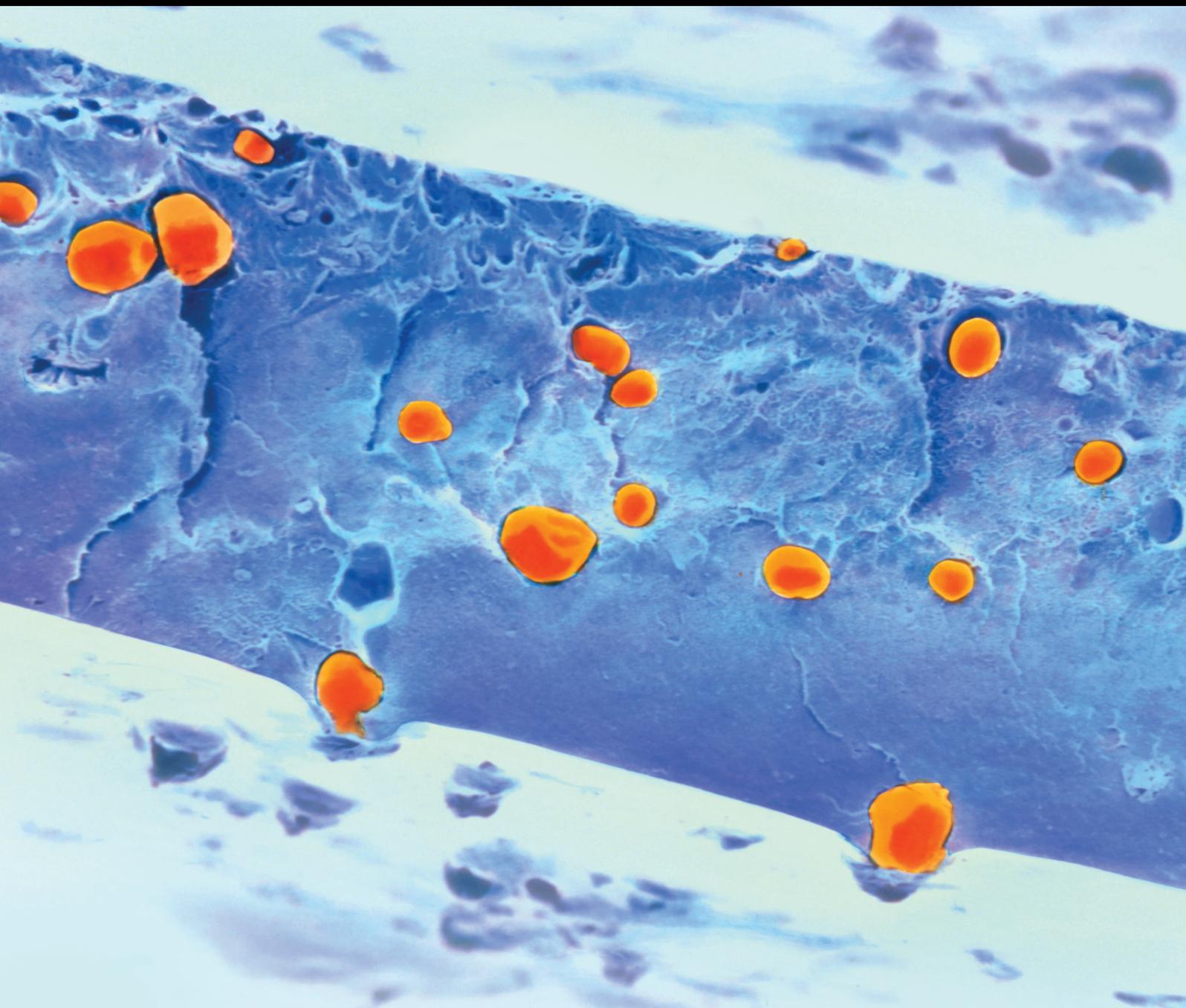


Natural Fiber Reinforced Polymer Composites

Guest Editors: Md. Saiful Islam, Adriana Kovalcik, Mahbub Hasan,
and Vijay Kumar Thakur





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Editorial

Natural Fiber Reinforced Polymer Composites

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The use of natural fibers as a reinforcement for various materials was recorded already in ancient Egypt; however, their rediscovery can be dated to the beginning of 20th century. Current special issue is devoted to the role of natural fibers as reinforcements for various biodegradable and nonbiodegradable polymer matrices. The application of natural fillers can be seen as an approach to adjust material performance of polymer composites supposing that filler/matrix interactions will be optimized and a hygroscopicity of natural fillers will be hindered. This special issue contains 16 papers that highlight a number of reasons for applications of natural fillers in polymer composites. In recent years the discussion about a balance in carbon footprint increased an attractiveness of natural fibers/fillers derived from agricultural sources predominantly from one-year plants.

One of the reasons given for using of fibers from one-year plants can be a quicker and economically favorable production of composites based on environmentally friendly, abundant renewable materials with short growth cycles. A large variety of natural fibers/fillers are available worldwide, although their chemical and physical nonuniformity in comparison with synthetic fibers often requires an inclusion of pretreatment steps as well as a precise characterization before their applications. S. Shahinur et al. in the paper "Characterization on the Properties of Jute Fiber at Different Portions" reported that physicomechanical properties of Jute Fibers vary within one batch, depending on a selected

cut position (lower part, middle part, and top of 250 mm long fibers). Md. M. Rahman et al. in the paper "Synthesis of Cotton from Tossa Jute Fiber and Comparison with Original Cotton" studied properties of synthesized cotton from Tossa Jute Fiber using the processing steps such as extraction in water, disintegration, drying, dewaxing, and delignification. This work shows that chemical structure and thermal stability of cotton from Tossa Jute Fibers are comparable with cotton fibers derived from cotton plant. N. Bidin et al. in the paper "Suitability of Aquatic Plant Fibers for Handmade Papermaking" advised aquatic plants such as *Scirpus grossus*, *Cyperus rotundus*, and *Typha angustifolia* as suitable materials for pulp and paper industry. B. Tisserat et al. in the paper "Ionic Liquid-Facilitated Preparation of Lignocellulosic Composites" introduced EMIMAc (ionic liquid) in the pretreatment step of lignocellulosic material (mixture of cotton and steam exploded wood) and various reinforcement fabrics to enhance the existing properties (especially mechanical) of polymer composites procured from renewable materials.

Another purpose of using natural filler can be a modification of rheological and mechanical properties of polymer composites without an increase of composites weight and costs. Papers within this issue address utilization of natural fibers as reinforcements for thermosets as well as thermoplastics. S. D. Salman et al. in the paper "Physical, Mechanical, and Morphological Properties of Woven Kenaf/Polymer

Composites Produced Using a Vacuum Infusion Technique” reinforced epoxy resins with plain woven kenaf fabric with fiber content of 35 wt.% and detected superior mechanical properties of composites cut in 0°/90° orientation.

V. A. Escócio et al. in the paper “Rheological Behaviour of Renewable Polyethylene (HDPE) Composites and Sponge Gourd (*Luffa cylindrica*) Residue” investigated effect of sponge gourd (cellulosic filler) in the concentration of 10–40 wt.% on rheological properties of high density polyethylene derived from sugarcane ethanol. This work shows that higher reinforcement of HDPE can be reached by an incorporation of cellulosic filler in the concentration above 20 wt.% but only with creations of agglomerates due to the low filler/matrix adhesion. The efficiency of fique fibres as a reinforcement low density polyethylene (LDPE) recycled from Tetra Pak was tested in the work of Hidalgo-Salazar et al. “Influence of Incorporation of Natural Fibers on the Physical, Mechanical, and Thermal Properties of Composites LDPE-Al Reinforced with Fique Fibers.” J. S. Won et al. in the paper “Mechanical Properties and Biodegradability of the Kenaf/Soy Protein Isolate-PVA Biocomposites” modified mechanical properties and biodegradability of soy protein isolate/poly(vinyl alcohol) by an incorporation of kenaf nonwoven fabric. Effects of natural filler such as rice husk and pineapple leaves fibers on thermal, morphological, and mechanical properties of composites based on various polymer matrices such as polyethylene, polypropylene, polyvinylchloride, and poly(lactic acid) were reviewed in the works of R. Arjmandi et al. “Rice Husk Filled Polymer Composites” and M. Asim et al. “A Review on Pineapple Leaves Fibre and Its Composites.” A fibre/polymer interfacial adhesion was highlighted as a main factor that influences final properties of natural fiber/polymer composites.

For practical uses of composites containing hygroscopic natural fibers it is very important to determine their mechanical properties under humid conditions to assess effect of moisture on their behavior. The issue of hygrothermal aging of kenaf fibers/polypropylene composites is addressed in the work of W. M. Haniffah et al. “Kenaf Fibre Reinforced Polypropylene Composites: Effect of Cyclic Immersion on Tensile Properties.” E. Muñoz and J. A. Garcia-Manrique in the paper “Water Absorption Behavior and Its Effect on the Mechanical Properties of Flax Fibre Reinforced Bioepoxy Composites” reported that composites based on biobased epoxy resin (SUPER SAP CLR Epoxy, Entropy Resins, USA) and 40 or 55 wt.% of flax fiber woven fabric processed by resin transfer moulding process (RTM) in spite of the natural hygroscopicity of flax fibers can be an alternative to composites based on petroleum-based resins and synthetic fibers. F. J. Aranda-García et al. in the paper “Water Absorption and Thermomechanical Characterization of Extruded Starch/Poly(lactic acid)/Agave Bagasse Fiber Bioplastic Composites” improved mechanical properties of thermoplastic starch by incorporation of agave bagasse fibers and/or poly(lactic acid) (PLA). Moreover, water absorption of thermoplastic starch/agave bagasse fibers/PLA composites was in this formulation reduced. Effects of acetylation on alfa fibers and grafting of polypropylene (PP) with maleic anhydride on the final interfacial compatibility and hydrothermal

stability of alfa fibers/PP composites were studied by N. Hamour et al. in the paper “Effects of MAPP Compatibilization and Acetylation Treatment Followed by Hydrothermal Aging on Polypropylene-Alfa Fiber Composites.”

The incorporation of natural fibers/filler requires a selection and a modification of common polymer processing methods and procedures to reach optimal physicomaterial properties of composites. M. D. Azaman et al. in the paper “Numerical Simulation Analysis of Unfilled and Filled Reinforced Polypropylene on Thin-Walled Parts Formed Using the Injection-Moulding Process” identified and compared residual stresses, volumetric shrinkages, and warpage in injected moulded thin-walled polypropylene specimens reinforced with 50 wt.% wood filler and 10 wt.% glass fibers. Z. Hutyrová et al. in the paper “Study of Surface Roughness of Machined Polymer Composite Material” investigated topography and surface properties of extruded wood fibers/HDPE composites and announced a presence of microcracks located on contacts between wood particles and polymer matrix.

This special issue provides up-to-date investigation of natural fibers as a source of renewable and biodegradable material available for use as reinforcements for polymers. Hopefully, this special issue will be beneficial to many scientists and move their research a small step forward.

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Research Article

Ionic Liquid-Facilitated Preparation of Lignocellulosic Composites

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Lignocellulosic composites (LCs) were prepared by partially dissolving cotton along with steam exploded Aspen wood and burlap fabric reinforcements utilizing an ionic liquid (IL) solvent. Two methods of preparation were employed. In the first method, a controlled amount of IL was added to preassembled dry matrix of cotton and Aspen wood with a burlap weave reinforcement. In the second method, IL solvent, cotton, and Aspen wood were mixed to produce a thick paste matrix that was subsequently pressed into the burlap weave reinforcement. The IL-based solvent was removed via water soaking, and the flexural and tensile properties of the LCs were examined. In this study, the matrix paste method produced a superior LC. Variables such as processing time (IL interaction time) and fabric weaves were found to influence the mechanical properties of the LCs. Although significant process optimization can still be realized, the mechanical properties of several of the LCs fabricated in this study were comparable to injection molded test specimens of neat high density polyethylene or neat polypropylene.

1. Introduction

There is an ever growing need to produce goods (e.g., fuels and consumer/industrial items) without petroleum [1–5]. Alternative sources of energy and feedstocks for materials and chemicals utilizing renewable resources are sought in order to lessen the dependence on petroleum, improve product performance, minimize environmental impact, and reduce costs [2]. Biofuels may be obtained by processing and fermenting lignocellulosic materials (i.e., waste wood, corn stover, and sugarcane bagasse).

About 8% of total petroleum products (i.e., crude oil and natural gas) are utilized in the manufacture of plastics [6, 7]. Bioplastic alternatives, whether biodegradable (polylactic acid or polyhydroxyalkanoates) or nondegradable (biopolyethylene or biopolyethylene terephthalate), are obtained by processing renewable resources into monomers [1]. Unfortunately, processing biosubstrates into monomers is often too energy intensive to be cost competitive with petroleum-based

monomers. An alternative is to directly incorporate biomaterials with thermoplastics to produce composites and thereby displace some of the plastics produced from bio- or oil-derived monomers. Lignocellulosic biomass from a variety of sources is routinely blended in percentages up to 50% with thermoplastics to produce biocomposites (i.e., wood plastic composites (WPCs)) [8–12]. While WPCs have certain economic and sustainability advantages, they also have inherent limitations such as the incompatibility issues occurring between the matrix (polyolefins) and the filler/reinforcement (lignocellulosic material). WPCs are difficult to recycle and, of course, still utilize substantial amounts of thermoplastics which continue to pose environmental problems [6, 13, 14].

Plastics are typically defined as synthetic materials made from a wide range of organic polymers, such as polyethylene, polypropylene, and nylon, that can be molded into shapes while being soft and then set into a rigid or slightly elastic forms [7, 10]. However, the term plastics can also be defined more generally as materials that can be easily shaped

or molded without regard to any thermoplastic reference. The focus of our research is to create biocomposites that are wholly composed of natural substrates but that are moldable. Furthermore, our goal is to generate composites that exhibit mechanical properties on par with petroleum-based thermoplastics. Other considerations are to produce these composites at a comparable cost to thermoplastics and employ sustainable processes that have a smaller environmental footprint than thermoplastics. In so far as this is possible, several intriguing synergies are apparent. First, inherit incompatibilities between natural and synthetic substrates may be avoided. Second, biocomposites composed of the same or similar materials should be easier to recycle (even becoming compostable) [15, 16]. Third, biocomposites may exhibit unique property combinations (i.e., strength, flexibility, and water transport) which are not easily obtained from synthetic polymers.

The concept of developing all-cellulose composites (ACCs), in which both the matrix and the reinforcement agents are cellulose-based, has been demonstrated [15–22]. Speaking broadly, ACCs are prepared by introducing a cellulose matrix around a fibrous (cellulosic) reinforcement material. Cellulose is the most abundant biopolymer in nature with an estimated production of 1.5×10^{12} tons/year and has mechanical properties (tensile strength: 13–17 GPa; tensile modulus: 138 GPa; density of 1.58 g/cm^3) on par or exceeding many of the common synthetic polymers [15, 16]. To create ACCs, a wet process is necessary, for example, dissolving cellulose in N,N-dimethylacetamide containing LiCl followed by its resolidification in the presence of reinforcement material [15]. Ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium acetate (EMIMAc) have also been utilized to prepare ACCs [23]. ILs may also be used to prepare composites using other biopolymers such as silk [21]. Although IL is currently expensive, it has certain advantages over other cellulose dissolving solvents such as being recyclable, relatively environmentally friendly, and very effective [19, 21–23]. In addition, finding large-scale uses for IL will undoubtedly reduce its manufacturing costs. In this work, we sought to fabricate complex, moldable composites composed primarily of lignocellulosic materials utilizing IL as the cellulose solvent. Unlike in other studies where highly refined cellulose materials were employed, we are interested in employing lower cost lignocellulosic ingredients with minimal processing to generate lignocellulosic composites (LCs). Wood, for example, is a composite tissue composed of cellulose and hemicellulose with lignin acting as the network fiber binding carbohydrate components into compact structures [2]. It is difficult to dissolve wood with conventional solvents because of the intricate relationship between lignin and polysaccharide constituents. Much interest exists in separating the lignin from the carbohydrates to manufacture biofuels and chemical feedstocks [24–28].

This report explores different approaches to adequately mix biomaterials and IL solvents to yield LCs. The influence of solvent exposure time (i.e., the time IL interfaced with the LC components) and the effect of employing different reinforcement types and weaves on the LC mechanical properties were

explored. We further compared the mechanical properties of the LCs generated specimen bars to that of injection molded bars composed of neat high density polyethylene (HDPE) or neat polypropylene (PP). This was done to determine if the LCs mechanical properties were comparable to thermoplastic resins. The cost of the unprocessed raw materials utilized in the LCs, cotton, \$0.58–0.69/lb, Aspen wood fiber, \$0.12–0.25/lb, and Jute burlap fibers, \$0.14–0.25/lb (<http://www.alibaba.com/>), suggests these LCs (\$0.35–0.40/lb) are cost competitive with thermoplastics (i.e., HDPE (\$0.52–0.70/lb) and PP (\$0.65–0.75/lb)) for use in a variety of applications (<http://www.plasticstoday.com/>).

2. Material Processing and Experimental Methods

2.1. Chemicals and Materials. The IL, EMIMAc (>98% purity), was obtained from IoLiTec Inc., Tuscaloosa, AL. Acetonitrile (ACN) ($\geq 99.5\%$ purity) was obtained from Sigma-Aldrich, St. Louis, MO. Reagents were used as received without any additional purification or modification.

Nonabsorbent (nonsterile/bleached) cotton (100% cotton) was obtained from U.S. Cotton Co., Lachine, Canada. Aspen steam exploded wood (SEW) was provided by USDA-Forest Service Southern Research Station, Pineville, LA. Aspen wood chips were soaked in water for 16 hr and then they were subjected to temperature of 190°C and pressure of 1.3 MPa for 5 min followed by the rapid release of pressure. Reinforcement fabrics employed were obtained from 23'' \times 40'' burlap bags, (ULine, Chicago, IL), burlap ribbons (Hobby Lobby, Oklahoma City, OK), and cotton canvas (DMC Corp., Kearny, NJ) (Table 1). The chemical composition of materials used in this study were cotton (94% cellulose), Aspen wood (57% cellulose, 20% hemicellulose, 16.3% lignin), and jute fiber (64–65% cellulose, 20–25% hemicellulose, 10–15% lignin) (<http://textilefashionstudy.com/>; <http://www.wikipedia.org/>). Materials were dried for 48 hr at 60°C prior to use.

2.2. Preparations. Two distinct procedures were conducted to obtain LCs. Table 1 summarizes the various treatments conducted in this research project.

2.2.1. Direct Application Method (DAM) of ILs. Dry matrix and reinforcement fiber weave were layered together (prior to adding solvent). Burlap fabric weaves were cut into 75 mm $L \times$ 25 mm W pieces. Cotton and SEW were mixed in a blender prior to use. The matrix material (0.8 g) was sandwiched between two layers of burlap weave, each ~ 0.45 g weight, in a rectangular silicone pan (75 mm $L \times$ 25 mm $W \times$ 27 mm H) (Freshware Inc., Alhambra, CA). IL of 3.5 mL of 1 M EMIMAc was applied to the surface of the burlap weave in a drop wise fashion and allowed to penetrate for 3 min. The LC sandwich was turned over and a second application of 1.75 mL IL was administered to the burlap weave. A total of 5.25 g of IL was administered to the composite components. LCs, still in silicone trays, were microwave heated at 50 watts for 10 minutes in Ethos EX microwave Labstation (Milestone Inc.,

TABLE 1: Weight percentages in test formulations.

Formulations*	Cotton	SEW	Burlap
DAM	10	50	40
MPM: tight burlap weave	10	45	45
MPM: burlap bag weave	10	45	45
MPM: wide burlap weave	10	52	38
MPM: cotton weave	15	65	20

*DAM represents the method employing direct application of IL on dry LC components; MPM represents the method of incorporation of matrix materials with IL followed by reinforcement with burlap layers.

Shelton, CT) during which time the microwave was stopped to periodically flip the LC sandwich. The LC samples were pressed between stainless steel plates and incubated in an oven at either 60°C or 80°C for 30, 90, and 1200 minutes and then they were transferred to containers containing 2000 mL deionized distilled water to remove IL. Water was replaced every hour for 4 consecutive hours. Composites were transferred to paper towels and pressed between stainless steel sheets under 4.6 MPa for 16 hrs until dried.

2.2.2. Matrix Paste Method (MPM) of ILs. To prepare the lignocellulose matrix, 0.2 g of cotton was immersed in 10 g solution of 1 mol EMIMAc:1 mol ACN in a rectangular silicone pan (75 mm $L \times$ 25 mm $W \times$ 27 mm H). The mixture was exposed to microwave heating for 15 s at 250 watts and then stirred with a microscapula. This heating and stirring process was repeated three additional times in order to obtain a partially viscous cotton paste. Next, 1 g of SEW was added to the paste by stirring then microwaved for 1 min at 50 watts; this heating and stirring process was repeated once more. LCs were created by applying the matrix material evenly to the bottom of a second rectangular silicone pan and then pressing a 75 mm $L \times$ 25 mm W piece of burlap bag fabric weave, weighing ~0.5 g, into the matrix; next a second layer of matrix was applied and an additional weave was applied followed by another layer of matrix. Silicone trays were incubated at 80°C for 1200 min and then transferred to trays containing deionized distilled water to remove IL. Water was replaced every hour for 4 consecutive hours at 25°C. LCs were then transferred to paper towels and pressed between stainless steel sheets under 4.6 MPa for 16 hrs at 60°C until dried. In some experiments, different fabric weaves were substituted for the burlap bag weave (Table 2).

2.3. Mechanical Property Measurements. LCs were punched with a clicker press fitted with specimen cutting dies to obtain ASTM test specimen sample bars: ASTM D790 flexural testing bar (12.7 mm $W \times$ 63.5 mm $L \times$ 1.5 mm thickness) and ASTM D638 Type V tensile testing bar (9.5 mm grip area \times 3.2 mm neck \times 63.5 mm $L \times$ 1.5 mm thickness \times 7.6 mm gage L). The Type V bars were used for the tensile strength property tests. The flexural bars were used to evaluate flexural properties.

Cut, dry LCs were conditioned for approximately 240 hours at standard room temperature and humidity (23°C and 50% RH) prior to any test evaluations. ASTM D638

TABLE 2: Properties of reinforcement fabric weaves employed in LCs.

Reinforcement types	Strand thickness (mm)	Openings (#/cm ²)	Opening size (mm ²)
Tight burlap weave	0.5	23.3	1.5
Burlap bag weave	1	15.5	1
Loose burlap weave	0.5	7.8	6
Cotton weave	0.5	15.5	3.1

Type V tensile bars were tested for tensile modulus (E), tensile strength (σ_u), and elongation at break (%El) using a universal testing machine (UTM) Instron Model 1122 (Instron Corporation, Norwood, MA). The speed of testing was 5 mm/min. Three-point flexural tests were carried out according to ASTM-D790 specification on the Instron UTM Model 1122 using flexural bars. The flexural tests were carried out using Procedure B with a crosshead rate of 13.5 mm/min. The flexural strength (σ_{fm}) and flexural modulus of elasticity (E_b) were calculated. Five specimens of each formulation were tested. The average values and standard errors were reported. Comparisons of the mechanical properties of the LCs with commercial polyolefins were conducted through normalization processes. The two common polyolefins tested were HDPE and PP matrix using Petrothene LS 5300-00 and Pro-fax SB891 (Equistar Chemical LP, Houston, TX). The specific physical properties and method to prepare injection molded tensile and flexural bars have been previously described [11, 12]. A 30-ton molding machine (Model Engel ES 30, Engel Machinery Inc., York, PA) using an ASTM family mold to obtain HDPE or PP test bars. Set point temperatures (°C) for the four zone injection molding barrel were feed = 160, compression = 166, metering = 177, and nozzle = 191. The mold temperature was 37°C. Type V bars were used for the tensile strength property tests. The flexural bars (12.7 mm $W \times$ 63.5 mm $L \times$ 3.2 mm thickness) were used to evaluate flexural properties of the composites. Type V bars (9.5 mm W grip area \times 3.2 mm neck \times 63.5 mm $L \times$ 1.5 mm thickness) were used to evaluate tensile mechanical properties of the composites. The average σ_u , E , %El, σ_{fm} , and E_b values of HDPE were 21.5, 339, 105, 279, and 894, respectively. The average σ_u , E , %El, σ_{fm} , and E_b values of PP were 25.2, 576, 82.2, 43.9, and 1386, respectively [11, 12].

3. Results and Discussion

3.1. Influence of Reaction Incubation Time. EMIMAc has been reported to dissolve 100 g microcrystalline cellulose per kg EMIMAc IL and 50 g maple wood flour per kg EMIMAc IL [27]. In contrast we employed ~1.3 g cotton/SEW/burlap with 5.25 g of IL to obtain our LC. Our aim was to procure an LC with the minimum amount of IL to reduce cost and limit denaturation to fiber reinforcements. Very little is known concerning how to prepare LC with IL and lignocellulosic ingredients as employed in this study. Therefore, we initially sought to determine how long should the LC mixture incubate with the IL solution (i.e., 1 M EMIMAc : 1 M ACN) to achieve adhesion among the ingredients (Figure 1).

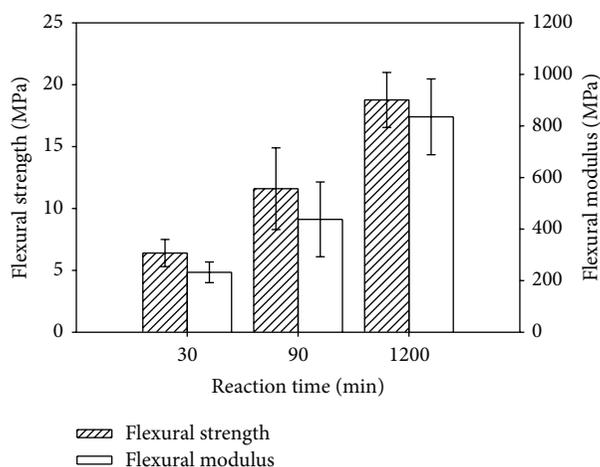


FIGURE 1: Effect of varying the incubation times using EMIMAc IL on the flexural properties of LCs. All LCs were subjected to a 60°C incubation temperature and soaked in water for 4 hrs.

Increasing the incubation reaction time from 30 min to 90 min dramatically improved the flexural properties of the LC. LCs reacted for 30 min versus 90 min at 60°C exhibited σ_{fm} and E_b values of 6.4 ± 1.1 and 232 ± 40 versus 11.6 ± 3.3 and 437 ± 144 , respectively. Therefore the LC/IL mixture that incubated for 90 min at 60°C exhibited a 81 and 88% increase in σ_{fm} and E_b values, respectively, compared to incubation for 30 min at 60°C (Figure 1). As shown in Figure 1, increasing the reaction time to 20 hours (i.e., 1200 min) further improved the mechanical properties of the resulting LC. The σ_{fm} and E_b values of the LC incubated for 1200 min at 60°C exhibited a 190% and 260% increase versus LC incubated for 30 min at 60°C. Although the optimum incubation time was not determined, it is clear that the IL solution can continue to react with the LC components for a considerable time span. Additionally, it should be noted that the amount of adventitious water in the IL solvent and biomaterial substrates may slow the mobilization of biopolymer (e.g., cellulose) considerably and it will be addressed in future work [27–33].

The IL must be removed from the LC for hydrogen bonding networks to be established between matrix and fiber components. Several solvents have been employed to remove IL from the treated biomass materials [33]. When the LC is introduced into water, an immediate swelling of the LC occurs along with a brownish discoloration of water. We replaced the water every hour for four consecutive hours and noted that substantially less of the brownish material was exuded from the LC each time the water was replaced. In other studies, data not shown, leaving the LC overnight in water did not improve the mechanical properties of the LC versus using a 4-hour soaking treatments. The influence of the soaking temperature was also examined using 25°C or 70°C. In both cases, the LC swelled considerably in the water. Furthermore, increasing the soaking temperature from 25°C to 70°C did not improve the mechanical properties of the LCs. For example, LCs water soaked for 30 min at 70°C exhibited σ_{fm} and E_b values that were 10% less than LCs water

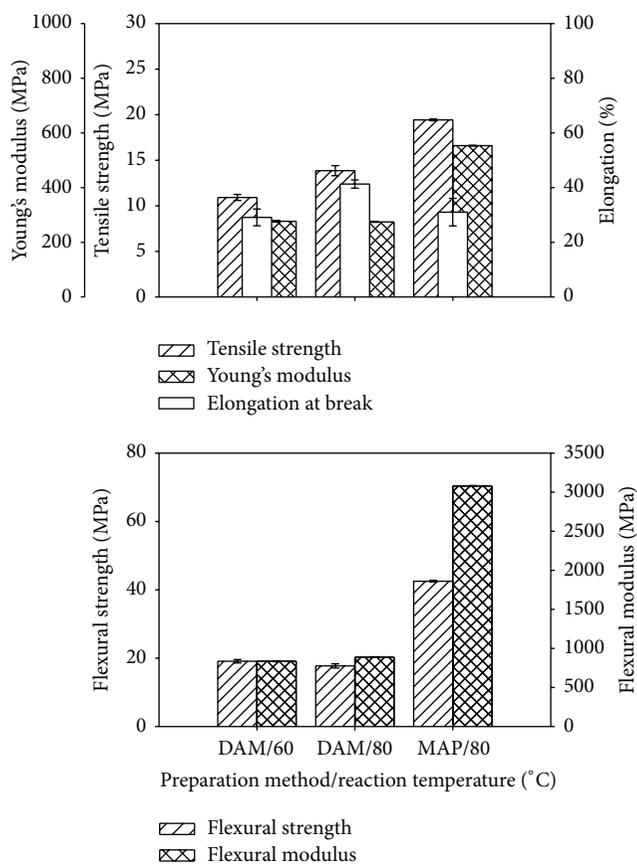


FIGURE 2: Influence of reaction incubation temperatures administered for 1200 min on the mechanical properties of LC. DAM designates the direct application method for applying IL to dry LC components; MPM indicates premixing matrix materials together with IL and then sandwiching this mixture between burlap layers.

soaked in 30 min at 25°C. In addition, we found it important to press the final LC to compress the components, reduce air spaces, and extrude excess water. LCs that were not pressed were physically weaker and exhibited much lower mechanical properties than pressed LCs.

The influence of incubation temperature on the mechanical properties was explored by incubating LCs at 1200 min at 60 and 80°C followed by mechanical properties testing. Employment of 80°C versus 60°C improved the σ_u and %El values by 27% and 42%, respectively, but it had little effect on the stiffness (E), σ_{fm} , or E_b values. The MPM (premixing the cotton and SEW with IL before sandwiching this mixture between the burlap layers) resulted in an LC with generally better mechanical values compared to LC prepared by the DAM of IL application (Figure 2). LCs prepared by MPM exhibited σ_u , E , σ_{fm} , and E_b values that were +40, +102, +140, and +247% higher than LCs prepared by the DAM. LCs prepared by MPM exhibited a decrease of 25% in %El values compared to LCs prepared by DAM. As seen in Figure 3, greater integration of the matrix with the burlap bag reinforcement fibers occurs in the LCs utilizing the MPM versus the DAM. LCs produced via the DAM clearly shows the outline of the original burlap bag weave (Figure 3(a)),

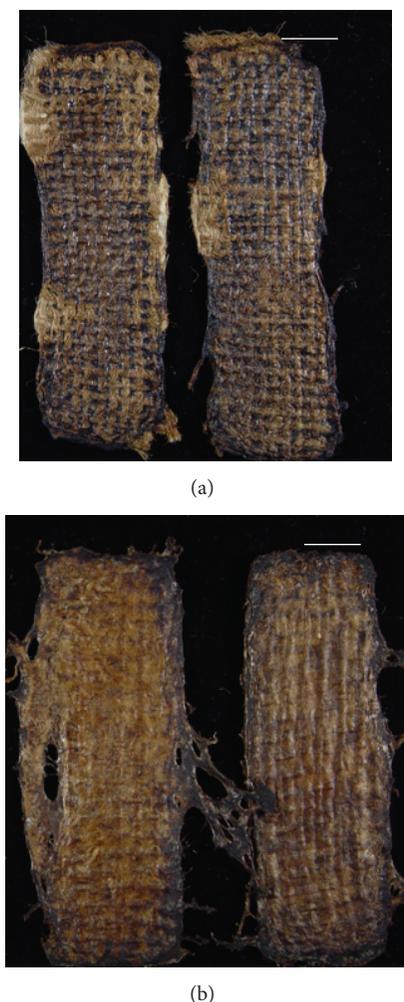


FIGURE 3: Examples of LCs employing the burlap bag weave fabricated using different preparation procedures. (a) LC obtained from the DAM. (b) LC obtained from MPM. Bar equals 12 mm.

while the MPM method shows a covering of the weave by the matrix materials (Figure 3(b)).

3.2. Influence of Reinforcement Types and Weaves. The influence of the reinforcement medium was investigated by employing burlap weaves of different strand thicknesses and opening sizes (Table 1; Figure 3). Relatively tight weave reinforcement materials produced an LC which had the lowest overall mechanical values of all the reinforcements tested (Figure 4). Visual examination showed that matrix material did not penetrate well between the openings and predominately coated only the outside portion of the weave. This resulted in an LC that exhibited high elongation values but low tensile and flexural values. Interestingly, the burlap bag weave which had thicker strands (1 mm), smaller opening sizes (1 mm²), and less openings (15.5/cm²) than the tight weave which had thinner strands (0.5 mm), larger opening sizes (1.5 mm²), and more openings (23.3/cm²) produced LCs with better mechanical properties. It should be noted that this

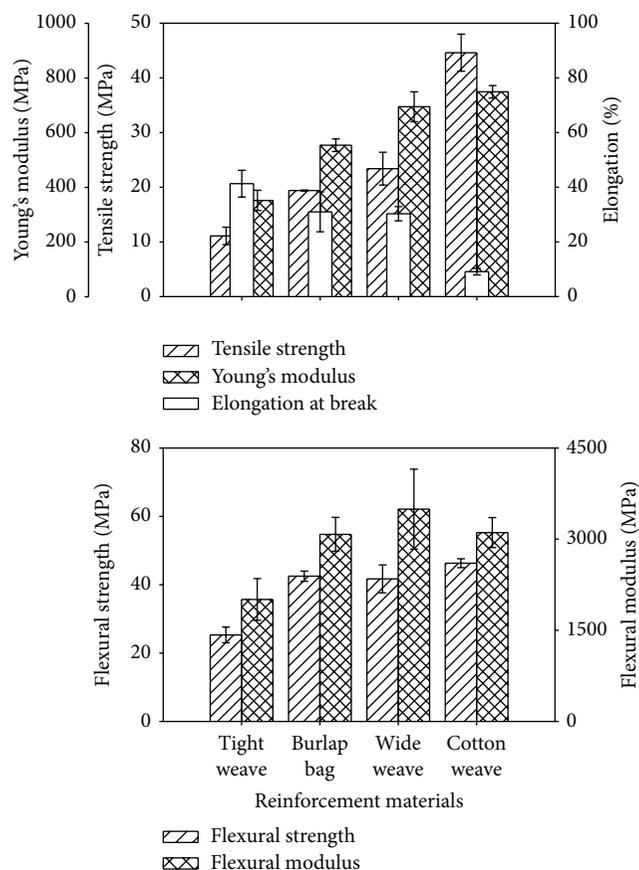


FIGURE 4: Mechanical properties of LC employing various reinforcement weave materials. LCs were prepared using the MPM method with a reaction incubation temperature of 80°C followed by 4 hrs of water soaking.

burlap bag weave had more loose fiber protrusions than the tight weave ribbon. This was due to the more highly refined state of manufacturing involved in manufacturing the tight weave burlap ribbon compared to the less expensive burlap bag weave. However, the burlap bag weave/LC exhibited σ_u , E , σ_{fm} , and E_b values that were +75, +57, +68, and +53% higher than tight weave/LC. The loose weave burlap/LC and cotton weave/LC exhibited the second best and best mechanical properties of the LCs tested. The cotton weave/LC exhibited the highest σ_u and E values at ~45 MPa and ~800 MPa, respectively (Figure 3). A likely explanation of these results is that increasing the interfacial area of the reinforcement allows for greater access of the matrix material (i.e., loose weave versus tight weave) to produce LCs that had higher mechanical properties.

Figures 5 and 6 graphically compare the mechanical properties of LCs with HDPE and PP by normalizing the LC to known HDPE and PP materials. For example, the σ_u , E , %EL, σ_{fm} , and E_b values of the wide weave/LC were 109, 205, 29, 149, and 391% of that of neat HDPE. Similarly, the σ_u , E , %EL, σ_{fm} , and E_b values of the wide weave/LC were 94, 124, 37, 95, and 252% of that of neat HDPE. These renderings clearly illustrate the influence of reinforced LCs compared

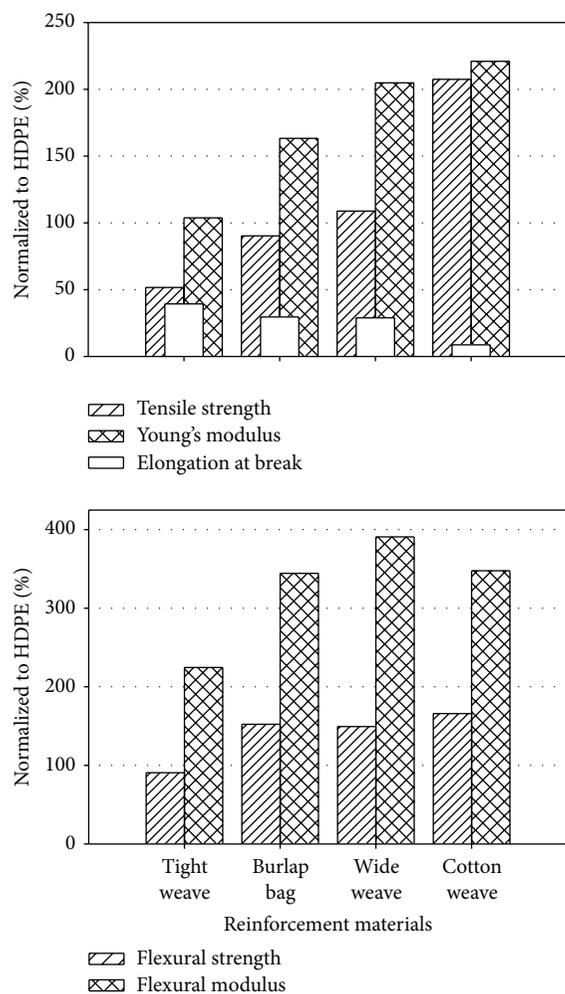


FIGURE 5: Normalized effect of reinforcement materials on the mechanical properties of LCs compared to HDPE.

favorably to commercial polyolefins. It is the contention of the authors that the LCs produced in this study may have merit to compete with polyolefins in certain short term applications. At this time, these LCs should not be considered as durable as polyolefins in terms of their mechanical properties, although they are more biodegradable. However, with appropriate surface functionalization and/or coatings, properties such as water absorption can be significantly altered in these LCs.

4. Conclusions

Relatively simple methods to produce LCs were demonstrated using IL. LCs were fabricated from dissimilar components such as cotton, SEW, and burlap fabric using either a direct application of IL solution to prepared dry components or by premixing the matrix materials (cotton and SEW) with IL then applying it to the burlap fabric. Other variables such as fabric weave patterns and solvent incubation time and temperature were found to significantly influence the mechanical properties of LCs generated. The methodologies employed produced LCs on par with synthetic polymers

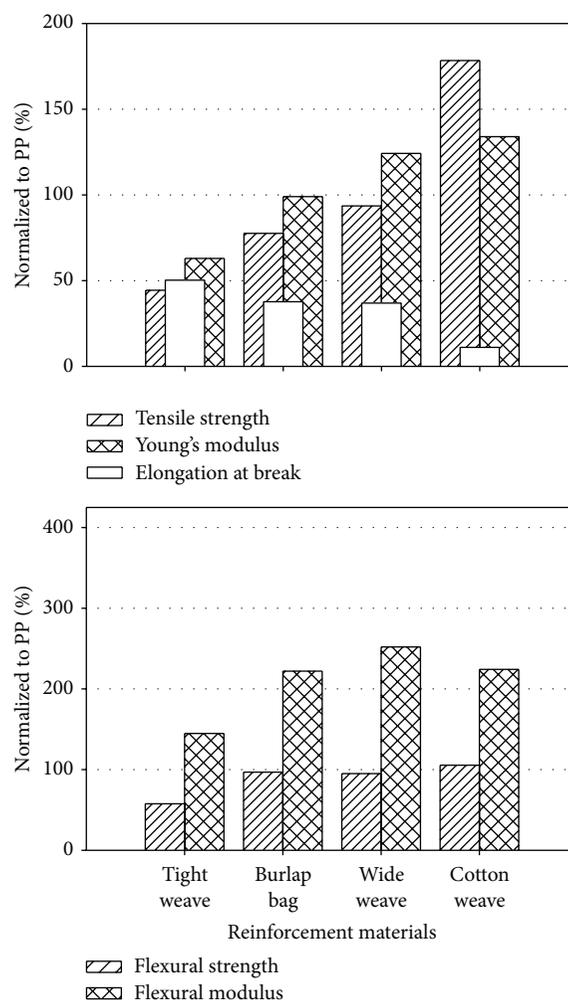


FIGURE 6: Normalized effect of reinforcement materials on mechanical properties of LCs compared to PP.

such as HDPE and PP. There are many remaining questions that need further investigation. As we continue to refine our process methods, optimized LCs will be subjected to chemical (e.g., X-ray diffraction), thermal characterizations and scanning electron microscopy examinations. In addition, studies will be conducted to decrease incubation periods by controlling the amount of adventitious water in substrates and solvent. Finally we are conducting studies to recover and recycle IL-based solvents.

Abbreviations

WPC:	Wood plastic composites
ACC:	All-cellulose composites
IL:	Ionic liquids
LCs:	Lignocellulosic composites
HDPP:	High density polyethylene
PP:	Polypropylene
EMIMAc:	1-Ethyl-3-methylimidazolium acetate
SEW:	Steam exploded wood
ACN:	Acetonitrile

DAM: Direct Application Method
 MPM: Matrix Paste Method
E: Tensile modulus
 σ_u : Tensile strength
 %El: Elongation at break
 σ_{fm} : Flexural strength
 E_b : Flexural modulus of elasticity.

Disclosure

Mention of a trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the US Department of Agriculture (USDA) or Bradley University.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Characterization on the Properties of Jute Fiber at Different Portions

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Natural fibers are environment-friendly, biodegradable, nonabrasive, and less costly and exhibit high initial modulus and high moisture absorption. However, they have nonuniformity in their mechanical, physical, chemical, and thermal properties at different portions. For this reason, long jute fiber was cut into three different portions and subsequently characterized using single fiber tensile test, differential scanning calorimetric, thermogravimetric analysis, X-ray diffraction, and scanning electron microscopy according to top, middle, and cutting portions. The crystallinity and moisture content were measured by XRD data and moisture absorption test of the different portions of the raw jute fiber, respectively. The middle portion had better mechanical, thermal, chemical, and crystalline properties compared to the other two portions of the jute fiber. The diameter gradually became thinner from cutting to top portions. Thus the middle portion of jute fiber would be the better choice while being used as reinforcement in composites.

1. Introduction

A broad variety of natural fibers are nowadays available that can be used as filler in green composites due to their better physicochemical and physicomechanical properties. In recent times the natural fibers have found new field of application as reinforcement in composites for replacing the man-made synthetic fibers such as carbon [1]. Environmental regulations brought paradigm shift in the composite market. Thus, the interest of the natural fiber reinforced polymer composite in the composite market and in engineering application has increased significantly [1, 2].

Natural fibers such as hemp, coir, bamboo, palm, and kenaf are easily available, inexpensive, light, renewable, biodegradable, and environmentally acceptable. Jute is a biodegradable, cheap, nontoxic, environment-friendly, and longest bast fiber. Due to the advent of cheap synthetic substitutes, bulk handling, containerization, and storage in

soils, jute and jute goods are losing market sharply in the countries. Diversified use of jute is therefore essential in order to prevent further decline of the jute sectors [2]. However, the physicomechanical properties of the jute fiber vary in a wide range. For this reason, jute fibers are not used in the large range in the diversified production sectors. In order to diversify the use of jute fiber, various chemical treatments were conducted on jute fiber. In some places, jute was mixed with other materials [3–8]. Uddin et al. blended top, middle, and bottom portion of jute with jute cotton and found significant variation in properties. The top and cutting portions had comparable results when blended with jute cotton [3, 4]. Shahinur reported that the tensile properties of different portions of the jute fiber became similar after chemical treatment. However the properties were different in three different portions in raw jute fiber [5]. Wang et al. prepared micro and nano fibrils from jute fiber using chemical treatment and reported better properties in the jute fibrils [6]. Teli and

Valia conducted acetylation on jute to improve oil absorbency [7]. However, raw jute fiber was not characterized properly and the thermal properties were not evaluated according to different portions. The chief weakness of natural fibers is that they have different properties in different portions due to different maturity of the cell in different portions. The deviation of the properties also varies in wide range as natural fiber contains a wide range of nonhomogeneity [9, 10]. As a result, jute composites prepared using different portion of the jute fiber will not show uniform properties. In order to investigate the properties of different portions of jute fiber, long jute fiber was cut into three portions (top, middle, and cutting) in the present research. Those portions were subsequently characterized using physical, mechanical, and thermal techniques.

2. Methodology

Jute fiber was collected from Bangladesh Jute Research Institute, Bangladesh. The origin of the fiber was Faridpur region situated at middle part of Bangladesh. The collected fibers were cut manually into three portions (top, middle, and cutting) of approximately 250 mm in length (Figure 1). The single fiber was characterized by tensile testing using 6353 Instron machine (Instron, USA) at the crosshead speed 5 mm/sec [10]. The fiber span length was 5 mm, 15 mm, 25 mm, and 35 mm. The span length effect was corrected by newly developed method [10]. The moisture content was measured by conventional method at room temperature, moisture, and rainy conditions. The surface morphology of the fiber was observed under a scanning electron microscope. The moisture absorption characteristics of the different portions were studied at distilled water, 10% HCl, and 10% NaCl using ASTM-D 570. Fiber crystallinity was measured by X-ray diffraction data. A Norelco type 120-101-85 Philips electronic diffractometer with nickel filtered copper $K\alpha$ was used. X-ray diffraction data were collected from the equatorial diffraction profiles using 5 to 15 steps scanning (2θ), method of "top of smoothed peak," fiber diagram. Thermal properties were measured using a thermogravimetric analyzer (TA Instruments SDT Q50) on 8–10 mg raw jute fiber at a heating rate of 5°C/min in a nitrogen atmosphere. Differential scanning calorimetric analysis was also carried out to measure thermal properties using a DSC Q10 (TA Instruments) thermal system with a sealed aluminum capsule. 10 mg jute fiber was used and the temperature was varied in between 0 and 500°C.

3. Results and Discussion

3.1. Surface Morphology. The whole jute fiber was cut into three portions as top, middle, and cutting/bottom (Figure 1). The surface morphology of the top, middle, and cutting portions was found different according to their thickness that was due to variation of the jute fiber maturity. The top fiber was immature, middle fiber was properly matured, and cutting portion was overmatured [11] (Figure 2). There were less pores and voids on the top portion fiber surface

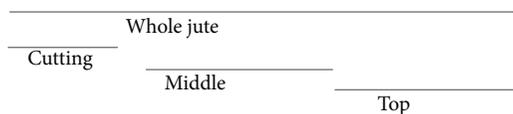


FIGURE 1: Cutting process of whole jute fiber.

as compared to the surfaces of middle and cutting portions. Physically top portion was branched in soft and light colour. Middle portion was beautiful in colour and glassy, while cutting portion was rough and dark in colour as compared to the top and middle portion [12]. The top portion had less diameter (40 μm) due to immaturity, while the middle and cutting portion had sufficient diameter due to their cellulose content [13]. The diameter of the middle and cutting portions was approximately 65 μm and 75 μm , respectively.

3.2. Tensile Properties. The tensile strength, Young's modulus, and strain to failure of middle portion jute fiber were higher as compared to the top and cutting portions (Figure 3). This was due to the higher cellulose content of the middle portion [13]. One important thing is that middle portion fibers were matured, whereas the top and cutting portions were immature and overmature, respectively [11]. The tensile strength and strain to failure for all portions decreased with span length. This is because the lower test span length was much affected by fiber properties and machine parameters. On the other hand, Young's modulus increased with span length as found in previous research [10, 11].

3.3. Moisture Content Results. The moisture content of raw jute fiber of different portions is shown in Figure 4. The middle portion of jute fiber showed exceptional results compared to the top and cutting portions due to its high cellulose and free hydroxyl (-OH) group content [13]. At room and moisture condition middle portion had lower moisture content than the other two portions; as a result mechanical and thermal properties of middle portion were higher compared to top and cutting portions [14].

3.4. Crystallinity Analysis. The XRD pattern, as well as crystallinity of the top middle and cutting portions, was similar (Figure 5). The crystallinity of the top portion of jute fiber was slightly higher as compared to the middle and cutting portions, which could be due to the presence of less dense fats and waxes or lignin in the top portion [15]. As a result there were less pores and voids on the top portion fiber surface. From the XRD data, it can be clearly seen that the width at half-height of the 002 at 29–18° and 29–24° was similar to top, middle, and cutting portions of the fibers. There was only a small difference in the positions of these peaks [16].

3.5. Thermal Properties

3.5.1. Thermogravimetric Analysis. The thermal properties of different portion of jute are shown in Figure 6 and tabulated in Table 1. The thermograph of individually three-portion

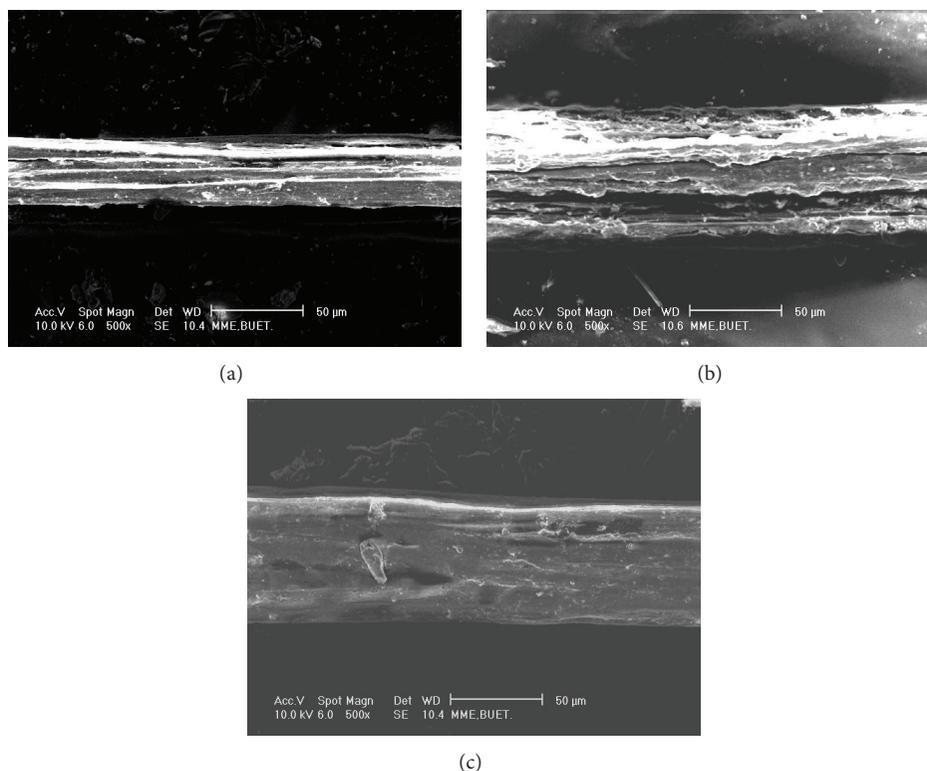


FIGURE 2: Surface morphology of (a) top, (b) middle, and (c) cutting portions of raw jute fiber.

TABLE 1: Thermal properties of different portions of jute fiber.

Portion	Degradation temperature ($^{\circ}\text{C}$) of		
	Moisture	Cellulose and hemicellulose	Lignin
Top	100	290	325
Middle	101	280	310
Cutting	100	285	320

jute fiber presented three stages (from 25 to 180 $^{\circ}\text{C}$, from 180 to 280 $^{\circ}\text{C}$, and from 280 to 500 $^{\circ}\text{C}$) of decomposition [17]. The middle portion of raw jute fiber had higher derivative change (Figure 6(a)) due to higher cellulose [13] content as compared to the top and cutting portion during increase in temperature. The thermal stability was similar to different portions but the weight change of the fiber rapidly changed in case of middle portion, followed by cutting and top portions, respectively. This was related to the moisture content of the different portions of jute fiber [5]. The first 10% weight loss (Figure 6(b)) occurred due to moisture evaporation and 20–30% weight loss occurred due to degradation of light materials such as hemicellulose and cellulose, while 70% weight loss occurred due to decomposition of heavy material like lignin of the jute fiber [17, 18]. The degradation temperature of cellulose was higher than the hemicellulose (25–290 $^{\circ}\text{C}$) and lignin (150–420 $^{\circ}\text{C}$). This was due to the fact that most of the cellulose structure was crystalline, which is strong and resistant to hydrolysis [19, 20]. After the removal of the free water, the degradation process began in the cellulose,

hemicelluloses, lignin constituents, and the associated linked water [17, 21].

DTGA curve showed a lower temperature peak at around 250 $^{\circ}\text{C}$ for top portion fiber, which was due to the decomposition of hemicellulose. For the middle and cutting portion this peak was not visible, indicating the removal of hemicellulose from the fiber. Furthermore, a large peak at a temperature around 320 $^{\circ}\text{C}$ was due to cellulose and lignin decomposition. At this stage, middle portion showed higher decomposition temperature compared to top and cutting portion of the jute fiber. This again proves that hemicellulose and lignin were less in the middle portion [17].

3.5.2. DSC Analysis. DSC curves of three portions of jute fibers are shown in Figure 7. Ball et al. reported that the endothermic reaction occurred due to volatilization (gases) of the molecules, whereas exothermic reaction occurred due to the formation of charring (solid residue) [18, 22]. The cutting portion shows a higher endothermic peak (around 100 $^{\circ}\text{C}$) for water evaporation compared to the top and middle portion (around 80 $^{\circ}\text{C}$). This result indicates that cutting portion has low hemicelluloses compared to middle and top. A small exothermic peak appeared at the temperature range of 250–290 $^{\circ}\text{C}$ for cutting portion. This peak mainly occurred due to decomposition of hemicelluloses and a portion of lignin degradation. This exothermic peak disappeared from the top and middle portion of the jute fibers indicating greater amount of hemicellulose and lignin missing from the respected jute portions.

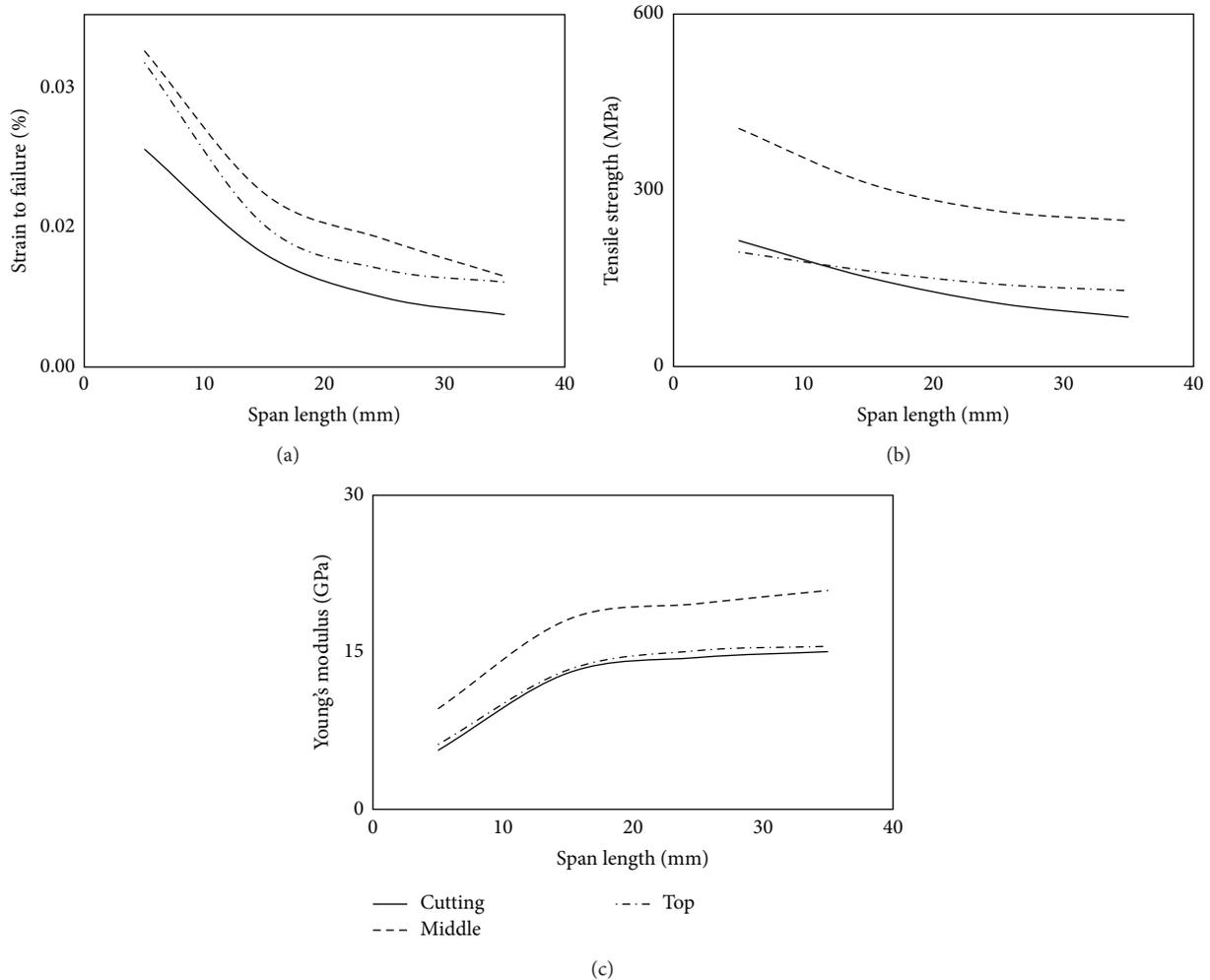


FIGURE 3: (a) Strain to failure, (b) tensile strength, and (c) Young's modulus of different portions of raw jute fiber.

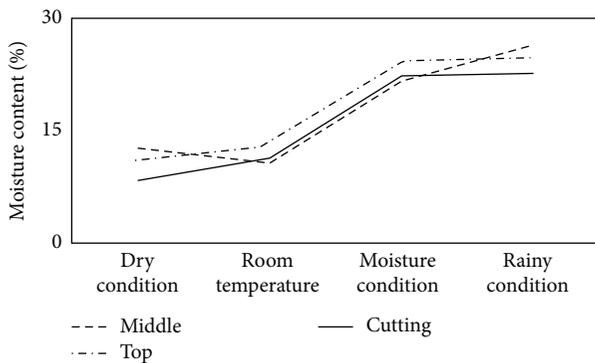


FIGURE 4: Moisture content of different portions of raw jute fiber.

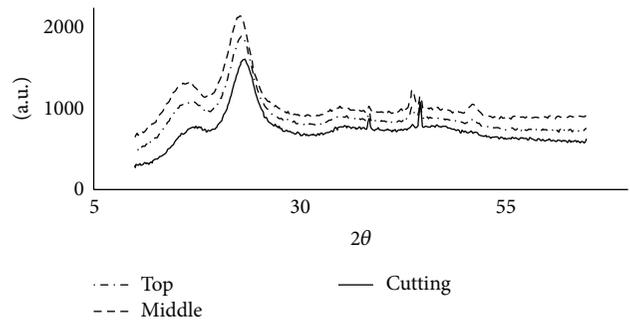


FIGURE 5: XRD pattern of the different portion of the raw jute fiber.

4. Conclusions

The present study investigated the physical, mechanical, and thermal properties of different portion jute fiber. Single fiber tensile test, differential scanning calorimetric analysis,

thermogravimetric analysis, X-ray diffraction analysis, and scanning electron microscopy on top, bottom, and cutting portions of jute fiber were carried out. The middle portion had higher tensile strength, strain to failure, and Young's modulus as compared to top and cutting portions. The surface of the cutting portion was rougher as compared to the

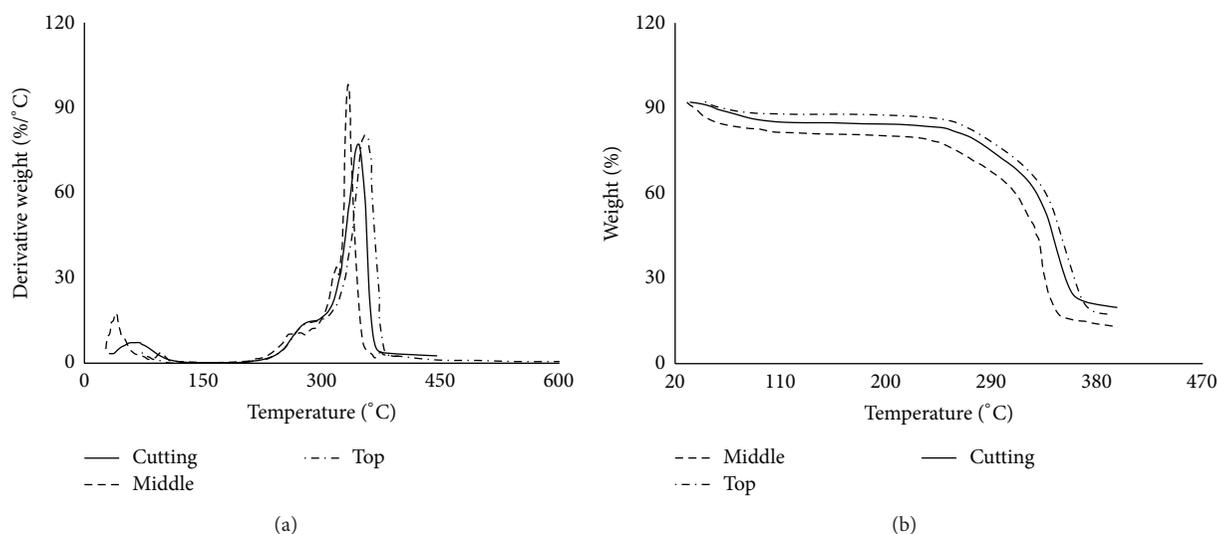


FIGURE 6: (a) DTGA and (b) TGA curves of different portions of raw jute fiber.

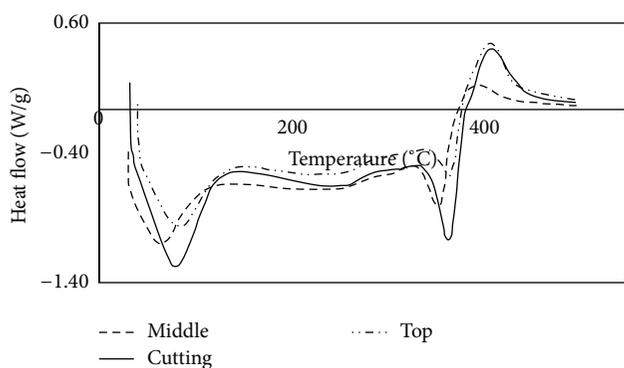


FIGURE 7: DSC curves of three portions of raw jute fibers.

top and middle portions. On the other hand, the crystallinity of different portions of jute fiber was similar. However, there was a small difference in the position of the peaks. The middle portion of jute fiber also had higher thermal stability as compared to the other two portions. Thus the middle portion should be used as reinforcement in composites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Synthesis of Cotton from Tossa Jute Fiber and Comparison with Original Cotton

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Cotton fibers were synthesized from tossa jute and characteristics were compared with original cotton by using FTIR and TGA. The FTIR results indicated that the peak intensity of OH group from jute cotton fibers occurred at 3336 cm^{-1} whereas the peak intensity of original cotton fibers occurred at 3338 cm^{-1} . This indicated that the synthesized cotton fiber properties were very similar to the original cotton fibers. The TGA result showed that maximum rate of mass loss, the onset of decomposition, end of decomposition, and activation energy of synthesized cotton were higher than original cotton. The activation energy of jute cotton fibers was higher than the original cotton fibers.

1. Introduction

In recent years, lignocellulosic materials have grown to be more attractive to the material engineering sectors. These materials, comprising lignin, hemicellulose, and cellulose, have become alternatives to conventional materials. This is due to their environmentally friendly nature and lignocellulosic materials are derived from plants. If the cellulose resources can be fully utilized, much energy can be saved and the environmental pollution can be decreased [1].

Jute is a natural biodegradable fiber, largely produced in India, China, and Bangladesh. In recent years, the development of biodegradable materials from renewable sources has increased [2]. Jute fibers are durable with many advantages, which include low cost, low density, and light weight. Jute fibers are conventionally used as packaging material and carpet backing. Nowadays, jute fiber of improved qualities has attracted its use in different areas, namely, technical textiles, jute gunny sack, jute gunny bag, jute yarn, household textiles, and so forth [3]. Therefore, it is important to develop

new products from jute to regain its economic importance. Original cotton fiber is a natural soft fiber obtained from the boll of the cotton plant.

The largest producing areas of cotton are China, India, Pakistan, Bangladesh, Republic of Uzbekistan, Brazil, Australia, Greece, and Syria. Original cotton is stable with many advantages such as low cost, light weight, and easy possessing. The original cotton fibers are conventionally used in medical sector and household textiles. Presently, original cotton fibers are increasingly used in different items, like paper, fiber pulp, food casing, textile mills, spinning mills, knitting mills, and so forth. The original cotton production, however, is less than the actual demand. Therefore, synthesized cotton fibers can be used to fulfill the high demand for original cotton.

Acetic acid and alkali processing is an effective alternative method to fabricate jute cotton fibers [4]. This method also includes dewaxing and delignification. The fabricated cotton fibers derived from jute fibers possess improved properties [5]. The synthesized jute cotton fibers can be used for diverse purposes. In this present work, a new technique and chemical

process were developed to prepare cotton from jute fibers, and the result was compared with the characteristics of original cotton fiber.

2. Materials and Methods

2.1. Materials. Chemicals used in this study were ethanol approximately 96% (C_2H_6O), hydrogen peroxide 35% (H_2O_2), supplied by Brightchem Sdn Bhd. Malaysia, toluene ($C_6H_5CH_3$), acetic acid (glacial) 100% (CH_3COOH), titanium (IV) oxide (TiO_2), and potassium hydroxide (solid KOH), supplied by Mallinckrodt Baker, Inc., Sweden. The jute fibers were collected from Bangladesh Jute Research Institute (BJRI), Dhaka, Bangladesh.

2.1.1. Fiber Extraction. The raw jute fibers were cleaned and then washed with tap water to remove dust and other undesirable elements. After that, the jute fibers were air-dried for two days under direct sunlight. The middle parts of the jute fibers were taken and chopped into lengths of approximately 3 mm. Then, the chop fibers were placed in a forced air convection oven for drying to remove the moisture content, with a temperature of $105^\circ C$ for 24 hours to ensure that all the moisture has evaporated.

2.1.2. Dewaxing. The dewaxing was done by applying the Leavitt-Danzer method. In this process, two types of chemicals were used, namely, toluene ($C_6H_5CH_3$) and ethanol (C_2H_6O), with ratios of 2:1. The extraction process was done using the extraction column (Soxhlet extractor, Round Bottom Flask, Liebig Condenser, Heater, Membrane, and Thermometer). Then, the chopped jute fibers were immersed in the extraction column. This process was continued for 3 hours at $150^\circ C$. The collected fibers were later placed in the forced air convection oven for 24 hours at $75^\circ C$.

2.1.3. Delignification. The delignification was implied using acetic acid (CH_3COOH) and hydrogen peroxide (H_2O_2) in present titanium oxide (TiO_2) in a round bottom vector vessel. Then, the dewaxed jute fibers were placed in the round bottom vessel. This process was continued for 3 hours at $130^\circ C$. After this, the collected fibers were carefully washed and placed in the forced air convection oven for 24 hours at $70^\circ C$.

2.1.4. Alkali Treatment. Potassium hydroxide (6%) (KOH) was placed in 1000 mL of conical flask and the delignified jute fibers were immersed in the solution for eight hours at $30^\circ C$ and $60^\circ C$, respectively. After that, the collected samples were carefully washed and placed in the forced air convection oven for 24 hours at $70^\circ C$. Dried fibers used as synthesis cotton fibers characterization are shown in Figure 1.

2.2. Microstructural Analysis

2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy. The infrared spectra of the synthesized cotton fibers from jute and original cotton fibers were recorded on a Shimadzu FTIR Spectrophotometer with dynamic alignment system sealed

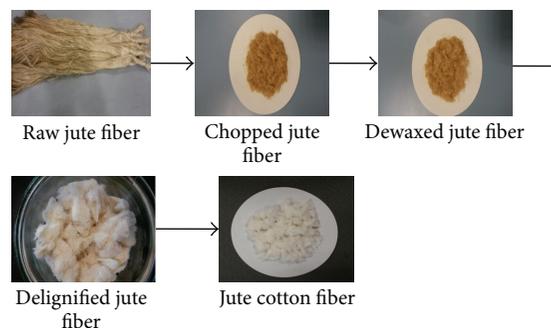


FIGURE 1: Flow chart of the synthesized jute cotton fibers.

interferometer with autodryer and wavenumber range was 350 to $7,800\text{ cm}^{-1}$. The obtained spectra are presented and discussed in Section 3.

2.2.2. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was used to study the thermal stability of synthesized cotton fibers from jute fibers and original cotton fibers. The thermal stability analysis was performed using Perkin-Elmer thermal analyzer (TGA). The specimen (10 mg) was heated from room temperature to $800^\circ C$ at a dynamic heating rate of $5^\circ C/min$ under N_2 using a flow rate of 100 mL/min .

3. Result and Discussion

3.1. Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectroscopic analyses of the cotton fibers from jute and original cotton fibers are shown in Figure 2. The wavenumber from 3600 to 3000 cm^{-1} corresponded to the stretching of H bonds in the OH groups [6, 7]. The IR spectrum showed the peak intensity of jute cotton fibers at 3336 cm^{-1} of OH groups whereas the original cotton fibers peak intensity was recorded at 3338 cm^{-1} .

Stretching of the C-H group of synthesized jute cotton fibers occurred at 2897 cm^{-1} while the original cotton fibers showed stretching at 2890 to 2362 cm^{-1} [8]. The C=O absorption band for jute cotton occurred at 1654 cm^{-1} and the original cotton fibers absorption band occurred at 1648 cm^{-1} [9]. The absorption band of synthesized jute cotton and original cotton fibers at 1313 and 1321 cm^{-1} can be attributed to the symmetrical deformation of NO_2 in the cellulose azo compound [10]. Therefore, the FTIR results proved that both synthesized jute cotton fibers and original cotton fibers possess similar properties.

3.2. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was carried out on the synthesized cotton fibers and original cotton fibers to determine the thermal stability. The thermal stability of synthesized cotton fibers and original cotton fibers is shown in Figure 3. The weight losses of synthesized cotton fibers and original cotton fibers can be illustrated in three stages: (1) dehydration of absorbed moisture and water ($<200^\circ C$), (2) the breaking of the cellulose

TABLE 1: Thermal characteristics of jute cotton fibers and original cotton fibers.

Sample names	T_i (°C) ^a	T_m (°C) ^b	T_f (°C) ^c	W_{T_i} (%) ^d	W_{T_m} (%) ^e	W_{T_f} (%) ^f	Activation energy, E_a (J/°K)
Jute cotton fibers	200	301	673	88.44	82.87	43.58	59.09
Original cotton fibers	39	296	492	81.32	71.74	35.10	52.25

^aTemperature corresponding to the beginning of decomposition.

^bTemperature corresponding to the maximum rate of mass loss.

^cTemperature corresponding to the end of decomposition.

^dMass loss of temperature corresponding to the beginning of decomposition.

^eMass loss of temperature corresponding to the maximum rate of mass loss.

^fMass loss of temperature corresponding to the end of decomposition.

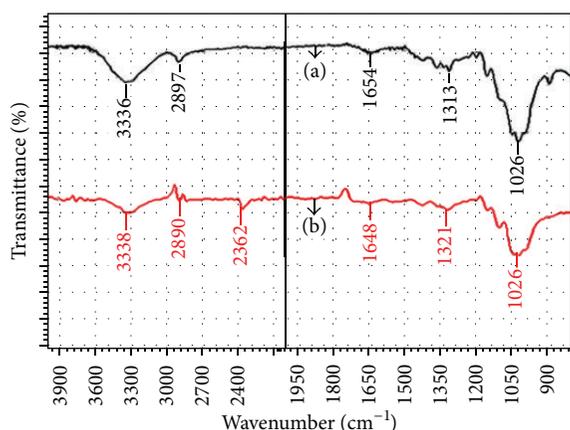


FIGURE 2: FTIR spectra of (a) jute cotton fiber and (b) original cotton fiber.

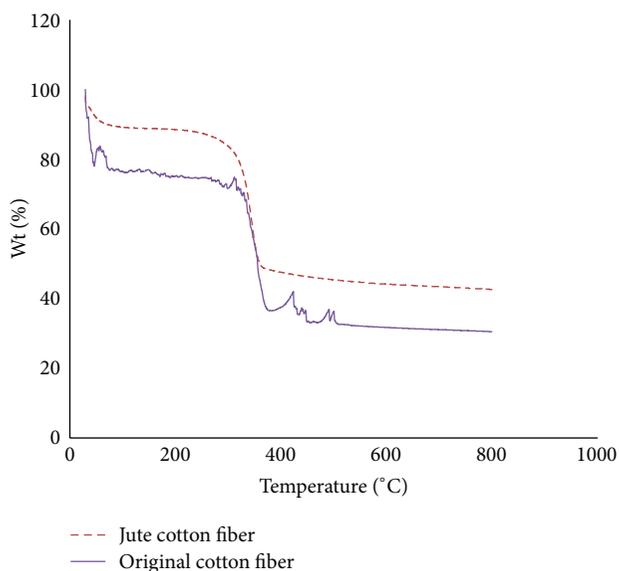


FIGURE 3: TGA curves of jute cotton fibers and original cotton fibers.

chain of C-C and C=O (200~380°C), and finally (3) aromatization (>380°C), the residual chair formation [11].

From the thermogravimetric analysis on synthesized cotton fibers, it is anticipated that dehydration is approximately

4.6% of water. According to Rahman et al. [12] there is no degradation up to 160°C. Above this temperature, the thermal property decreases gradually and decomposition occurs. The initial and final temperature decompositions (T_m , T_f) of jute cotton fibers were slightly higher than that of original cotton fibers which is shown in Table 1. The larger activation energy showed higher stability. The activation energy of jute cotton fibers was slightly higher than the original cotton fibers. Therefore, it can be assumed that the synthesized jute cotton fibers and original cotton fibers possess similar properties regarding thermal stability.

4. Conclusions

In this study, jute cotton fibers were synthesized by chemical processes. The FTIR spectrum showed that synthesized jute cotton fibers characteristic band was very similar to the original cotton fibers. The TGA result also showed that the maximum rate of mass loss, onset of decomposition, end of decomposition, and activation energy for synthesis jute cotton fibers were slightly higher than original cotton fibers. It can be concluded that synthesized cotton fiber characteristics were similar to the original ones.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Suitability of Aquatic Plant Fibers for Handmade Papermaking

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Increasing concerns for future fiber supplies in pulp and paper industries has shifted interest in nonwood sources from agriculture residues and aquatic plants. Aquatic plants with short growth cycles, in abundance, and with low lignin are a potential fiber source. Five aquatic plant species, *Cyperus digitatus*, *Cyperus halpan*, *Cyperus rotundus*, *Scirpus grossus*, and *Typha angustifolia*, were examined for fiber dimensions and chemical composition (cellulose, lignin) and compared with other nonwood plants. All aquatic plants possessed short (length, 0.71–0.83 mm) and thin (diameter, 9.13–12.11 μm) fibers, narrow lumen (diameter, 4.32–7.30 μm), and thin cell wall (thickness, 2.25–2.83 μm) compared with most other nonwood plants. Slenderness ratio ranged from 73.77 to 89.34 with *Typha angustifolia* having the highest ratio. Except for *Scirpus grossus*, the flexibility coefficient ranged from 52.91 to 58.08. *Scirpus grossus* has low Runkel ratio, 0.84 ± 0.17 . Fiber characteristics, short and thin fibers, Slenderness ratio >60 , flexibility coefficient within 50–75, and Runkel ratio <1 , are suitable for papermaking. Cellulose content of *Cyperus rotundus* ($42.58 \pm 1.32\%$), *Scirpus grossus* ($36.21 \pm 2.81\%$), and *Typha angustifolia* ($44.05 \pm 0.49\%$) $>34\%$ is suitable for pulp and papermaking. Lignin content in aquatic plants in the present study ranged 9.54–20.04% and below the wood lignin content of $<23\text{--}30\%$ encountered in pulp and papermaking. Handmade paper sheets produced for paperboard, craft, and decorative purposes are with permissible tensile strength, breaking length, and low moisture content.

1. Introduction

Population growth, better literacy, and development of communication and industrialization in developing countries increase worldwide paper products demand continuously [1]. In 2005, 17.4 million metric tons (9.27%) of nonwood fibers from 187.6 million metric tons global production of virgin pulp for paper and paperboard are produced [2]. In many countries, quantities of available wood are insufficient to meet the requirements and demands of pulp and paper especially in Mediterranean countries like Spain, Italy, and Greece [3–5]. In Malaysia, over one million tons of papers were produced in 2005 [6]. This would mean that more tropical trees need to be felled to sustain papermaking industry to meet the paper requirement and demand. To reduce the loss of rainforests, an attempt was made to find the alternative source of fiber for paper. Some alternatives have been used to

replace the wood fiber with nonwood derived fibers [1] from agriculture residues such as wheat and rice straw, sorghum stalks, jute, and hemp for paper production [7, 8].

Another alternative source of fibers for paper production is from aquatic plants found in lakes, ditches, rivers, ponds, and estuaries. They have short life cycle, grow massively, and due to their abundance can cause problems in irrigation channels water bodies [9, 10]. Besides, excessive growth of these aquatic plants can influence water management and ecosystem in ways such as affecting drainage, aesthetics, fishing activities, flood control, irrigation, and recreational and land values [11]. One way to control these plants is to use them as an alternative source for papermaking. Aquatic plants are nonfood plants and they have large differences in their physical and chemical characteristics [12, 13]. According to Ververis et al. [5], fiber dimension, lignin, and cellulose content of nonwood plants determine their suitability for

paper production. Under certain conditions, tearing resistance of the paper is highly dependent on fiber dimension, that is, fiber length [14]. Although the major source of fiber for paper production is from wood plant, nonwood aquatic plants with less lignin content have potentials to be used as an alternative fiber source [13].

Handmade paper industry is an environmental friendly and very promising industry for local entrepreneurship. Papers made from aquatic plants have multiple uses. They can be used for writing, food wrapping, tissue paper, and book mark and can be commercialized as value added materials for handmade crafts. Hence, the objectives of this study was to examine the fiber characteristics, derived values, and chemical composition of five aquatic plant species and compare them with other nonwood plant species that have been used to produce pulp and paper to determine their suitability for handmade papermaking. Additionally, handmade paper sheets produced of selected aquatic plants were tested for their quality with respect to tensile strength, breaking length, and moisture content.

2. Materials and Methods

2.1. Sample Collection. Aquatic plants, *Cyperus digitatus*, *Cyperus halpan*, *Cyperus rotundus*, *Scirpus grossus* and *Typha angustifolia*, found in abundance in ponds (N 02° 59.109', E 101° 41.432') at Universiti Putra Malaysia and wetland areas (N 02° 59.163', E 101° 39.000') around Selangor, Malaysia, were chosen and collected for this study. Plants were cleaned, leaves were removed, and stems were kept for determination of fiber dimension and derived values. Fresh stems were dried for determination of chemical composition and papermaking as described in detail below.

2.2. Fiber Dimension. Stems of aquatic plant were chopped into small pieces of 1 to 3 cm in length using a knife. One gram (1g) of stems was placed in a test tube and macerated with 10 mL 33.5% nitric acid (HNO₃) and boiled in water bath at 80°C for 2 hours. Macerated stems containing fibers were rinsed with distilled water to remove yellow stains of HNO₃ and placed in a small flask containing 50 mL distilled water. A drop of macerated fiber suspension was placed on microscope slide and a drop of Safranin was used to enhance the cell wall visibility. Fiber diameter, fiber length, cell wall thickness, and lumen diameter were viewed and measured, and image was captured and recorded under calibrated Axioskop NIKON compound microscope. The fiber dimensions determination was following the method of Ververis et al. [5]. All fiber dimensions were used to determine the derived values, slenderness ratio, flexibility coefficient, and Runkel ratio, following Tamolang [15] and calculated as shown below.

Slenderness ratio = fiber length (μm)/fiber diameter (μm).

Flexibility coefficient = fiber lumen diameter (μm)/fiber diameter (μm) \times 100.

Runkel ratio = cell wall thickness (μm)/fiber lumen diameter (μm) \times 2.

2.3. Chemical Composition. Of the five aquatic plant species, *Cyperus rotundus*, *Scirpus grossus*, and *Typha angustifolia* were chosen based on their fiber dimensions and derived values (lower and higher values as determined from Section 2.2 above) for evaluation of their chemical composition. The stems were ground and sieved with 250 μm sieve. Two grams (2g) of sample was weighted and placed in cellulose thimble and the cellulose was extracted by using Soxhlet apparatus with 2:1 alcohol acetone solution. After 4 hours of extraction, sample was placed in desiccators until obtaining the constant weight. The cellulose content determination was performed in triplicates. The cellulose, hemicelluloses, and lignin contents were calculated based on the formula described by Moubasher et al. [16] as follows.

$$\text{Cellulose content} = (Y - Z)/W \times 100.$$

$$\text{Hemicelluloses content} = (X - Y)/W \times 100.$$

$$\text{Lignin content} = (Z - V)/W \times 100.$$

V = weight of glass thimble (g), W = weight of extractive-free sample (g), Y = weight of glass thimble with sample after being treated with KOH (g), and Z = weight of the glass thimble with sample after being hydrolyzed with H₂SO₄ (g).

2.4. Pulping and Papermaking. Hundred gram (100 g) of dried stems of *Cyperus rotundus*, *Scirpus grossus*, and *Typha angustifolia* was cooked with 20 g sodium carbonate (Na₂CO₃) and 2 L of water at 140°C for 2 hours by using induction cooker. After 2 hours, the cooked samples were cleaned under water flow to remove the chemical and blended by using electronic blender. 50 mL of starch solution (1g of starch diluted in 1000 mL of distilled water) was then added to the pulp in an electronic mixture. Mould and deckle pouring method and couching technique was used in the papermaking process according to Hiebert [17].

2.5. Paper Quality. Moisture content of the produced paper sheet was determined by placing one gram (1g) of paper sheet on AD-4715 Infrared Moisture Determination Balance. The tensile strength and breaking length were tested for the paper sheet strips by using modified TAPPI (Technical Association of the Pulp and Paper Industry) 494 om-06 [18] standard method of tensile properties for paper and paperboard. Tensile strength and breaking length were calculated as shown below.

Tensile strength (kN/m) = Maximum breaking force (kN)/width of paper strip (m).

Breaking length (km) = 102 000 \times (Tensile strength (kN/m)/grammage (g/m²)).

2.6. Statistical Analysis. One way analysis of variance (ANOVA) followed by post hoc Duncan's multiple range test ($p < 0.05$) were conducted using SPSS program to compare aquatic plants species fiber dimensions, derived values, chemical composition, tensile strength, and breaking length. Principle Component Analysis (PCA) based on Bray Curtis similarity index was carried out using XLSTAT software

(Windows version 2013) to obtain the relationship between fiber dimensions, derived values, and chemical composition of aquatic plant species in this study with other nonwood plant species that have been used to produce different type of papers.

3. Results and Discussion

3.1. Fiber Dimensions and Derived Values. The fiber lengths of the aquatic plants ranged from 0.71 to 0.83 mm and are relatively shorter than those of other nonwood plants (Table 1). Of the five species, *Scirpus grossus* possessed longer fiber length (0.83 ± 0.02 mm), wide fiber diameter (12.11 ± 0.98 μ m), lumen diameter (7.30 ± 0.89 μ m), higher flexibility coefficient (58.08 ± 4.07), and low Runkel ratio (0.84 ± 0.17). Fiber length of *Scirpus grossus* is comparable with crop plants, *Zea mays* (0.88 mm). Besides fiber length, fiber diameter, lumen diameter, and cell wall thickness of nonwood plants also varied depending on the plant species and the parts (leaves, stems) from which the fibers are derived (Table 1) and this supported the observation made by Ilvessalo-Pfaffli [19]. As a comparison with hard-wood plant such as *Populus tremuloides* for kraft pulp, the fiber lengths are longer, 1.0–1.3 mm, and are reported to be suitable for coated paper production [20]. However, longer fiber length tends to give less fine of sheet structure [21, 22].

Derived values (slenderness ratio, flexibility coefficient, and Runkel ratio) measure the ability of fibers to bind each other in the paper sheet. Slenderness ratio for aquatic plant species studied ranged from 77 to 89.34, a ratio >60 which is attributed to the thin fibers (cf. with other nonwood plants, Table 1) suitable for producing high quality paper [5]. A combination of short and thin fibers usually will produce a good slenderness ratio, which is related to tearing resistance, paper sheet density, and pulp digestibility [28]. Comparatively, these values are close to slenderness ratio of 69.17–81.07 of *Hibiscus cannabinus* used to produce quality paper [29]. The trend of flexibility coefficient categorically placed *Scirpus grossus* (58.08) as the highest followed by *Cyperus halpan* (53.54) and *Cyperus digitatus* (52.91) and these values are relatively high compared with other aquatic plant, *Arundo donax* internode (49.20), commercial plant *Bambusa tulda* stalk (20.29), and crops plant of *Saccharum* sp. baggase (29.29) and are comparable with *Zea mays* residue (54.27) [5, 25–27]. Except for *Scirpus grossus*, *Cyperus halpan*, and *Cyperus digitatus* the flexibility coefficient (52.91–58.08) of aquatic plant species is within the preferable flexibility coefficient range of 50–75 [30]. Runkel ratio is good in *Scirpus grossus* (0.84 ± 0.17) and *Cyperus digitatus* (1.06 ± 0.14) compared with crop plants, *Saccharum* sp. (2.46) and commercial plant, *Bambusa tulda* (3.93) [25, 27]. The Runkel ratio >1 (e.g., 1.52 ± 0.18 as in *Typha angustifolia*) indicated that it is less flexible and stiffer and that it forms bulkier paper [5]. Low Runkel ratio and high fiber length resulted in good pulp strength properties [31]. Runkel ratio <1 is related to high flexibility coefficient [32] and gives good mechanical strength properties to the paper produced [28].

The principal component analysis (PCA) was performed to assess similarity in the fiber characteristics and derived

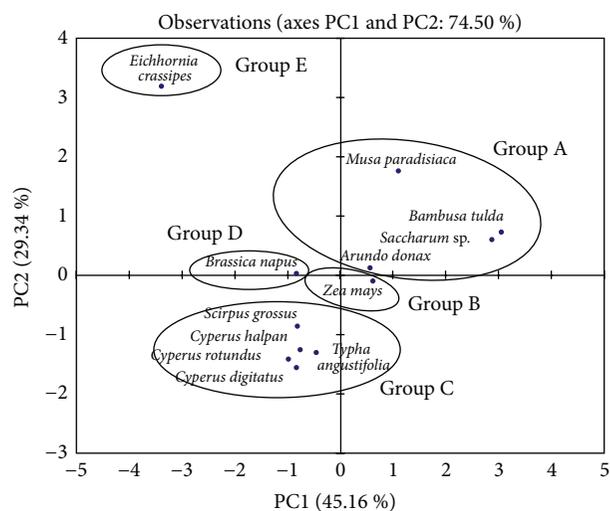


FIGURE 1: Principal component analysis (PC1 and PC2) of five aquatic plant species compared with other nonwood plant species based on their fiber dimensions and derived values.

values (slenderness ratio, flexibility coefficient, and Runkel ratio) of the aquatic plant species with other nonwood plants (Table 1) that have been tested for paper production (Table 2). The obtained results based on Bray-Curtis similarity index at 50% similarity showed the total variance of the first two components is 74.50% (PC1 has a total variance of 45.16% and PC2 29.34%) and the species were clustered into five distinct groups (A, B, C, D, and E, Figure 1). Aquatic plant species, *Cyperus digitatus*, *Cyperus halpan*, *Cyperus rotundus*, *Scirpus grossus*, and *Typha angustifolia*, are clustered in only one group, C, independent of four other nonwood plant species, group A (*Musa paradisiaca*, *Bambusa tulda*, *Saccharum* sp., and *Arundo donax*), group B (*Zea mays*), group D (*Brassica napus*), and group E (*Eichhornia crassipes*). Species in group B, D and E are suitable for production of writing or printing paper [5], composites and paperboard [22] and fiber plate, rigid cardboard and cardboard paper [26] (Table 2). According to Enayati et al. [1] and Kasmani et al. [33], a combination of nonwood/softwood and hardwood fibers can be promising and can have potential in papermaking.

3.2. Chemical Composition. Among the species studied, *Typha angustifolia* possessed comparatively higher percentages of cellulose and hemicelluloses content, $44.05 \pm 0.49\%$ and $54.84 \pm 4.27\%$, respectively. The cellulose content of all aquatic plant species was high and comparable with vegetable plants, *Brassica napus* (34.50%) and other aquatic plants, *Arundo donax* (36.70%), and *Typha* (pati) (36.80%) (Table 3). In addition, the percentage of cellulose content >40% was comparable with *Hibiscus cannabinus* [5], used to produce quality paper [29]. The holocellulose, a combination of cellulose and hemicellulose amounts to >65–70% of reported plant dry weight [34]. The cellulose content >34% indicates the plants are suitable for pulp and paper manufacturing. Cellulose content affects the strength and makes the fiber strand liable to natural and synthetic dye binding while

TABLE 1: Comparison of fiber dimension and derived values of aquatic and other nonwood plant species.

Species	Part	Fiber length (mm)	Fiber dimension				Derived value			Reference (s)
			Fiber diameter (μm)	Lumen diameter (μm)	Cell wall thickness (μm)	Slenderness ratio	Flexibility coefficient	Runkel ratio		
(1) <i>Cyperus digitatus</i>	S	0.72 ± 0.03^b	9.64 ± 0.39^{bc}	5.15 ± 0.40^{bc}	2.25 ± 0.14^b	76.85 ± 4.31^{ab}	52.91 ± 2.85^{ab}	1.06 ± 0.14^{ab}	Present study	
(2) <i>Cyperus rotundus</i>	S	0.71 ± 0.02^b	9.13 ± 0.47^c	4.32 ± 0.37^c	2.41 ± 0.16^{ab}	81.57 ± 4.95^{ab}	46.63 ± 2.56^{bc}	1.28 ± 0.13^{ab}	Present study	
(3) <i>Cyperus halpan</i>	S	0.73 ± 0.04^b	11.08 ± 0.55^{ab}	6.02 ± 0.53^{ab}	2.53 ± 0.18^{ab}	69.01 ± 4.52^b	53.54 ± 3.11^{ab}	1.02 ± 0.15^a	Present study	
(4) <i>Scirpus grossus</i>	S	0.83 ± 0.02^a	12.11 ± 0.98^a	7.30 ± 0.89^a	2.41 ± 0.16^{ab}	73.77 ± 7.32^{ab}	58.08 ± 4.07^a	0.84 ± 0.17^a	Present study	
(5) <i>Typha angustifolia</i>	S	0.83 ± 0.02^a	10.01 ± 0.66^{bc}	4.35 ± 0.42^c	2.83 ± 0.18^a	89.34 ± 5.62^a	42.52 ± 2.19^c	1.52 ± 0.18^b	Present study	
(6) <i>Eichhornia crassipes</i>	Lf	1.60	5.50	9.00	2.50	290.90	163.64	0.56	Goswami and Saikia [23]	
(7) <i>Arundo donax</i>	In	1.22	17.30	8.50	4.40	70.50	49.20	1.00	Ververis et al. [5]	
(8) <i>Musa paradisiaca</i>	S	1.55	22.00	14.20	5.50	70.50	64.55	0.77	Goswami et al. [24]	
(9) <i>Saccharum</i> sp.	Bg	1.51	21.40	6.27	7.74	70.56	29.29	2.46	Agnihotri et al. [25]	
(10) <i>Zea mays</i>	Rs	0.88	20.12	10.92	4.59	44.08	54.27	0.84	Kiaei et al. [26]	
(11) <i>Bambusa tulda</i>	St	1.89	17.00	3.45	6.78	111.20	20.29	3.93	Sharma et al. [27]	
(12) <i>Brassica napus</i>	St	1.20	13.10	8.60	2.25	91.00	64.00	0.58	Tofanica et al. [22]	

All values are given as mean \pm S.E. Alphabets in the same column indicate significant difference at $p < 0.05$ (DMRT), a > b > c. Aquatic plants (no. 1-7); crop plants (no. 8-10); commercial plants (no. 11); vegetable plants (no. 12). S: stem; Lf: leaf; In: internode; Bg: bagasse; Rs: residue; St: stalk.

TABLE 2: Types of paper produced from aquatic and other nonwood plant species.

Species	Part	Parameter tested	Paper properties tested	Paper types	Reference (s)
(1) <i>Eichhornia crassipes</i>	Lf	Physical properties	Fiber dimension, derived value	Greaseproof paper	Goswami and Saikia [23]
		Chemical properties	Cellulose, hemicelluloses, pentosan		
(2) <i>Arundo donax</i>	In	Paper properties	Degree of freeness, burst index, tear index, tensile index	Printing and writing paper	Ververis et al. [5]
		Physical properties	Fiber dimension, derived value		
(3) <i>Musa paradisiaca</i>	S	Chemical properties	Cellulose, lignin, ash	Greaseproof paper	Goswami et al. [24]
		Paper properties	Slenderness ratio, tearing resistance		
(4) <i>Saccharum</i> sp.	Bg	Physical properties	Fiber dimension, derived value	Writing and printing paper	Agnihotri et al. [25]
		Chemical properties	Cellulose, hemicelluloses, lignin, ash, silica		
(5) <i>Zea mays</i>	Rs	Paper properties	Burst index, tear index, tensile index, blister, double-fold number, degree of freeness	Fiber plate, rigid cardboard and cardboard paper	Kiaei et al. [26]
		Physical properties	Fiber dimension, derived value		
(6) <i>Bambusa tulda</i>	St	Chemical properties	Holocellulose, cellulose, hemicelluloses, ash, silica	Writing and printing paper	Sharma et al. [27]
		Paper properties	Tensile index, tear index, burst index, double-fold number		
(7) <i>Brassica napus</i>	St	Physical properties	Fiber dimension, derived value	Composites, paper and paperboard	Tofanica et al. [22]
		Chemical properties	Cellulose, lignin, ash		
		Physical properties	Fiber dimension, derived value		
		Chemical properties	Cellulose, holocellulose, lignin, ash		
		Physical properties	Fiber dimension, derived value		
		Chemical properties	Cellulose, holocellulose, pentosan, lignin, ash, silica		

Aquatic plants (no. 1-2); crop plants (no. 3-5); commercial plants (no. 6); vegetable plants (no. 7). Lf: leaf; In: internode; S: stem; Bg: bagasse; Rs: residue; St: stalk.

TABLE 3: Chemical composition of aquatic and other nonwood plant species.

Species	Part	Chemical composition (%)			Lignin	Types of paper produced	References
		Cellulose	Hemicellulose				
(1) <i>Cyperus rotundus</i>	S	42.58 ± 1.32 ^a	45.64 ± 1.12 ^a	9.54 ± 1.08 ^b	Cardboard, paper and paperboard	Present study	
(2) <i>Scirpus grossus</i>	S	36.21 ± 2.81 ^b	49.88 ± 0.71 ^a	13.44 ± 3.90 ^a	Cardboard, paper and paperboard	Present study	
(3) <i>Typha angustifolia</i>	S	44.05 ± 0.49 ^a	54.84 ± 4.27 ^a	20.04 ± 3.37 ^a	Cardboard, paper and paperboard	Present study	
(4) <i>Typha</i> (pati)	Wh	36.80	n/a	16.20	Cottage industry	Jahan et al. [35]	
(5) <i>Arundo donax</i>	In	36.70	n/a	18.50	Printing and writing paper	Ververis et al. [5]	
(6) <i>Musa paradisiaca</i>	S	59.18	n/a	18.21	Greaseproof paper	Goswami et al. [24]	
(7) <i>Zea mays</i>	Rs	47.33	n/a	21.33	Fiber plate, rigid cardboard and cardboard paper	Kiaei et al. [26]	
(8) <i>Bambusa tulda</i>	St	47.00	n/a	25.70	Printing and writing paper	Sharma et al. [27]	
(9) <i>Brassica napus</i>	St	34.50	n/a	20.60	Composites, paper and paperboard	Tofanica et al. [22]	

Mean in column with the different superscript (a > b > c) is significantly different (DMRT, $p < 0.05$) for present study. Aquatic plants (no. 1-5); crop plants (no. 6-7), commercial plants (no. 8); vegetable plants (no. 9). n/a: not available; S: stem; Wh: whole; In: intermode; Rs: residue; St: stalk.

TABLE 4: Measurement for determination of paper quality of selected aquatic plant species.

Species	Tensile strength (kN/m)	Breaking length (m)	Moisture content (%)
<i>Cyperus rotundus</i>	1.69 ± 0.18^a	731.68 ± 72.75^a	10.11 ± 0.04^b
<i>Scirpus grossus</i>	1.52 ± 0.21^a	612.39 ± 34.05^a	13.08 ± 0.41^a
<i>Typha angustifolia</i>	0.94 ± 0.20^b	410.11 ± 82.85^b	13.13 ± 0.11^a

All values are given as mean \pm S.E. Different alphabets in the same column of parameter indicate significant difference at $p < 0.05$; that is, $a > b$.

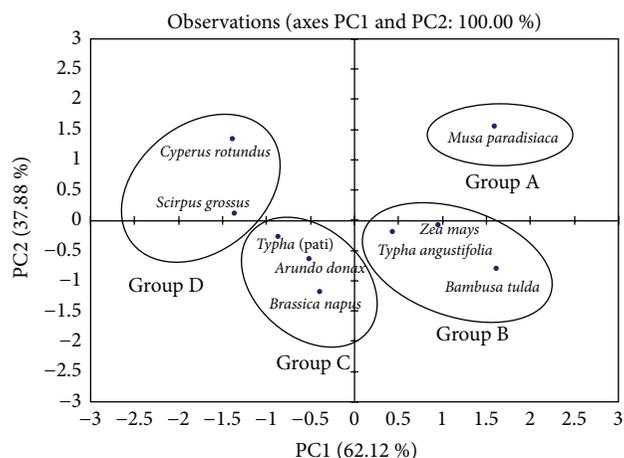


FIGURE 2: Principal component analysis (PC1 and PC2) of three aquatic plant species compared with other nonwood plant species based on their cellulose and lignin composition.

hemicelluloses is responsible for the water absorption by plant fibers and reduces internal fiber stress.

Lignin content was higher in *Typha angustifolia* ($20.04 \pm 3.37\%$) followed by *Scirpus grossus* ($13.44 \pm 3.90\%$) and it was lowest in *Cyperus rotundus* ($9.54 \pm 1.08\%$). *Cyperus rotundus* has the lower lignin content compared with *Typha (pati)* (16.20%) [35], *Arundo donax* (18.50%) [5], *Musa paradisiaca* (18.21%) [24], and *Zea mays* (21.33%) [26]. Moreover, lignin content in *Typha angustifolia* was similar with *Brassica napus* ($19.21\text{--}20\%$) [22, 36]. The lignin content for these studied species was lower than wood fiber lignin content of 23–30% for pulp and papermaking [13]. Dutt and Tyagi [28] reported that lignin content in *Eucalyptus* sp. was $>25\%$. However, all three species can be pulped in one-third of the time needed for hardwoods and softwood due to the lower lignin content [5]. Lignin was considered undesirable component during pulping and papermaking due to its unstable color and for being relatively dark and its hydrophobic surface caused unfavorable interfiber bond formation of hemicelluloses and cellulose [37].

Comparison of chemical composition of aquatic plants and other nonwood plants (vegetables, crops, and commercial plants) with their type of paper is shown in Table 3. The present study data and available data on nonwood plants were ordinated with PCA using lignin and cellulose composition. The biplot generated four main clusters (Figure 2). Aquatic plants are in two clusters: *Typha angustifolia* is in group B with *Zea mays* and *Bambusa tulda* while *Cyperus rotundus* and *Scirpus grossus* are in group D. Based

on fiber characteristics, cellulose and lignin content, plants in group B, can be utilized for production of fiber plate, rigid cardboard, cardboard paper, writing and content of printing paper (Table 3, [25, 27]). In group C, paper sheets derived from fibers and cellulose from these plants had been tested and were suitable for handmade paper in the cottage industry, composites, paperboard, and writing and printing paper (Table 3, [5, 22, 35]) for decorative purposes.

3.3. Paper Quality. *Cyperus rotundus* has the highest tensile strength (1.69 ± 0.18 kN/m) and breaking length (731.68 ± 72.75 m) (Table 4). The tensile strength of paper sheets produced from aquatic plants, *Cyperus rotundus*, *Scirpus grossus*, and *Typha angustifolia*, in this present study is in the range of 0.94–1.69 kN/m and this reflected the intimate structure of paper [38]. Its individual fibers, their arrangement, and the extent to which they are bonded to each other are key factors which contribute to tensile strength. Long fibers generally produced paper with higher tensile strength properties than paper from short fiber. However, interfiber bonding is considered as the most important factor contributing to the paper tensile strength. Jeyasingam [39] mentioned that breaking length for *Hibiscus cannabinus* was 4000 m ten times higher than the present study range of 410.11–731.68 m. Jahan et al. [40] also found that the breaking length of nonwood raw materials such as jute, cotton stalks, corn stalks, bagasse, saccharum, rice straw, and wheat straw varies in the range of 5511–7550 m. In addition, the breaking length values are in the range of 3650–5300 m for different types of paper, that is, offset, rag bond, and news print papers [38]. Hierarchically, paper moisture content was *Typha angustifolia* ($13.13 \pm 0.11\%$) $>$ *Scirpus grossus* ($13.08 \pm 0.41\%$) $>$ *Cyperus rotundus* ($10.11 \pm 0.042\%$). Moisture in paper varies from 2% to 12% depending on relative humidity, type of pulp used, degree of refining, and chemical used. Ideally a good quality paper possessed properties of comparatively high tensile strength and breaking length and lower moisture content. Other than being used for craft, wrapping, or decorative purposes, fibers derived from aquatic plant species as in this study may be suitable for newsprint production as their tensile strength is in the range of newsprint paper (0.90–1.79 kN/m) as reported by Caulfield and Gunderson [38].

4. Conclusion

Scirpus grossus, *Cyperus rotundus*, and *Typha angustifolia* are suitable aquatic plants species for papermaking based on their fiber characteristics, chemical composition, and physical properties. An abundance and availability of these plants can provide sustainable large biomass as raw fibers for pulp

and paper production. Handmade paper sheets produced for paperboard, writing, and printing paper used for craft, wrapping, and decorative purposes are with permissible tensile strength, breaking length, and low moisture content.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Water Absorption Behaviour and Its Effect on the Mechanical Properties of Flax Fibre Reinforced Bioepoxy Composites

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In the context of sustainable development, considerable interest is being shown in the use of natural fibres like as reinforcement in polymer composites and in the development of resins from renewable resources. This paper focuses on eco-friendly and sustainable green composites manufacturing using resin transfer moulding (RTM) process. Flax fibre reinforced bioepoxy composites at different weight fractions (40 and 55 wt%) were prepared in order to study the effect of water absorption on their mechanical properties. Water absorption test was carried out by immersion specimens in water bath at room temperature for a time duration. The process of water absorption of these composites was found to approach Fickian diffusion behavior. Diffusion coefficients and maximum water uptake values were evaluated; the results showed that both increased with an increase in fibre content. Tensile and flexural properties of water immersed specimens were evaluated and compared to dry composite specimens. The results suggest that swelling of flax fibres due to water absorption can have positive effects on mechanical properties of the composite material. The results of this study showed that RTM process could be used to manufacture natural fibre reinforced composites with good mechanical properties even for potential applications in a humid environment.

1. Introduction

The environmental consciousness as well as the government legislation around the world has encouraged the academic and industrial researches to develop eco-friendly, sustainable, and biodegradable composite materials, thus often referred to as “green composites” [1]. Renewable and biodegradable materials as alternative to synthetic fibres and polymers derived from petroleum used in traditional fibre reinforced polymer composites [2, 3].

The interest in natural plant fibres (flax, hemp, jute, kenaf, etc.) [4–7] as reinforcement in polymer matrix has grown quickly in the last decade. Several advantages in comparison with synthetic fibres can explain it. They have low density, are annually renewable, and therefore are low in cost. Natural fibres are biodegradable, are crucial at the end of life of products, and have comparable specific strength and modulus as traditional glass fibres. Industries as automotive [8, 9] and construction [10] have started the manufacturing of products using natural fibre, to improve the environmental impact

of the product due to the inexpensive price of natural reinforcements.

There are also some drawbacks in the use of natural fibre reinforced composites. Hydrophilic natural fibres are incompatible with hydrophobic thermosetting resins, and it is necessary to improve the adhesion between fibre and matrix, the use of chemical treatments [11, 12]. Natural fibres as reinforcement have been limited by their susceptibility to water absorption, due to their chemical composition being rich in cellulose, hydrophilic in nature. Water absorption results in the swelling of the fibre that could reduce the mechanical and dimensional properties of the composites [13–15] as a result of the appearance of microcracks at fibre-matrix space.

There are three major mechanisms [13, 16–18] of water absorption in fibre reinforced polymer composites: diffusion, capillary, and transport of water molecules, respectively. Diffusion mechanism occurs inside the microgaps between the chains of polymers. Capillary transport mechanism occurs in the gaps at fibre-matrix interface space, if during manufacturing process the impregnation of the reinforcement with

TABLE 1: Structural composition of flax fibre.

Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Pectins (wt%)	Microfibril angle (degree)	Moisture content (wt%)
71	18.6–20.6	2.2	2.3	6–7	10

TABLE 2: Comparison of the properties of flax and glass fibre.

Fibre	Density (g/cm ³)	Elongation at break (%)	Tensile strength (MPa)	Tensile modulus (GPa)
Flax	1.5	2.7–3.2	500–900	50–70
E-glass	2.5	2.5	2000–3500	70

the matrix has been incomplete. In natural fibre composites, the transport of water molecules through the microcracks that can appear in the matrix is especially important, as a result of the fibre swelling. According to this mechanisms, there are three cases of diffusion behavior [19, 20] known as Fickian diffusion model, anomalous or non-Fickian, and an intermediate case between Fickian and non-Fickian.

The manufacturing of natural fibre composites includes the use of thermoplastics polymer such as polypropylene, polyethylene, and polyamides combined with the natural fibre random mat or short fibres through injection molding, compounding, extrusion, or thermoforming processes. Automotive industry is a clear example, where their use for nonstructural components can be found [21] as interior glove box and door panels or exterior floor panels. In the case of natural fibre reinforced thermosetting matrix composite, the most used manufacturing process in the literature has been hand lay-up and liquid compression molding, for nonwoven or random mats due to the low costs associated with these techniques. Nowadays, research and industrial applications focus on the aligned natural fibre composites applications using continuous natural textile reinforcements like unidirectional (UD), woven, and noncrimp fabrics, at this time, commercially available. The potential of use of natural fibre fabrics will improve significantly the composite properties for engineering applications or high performance natural fibre composites. Additionally, in combination of thermosetting polymer matrices, it will allow the use of well-established manufacturing techniques as liquid composite moulding (LCM) processes, as resin transfer moulding (RTM) or vacuum infusion. Only a few studies [22] have been focused on the processing of natural fiber composites by LCM processes. This study will focus on the manufacture of flax fibre woven fabric reinforced bioepoxy composites by RTM process and the evaluation of their mechanical properties. In order to study the potential of use of these composites in outdoor applications or humid environmental conditions, the water absorption behavior of flax fibre bioepoxy composites at room temperature and various weight fractions of fibre has been investigated as well as its effect on the mechanical properties (tensile and flexural).

2. Materials and Methods

2.1. Materials. A 200 g/m² flax fibre balanced woven fabric (0°/90°), supplied by Lineo, Belgium, has been used as textile

reinforcement for the manufacturing of bioepoxy matrix composites. Table 1 shows the chemical composition of flax fibres [12]. Table 2 [1] shows the properties (mechanical and physical) of flax fibre compared to glass fibre.

A commercially available biobased epoxy resin, Super Sap CLR Epoxy supplied by Entropy Resins, USA, was used as polymer matrix in this work. According to technical data sheet of the manufacturer, Super Sap CLR Epoxy is a modified liquid epoxy resin. As opposed to traditional epoxies that are composed primarily of petroleum-based materials, this biobased epoxy resin contains in its chemical formulation (trade secret) biorenewable materials sourced as coproducts or waste of other industrial processes such as wood pulp (epoxidized pine oils) and biofuels production (nonfood grade vegetable oils). The biocontent by mass value is between 30.8% and 45.2% and uses biocarbon content number (ASTM D6866) and molecular structure to calculate total percentage of mass derived from biosources.

Super Sap INF Hardener is the curing agent employed. According to technical and material safety data sheets supplied by the manufacturer, it is a cycloaliphatic polyamine. Resin and hardener were mixed to a weight ratio of 100 : 33. The epoxy system (resin-hardener) has a biocontent by mass between 21% and 30%.

2.2. Manufacturing Process. Liquid composite moulding process (LCM) consists of the manufacture of composites from polymer matrix by the impregnation of a dry fibrous fabric inside of an enclosed mold with a low viscosity resin. The resin is injected into the mold by the pressure difference between the resin inlet and the air outlet. The pressure difference can be either positive as resin transfer moulding (RTM) process shown in Figure 1 or negative as vacuum injection process. The process begins with the injection of the resin into the mold and ends when the resin completes the chemical reaction of curing and the part is ejected. The polymerization reaction is highly exothermic and its duration is widely variable and depends on the type of resin, inhibitor used, mold temperature, and especially the ratio of resin to inhibitor. The injection pressure must be low enough to give the proper fabric impregnation and to ensure that it does not become displaced by resin flow inside the mold. This pressure varies between 0.5 bar in vacuum injection and 3 bar for pressure injection.

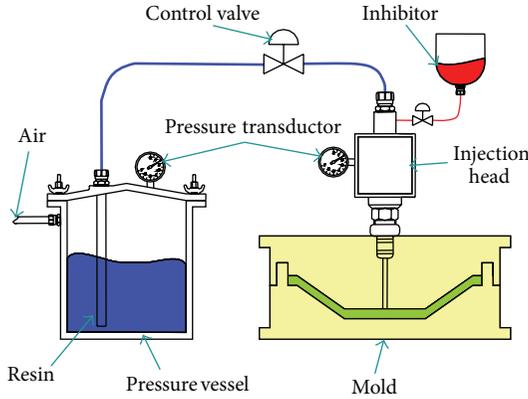


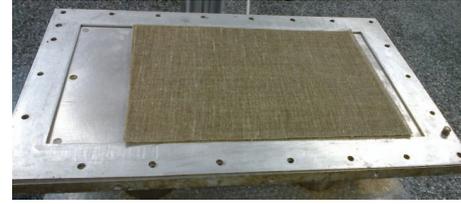
FIGURE 1: RTM manufacturing process under constant injection pressure.

The principal advantages of these LCM processes compared to the traditional hand lay-up are

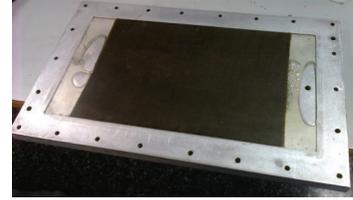
- (i) elimination of manual impregnation, avoiding risks to workers from inhalation of toxic styrene vapour present in thermosetting resins,
- (ii) both sides of the component having a good surface quality due to the closed mold,
- (iii) preventing induced anisotropy of the fabric, since it is preplaced into place before impregnation,
- (iv) increasing production rate due to the automation of some phases of the process.

In this study, resin transfer moulding process was used to manufacture 400×260 mm green composite laminates. To achieve different fibre volume fractions 0.4 and 0.55, a different number of layers of flax fabric were placed in the rigid mold, 6 and 8 layers, respectively. A metallic frame with the thickness (3 mm) of the composite laminate was placed between top and bottom aluminum mold. The mold was closed and resin injection was performed at a pressure of 1 bar, with vacuum assistance. The laminates were cured for 24 h at room temperature. Laminates were removed from the mold and finally postcured at 50°C for 2 hours in an oven. Figure 2 shows the flax fibre fabric reinforcement placed in the mold before resin injection and manufactured composite laminate.

2.3. Water Absorption Tests. To study the behaviour of water absorption of the flax fibre reinforced bioepoxy composites, water absorption tests were carried out according to UNE-EN ISO 62:2008 [23]. Composite samples were immersed in a water bath (deionized, 23°C) during a time period until the saturation was reached. Five specimens from each fiber volume fraction with dimensions $250 \text{ mm} \times 25 \text{ mm} \times 3 \text{ mm}$ (tensile samples) and $90 \text{ mm} \times 15 \text{ mm} \times 3 \text{ mm}$ (flexural samples) were cut from composite panels. An oven was used, firstly to dry all the samples at 50°C during 24 h, and then they were cooled to room temperature. The drying process was repeated, until the weight of the specimens was constant (mass m_1). After 24 h, the samples were removed from the water and were weighed (mass m_2) using a digital scale



(a)



(b)

FIGURE 2: Flax fibre fabric and flax fibre reinforced composite.

immediately after they were dried with dry cloth. This process was repeated, to weigh the specimens regularly (mass mt) over 32 days of water immersion.

At different periods of time, the percentage of weight gain was calculated and it was plotted versus square root of water immersion time. As a result, the average value was reported. The difference of weight between the sample in dry conditions and that after water immersion at time t was obtained as follows:

$$M_t (\%) = \frac{mt - m_1}{m_1} * 100, \quad (1)$$

where mt is the weight of the sample at time t during water immersion and m_1 is the weight of the dry sample at initial time.

According to the model developed [23] in order to describe the water absorption of one material following Fickian behavior or Fick's diffusion laws, the moisture content $c(t)$ as function of the time can be expressed as function of diffusion coefficient (D), the weight moisture (c_s) in the saturated material, and their thickness (d) as the following equation:

$$c(t) = c_s - c_s \frac{8}{\pi^2} \sum_{k=1}^{20} \frac{1}{(2k-1)^2} \exp \left[-\frac{(2k-1)^2 D \pi^2}{d^2} t \right]. \quad (2)$$

Therefore, if water absorption behavior follows Fickian diffusion pattern, it can be described with the following formula [13, 14, 24]:

$$\frac{M_t}{M_\infty} = 4 \sqrt{\frac{Dt}{\pi h^2}}. \quad (3)$$

At initial absorption stage, water absorption (M_t) at time t increases linearly with \sqrt{t} and M_∞ denotes the quantity after infinite time or maximum weight gain when material approaches at saturation point. The average diffusion coefficient (D) of the composites was calculated by

TABLE 3: Water absorption and diffusion coefficients of flax fiber composites after the immersion in water.

Fibre volume (%)	Saturation water absorption M_s (%)	Slope (k)	Diffusion coefficient, D , $\times 10^{-6}$ (mm^2/s)
40 (6-layer flax)			
Tensile specimen	6.23	6×10^{-5}	1.63
Flexural specimen	6.56	6×10^{-5}	1.47
55 (8-layer flax)			
Tensile specimen	8.71	1×10^{-4}	2.32
Flexural specimen	9.76	1×10^{-4}	1.85

the measurements of weight gain and the initial slope of the weight gain curves versus square root of time, as follows:

$$D = \pi \left(\frac{kh}{4M_\infty} \right)^2, \quad (4)$$

where h is the thickness of the specimens, M_∞ is the maximum weight gain, and k is slope of the initial plot $M(t)$ versus \sqrt{t} .

2.4. Mechanical Tests

2.4.1. Tensile Test. To evaluate the tensile properties of the dry composite samples and of the samples with water absorption, tensile tests were conducted according to UNE-EN ISO 527-4:1997 [25]. An Instron 5960 universal testing machine with a load cell of 30 kN was used with a crosshead speed 2 mm/min. Ten rectangular specimens of each fibre content were cut from the manufactured composite laminates. Five specimens (250 mm \times 25 mm \times 3 mm) were tested for each case, dry or wet samples. Stress-strain curves were obtained and the average values for tensile strength, tensile strain at tensile strength, and tensile modulus were reported as a result.

2.4.2. Flexural Test. Flexural tests were conducted according to UNE-EN ISO 14125:1999 [26] to determine the flexural properties of the flax composites with and without water absorption. Universal testing machine (Instron 5960, 30 kN load cell) was used to carry out three-point bending tests, with a span of 60 mm between supports and a crosshead speed applied of 2 mm/min. Ten rectangular specimens of each fibre content were cut from the manufactured composite laminates. Five specimens (90 mm \times 15 mm \times 3 mm) were tested for each case, dry or wet samples; the average values for flexural strength, strain, and modulus were reported as a result.

2.4.3. Morphological Analysis: SEM. The tensile fracture surfaces of dry and water immersed composite specimens were observed with (SEM) JEOL-JSM 6300, 20 kV scanning electron microscope. To make the samples conductive, it is necessary to vacuum-coat them with a thin film of gold.

3. Results and Discussion

3.1. Water Absorption Behavior. The water absorption of the composite samples was calculated with (1). The weight gain (%) as a function of square root of time for the tensile and

flexural specimens after water immersion at room temperature and different content of fibre is shown in Figure 3.

For the samples with 6 layers of flax (0.40 fibre volume fraction) after 768 h of water immersion, the maximum percentage weight gain is 6.23% for tensile samples, and 6.56% for flexural samples. This slight difference for the same fibre volume fraction can be explained due to the variability of the natural constituents of the fibre. Plant fibre reinforcements can exhibit significant inconsistency in their properties. Chemical composition, dimensions, and surface density of the fibre can be affected due to the conditions of the growing [27, 28].

In the same way, maximum percentage weight gain for the specimens with 8 layers of flax (0.55 fibre volume fraction) immersed for 768 h is 8.71% for tensile samples, and 9.76% for flexural samples.

As can be seen, for all the samples, the process of water absorption is at the beginning linear. After it slows and finally after extended immersion time, the samples approaches to the saturation stage. Therefore, for all the samples, its behavior of water absorption can be modeled as diffusion process type Fickian.

As the fibre volume fraction increases, for all samples, the initial rate of the process and the maximum water absorption increases. This phenomenon can be explained [29] by the hydrophilic nature of vegetable fibres, as flax fibres, due to the fact that they are cellulose fibres. If the vegetal fibres are exposed to a process of water absorption, the fibre swells. Besides, as a result of the swelling, microcracks can appear in a brittle matrix as epoxy resin and, in turn, can lead to largest transport of water through the fiber matrix interface.

Table 3 shows saturation water absorption values and the diffusion coefficients calculated for water immersed specimens at room temperature (23°C). The results show that the diffusion coefficient and maximum water content values increase as the fibre content increases. Samples with a higher fibre content have a greater diffusion coefficient, due to the fact that absorption of water is higher, as a result of a higher content of cellulose. The formation of microcracks at the interface region, induced by fibre swelling, can increase the diffusion transport of water via them. Furthermore a capillarity mechanism becomes active; water molecules flow through the interface of fibre and matrix, leading to a greater diffusivity [30]. The difference of diffusion coefficient values for the same fibre volume fraction composites can be explained again, due to the scattering of natural constituents of the fibre, and it can be assumed.

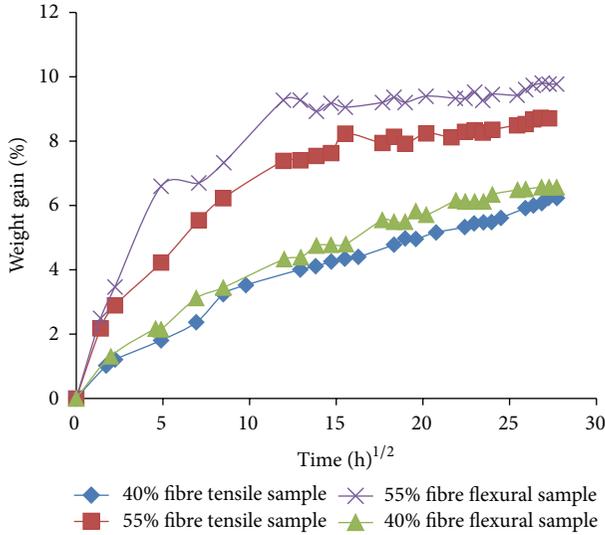


FIGURE 3: Curves of water absorption for the different flax composite samples.

3.2. Effect of Water Absorption on the Mechanical Properties

3.2.1. Tensile Properties. Figures 4 and 5 show the results of the tensile strength and strain versus fibre volume, respectively, for the samples without (dry) and with water absorption (768 h water immersed). For the dry samples, their tensile strength increases with the increase of fibre content. This enhancement in flax reinforced composite strength is the result of higher loads supported by the fibres, due to the higher load transfer from the matrix to them. As it can be seen, the water immersed samples have a higher tensile strength compared to tensile strength of the dry samples. It may be attributed to the swelling of the fibres as a result of the water absorption in high quantities. The gaps between the fibre and the matrix that can appear during manufacturing process due to a poor impregnation or the shrinkage of the resin cure could be filled up and therefore can eventually lead to an improvement of the mechanical properties, in this study, an increase of the tensile strength.

This effect was reported by Karmaker et al. [31]; it was studied if the fibre swelling by the water absorption could fill up the gaps between jute fibers and polypropylene matrix, as a result of the thermal shrinkage of the matrix melt. To fill up these gaps, can result, during the fracture stage, in a higher shear strength between the fibers and matrix. Dhakal et al. [13] found that the ultimate tensile stress of hemp reinforced unsaturated polyester composites with a fibre volume fraction of 0.26 (5-layer nonwoven hemp fibre) after a period of water immersion was higher compared to the same samples without water absorption. It was also attributed to the filling up of the gaps between fibre and the matrix, as a result of the swelling of the fibre.

The microcracks that can appear in a brittle matrix (as an epoxy resin) due to the fibre swelling can lead to a weak bonding between the fibres and the matrix and in turn can lead to composite failure. However in this study, this effect

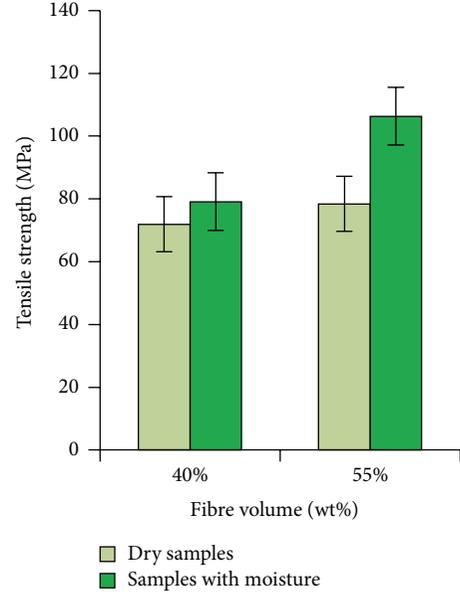


FIGURE 4: Tensile strength versus fibre volume.

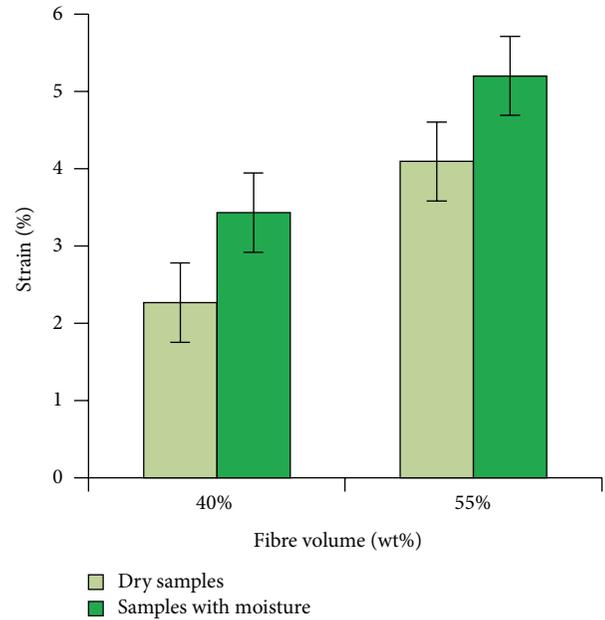


FIGURE 5: Tensile strain versus fibre volume.

seems to have less influence. The resin used as matrix is an epoxy resin modified with the addition of epoxidized pine oil. Epoxidized vegetable oils (EVO) can form elastomeric networks [32] as a result of its polymerization with the suitable curing agent. EVO can be added into conventional synthetic epoxy resin to be used as natural plasticizer or toughening additive [33–35] to reduce its rigid and brittle behavior.

After immersion in water, Figure 4 shows that the tensile strength of the samples reinforced with 6 flax layers increases 10%, and the same behavior is observed for the samples with 8 layers, where the tensile strength increases 35%.

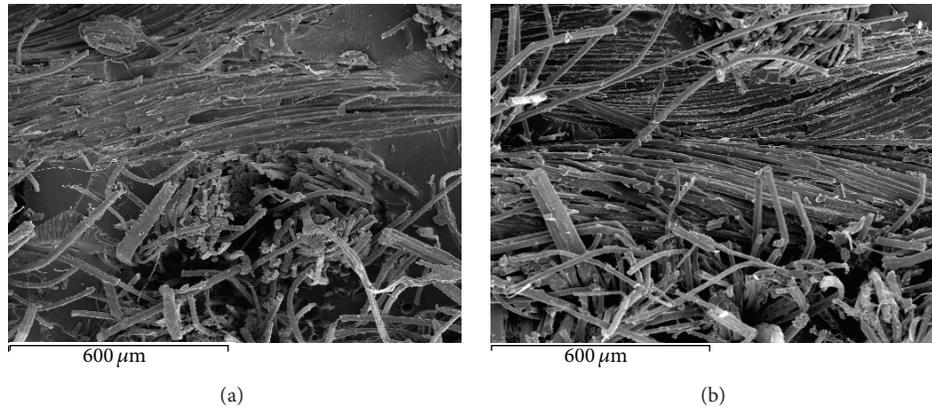


FIGURE 6: SEM tensile fracture images of dry composite samples with fibre content (a) 40 wt%, (b) 55 wt%.

As can be seen in Figure 5, for all the samples with water absorption, the tensile strain values increase compared to the values of the dry samples. For 40 wt% flax reinforced samples, the strain increases 51% and 27% for 55 wt% flax samples. It can be due to the water absorption causing the plasticization of flax composite samples. As it was reported for similar composites [36, 37], the water absorbed by the composite causes mainly the swelling of natural reinforcement, but also the plasticization of both the resin and the natural fibres.

Dhakal et al. [13] have reported similar results for hemp fibre reinforced unsaturated polyester composites, where it was found that the failure tensile strain values for samples with different fibre volume fractions increase after water absorption process, compared to the values obtained before the immersion in water.

The effect of water absorption on mechanical properties of the composite can be understood if its effect on their constituents, the matrix, the fibre, and the fibre-matrix interface region is studied. The SEM micrographs of the tensile fracture surface of composite specimens support these results.

3.2.2. SEM Micrograph of Tensile Fracture Surface. Figures 6(a) and 6(b) show the SEM images of the tensile fracture surface of flax reinforced epoxy composites without water absorption (dry samples) with fibre contents of 40 and 55 wt%, respectively. Fibre breakage, matrix fracture, fibre debonding, and fibre pull-outs can be observed after tensile test for both composites. It is clearly seen in the images, the fibre content on the fracture surface. The composite with lower fibre content (40 wt%) shows an increase in matrix rich regions compared to the composite with higher fiber content (55 wt%). Lower fibre content will lead to low mechanical properties, due to the fact that there are less fibres that can support the transferred load from the matrix.

For all water immersed samples in Figure 4, tensile strength increased compared to the dry specimens. Water caused the swelling of the fibres, and it was attributed to the filling up of the gaps between the fibre and the matrix. This effect could lead specifically to an increase in the mechanical properties of the composite. Gaps formed during the manufacturing process due to a poor impregnation of

the reinforcement or to thermal shrinkage of the resin cure. With the swelling of the fibre, the empty space fibre-resin can disappear, and the fibres exert pressure on the matrix, which results in a perfect adhesion. The SEM image in Figures 7(a) and 7(b) shows matrix region for 40 wt% fibre reinforced sample in dry conditions and for 40 wt% water immersed sample, respectively. This SEM image shows an enhanced or stronger bonding between the fibers and the matrix in wet conditions compared to the other sample in dry conditions, which results in a more efficient transfer of stress along the fibre-matrix interface before composite failure. Therefore in this case, it results in an increase of the composite strength after water immersion. Similar effect was also observed in dry and water immersed samples with 55 wt% fibre content.

In addition, the fracture surface of dry samples after tensile test showed flax fibre breakage in a more brittle manner, compared to fracture surface of water immersed samples, as it can be observed in Figures 8(a) and 8(b) for 40 wt% fiber content composite sample. In wet conditions, it is seen that fibre surface is rougher and some split into thinner fibrils occurs, caused by water absorption. The plasticization of flax composite samples caused by water absorption was found to increase the tensile strain values of all samples after water immersion compared to dry samples. The matrix rich zones seem to show the same behavior before and after the water absorption, and besides, they are not perceptible microcracks in the matrix around the fibre, in the case of the water immersed samples, maybe due to the higher flexibility of the epoxy resin used. Similar fracture surface was also observed in dry and water immersed samples with 55 wt% fibre content. Note that wet samples probably lost part of the water uptake during the sample preparation for SEM.

3.2.3. Flexural Properties. Figures 9 and 10 show the results of the flexural strength and strain versus fibre volume, respectively, for the samples without (dry) and with water absorption (768 h water immersed).

For the dry samples flexural strength increased as fibre content increases. This enhancement of the composites flexural strength is due to the increase of transferred load to the fibres, because of the higher adhesion at interface zone

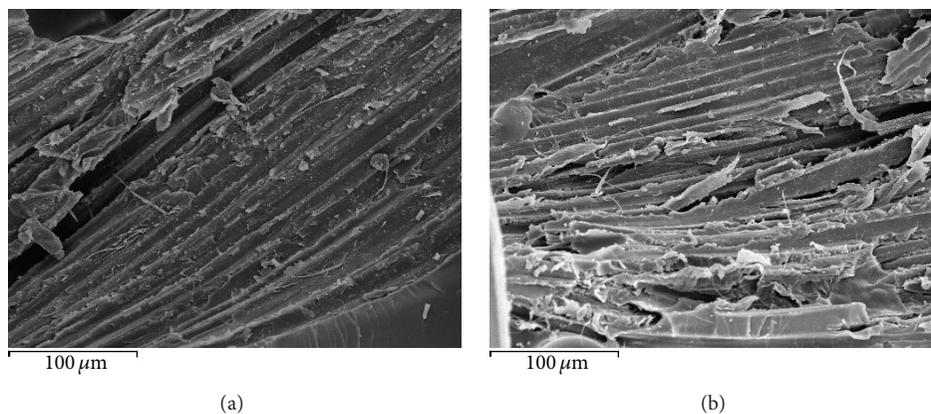


FIGURE 7: SEM images of fibre-matrix adhesion of 40 wt% fibre content samples (a) in dry conditions and (b) after water immersion.

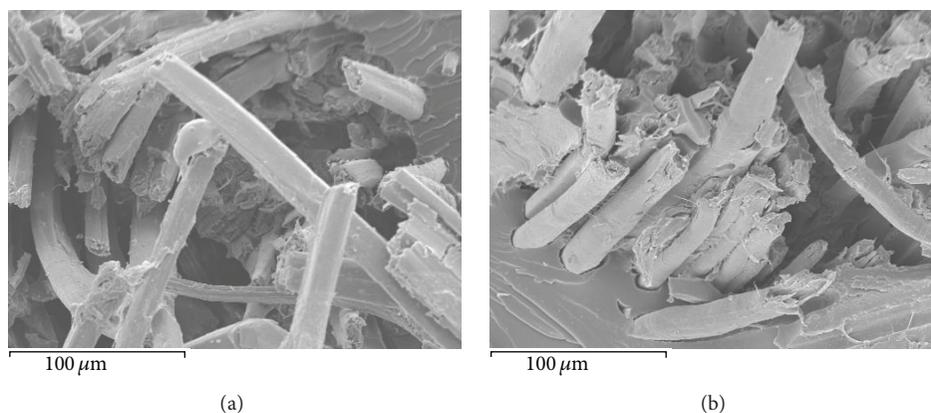


FIGURE 8: SEM images of fracture surface and fibre breakage: (a) dry composite sample, (b) water immersed composite sample.

(fibre-matrix) region, and due to the property of cellulose fibres as flax fibre to support bending loads [38].

The flexural failure mode for both dry and water immersed samples occurs in the same way. The specimen fails suddenly in a linear mode at the bottom surface of the specimen. As a result of the fact that there is no interlaminar failure at the thickness of the specimen, shear failure mode does not occur.

As the fibre volume fraction increases (Figure 9), flexural strength for water immersed samples decreases. This decrease can be attributed to the increase in the percentage of water absorption that can lead to the formation of higher number of microcracks as a result of fibre swelling which in turn weaken fibre-matrix interface region when bending loads are applied.

In this study, to observe that the 6 flax layers' samples (40 wt% fiber content) have a higher flexural strength after water immersion, compared to dry samples, an increase of 25.5% was found. It could be due to swelling of the fibres, previously mentioned, that can fill up the gaps between fibre and matrix, increasing the bonding between them, which results in an increase of mechanical properties. However for 55 wt% specimens (8-layer flax), flexural strength of the water immersed samples decreases by 20% compared to dry samples.

An increase of water absorption quantity (Figure 3) as occurs in the 55 wt% fibre flexural specimens compared to 40 wt% fibre specimens decreases their flexural strength. It may be caused by the weak interfacial adhesion between fibre and matrix [15], as a result of the appearance of hydrogen chemical bonds between the cellulose fibre (flax fibres) and the water molecules [37].

Flexural strain of the samples with water absorption, as can be seen in Figure 10, increased compared to dry samples. After water immersion, once the loss of cellulose has taken place [39] natural fibre reinforced composites approach to be ductile. The molecules of water behave as plasticizer elements, leading to an increase of the maximum strain of the composite after water absorption [40].

3.2.4. Effect of Water Absorption on Tensile and Flexural Modulus. Table 4 lists the obtained values of tensile and flexural modulus of the samples without (dry) and with water absorption (wet, 768 h water immersed) after tensile and flexural tests. A change was found in the values of modulus as a result of the water absorption. Tensile modulus decreased for all samples after water immersion compared to dry specimens. Tensile modulus decreases 28% and 21% for 0.4 and 0.55 fiber volume fraction samples, respectively.

TABLE 4: Tensile and flexural modulus values of flax composite.

Composite specimens	Fibre volume (wt%)	Tensile modulus (GPa)		Flexural modulus (GPa)	
		Dry	Wet	Dry	Wet
6-layer flax	40	7.24	5.16	7.77	8.67
8-layer flax	55	7.67	6.06	6.96	4.82

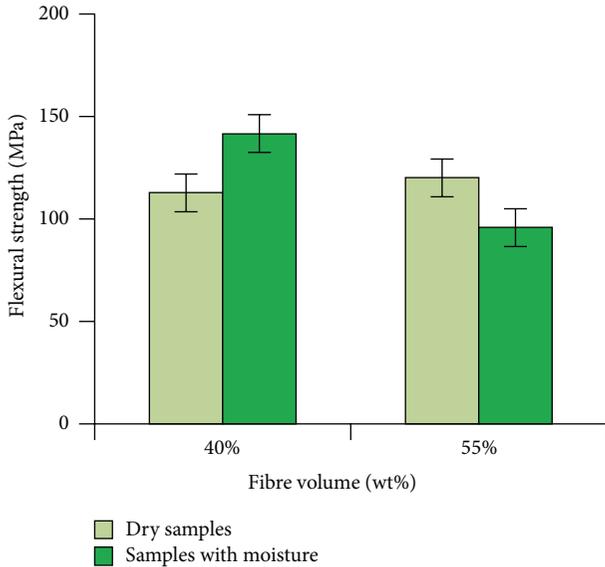


FIGURE 9: Flexural strength versus fibre volume.

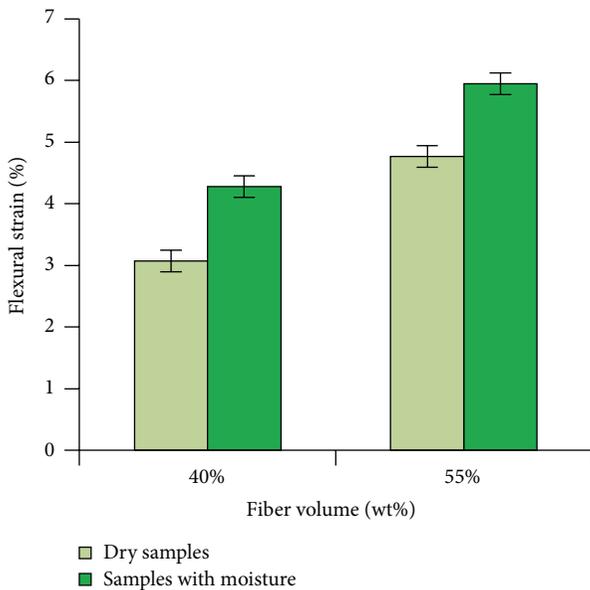


FIGURE 10: Flexural strain versus fibre volume.

Tensile modulus as being dependent on the fibre property in a composite material can be affected as a result of water absorption, whereas the tensile strength of the composite is more sensitive to fibre-matrix interface region properties.

Water absorption does not affect in negative way the flexural modulus. The effect of water absorption is different

depending on the fibre volume fraction. Flexural modulus of 40 wt% fibre content wet specimens increases 11% compared to dry samples. However, flexural modulus decreases in specimens with higher fibre content, hence higher water content. The flexural modulus of 55 wt% fibre wet samples decreases by 30% compared to dry samples. It is possible to assume the effect of the water absorption on the fibre and its effect on the modulus to be less critical for flexural failure than in tensile failure mode.

4. Conclusions

This study showed that RTM process could be used to produce high performance natural fibre composites with flax fibre fabric and bioepoxy matrix. This process is an environmental friendly alternative to the use of petroleum-based synthetic fibers and resins. The effect of water absorption on the mechanical properties of flax reinforced bioepoxy composites has been studied by the immersion of the samples in water at room temperature. It shows that water absorption increases with an increase in fibre weight fraction due to a higher cellulose content. At room temperature, it was found that composites follow water absorption Fickian behavior. The diffusion coefficient values obtained in the order of 10^{-6} mm²/s are in agreement with the range of values reported, for other natural fibre reinforced composites. It can be concluded that the results suggest that swelling of flax fibers in the composite material as a result of water absorption can have positive effects on mechanical properties. Tensile strength of all water immersed studied specimens is higher compared to the dry samples due to a stronger interfacial bonding between the fiber and the matrix. Flexural properties decrease as water absorption content increases. Tensile modulus was found to decrease with water absorption as a sensitive property of the fibre. Flexural modulus decreases in higher fibre content specimens after water absorption. This flax fibre composites show their potential use in outdoor applications due to the exposure to water absorption not affecting negatively their mechanical properties.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Water Absorption and Thermomechanical Characterization of Extruded Starch/Poly(lactic acid)/Agave Bagasse Fiber Bioplastic Composites

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Water absorption and thermomechanical behavior of composites based on thermoplastic starch (TPS) are presented in this work, wherein the concentration of agave bagasse fibers (ABF, 0–15 wt%) and poly(lactic acid) (PLA, 0–30 wt%) is varied. Glycerol (G) is used as starch (S) plasticizer to form TPS. Starch stands as the polymer matrix (70/30 wt/wt, S/G). The results show that TPS hygroscopicity decreases as PLA and fiber content increase. Storage, stress-strain, and flexural moduli increase with PLA and/or agave bagasse fibers (ABF) content while impact resistance decreases. The TPS glass transition temperature increases with ABF content and decreases with PLA content. Micrographs of the studied biocomposites show a stratified brittle surface with a rigid fiber fracture.

1. Introduction

Nowadays, the interest in bioplastics is growing for market niches such as packaging, agriculture, or automotive parts among others. They are classified in biodegradable and biobased/nonbiodegradable. In 2014, their total global production capacity reached 1.67 million tons, where 643,000 tons corresponded to biodegradable plastics [1]. By 2018, the production capacity is expected to reach more than 6 million tons, where 1.06 million will correspond to the biodegradable type [1]. The main sources of biomass to produce bioplastics are grains (usually corn), sugar cane bagasse, potatoes, and castor oil. It is reported that other natural sources such as cellulose and corn stover will also become an important raw material [1].

Since starch (S) is an economical biopolymer that is contained in many natural products, it is attractive as a source to make biodegradable plastics [2]. In dry form, depending on the source and characterization method, starch shows a melting temperature (T_m) that varies from 200°C [2] to 220 [3] or even 240°C [4]; however, with 10 % of humidity, its T_m decreases to 160°C [3]. It is mainly composed of amylose and

amylopectin which show very different physical and chemical properties [2, 4, 5].

Starch has to be plasticized to lower its high T_m [3] and processing temperature to avoid degradation before [6] it melts. Plasticification with water, glycerol, sorbitol, sugars, or amino acids lowers its T_m and its glass transition temperature (T_g) [6] forming a thermoplastic starch (TPS) and increasing its moldability. Glycerol (G) is the plasticizer most commonly used for starch in proportions ranging from 20 to 50% by weight. Unfortunately, materials based on starch have low mechanical properties because of its hydrophilic character [7–9]. To overcome that problem, TPS has been mixed with other polymers (forming polymer blends) [3, 4], or with reinforcing agents (e.g., natural or synthetic fibers) [2, 5, 7]. Natural fibers as reinforcing materials offer some advantages; among them the following may be mentioned: improvement of some mechanical properties of the polymer matrix [10, 11], minimization of environmental pollution [9], and lower production costs; however, natural fibers present the limitation that processing temperatures are restricted to less than 200°C.

TABLE I: Composite formulations.

S, g	G, g	TPS*, g	PLA, g	ABF, g	PLA wt% in polymer blend [•]	ABF wt% in composite [▼]
70	30	100	0	0	0	0
63	27	90	10	0	10	0
56	24	80	20	0	20	0
49	21	70	30	0	30	0
70	30	100	0	11.11	0	10
63	27	90	10	11.11	10	10
56	24	80	20	11.11	20	10
49	21	70	30	11.11	30	10
70	30	100	0	17.65	0	15
63	27	90	10	17.65	10	15
56	24	80	20	17.65	20	15
49	21	70	30	17.65	30	15

*TPS represents the mixture of S and G. [•]Polymer blend represents the mixture of TPS and PLA. [▼]Composite represents the mixture of TPS, PLA, and ABF.

Dufresne and Vignon in an early work on starch/fiber composites reported that thermomechanical properties of potato starch films were improved when they were mixed with cellulose nanofibers, showing also a decrease in moisture sensitivity, while maintaining biodegradability. Additionally, they found that increasing the glycerol content the equilibrium moisture increased and that such parameter decreased when the fiber content was augmented [5].

Huneault and Li studied mixtures of TPS with poly(lactic acid) (PLA) using maleic acid as a compatibilizer. They reported that Young modulus (E) and tensile strength increased when PLA content was increased [12]. An increase in E and tensile strength of TPS was reported using poly(lactic acid) fibrillation for reinforcement [13].

Although there are several works that follow the effect of PLA or natural fibers on moisture absorption and mechanical properties of TPS, there are very few reports on the effect of the simultaneous addition of both materials to the TPS. Furthermore, there is only scarce data on properties of TPS composites containing cellulosic fibers that were obtained as a byproduct of an industrial process. Teixeira et al. reported the use of cassava bagasse to obtain fiber reinforced TPS and PLA/TPS blends, but tensile strength did not increase significantly and the fiber essentially acted as a filler [14]. Castaño et al. found that reinforcing a TPS/PLA/PVA blend with pehuen cellulosic husk, the increase on mechanical properties was small [15]. Using pineapple fibers in TPS/PLA blends, an improvement in mechanostatic properties and water resistance was reported [16]. Cellulose derivatives have also been used to reinforce starch [17].

Using PLA [18, 19] or PCL [20] as polymer matrix with *agave sisalana* (sisal) as reinforcer, the results showed an increase in storage [18, 19], flexural [18], and tensile moduli [20].

In this work, the effects of the amount of PLA and/or agave bagasse fibers on moisture absorption and mechanical and thermal properties of TPS are reported. This is the first report on the application of agave bagasse fibers to reinforce TPS/PLA blends, which are discarded fibers from industrial processes.

2. Experimental

2.1. Materials. The materials used in this work were corn starch (IMSA) with 10% humidity, glycerol QP (Golden Bell Products), agave bagasse (tequilana Weber blue var.) fiber, PLA (Ingeo Biopolymer 3521D Industries Leben), and Magnesium Nitrate (Fermont). To prepare TPS, after the starch was dried for 24 h at 60°C, it was manually mixed with glycerol (30 wt%) until a homogeneous mixture was obtained. TPS was mixed with different amounts of PLA and/or fiber (Table 1), in a corotating twin-screw extruder (Leistritz Micro 27 equipment GL/GG 32D) to obtain a continuous cord of polymer blend or composites that were pelletized after extrusion. The pellets of the different materials were first dried at 60°C until a constant weight was obtained; then, they were molded by thermal compression in a Schwabenthan Polystat 200T compression equipment at 180°C and 200 bars during 2.5 minutes, maintaining pressure for 10 more minutes during the cooling stage.

2.2. Equilibrium Moisture. First, composites were dried at 60°C for 24 h; then the material was weighed and placed at 25°C in a closed chamber maintained at a relative humidity of 53% (saturated solution of magnesium nitrate). The composites weight was recorded periodically until a constant weight was obtained.

2.3. Mechanical Tests. Mechanodynamic tests were carried out following ASTM D5023-01, using a thermomechanical analyzer (TA Q800 DMA) and the following conditions: temperature range, -85°C to 150°C, heating rate, 2°C/min, three-point bending clamp, and frequency of 1 Hz. Mechanostatic tests were carried out at 25°C following ASTM D638-04 for stress-strain (Instron 4411, crosshead speed: 5 mm/min), ASTM D790-03 for flexure (Instron 4411), and ASTM D6110-04 (Instron, Ceast 9050) for Charpy impact testing.

2.4. Thermal Characterization. Thermal behavior of the samples was followed by DSC (Q Series DSC Q100, TA

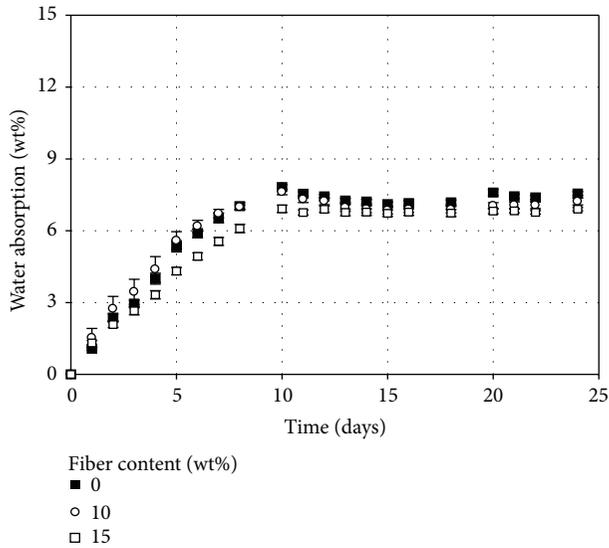


FIGURE 1: Moisture absorption of TPS/PLA/Fiber composites as a function of time for the polymer blend and composites containing 20 wt% PLA.

Instruments), using ASTM D3418-03. Heating rate was 10°C/min from 20 to 180°C.

2.5. Morphology. Samples were observed by Field Emission Scanning Electronic Microscopy (FE-SEM (Tescan, Mira3)). The samples were frozen in liquid nitrogen for 5 minutes before fracture. Subsequently, the samples were dried at 60°C before FE-SEM observation.

3. Results

3.1. Moisture Absorption. Figure 1 shows moisture absorption of the polymer blend and the composites containing 20 wt% PLA. Such figure illustrates that the rate of moisture absorption decreases as the ABF content increases and that equilibrium is reached in approximately two weeks. Similar moisture absorption behavior was obtained for the other materials.

For moisture absorption, it can also be noticed that an increase in ABF content reduces the equilibrium moisture value (Figure 2); that behavior can be explained in terms of the lower hydrophilic character of the fiber comparing with the TPS. Like in this case, it has been reported that composites of TPS with sugarcane bagasse fibers showed a decrease in moisture equilibrium when fiber content was increased [21]. Additionally, since PLA is a less hydrophilic polymer than TPS, independently of fiber content, increasing PLA concentration causes a decrease in the moisture absorption capacity of the composite (Figure 2).

3.2. Thermomechanical Analysis. In Figure 3 the storage modulus (E') is presented as a function of temperature for the composites containing 20 wt% of PLA. There, an overlapping plateau for the 3 samples can be observed from -30 to 40°C;

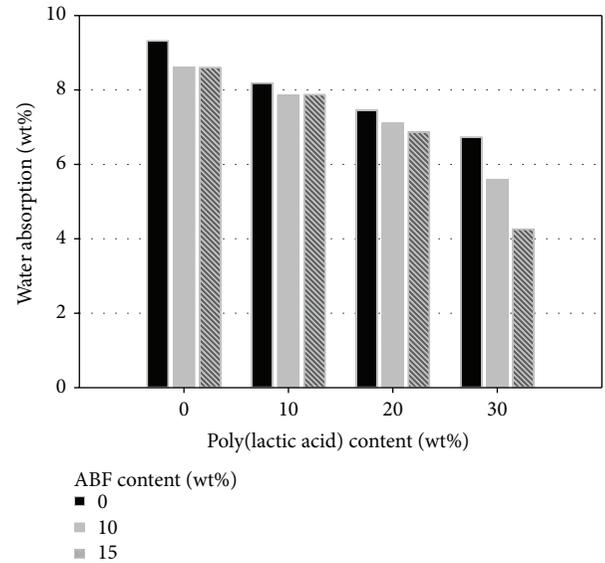


FIGURE 2: Equilibrium moisture of polymer blends and composites varying PLA content.

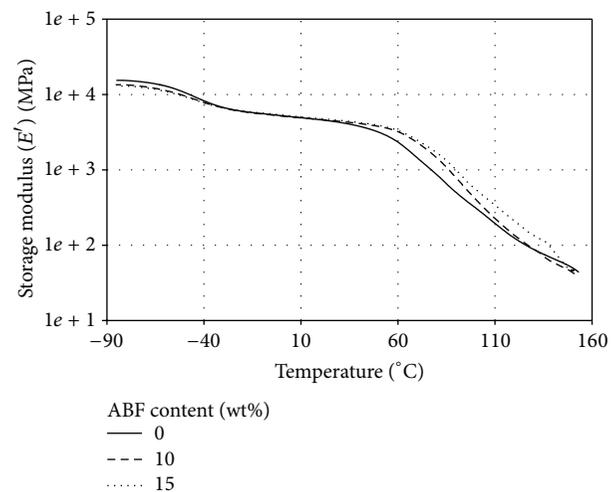


FIGURE 3: Storage modulus as a function of temperature for the polymer blend and composites containing 20 wt% of PLA.

however, the composites maintain the plateau E' value for about 10°C more than the polymer blend. Such additional temperature resistance before E' decay is important for outdoor thermoplastic applications and indicates that the fiber acts as a reinforcing material due to its rigidity and hydrogen bonding between the polymer blend and the ABF. Similar storage modulus behavior was obtained for the other composites. Such type of effect has been reported for TPS reinforced with cellulose fibers [22].

The storage modulus at 25°C of the studied composites is shown in Figure 4. Such figure indicates that higher storage moduli are obtained with the inclusion of ABF and/or PLA, and such increase is larger as more PLA and/or ABF are added. The reinforcement effect of PLA and ABF along with hydrogen bonding leads to a decrease in chains mobility. It

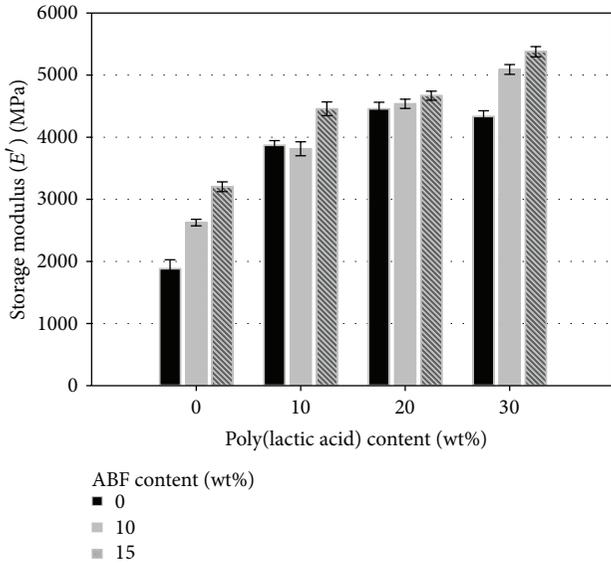


FIGURE 4: Storage modulus of polymer blends and composites at 25°C, varying PLA content.

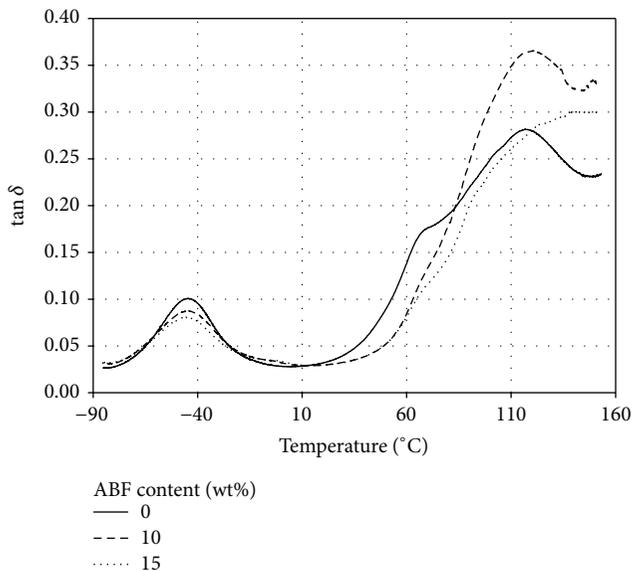


FIGURE 5: $\tan \delta$ versus temperature for polymer blend and composites containing 20 wt% PLA.

has been reported that modulus increases with fiber content [7, 22, 23] due to the high compatibility between TPS and cellulose fillers [5, 10]. Reports about it include bleached leaf wood fibers [24], fibers from bleached eucalyptus pulp [25], flax and ramie fibers [26], wood pulp [27], and tunicin whiskers [28–30].

Figure 5 shows $\tan \delta$ versus temperature for the composites containing 20 wt% of PLA. This figure shows that the peaks appear in three regions: (a) around -55°C (T_g of glycerol), (b) at $54\text{--}57^\circ\text{C}$, which is attributed to T_g of PLA, and (c) at $115\text{--}130^\circ\text{C}$ that corresponds to T_g of S.

TABLE 2: T_g of starch in polymer blends and composites.

PLA content in polymer blend, wt%	ABF content in composites, wt%		
	0	10	15
10	120°C	124°C	132°C
20	115°C	120°C	130°C
30	111°C	114°C	127°C

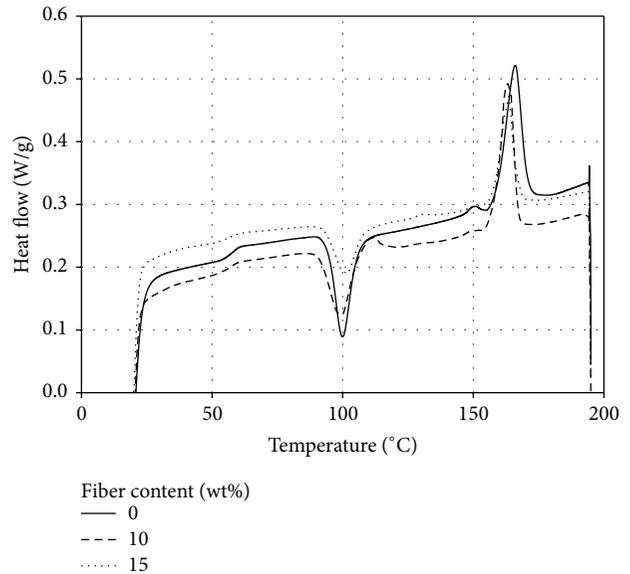


FIGURE 6: Thermograms of the polymer blend and composites containing 20 wt% of PLA.

Using $\tan \delta$ results of the polymer blend and composites containing different amounts of PLA and ABF, the T_g values of TPS are presented in Table 2. The values indicate that an increase in PLA content promotes a decrease in T_g ; such behavior can be explained by the lower T_g value of PLA compared to that of the starch ($T_g > 110^\circ\text{C}$) [3, 4]. In Table 2, it can also be noticed that for constant PLA content, there is an increase in T_g as fiber content increases; the T_g displacement can be attributed to the decrease of starch chains mobility and the H-bond interactions between ABF and TPS [7, 22, 24].

3.3. Thermal Analysis. The DSC thermogram (Figure 6) shows the thermal transitions of the polymer blend and composites containing 20 wt% of PLA. For the curves, at approximately 60°C , a change in slope can be observed due to the T_g of PLA. Those temperature values are presented in Table 3. The small decrement in T_g for the composites with respect to the pure PLA obtained here (62°C) can be attributed to glycerol migration, as Li and Huneault reported [31]. In addition, Martin and Avérous reported a small decrease in T_g of PLA by the presence of glycerol [32]. For the composites containing the larger amount of fiber (15 wt%), the T_g of PLA shows a slight decrease by enhanced PLA chain mobility. Jaafar et al. reported a decrease in T_g of PLA, which

TABLE 3: T_g of PLA in polymer blends and composites.

PLA content in polymer blend, wt%	ABF content in composites, wt%		
	0	10	15
10	57.0°C	57.1°C	54.5°C
20	57.0°C	57.3°C	55.5°C
30	57.0°C	57.0°C	56.0°C

TABLE 4: T_c of PLA in polymer blends and composites.

PLA content in polymer blend, wt%	ABF content in composites, wt%		
	0	10	15
10	100.0°C	100.7°C	99.1°C
20	99.9°C	99.8°C	101.0°C
30	98.9°C	100.4°C	100.2°C

TABLE 5: T_m of PLA in polymer blends and composites.

PLA content in polymer blend, wt%	ABF content in composites, wt%		
	0	10	15
10	163.0°C	164.5°C	161.0°C
20	165.9°C	163.6°C	163.4°C
30	166.1°C	165.9°C	163.2°C

they attributed to the inclusion of Kenaf fibers that increased PLA chains mobility because fibers separate PLA chains [33].

The exothermic peak that appears at approximately 100°C is related to PLA crystallization (T_c), as a result of the interaction of PLA and TPS, [32]. T_c values are shown in Table 4, where no noticeable effect can be seen for a fiber or PLA concentration increase (equivalent to TPS concentration decrease). Teixeira et al. reported a small decrease in the T_c of PLA using cassava bagasse [14].

For the polymeric materials of Figure 6, the small variation in the slope of the curves indicates that the T_g of S appears at 110–130°C. Those values correspond to the $\tan \delta$ peaks shown in Figure 5.

Figure 6 also shows peaks between 110 and 130°C due to T_g of starch, which coincide with the T_g obtained by mechanodynamic tests, which confirms that increasing fiber content increases T_g .

The endothermic peaks at the high temperature zone correspond to PLA melting temperature (T_m). The peak temperature values presented in Table 5 show that slight changes in PLA melting temperature correspond to an increase with PLA content and a decrease with ABF addition. Such decrease can be explained by the interference that fibers may cause to allow PLA crystallization. Before the PLA melting peaks, the correspondent small shoulder is attributed to rearrangement of lamellar fractions formed during PLA crystallization [34], or premelting of small crystals.

3.4. Mechanostatical Tests. Even though mechanodynamic tests allowed the thermomechanical characterization of

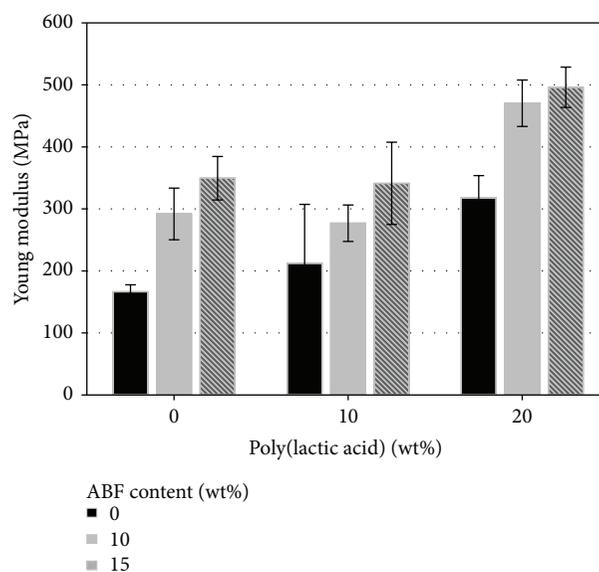


FIGURE 7: Young modulus of polymer blends and composites at 25°C, varying PLA content.

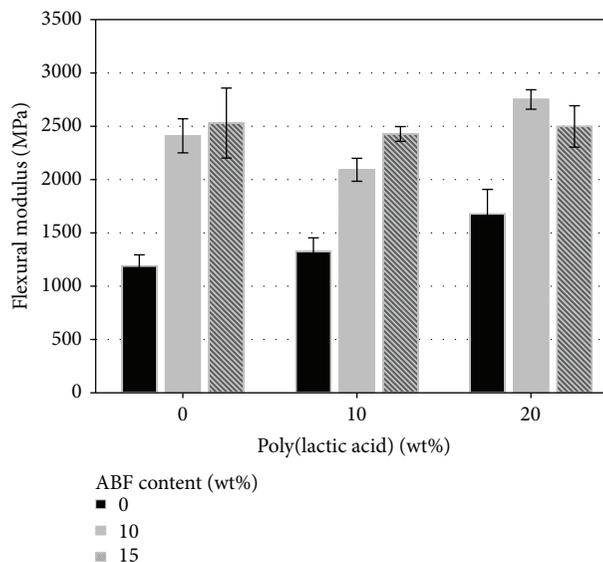


FIGURE 8: Flexural modulus of polymer blends and composites at 25°C, varying PLA content.

extruded materials, mechanostatical tests of some of the composites are included to confirm their moduli values pattern, as well as to determine impact resistance behavior. In Figure 7 Young modulus of polymer blends and composites as a function of PLA and fiber content is shown. The inclusion of PLA and/or ABF promotes an increase in modulus. Those patterns are in agreement with the storage modulus values obtained at 25°C (Figure 4).

Figure 8 shows flexural modulus of the polymeric materials as a function of PLA and fiber content. For this parameter, an increase in PLA and/or fiber content leads to composites

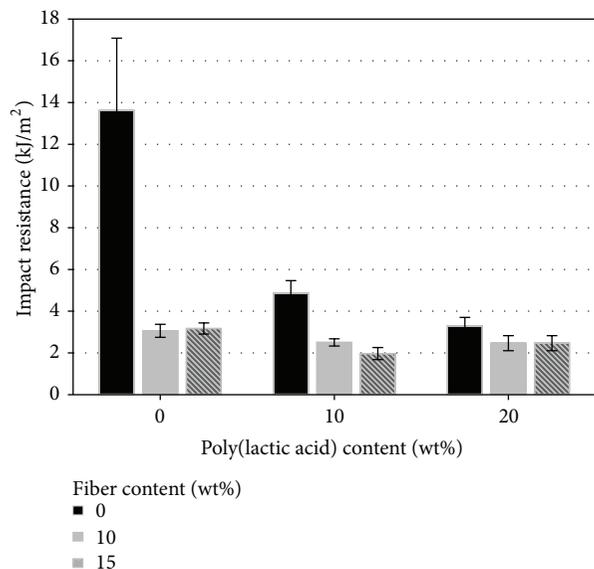


FIGURE 9: Impact resistance of polymer blends and composites at 25°C varying PLA content.

with higher flexural modulus, supporting the results obtained for the other moduli.

In Figure 9, it can be noticed that the increase in rigidity of the TPS caused by the addition of PLA and/or ABF leads to a large decrease in impact resistance.

3.5. Morphology. In Figure 10, micrographs of fractured samples of (a) TPS, (b) polymer blend containing 20 wt% of PLA, and (c) 80 TPS/20 PLA w/w, with 15 wt% ABF composite are shown. In Figure 10(a), uniform gelatinized starch granules can be observed. Figure 10(b) shows a stratified brittle surface. The fibers in the composite can be seen in Figure 10(c), and a rigid fracture is noticed.

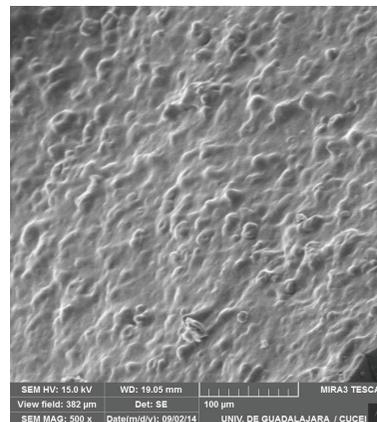
4. Conclusions

Blends of TPS and PLA and composites of TPS/PLA/ABF prepared by extrusion followed by compression molding were characterized. The reinforcing effect of PLA and/or ABF in TPS led to an increase in moduli and a decrease in moisture absorption and impact resistance. The TPS glass transition temperature increased with ABF content and decreased with PLA content.

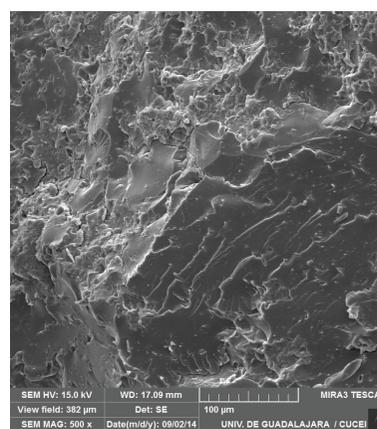
The reinforcing effect of PLA was enhanced by the incorporation of ABF, although the reduction in impact resistance is not convenient. That kind of behavior is expected generically for rigid materials; nevertheless, the wood appearance and biodegradability, along with the increase in moduli as well as thermal resistance, and the decrease in water absorption justify the production of this type of composites for many applications.

Conflict of Interests

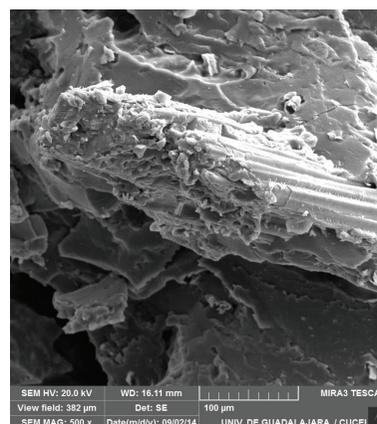
The authors declare that there is no conflict of interests regarding the publication of this paper.



(a)



(b)



(c)

FIGURE 10: SEM images of polymeric materials: (a) TPS, (b) polymer blend containing 20 wt% PLA, and (c) 80 TPS/20 PLA w/w, with 15 wt% ABF composite.

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Research Article

Rheological Behavior of Renewable Polyethylene (HDPE) Composites and Sponge Gourd (*Luffa cylindrica*) Residue

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The present study reports the results of rheological behavior of renewable composites, based on a matrix of high density polyethylene (HDPE), made from ethanol distilled from sugarcane, and lignocellulose filler from waste generated in the processing of sponge gourds for bathing use. The composites were prepared with 10, 20, 30, and 40%wt of filler in a twin-screw extruder. The materials were analyzed in a parallel plate rheometer and a melt-flow indexer. The composite morphology was determined by scanning electron microscopy. The composite viscosity increased with filler content, suggesting possible formation of filler agglomerates. This result was confirmed by Cole-Cole diagrams.

1. Introduction

Knowledge of the rheological properties of melted polymers is important because it permits selecting the best material for a determined application and processing technique [1]. Molar mass, size distribution of macromolecules, number of structural conformations, and the possible entanglement of polymer chains are factors responsible for the large differences in flow between various polymers during processing. The flow properties of viscoelastic fluids also depend on temperature, deformation rate, and processing time [2].

Besides these aspects, during processing, by either extrusion or injection molding, polymers are subjected to various types of deformation due to the complex geometry of the devices used. Rheological testing provides information on the deformations and strains of polymers and their composites under flow conditions, to enable understanding and predicting their final morphology and thus their properties [3].

There are only a few reports in the literature on the rheological behavior of HDPE composites of fossil origin (called conventional HDPE here) combined with cellulose.

To the best of our knowledge, there are no published studies of composites made of totally renewable polyethylene. González-Sánchez et al. [4] studied the rheological behavior of composites made of HDPE or polypropylene (PP) with 10, 25, 40, and 48% by weight of cellulose fiber before and after five reprocessing cycles. The fiber used was eucalyptus pulp. The effects of shear rate, fiber content, and type of matrix were analyzed in the virgin and reprocessed composites. The rheological data, obtained by capillary rheometry, scanning electron microscopy, and thermogravimetry, showed a decline in viscosity of the HDPE reprocessed at low shear rates. This decrease was more pronounced in the composites containing higher fiber concentrations, due to the thermal degradation of the fibers at low shear rates (lower than 100 s^{-1}). The authors also observed a greater loss of pseudoplasticity of the PP composites than those made with HDPE. In another study of HDPE composites, Li and Wolcott [5] also assessed the rheological properties with a capillary rheometer and used different cellulose filler, from maple and pine logs with different diameters. The authors observed

the wall slip velocity and its dependence on the wood content, type of filler, and shear stress. According to literature [6, 7], the wall slip effects are generally observed in the flow of highly viscous two-phase materials in rheometers, pipes, or any channel with smooth walls. Near the smooth, solid boundary, the local microstructure is depleted because the suspended particles could not penetrate the solid walls. Li and Wolcott [5] also analyzed the extensional flow, finding that the extensional viscosity is more dependent on the wood content than on the species. Mohanty and Nayak [8] studied the viscoelastic behavior of composites of HDPE and sisal fiber, also using capillary rheometry. They observed that the composites viscosity increased with the incorporation of fiber, a finding also reported by other researchers, and that treatment of the polyethylene with maleic anhydride caused an increase in the viscosity due to the better adhesion of the polymer matrix to the fiber, which was confirmed by scanning electron microscopy. Besides this, other dynamic properties (storage modulus, G' , loss modulus, G'' , and $\tan \delta$) also increased with cellulosic reinforcement.

The objective of this study was to investigate the rheological behavior in a parallel plate rheometer of a totally renewable composite made of polyethylene derived from ethanol with different concentrations of added filler from sponge gourd processing residue (10, 20, 30, and 40%wt).

2. Experimental

2.1. Raw Materials. The high density polyethylene (HDPE) SHC 7260 (Braskem, Brazil) was obtained from sugarcane ethanol. Its density is 0.959 g/cm^3 and the melt-flow index is 7.2 g/10 min (190°C ; 2.16 g). The sponge gourd residue (cellulosic filler) was provided by the company Bushings Bonfim, state of Minas Gerais, Brazil. This filler has density of 1.3 g/cm^3 , particle size of $<0.15 \text{ mm}$, and moisture content of 10.7% by weight.

2.2. Composite Preparation. The HDPE composites with 10, 20, 30, and 40%wt of sponge gourd residue were processed in a Tecktril model DCT-2 corotating interpenetrating twin-screw extruder. The cellulosic filler was conditioned before processing in an oven with air circulation for 24 hours at a temperature of 60°C . Before addition of the material in the extruder, the polymer and the milled filler were manually premixed. The extrusion conditions were as follows: rotating speed of 300 rpm; feeder rotation of 15 rpm; temperature in processing zone 1: 90°C , zones 2 to 5: 140°C , zones 6 to 9: 160°C , and head: 180°C . The obtained pellets were heated at 60°C to remove moisture.

2.3. Composite Characterization

2.3.1. Melt-Flow Index (MFI). Before performing this test, the samples, in the form of pellets, were dried in an oven with air circulation for 24 hours at 60°C . The melt-flow index (MFI) (ASTM D1238) [9] was measured in a Dynisco Kayeness Polymer Test Systems model LMI 4003 melt indexer.

2.3.2. Melt Rheology. The oscillatory flow measurements, namely, the complex viscosity, η^* , the storage modulus, G' , and the loss modulus, G'' , of the pure HDPE and its composites were determined in a TA Instruments rheometer, model AR 2000. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials. Dynamic frequency sweep test (strain: 0.3%; frequency: 0.1 to 600 rad/s; and temperature at 170°C) was subsequently performed to determine the dynamic properties of the materials, using a parallel-plate geometry with 25 mm of diameter and a gap set at 0.5 mm.

Stress relaxation experiments are the fundamental way in which relaxation modulus, $G(t)$, can be defined. The relaxing stress data are used to determine $G(t)$ directly,

$$G(t) = \frac{\tau(t)}{\gamma_0} \quad (1)$$

The stress relaxation tests were conducted at a constant strain of 0.3% and at a temperature of 170°C .

2.3.3. Surface Morphology and Dispersion Characteristic. The morphology of the samples was examined by SEM using a Jeol model JSM-6510LV microscope. Gold sputtering of the specimens fractured in the impact test was carried out using a Denton Desk V vacuum sputter system. The samples were fractured at room temperature.

3. Results and Discussion

3.1. Melt-Flow Index (MFI). The melt-flow index (MFI) is a physical parameter that is widely used to evaluate the ability of a polymer to flow when melted. The MFI value (Figure 1) declined as the sponge gourd residue concentration increased, due to the increased viscosity of the HDPE/filler system compared to the pure HDPE. With the addition of 10% by weight of cellulose, the MFI decreased by 19%, while for a filler content of 20%wt the decline was 43% and with addition of 40%wt the decrease was 83% in relation to the pure HDPE.

By the rule of mixtures criterion [10], the addition of 10%wt of cellulose filler should cause a decrease of 10% in the MFI, but this did not occur. Instead, the result of the property for this composition was 6.8 g/10 min (20% lower than for the pure polymer). Similar MFI behavior was observed by Mohanty and Nayak [11] for conventional HDPE composites obtained from petroleum and bamboo fiber. Cellulosic fillers are incompatible with the polymer matrix and have a tendency to form aggregates during processing [12], which might further impede the flow of the polymer matrix.

3.2. Melt-State Rheology. Viscosity is one of the most commonly used parameters to investigate the behavior of polymer materials during processing, since the majority of transformation processes occur in shear flows. The measure of storage modulus (G') and loss modulus (G''), which are related, respectively, to the energy stored and dissipated during a cycle, is also widely used to study the processing of polymer materials. The storage modulus depends on the rigidity of

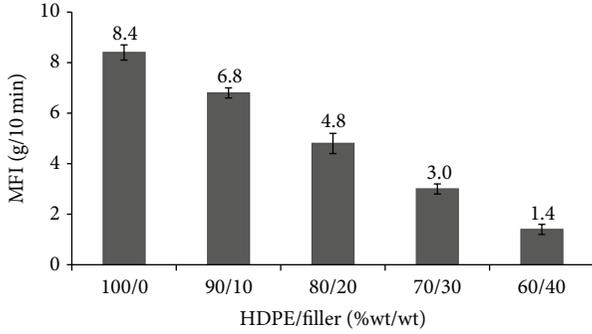


FIGURE 1: Melt-flow index of composites of renewable HDPE and sponge gourd filler.

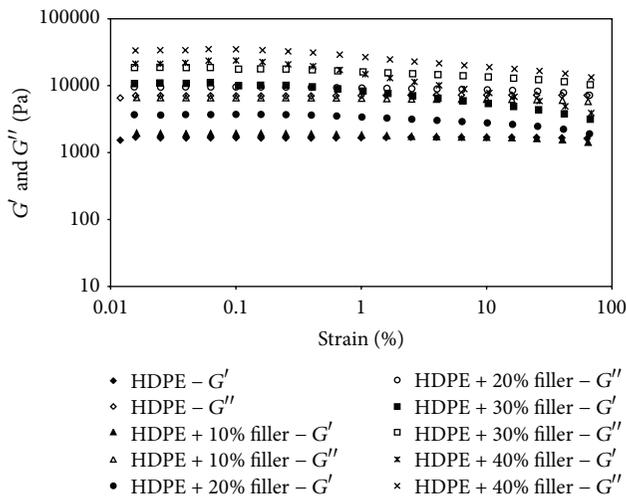


FIGURE 2: Strain sweep results for neat renewable HDPE and its composites containing different wt% of sponge gourd filler.

the macromolecules and their entanglement, while the loss modulus depends on the bonds, which control conformational changes in chain segments and the displacement of one chain in relation to another [2]. In turn, the rheology of composites is influenced by the interactions that occur between the polymer matrix and the filler, along with the structure, size, and shape of the particles and the quality of their dispersion throughout the melted matrix [13–15].

Strain sweep tests were conducted at 170°C in nitrogen atmosphere with a constant frequency of 1 Hz and in the strain range of 0.01 to 100%. As it can be seen in Figure 2, the response of all samples does not depend on the strain (both G' and G'' exhibit a constant plateau), and the behavior is well within the linear viscoelastic region. However, the plateau region shortens with higher cellulosic filler contents in HDPE matrix, 30 and 40 wt%. It can also be seen that G'' is dominating over G' for all composites analyzed, indicating that the overall behavior is dominated by viscous segmental frictions. The composite with 10 wt% of filler exhibits quite similar trend as neat HDPE. As filler content increases, the gap between G'' and G' values decreases, showing that viscous behavior becomes less pronounced with higher filler

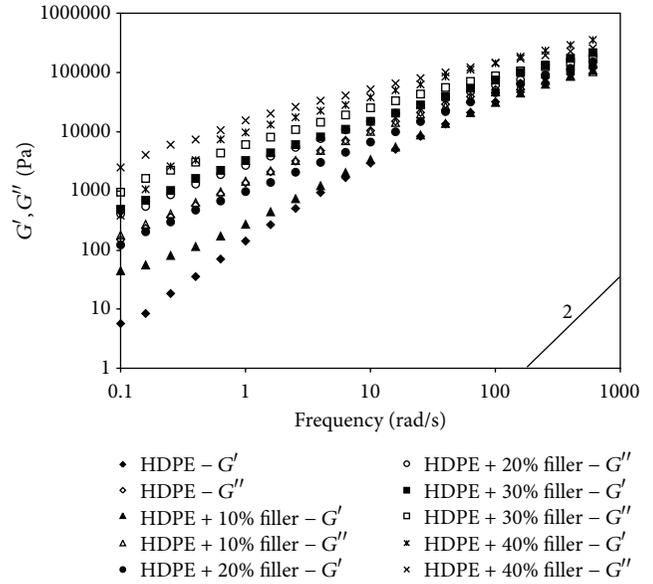


FIGURE 3: Variation of the storage modulus, G' , and loss modulus, G'' , as a function of frequency for neat renewable HDPE and its composites containing different wt% of sponge gourd filler.

loading in HDPE matrix and a tendency to a gradual switch from viscoelastic liquid-like to solid-like behavior occurs. From the above experiments, the strain was then set at 0.3% to ensure that the response of all materials would be within the linear viscoelastic region.

Small amplitude oscillatory shear measurements were performed at 170°C and 0.3% strain. The dynamic moduli, G' and G'' , are showed in Figure 3 for HDPE and HDPE/filler composites. The obtained behavior in frequency sweep is in accordance with the results of strain sweep. In fact, HDPE and HDPE composites exhibit $G'' > G'$ in a wide frequency range, indicating that the materials present a pronounced viscous behavior; however, as filler content increases, the gap between G'' and G' tends to decrease and a characteristic solid-like behavior tends to occur.

According to Jiang et al. [16], a homopolymer with narrow molecular weight distribution presents a characteristic terminal behavior of $G' \propto \omega^2$. In the present study, the neat HDPE did not deviate significantly from the standard terminal behavior, $G' \propto \omega^{1.18}$. As filler was added in HDPE matrix, a deviation from $G' \propto \omega^{0.96}$ for 10 wt% filler to $G' \propto \omega^{0.69}$ for 40 wt% filler was observed. This behavior indicates a solid-like viscoelastic behavior as filler content is increased. In other words, the addition of sponge gourd filler in the HDPE matrix prevents a complete relaxation due to physical jamming.

The frequency at which G' and G'' moduli curves cross each other reflects the transition from viscous to elastic response of the viscoelastic melts [17].

Table 1 shows the crossover point ($G' = G''$) and the frequency values, ω_c , where these cross points occurred.

The results show that a decrease of up to 20wt% of filler in the HDPE matrix in the cross point and in the crossover

TABLE 1: Modulus and frequency values in the cross point G'/G'' for the compositions analyzed.

Sample codes	Cross point, $G' = G''$ (Pa)	ω_c (rad/s)
HDPE	101700	398
HDPE + 10% filler	89590	398
HDPE + 20% filler	76340	158
HDPE + 30% filler	108400	158
HDPE + 40% filler	148900	100

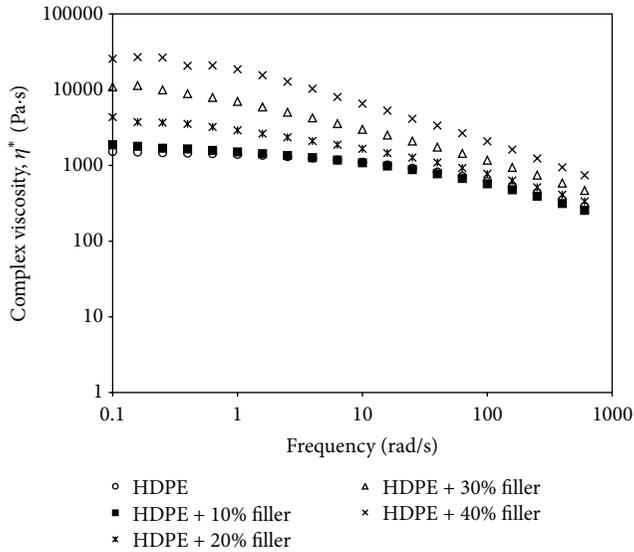


FIGURE 4: Variation of the complex shear viscosity as a function of frequency for neat renewable HDPE and its composites containing different wt% of sponge gourd filler.

frequency values was observed. It indicates that materials with more elastic behavior tend to be produced, but at the same time the composites present a shear thinning behavior as frequency increases. As filler content was further added to HDPE matrix (30 and 40 wt%) an increasing cross point value was observed, while crossover frequency values still decreased. This behavior can be related to a characteristic of solid-like behavior more pronounced in these high load composites, as compared with the other compositions. Probably it occurred due to the tendency to form aggregates during processing when higher filler contents are present, which might further hinder the HDPE matrix flow, as mentioned before.

The variation of the complex viscosity as a function of frequency (Figure 4) is another way to show these latest results.

Figure 4 shows that neat HDPE and 10 wt% filler composition present similar flow behavior in the whole frequency range analyzed. Only at low frequency values, the composite presents a slightly higher viscosity values in relation to neat HDPE. When 20 wt% of filler was added, higher viscosity values were obtained, but a frequency-thinning characteristic can also be observed, reaching similar flow behavior in

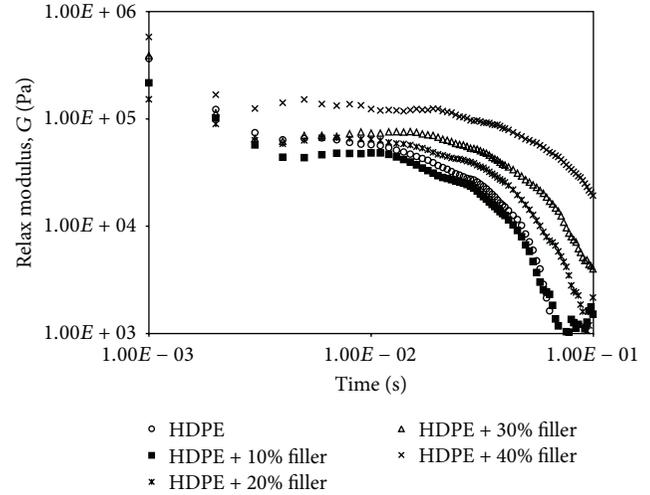


FIGURE 5: Variation of relaxation modulus with time for neat renewable HDPE and its composites containing different wt% of sponge gourd filler. The experiments were performed at a constant strain of 0.3% in nitrogen atmosphere.

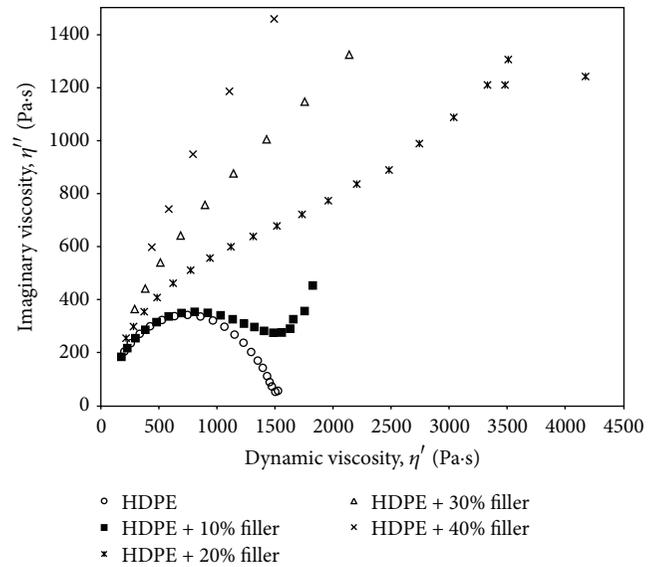


FIGURE 6: Cole-Cole representation of the viscoelastic properties of neat HDPE and HDPE/filler composites.

relation to the neat HDPE and 10 wt% filler composition at higher frequencies. Probably it occurred due to the fact that up to 20 wt% of filler aggregates can disentangle, allowing polymer chain to flow. However at higher filler contents, disentanglement processes become more difficult in the frequency range analyzed and thus higher viscosity values were observed.

The variation of the relaxation modulus with time is reported in Figure 5. The results show that $G(t)$ ($G(t) = \sigma(t)/\gamma_0$) of HDPE presents a behavior similar to a polymer with high molecular weight and narrow distribution; that is, a plateau zone appears in which the modulus is nearly

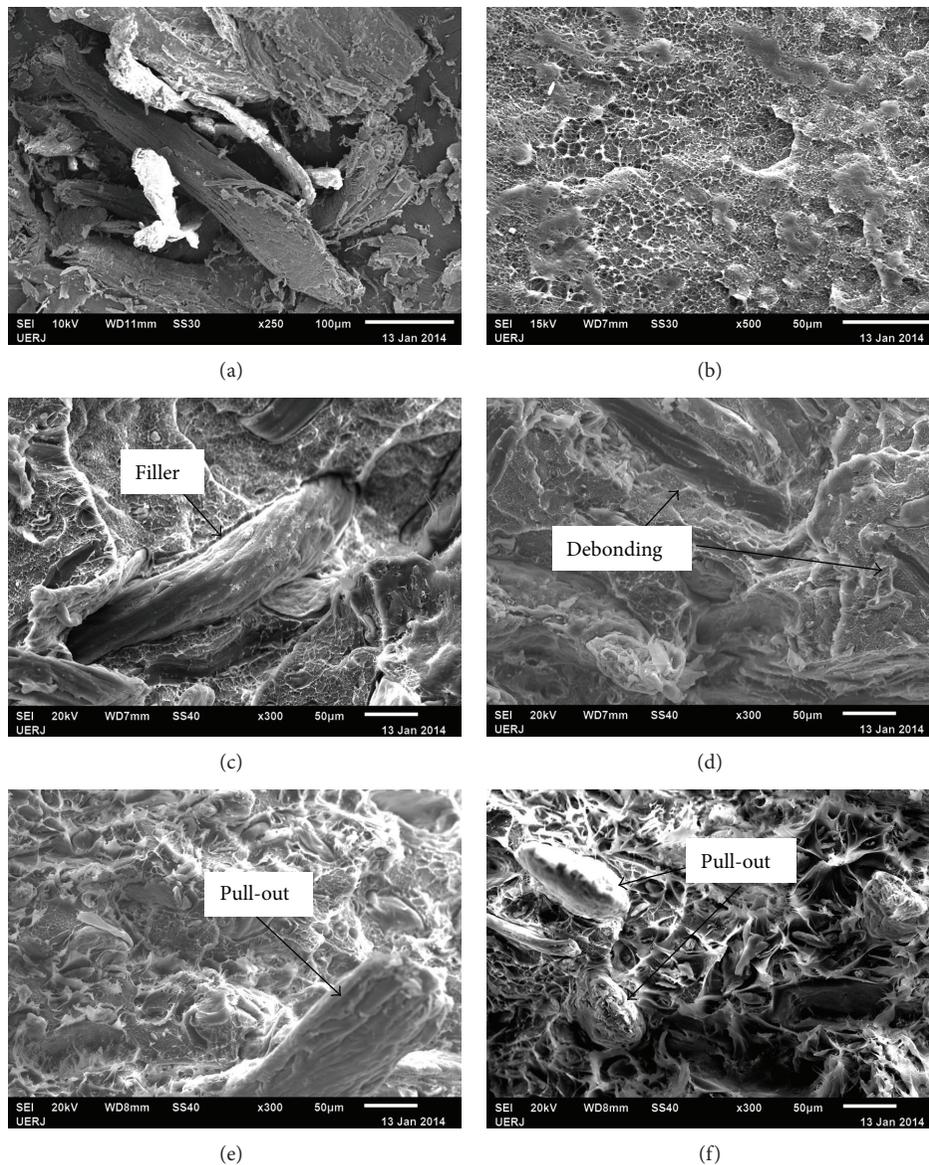


FIGURE 7: SEM micrographs of fracture surfaces for the following samples: sponge gourd residue with particle size $< 0.15\text{ mm}$ (a), renewable HDPE (b), and renewable HDPE/cellulosic filler composites: (c) 90/10%wt/wt, (d) 80/20%wt/wt, (e) 70/30%wt/wt, and (f) 60/40%wt/wt.

constant. At longer times, flow occurs and the $G(t)$ curve moves towards a “terminal zone,” where the modulus relaxes at sufficiently long times. For HDPE/filler composite with 10 wt% filler a similar behavior is observed in relation to neat HDPE for long times. As filler was added in HDPE matrix, $G(t)$ extends to long time and the magnitude of $G(t)$ value increases with the filler concentration. This behavior is another indication for the formation of filler aggregates (such as “temporary network”) when higher filler contents are added, hindering the occurrence of relaxation processes. At even longer periods of time, the “network” disentangles and a decrease of $G(t)$ values is once again observed.

Linear viscoelastic characteristics derived from the results of rheological measurements are also shown in a different representation in Figure 6, using the so-called Cole-Cole

plots for HDPE and HDPE/filler composites. In this representation, the η'' parameter (where $\eta'' = G''/\omega$), the so-called imaginary viscosity, is plotted against dynamic viscosity, η' (where $\eta' = G'/\omega$). The plot should be a perfect arc if higher order structures are absent and the relaxation behavior of the melt can be described by a single relaxation time [17]. According to Ábrányi et al. [18], studies on heterogeneous systems in melts containing network, the elastic component of viscosity (η'') increases and the structure has a larger relation time.

Data shown in Figure 6 indicate that the addition of filler leads to an increase of the elastic behavior of the composites and larger relaxation times can be observed as increasing filler loads are added in HDPE matrix, indicating the presence of filler aggregates.

3.3. Morphology Analysis. Figure 7 shows scanning electron microscope (SEM) images of the filler alone, with particle size smaller than 0.15 mm, pure HDPE, and composites. Figure 7(a) shows the irregularities of the sponge gourd filler, which is characteristic of natural fibers. Figure 7(b) shows the fracture surface of the pure HDPE, with slight roughness, after being submitted to impact resistance test, conducted at room temperature, a factor that can explain this roughness. Some displacement of fibers can be seen in Figures 7(c) and 7(d), which increases on rising filler content, due to the low adhesion of the polymer/filler interface. Finally, Figures 7(e) and 7(f) show the pull-out of the fillers and also the greater surface roughness of the composite with 40%wt filler. Filler agglomeration can be observed, corroborating the rheological results.

4. Conclusion

The rheological behavior of the composites comprising renewable HDPE and cellulosic filler showed that the viscosity of the system increases with higher filler content. This result suggests that the filler acts as a barrier to chain flow. According to Cole-Cole diagram, this system forms agglomerates due to the incompatibility of the matrix and filler. The melt-flow index results show values lower than expected, also corroborating the possible formation of filler agglomerates in the composite. Strain and frequency sweep analysis showed that, with the increase filler content, the gap between G'' and G' values decreases, showing that viscous behavior becomes less pronounced with higher filler loading in HDPE matrix and a tendency to a gradual switch from viscoelastic liquid-like to solid-like behavior occurs. The SEM micrographs allowed observing roughness at the fracture surface and fracture mechanisms in the composites such as pull-out, displacement of filler, and formation of agglomerates, a consequence of the low adhesion between the polymer matrix and cellulosic filler. These results are in accordance with rheological behavior observed. It can therefore be concluded that it is possible to obtain composites made from totally renewable polymer with good rheological properties, enabling reduction of negative environmental impacts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Effects of MAPP Compatibilization and Acetylation Treatment Followed by Hydrothermal Aging on Polypropylene Alfa Fiber Composites

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This work investigates the effect of hydrothermal aging on the properties of polypropylene/alfa fiber composites. Hydrothermal aging was induced in an environmental testing chamber at 65°C and 75% relative humidity (RH) over a 1000 h period. At the beginning ($t = 0$ h), the results showed that Young's moduli of the untreated alfa fibers and the acetylation-treated fibers increased by 21% and 36%, respectively, compared with the virgin polypropylene (PP). Additionally, Young's moduli decreased by 7% for the compatibilized composites composed of maleic anhydride grafted polypropylene (MAPP). After 1000 h of aging, Young's moduli decreased by 36% for untreated alfa fibers and 29% for the acetylation-treated alfa fibers and the compatibilized composites. Significant degradation was observed in the untreated alfa fiber samples. The Fourier transformed infrared (FTIR) allows us to distinguish the characteristic absorption bands of the main chemical functions present in the composite material before and after aging. The thermal properties showed that the thermal stability and the degree of crystallinity of the composites decreased after hydrothermal aging; this result was corroborated by the dynamical mechanical analysis (DMA) results.

1. Introduction

In recent years, substantial attention has been focused on the development of environmentally friendly composites that combine synthetic polymers with plant-based fibers. Natural fibers such as alfa [1, 2] olive husk [3], wood [4, 5], luffa [6], coir [7], hemp [8], kenaf [9], and sisal [10] have been widely used in composites. They are used as reinforcement for the polymer matrix and have good potential to replace conventional fibers (glass, carbon, etc.) in certain applications [11]. Moreover, lignocellulosic fibers are a biodegradable material obtained from renewable and abundant sources with low extraction prices [12]. However, the hydrophilic nature of natural fibers can be a disadvantage for composite manufacturing because these fibers lack compatibility with

hydrophobic polymeric matrices, which may result in poor performance. To solve this problem, chemical modification of natural fibers or the use of compatibilizer agents has been necessary. However, composites based on natural fibers present poor dimensional stability when in contact with water [13]. The possibility of using these materials in outdoor applications necessitates analyses of their mechanical behavior under the influence of hydrothermal aging [14]. Lignocellulose fibers (or plant fibers) contain many hydroxyl groups and readily interact with water molecules via hydrogen bonding. In contrast to glass fibers, in which water adsorption occurs at the surface, lignocellulosic fibers can interact with water throughout their bulk. The quantity of sorbed water depends on the relative humidity of the surrounding atmosphere and the degree of crystallinity. All of the hydroxyl groups in the

TABLE I: Overview of the samples tested.

Designations		Analysis					
Abbreviations	Compositions	FTIR	Tensile test	ATG/DSC		DMTA	SEM
			Aging Kinetic Analysis (h)				
Virgin PP	100% PP	0; 1000	0; 150; 400; 600; 800; 1000	0; 1000	0; 1000	0; 1000	0; 1000
F20UT	Fiber 20 wt% + 80% PP	0; 1000	0; 150; 400; 600; 800; 1000	0; 1000	0; 1000	0; 1000	0; 1000
F20AT	Acetylated fiber 20 wt% + 80% PP	0; 1000	0; 150; 400; 600; 800; 1000	0; 1000	0; 1000	0; 1000	0; 1000
F20AMAT	Fiber 20 wt% + 5 wt% Compatibiliser + 75% PP	0; 1000	0; 150; 400; 600; 800; 1000	0; 1000	0; 1000	0; 1000	0; 1000

amorphous phase are assumed accessible by polar solutions, which is unlike crystalline phases, in which only the surfaces are available for water sorption. Therefore, swelling by water uptake can lead to microcracking of composites and the degradation of mechanical properties [13, 15].

This study aims to improve the understanding of the effect of hydrothermal aging of PP/alfa fiber composites. In addition, this study investigates the modification of interfacial adhesion forces between the alfa fibers (high hydrophilicity) and the PP matrix (strongly hydrophobic) to increase their compatibility using two different methods. The first method was based on the chemical treatment of alfa fibers through acetylation by reacting the hydroxyl groups of the lignocellulosic material with the acetyl groups of acetic anhydride (Ac). The second method consisted of using the well-known polymer maleic anhydride grafted polypropylene (MAPP) as a compatibilizer to improve the interfacial bonding between the alfa fibers and the PP matrix. These two composites were compared to a PP/untreated alfa fiber composite. The three composite materials obtained were studied using several analytical techniques, including FTIR spectroscopy, the measurement of tensile and dynamic mechanical properties (DMA) and thermal stability (TGA, DSC), and SEM observations.

2. Materials and Methods

2.1. Materials. Alfa plants were collected in western Algeria. After in-house decortication, the fraction of the material obtained after sieving through a 100 μm mesh was used. The chemical composition of the alfa grass was mainly lignin (29 wt%), cellulose (45 wt%), and hemicelluloses (20 wt%). These constituents were determined using previously described chemical procedures [16]. The isotactic polypropylene (PP500P[®]) used in this study as the matrix was provided by SABIC (Saudi Arabia) with a melt flow index (MFI) of 3 g/10 min (230°C/2.16 kg) (ASTM D-1238) and a density of 0.9 g·cm⁻³ (values from supplier datasheets). Maleic anhydride (MAPP), supplied by ARKEMA (France), has a melt flow index (MFI) of 2.63 g/10 min (190°C/235 g, technical notice). Acetic anhydride (Ac, 98%), acetic acid, and sulfuric acid were provided by Sigma-Aldrich.

2.2. Acetylated Alfa Fibers. Dry alfa fiber (15 g) was placed in a round-bottom flask with 72.5 mL acetic acid. The reaction was performed in a thermostatic bath at 35°C for 45 min under mechanical stirring. Then, 24 mL of acetic acid was

added along with 0.1 mL of concentrated H₂SO₄ and the bath was maintained for 1 h. After this step, the mixture was cooled to 18°C for the slow addition of acetic anhydride (40 mL) with 0.6 mL concentrated H₂SO₄ over 3 h with constant stirring. A temperature of 24°C was maintained for more than 15 min. Then, the temperature was slowly increased to 50–55°C and the reaction continued for 3 h. This mixture was vacuum filtered, washed with distilled water, and then dried in an oven at 50°C for 24 h [17].

2.3. Composite Processing. Different formulations of PP/alfa fibers were prepared using “corotating” twin-screw extrusion. In addition to neat PP, PP/untreated alfa fiber composites, PP/alfa fiber composites treated with acetic anhydride, and a compatibilized composite were prepared after twin-screw extrusion. The formulations were injected using an injection press (ERINKA mark) connected to the compounder. Tensile specimens (ISO 527-5B) were obtained as the output of the injection-molding machine. The mould temperature were kept at 180 and 30°C, respectively at different pressures (4 bar for preinjection and 5 bar for injection). Table 1 shows an overview of the samples tested.

2.4. Hydrothermal Aging Treatment. The alfa fiber/polypropylene composites were placed in a Secasi Technologies (SLH41/08P, France) environmental testing chamber equipped with a relative humidity controller with a precision of $\pm 2\%$ to $\pm 5\%$. Demineralized water was used throughout the duration of treatment to ensure the neutrality of the environment. A relative humidity (RH) of 75% and temperature of 65°C were used to conduct the aging treatments. The samples were aged for different periods: 150, 400, 600, 800, and 1000 h (approximately 6 to 41 days).

2.5. Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra of the PP and PP/alfa fiber composites with and without aging were recorded using an FTIR SHIMADZU FTIR-8400S in the range of 4000–500 cm⁻¹. The equipment was operating in absorbance mode with 4 scan, at a resolution of 4 cm⁻¹, meaning a displacement of the mirror of 0.25 cm. Thin films, which were between 60 and 80 μm in thickness, were prepared by compression molding at 180°C for 2 min.

2.6. Thermogravimetric Analysis (TGA). Thermogravimetric analysis (TGA) was performed using a Hi-Res TG 2950 (TA instruments) in an inert atmosphere at a heating rate of 10°C/min. The sample weights were in the range of 10–20 mg,

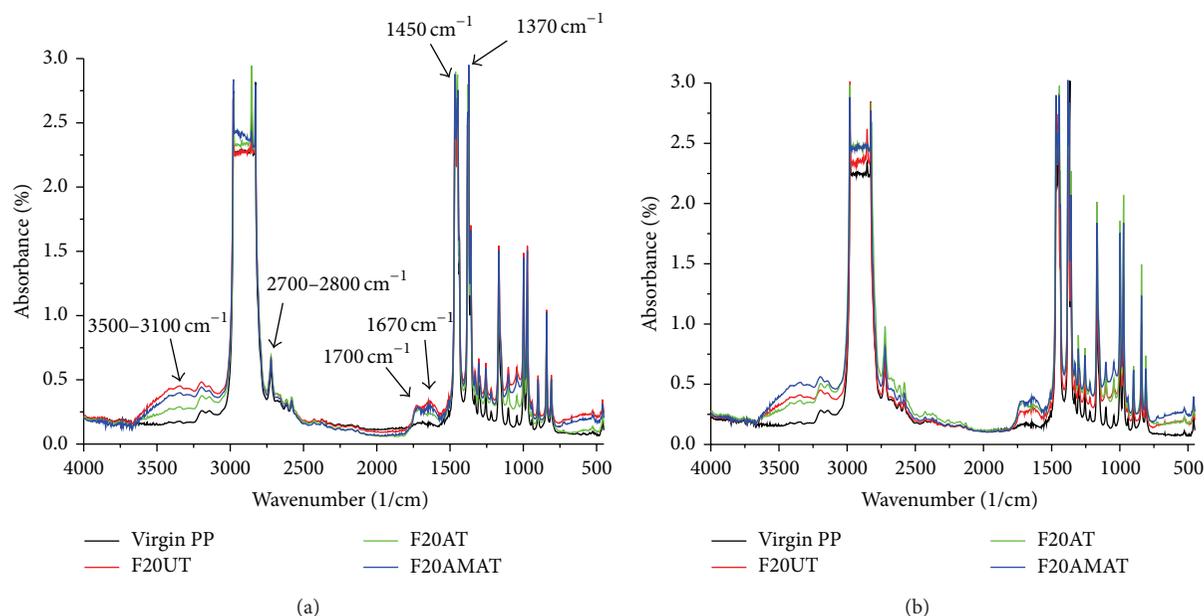


FIGURE 1: FTIR spectra of the PP/alfa fiber composites: (a) before aging and (b) after aging.

and they were scanned in the temperature range of 20°C to 700°C.

2.7. Differential Scanning Calorimetric Analysis (DSC). The DSC measurements were conducted using a DSC-2920 (TA instrument) differential scanning calorimeter with nitrogen as the purge gas. Samples of approximately 5–10 mg were analyzed in the temperature range of –50 to +200°C. To erase the thermal history, the first cooling and the second heating thermograms were recorded with the following scanning rate: 10°C/min in the first cooling and 10°C/min in the second heating. The melting peak (T_m) was obtained. The melting temperature (T_f), melting enthalpy (ΔH_f), crystalline index (X_c), crystallization temperature (T_c), and crystallization enthalpy (ΔH_c) were determined from the DSC thermograms, and the values are reported in Table 3.

2.8. Tensile Tests. Quasi-static tensile tests were carried out using a Macro Test Well 108-2kN testing apparatus in a climatic room where the temperature was 23°C at 65% RH according to ISO 527-5B. The speed was 50 mm/min. The tests were performed at least three times for each sample, and the results were averaged arithmetically.

2.9. Dynamic Mechanical Analysis (DMA). Dry and moisture-saturated samples were subjected to dynamic mechanical analysis (DMA) using a tension cantilever system DMA Q800 (TA Instruments) at a frequency of 1 Hz and a driving force of 8 N. The dynamic storage moduli of each specimen were determined as a function of humidity from 10% to 100% (isotherm of 40°C).

2.10. Scanning Electron Microscopy (SEM). Scanning electron microscopy (SEM) was used to monitor the fracture surface

of the composites after the samples were frozen in liquid nitrogen. SEM analysis was performed using a TM 1000 Tabletop Microscope (Hitachi).

3. Results and Discussion

3.1. FTIR Analysis. To analyze the behavior of PP containing fibers as a function of the treatment and the applied hydrothermal aging, as well as the influence of aging on the mechanical and thermal behavior, spectroscopic techniques were employed to study the formation of radical and chemical species that affect the structure and final behavior of the composite. The technique employed was infrared (FTIR) spectroscopy. The results obtained and the FTIR spectra for the PP/untreated alfa fiber composites are shown in Figure 1(a). The results presented in Figure 1(a) show the presence of aldehyde carbonyl groups (C=O) at the stretch frequency of approximately 1700 cm^{-1} , C–H absorption within the range of 2700–2800 cm^{-1} , and asymmetric stretching of the cis and trans C=C at approximately 1670 cm^{-1} . Absorption bands typical of PP were also observed at frequencies between 1450 cm^{-1} for the $-\text{CH}_2$ bond and 1370 cm^{-1} for the $-\text{CH}_3$ bond. We also noticed the appearance of the absorption band between 3500 and 3100 cm^{-1} , which increases in intensity after aging Figure 1(b), reflecting elongation of the hydroxyl vibration of water molecules (OH) associated with the diffusion of the liquid within the matrix and fiber interface/matrix [18, 19].

In addition, the FTIR spectra results for the F20AT (PP/treated alfa fiber by acetylation) and F20AMAT (PP/alfa fiber/MAPP) composites are shown in Figures 1(a) and 1(b). As in the case of the virgin matrix and the untreated composite the spectra of F20AT F20AMAT composite present the same absorption bands. This result suggests that the presence

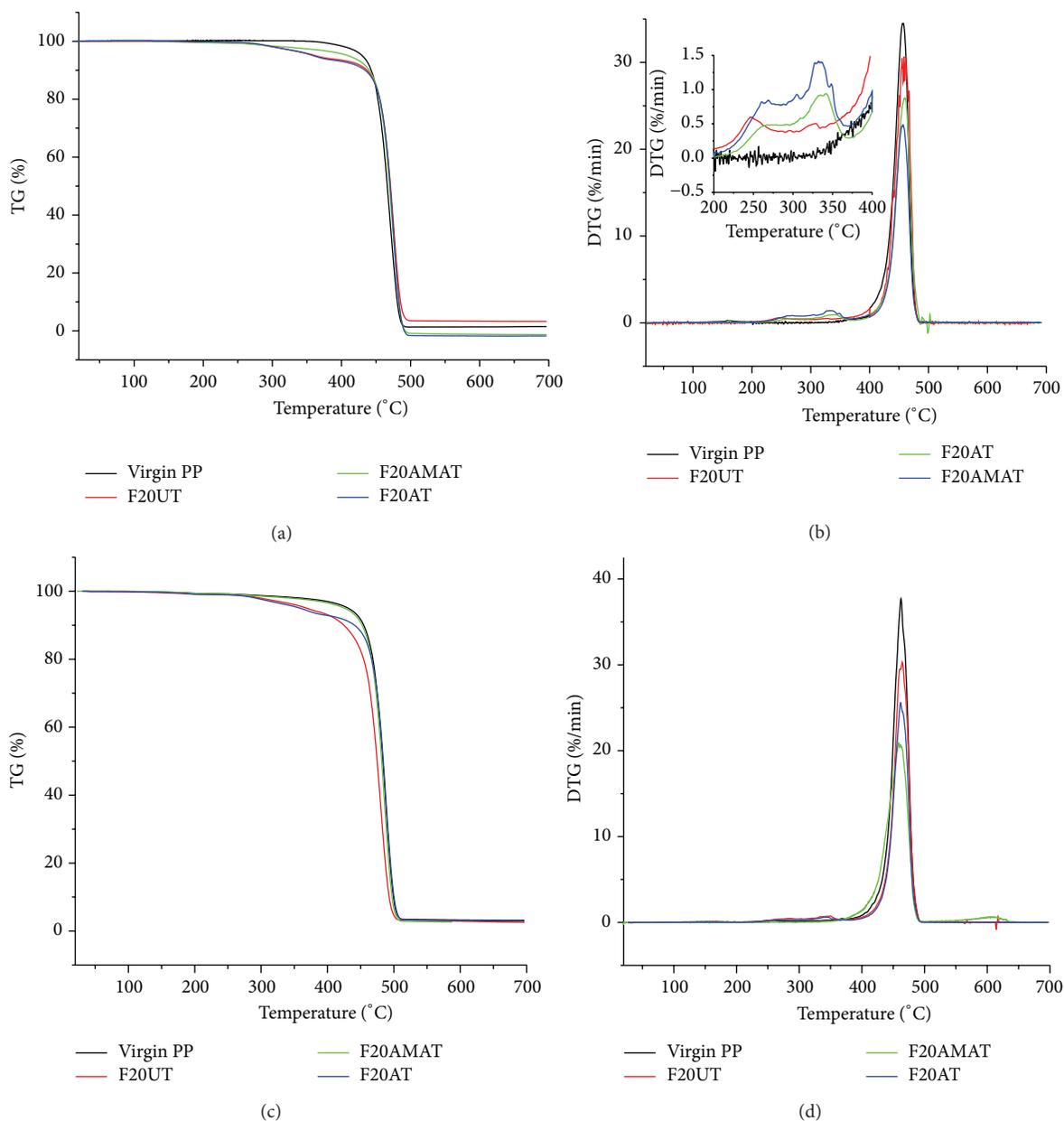


FIGURE 2: Thermal degradation behavior of the composites: ((a), (b)) before aging and ((c), (d)) after aging.

of a compatibilizing agent and the chemical modification by acetylation of fibers have no effect on the composite during the hydrothermal aging.

3.2. Thermogravimetric Analysis (TGA). Thermogravimetric analysis was used to determine the degradation temperature of the composites, as well as their components, under nitrogen atmosphere. Figure 2 clearly shows that the thermal degradation profiles of the composites with and without aging are similar. One stage of polypropylene degradation was recorded, which is unlike composites, whose degradation occurs in two steps [20]. Indeed, the PP decomposes from 400°C and gives mainly propylene trimer [21]. Beyond

500°C, oligomers of other monomers are also formed, and approximately 0.8% of char is recovered at the end of its decomposition. However, the thermal degradation of the alpha fiber-filled PP composites occur in a two-step process, this result was confirmed in derivative thermogravimetric curve (DTG) (Figure 2(b)). The first thermal degradation step may correspond to lignin and polysaccharide polymers (hemicellulose and cellulose). The second step was attributed to degradation of the polymer (PP) [22].

The incorporation of the untreated alfa fiber in polypropylene led to a decrease in the onset decomposition temperature; this decrease is probably caused by the decomposition of the components of the alfa fiber (cellulose,

TABLE 2: TGA data for neat PP and PP/alfa fiber composite materials.

Formulations		T_{onset} (°C)	V_{max} (%/min)	Char (Wt. %)
Before aging	Virgin PP	431	34.6	0.34
	F20UT	362	30.0	2.50
	F20AT	394	25.4	3.19
	F20AMAT	360	21.8	3.63
After aging	Virgin PP	393	35.0	0.23
	F20UT	353	29.8	3.26
	F20AT	395	24.1	3.54
	F20AMAT	307	20.5	3.42

TABLE 3: Crystallinity rates of neat PP and PP/alfa fiber composite materials.

Formulations		T_f (°C)	ΔH_f (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
Before aging	Virgin PP	116	94.2	169	77.0	36.8
	F20UT	115	87.0	170	74.4	44.5
	F20AT	116	83.4	170	74.5	44.5
	F20AMAT	115	80.1	170	72.4	43.3
After aging	Virgin PP	116	85.1	170	72.0	34.4
	F20UT	116	81.8	169	68.9	41.2
	F20AT	116	81.4	170	67.2	40.2
	F20AMAT	117	78.2	169	69.1	41.3

hemicellulose, and lignin). However, the thermal stability slightly improved for the PP/alfa fiber composites with the compatibilizing agent MAPP compared with the composites modified by acetylation and untreated composites, which is explained by the improved compatibility and adhesion of the fibers to the PP matrix [3].

The typical degradation temperatures of virgin PP and the PP/alfa fiber composites are summarized in Table 2. Moisture plays an important role in influencing the mechanical behavior, as well as the long-term durability, of the composites. Figures 2(c) and 2(d) show the thermograms for virgin PP and PP/alfa composites after aging. The derivatives of the mass loss curves are also displayed to highlight the differences between the samples.

The maximum degradation rate (V_{max}) decreased after aging. For the untreated composite (F20UT), the V_{max} decreased from 30 to 29 (%/min). Clearly, this decrease was due to the lignin, which acts as a heat stabilizer in the PP. However, the treated composite showed the same tendencies. The V_{max} decreased from 25 to 24 (%/min) and from 21 to 20 (%/min) for F20AT and F20AMAT, respectively. This decrease is due to the increase of the thermal stability.

3.3. Differential Scanning Calorimetry (DSC) Analysis. The percent crystallinity was obtained from DSC analysis using the following relation [23, 24]: $X_c (\%) = ((\Delta H)/(\Delta H_m \cdot \omega)) * 100$, where ΔH and ΔH_m are the heat of fusion of PP and 100% crystalline PP, respectively. A value of $\Delta H_m = 209$ J/g for PP [25] was used, and ω is the reinforcement content. The crystallinity of virgin PP and the PP/alfa fiber composites decreased after aging; the crystallinity of virgin PP decreased by 6% after aging, and the crystallinity of the

F20UT composite (PP/untreated alfa fiber) decreased by 7% after aging. Crystallinity reductions for the F20UT, F20AT, and F20AMAT composites were observed after hydrothermal aging (Table 3). Beg and Pickering [23] found similar results and explained that this reduction is related to the decrease of the molar mass of macromolecular chains. The other authors [26] have explained the crystallinity reduction by the decrease of the structural irregularity.

3.4. Effects of Hydrothermal Aging on the Mechanical Properties. Mechanical tests were performed on all of the samples before and after aging; the results are shown in Figures 3(a) and 3(b). In general, the mechanical properties of these materials decreased after moisture uptake due to the effect of the water molecules, which change the structure and properties of the fibers and the matrix as well as the interface between them [27]. After the water molecule penetrates the composite materials, the fibers tend to swell. The matrix structure can also be affected by the water uptake by processes such as chain reorientation and shrinkage. Additionally, water molecules are inserted between the macromolecular chains of polypropylene weakening secondary link of Van der Waals and therefore they reduce the interactions between these chains that can move freely. For this reason we can say that the water acts as a plasticizer. Hydrothermal aging causes the degradation of fibers in a thermoplastic matrix. Water absorption and its effects contribute to the loss of compatibilization between the fibers and the matrix, which results in debonding and weakening of the interface adhesion [27].

According to the obtained tensile strength results (Figure 3(a)), the values at the beginning ($t = 0$ h) are slightly

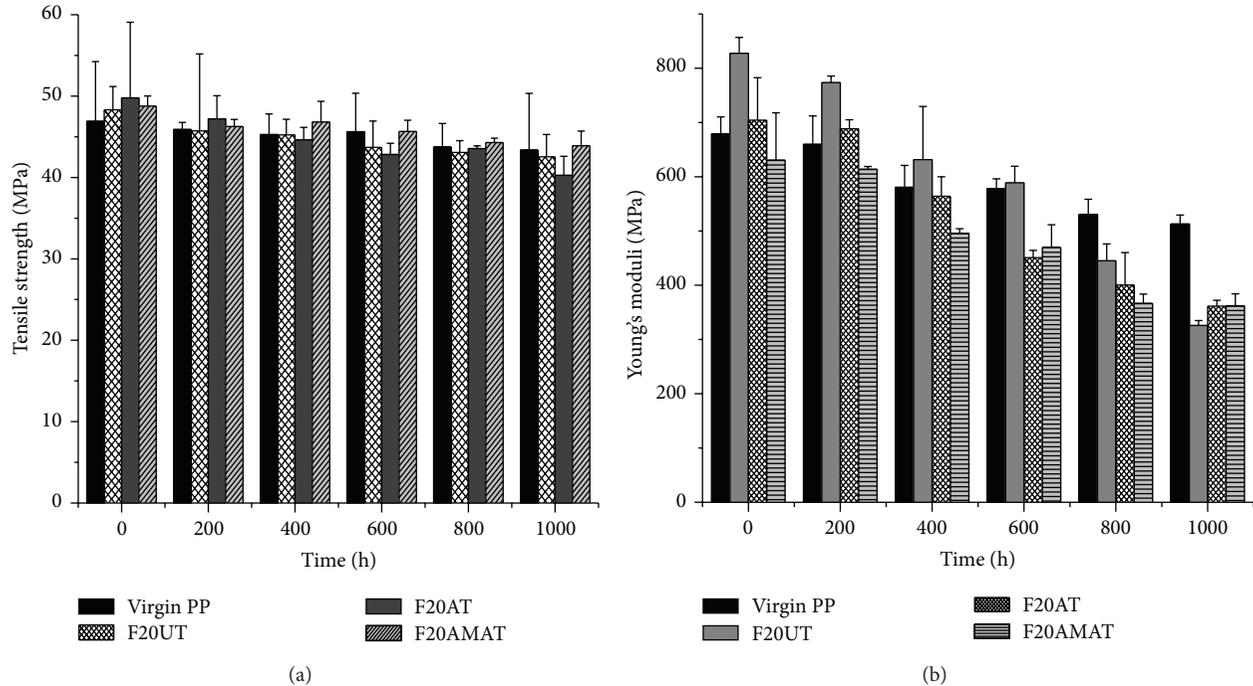


FIGURE 3: Evolution of the mechanical properties of the PP/alfa fiber composites: (a) tensile strength and (b) Young's moduli.

increased compared with those of the PP matrix after 1000 h. A slight decrease was observed for all of the composite mixtures.

At the beginning ($t = 0$ h), Young's moduli of the F20UT and F20AT composites were higher than that of the PP matrix, which was due to the fiber stiffness, in both of the different composites. However, the F20AMAT composite had the lowest Young modulus, which can be explained by the plasticization due to the MAPP compatibilizer. After 1000 h, the modulus decreased with exposure time to temperature and moisture, which acts as a plasticizer. Similar degradation behavior was observed by Hammiche et al. and Chen et al. [28, 29]. Finally, the changes in the mechanical properties coincided with the structural modification and chemical changes deduced from the FTIR characterization.

3.5. Dynamic Mechanical Analysis (DMA). Dynamic mechanical analysis is a method for measuring the viscoelasticity of polymers. This method enables the study and characterization of the mechanical properties as the storage moduli, E' , which represents the stiffness and the elastic component of the material. E' expresses the material's ability to store mechanical energy and to fully transfer the energy in the form of elastic deformation. The dynamic mechanical properties of virgin PP and the PP/alfa fiber composites with and without modification were evaluated. The storage moduli, E' , as a function of humidity is depicted in Figure 4(a). In the case of the matrix, the storage moduli, E' , significantly decreased with moisture due to gradual softening of the material and increased segmental mobility. Regardless of the humidity, after the addition of fibers (F20UT), a significant increase in the storage modulus was

observed, as expected. This result revealed that there is an effective stress transfer across the interface, which improves the stiffness of the composite. For the systems based on the compatibilized composites (F20AMAT), the storage moduli were slightly lower compared with those of the materials based on nonmodified fibers. This reduction can also be explained by a reduction of the stiffness. This result confirms the data obtained from the tensile measurements, which show a decrease in tensile modulus at room temperature for the compatibilized composites.

With increasing humidity, the E' values of the matrix PP and the composite systems decreased. However, for composites, the decreased matrix moduli are arguably compensated for by the fiber stiffness. The effects of hydrothermal aging on the dynamic mechanical behavior after aging are shown in Figure 4(b). The storage moduli of the composites containing fibers (treated or not) were slightly lower than that of the PP matrix. This decrease reflects several concurrent phenomena, which are reversible. The reversible phenomena are summarized by the plasticization caused by the presence of water. The hydrophilic nature [30] of natural fibers is considered to decrease the resistance of the composite in a humid environment. From these results, it can be deduced that a study of the behavior of the composites in a humid atmosphere is necessary not only to estimate the effects of aging but also to better understand the mechanisms involved to minimize them. Presumably, the first water molecules entering the polymer will act strongly on the matrix. These water molecules can initially spread in space (free volume and porosity) before reaching the polar sites, after which they generate swelling and, as a consequence, a change in thermomechanical properties. The mechanism of plasticization,

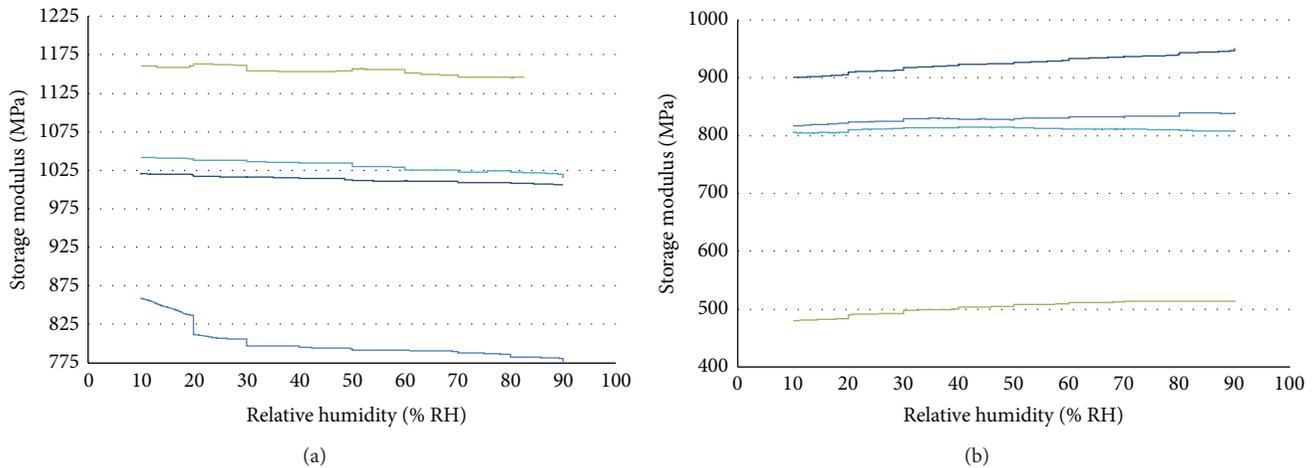


FIGURE 4: Variation of storage moduli versus humidity (DMTA analyses): (a) before aging and (b) after aging for (blue line) virgin PP, (green line) F20UT, (light blue line) F20AT, and (black line) F20AMAT.

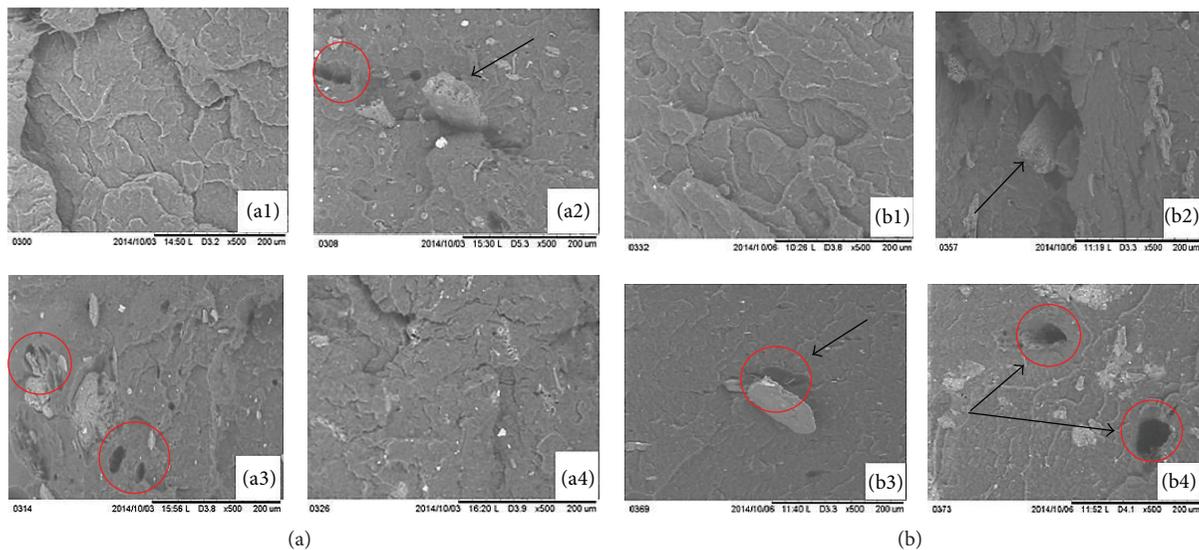


FIGURE 5: SEM micrographs of fractured surfaces (a) before aging and (b) after aging for composites: ((a1), (b1)) virgin PP, ((a2), (b2)) F20UT, ((a3), (b3)) F20AT, and ((a4), (b4)) F20AMAT.

which is generated by the diffusion of water molecules in the amorphous phase, may be responsible for such damage.

3.6. Scanning Electron Microscopy (SEM). The morphology and facies rupture were observed to evaluate changes induced by fiber incorporation in the polymeric matrix because the functional properties of the resulting material are directly related to the surface features of the composite and the interfacial adhesion between its components. The results are represented in Figures 5(a) and 5(b), which correspond to the fracture surface before and after hydrothermal aging, respectively. In particular, in Figure 5(a1), the facies of virgin PP before aging exhibits a very smooth relief. In contrast, in Figure 5(b1), the surface exhibits very few defects after 1000 h, likely because the surface of the virgin PP did not undergo degradation. As expected, the SEM micrographs

show that the addition of F20UT to the PP matrix before aging (Figure 5(a2)) resulted in a gap or void between the fiber elements and matrix. We can also notice the presence of aggregates in the F20UT composite. The formation of these aggregates affect negatively a dispersion of the alfa fiber in the matrix inducing the debonding which increased after aging (Figure 5(b2)) between these two components. The debonding load/matrix was often accompanied by shrinkage of the polymer around the load and can be reversed after the first instance. This phenomenon is attributed to hydrolysis of the polymer matrix by water [31]. The same result was observed for the formulations F20AT and F20AMAT (Figures 5(b3) and 5(b4)). Therefore, sample degradation was caused by debonding at the load/matrix interface. As a result, hollows and wide grooves that amounted to cracks were visible [32].

4. Conclusion

This study addresses the evolution of properties of untreated and treated alfa fiber-reinforced polypropylene composites during hydrothermal aging. Regardless of the type of treatment (acetylation by acetic anhydride or addition of the MAPP compatibilizing agent), the PP/alfa fiber composites showed a reduction in tensile moduli after aging. This decrease can be plausibly explained by the hydrophilic nature of the fiber that absorbs more moisture and causes swelling of the PP matrix. Rupture facies confirmed the debonding of alfa fiber elements, which in turn may participate in the decrease in mechanical properties of the composite. Concerning thermal properties, the incorporation of acetylation-treated and untreated alfa fibers before aging improved the thermal stability of the composites. In addition, the use of MAPP compatibilizer provided improved thermal stability compared with that observed with the acetylation-treated and untreated alfa fibers. After hydrothermal aging, the treated composites displayed a higher thermal stability, as evidenced by the increase in the onset temperature and the decrease of the maximum rate of degradation. This effect might be due to the stronger interactions between the fiber and matrix caused by the formation of covalent bonds at the interface in the presence of MAPP. The degrees of crystallinity of the treated and untreated samples decreased after hydrothermal aging due to the humidity; this change was corroborated by the DMA results.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Review Article

A Review on Pineapple Leaves Fibre and Its Composites

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Natural fibre based composites are under intensive study due to their ecofriendly nature and peculiar properties. The advantage of natural fibres is their continuous supply, easy and safe handling, and biodegradable nature. Although natural fibres exhibit admirable physical and mechanical properties, it varies with the plant source, species, geography, and so forth. Pineapple leave fibre (PALF) is one of the abundantly available wastes materials of Malaysia and has not been studied yet as it is required. A detailed study of chemical, physical, and mechanical properties will bring out logical and reasonable utilization of PALF for various applications. From the socioeconomic prospective, PALF can be a new source of raw material to the industries and can be potential replacement of the expensive and nonrenewable synthetic fibre. However, few studies on PALF have been done describing the interfacial adhesion between fibres and reinforcement compatibility of fibre but a detailed study on PALF properties is not available. In this review, author covered the basic information of PALF and compared the chemical, physical, and mechanical properties with other natural fibres. Furthermore, it summarizes the recent work reported on physical, mechanical, and thermal properties of PALF reinforced polymer composites with its potential applications.

1. Introduction

Industries are widely using plant fibres for numerous applications from many resources. In the middle of 20th century, synthetic fibres rose up drastically, and natural fibres industries collapse its market shares. For promoting natural fibre and material, year 2009 is considered as international year of natural fibre (IYNF), which is highly supportive to famers, agriculture, environment, and market demands. Composite market of United States has been recorded 2.7–2.8 billion pounds from 2006 to 2007. On the basis of compound annual growth rate of 3.3%, it is estimated to cross over 3.3 billion pounds [1]. In 2009, Thailand produces 1.894 million tonnes, the Philippines produced 2.198 million tonnes, and Brazil produced only 1.43 million tonnes. In 2001

the production of Costa Rica, Cote d'Ivoire, and Philippines were 322,000 tonnes, 188,000 tonnes, and 135000 tonnes, respectively [2]. The most important property of natural fibre is biodegradability and noncarcinogenic which bring it back into fashion, with an advantage of being cost-effective. The versatile nature of it makes it suitable for automobiles, railway coach, building construction, partition wall cabinets, or furniture for machinery uses and packaging. Natural fibres are important agricultural biomass contributing to Malaysian economy. The huge and wide range availability of natural fibre can reduce the pressure on forest and agriculture. The usage of diverse raw materials will help to keep a ecological balance in nature. Generally agriculture materials and forest product produce 30–40% waste materials, which can also be used in value added processing. The low density

natural fibres can also be utilised as per the aim of utility. For example, a grass fibre can be a good alternative for low load bearing products [3]. It has cumulative advantage of light weight (low density), cheaper source, low wages, being noncarcinogenic, and biodegradability [4–6]. Scientists and engineers are having great interest to find out new sources of raw materials that possess comparable physical and mechanical properties to synthetic fibres. Various other parameters to be considered while selecting raw materials are being cheap, being ecofriendly [7], absence of health hazards, high degree of flexibility [8], lower plant's age, easy collection, and regional availability which directly influence the suitability of natural fibres [9, 10]. Above all the natural fibres are renewable resource, thus providing a better solution of sustainable supply, like it has low cost, low density, least processing expenditure, no health hazards, and better mechanical and physical properties [11–16]. The main drawback of natural fibre is moisture absorption, so it is bound to change its surface property by using chemicals [17]. Synthetic fibre reinforced polymers were costly and have an impact on environment [18]. There are many plant fibres available which has potential to be applied in industries as raw materials such as pineapple, kenaf, coir, abaca, sisal, cotton, jute, bamboo, banana, Palmyra, talipot, hemp, and flex [16–21]. Pineapple leaf fibre (PALF) is one of the waste materials in agriculture sector, which is widely grown in Malaysia as well as Asia. After banana and citrus, pineapple (*Ananas comosus*) is one of the most essential tropical fruits in the world [22]. Commercially pineapple fruits are very important and leaves are considered as waste materials of fruit which is being used for producing natural fibres. The chemical composition of PALF constitute holocellulose (70–82%), lignin (5–12%), and ash (1.1%). Pineapple (PALF) has tremendous mechanical properties and can be applied in making of reinforced polymer composites [23, 24], low density polyethylene (LDPE) composites, and biodegradable plastic composites. Physical and mechanical properties of composites like viscoelastic behaviour processing, tensile strength, flexural strength, and impact are dependent on length of fibre, matrix ratio, and fibre arrangement [25, 26]. The main drawbacks PALF is hydrophilic nature; it does not make good bonding with hydrophobic matrix, particularly at high temperatures [27]. Interfacial quality between PALF and polymer could be enhanced by using chemical treatments like dewaxing, treatment with NaOH, cyanoethylation, and grafting of acrylonitrile monomer onto dewaxed PALF [24]. Moreover, the surface modification by chemicals like sodium hydroxide (NaOH), 2,4-dinitrochlorobenzene, benzoyl peroxide (BPO), and BPO/acetylation can minimize water absorption and improves the mechanical properties [28]. The moisture absorption of chemically modified PALF-reinforced LDPE composites shows considerably less moisture content [29]. Bonding agent resorcinol (reso), hexamethylenetetramine (Hexa), and silica have good affinity for PALF-natural rubber (NR) and exhibits better adhesion [30].

Nowadays, biocomposite reinforced materials are widely accepted in place of traditional materials in high strength and several light weight applications. Such composite materials exhibit good strength by weight ratio, high tensile and

flexural strength, high creep resistance, and high compactness. Natural fibres reinforced into bioplastics are a good example of green composites, which is easily degradable by bacteria and enzyme [31]. The major problem of natural fibres as a reinforced material is improper contact of adherent surface and polymer matrix with a bad interaction load transformation from matrix to fibre [32]. Thus, to enhance the adhesion property of fibres, it needs surface modification by using appropriate chemicals. These modification methods can be alkaline treatment [33] grafting with malic anhydride copolymer [34] and using saline coupling agent [35].

2. Natural Fibre

It is believed that source of petroleum based products are limited and uncertain. So an alternative with cheap sustainable and easily available raw material is required. The countries growing plant and fruit are not for only agricultural purpose but also to generate raw materials for industries. Most of the developing countries trade lignocellulosic fibres for improving economic condition of poor farmers as much as country support. Recently polymer composites containing cellulosic fibres are under focus in literature as well as industries. Table 1 shows the annual natural fibre production from various sources. Near about 30 million tonnes of natural fibres are produced every year and used as component of many manufacturing processes like clothing, packaging, paper making, automobiles, building materials, and sports equipment [1]. Natural fibres composites are eye-catching to industry because of its density and ecofriendly nature over traditional composites [36]. Other than plant fibres, various animal fibres also have different types such as products from the wool, silk, feathers, avian fibre, and animals hairs which are prime resource. Fruit fibres are taken from fruits like coconut (coir) fibre. Stalk fibres are collected from husk and straw of crops like wheat, rice, barley, and so forth. Tree wood can also be used as fibre. Natural fibres have been used for a long time in many developing countries as cement materials [37].

These fibres are thread-like structure of various sizes; it can be used in rope or threads making; now it is major component of biocomposite materials like boards, paper, and many structures [17].

The performance of natural fibre varies with part of the plant that is used for fibre extraction, age of plant, fibre extraction process, and many more factors [38]. It can be extracted from the bast stem, leaf, and seeds from the plants in a bundle form; therefore it is also called fibre bundles; extraction method of fibres is similar in both bast stem and leaf, while seed fibres have many methods like cotton lint extracted from ginning process. The strip fibre bundle is extracted from stem and leaf; decorticator technique is recommended. Retting technique prefers to use chemicals and biological treatment for removing fibres from stem; retting is basically two types: dry retting and water retting [39]. Dew retting is most popular in Europe, but its quality is not good as much as water retting. Water retting technique is being used in Asian countries [40].

TABLE 1: Annual production of natural fibres and sources [41–43].

Fibre source	World production (10 ³ Tons)	Origin
Abaca	70	Stem
Bamboo	10,000	Stem
Banana	200	Fruit
Broom	Abundant	Stem
Coir	100	Stem
Cotton Lint	18,500	Stem
Elephant grass	Abundant	Stem
Flax	810	Stem
Hemp	215	Stem
Jute	2,500	Stem
Kenaf	770	Stem
Linseed	Abundant	Fruit
Pineapple	Abundant	Leaf
Caroa	—	Leaf
Nettles	Abundant	Stem
Oil palm fruit	Abundant	Fruit
Palm rah	Abundant	Stem
Ramie	100	Stem
Roselle	250	Stem
Rice husk	Abundant	Fruit/grain
Rice straw	Abundant	Stem
Sisal	380	Stem
Sun hemp	70	Stem
Wheat straw	Abundant	Stem
Wood	1,750,000	Stem
Sugarcane bagasse	75,000	Stem
Cantala	—	Leaf
China jute	—	Stem

Natural fibres have systematic internal cell wall structure which is divided into three major structural parts [80]. The microfibril angle and arrangement inside the cell wall decide the properties of fibres [81]. Cell wall mainly consists of two cell walls, primary cell wall (S1) and secondary cell wall (S2). Primary cell wall propagates at the time of growth of plant. Secondary cell wall is made up by three layers and each layer carries long chain of microfibril [82]. Amount of cellulose increases from S1 to S2 steadily and hemicelluloses content remains the same in each layer but lignin content shows reciprocal trend to cellulose. Hemicelluloses molecules are net-like structure and make bond with cellulosic fibrils. Cellulose-hemicelluloses make network together and lignin and pectin provide an adhesive quality. These adhesive properties are responsible for strength and rigidity of cellulosic fibres. Secondary layer (S2) decides the physical and mechanical strength of fibres. Normally high level of cellulose content and lower microfibrillar angle provide better strength properties [55, 83]. In general synthetic fibres show better mechanical and physical properties compared to the natural fibre whereas the specific modulus and elongation at break are better in natural fibres than the synthetic fibres, which is considered as an important factor in polymer engineering composites [49].

The major chemical composition of fibres like coir, banana, pineapple leaf, sisal, Palmyra, sunhemp, and so forth are cellulose and lignin discussed in Table 2. Natural fibres are constitutes of cellulose and lignin; these celluloses consist of many fibrils along the length which is, associated with hydrogen bond to provide strength and flexibility [84].

The fibre selection depends on the length, strength, and purpose of usage. Table 3 discusses the physical and mechanical properties of various cellulosic fibres, with their respective density, microfibril angle, Young's modulus, and fibre elongation of fibres that determine the overall properties of the fibres [43]. Cell dimension of lignocellulosic fibres depends on the species, maturity, and location of the plant and also on the fibre extraction conditions [1].

It is believed that the resins produced from petroleum products are not fully biodegradable. However the composite produced from such matrix resin with reinforced natural fibres is considered biodegradable. Matrix material of thermosets and thermoplastics should be compatible for the natural composites [85–87]. The thermoset composite formulation is more complex than thermoplastic. It depends on many parameters like flowing agents, resin, curing agents, catalysts, and hardeners. Such composites need to be chemically cured by using perfect cross-linkage with all direction setup structure. The cross-linked structures are tough, creep resistant, and highly solvent resistant. Fibre loading can enhance the property up to 80% because of alignment of fibres. Thermoplastics provide more advantage over thermoset polymers. Thermoplastics matrix composite is having low processing cost, design flexibility, and ease of moulding complexity. It is very simple method for processing of composites such as extrusion or injection moulding methods. In thermoplastics, most of the work has been done with polyethylene, polypropylene, polystyrene, and polyvinyl chloride (PVC) polymers. These polymers require temperature below 200°C temperature which is suitable for natural fibres and avoid thermal degradation. In thermoplastic composites, fibres distribution plays an important role to achieve quality products. Since natural fibre varies its properties, such as length density, it is very difficult to control the mass production. Natural fibres are highly affected by its growing environment such as composition of soil, temperature, humidity, and frost. Plantation and harvesting methods can also cause variation in density [88]. Natural fibres are tough, elastic and demonstrate good mechanical strength. The composite from natural fibres is introduced for commercial purpose and becomes a good alternative of glass reinforced composites in many uses. A comparison of various parameters between natural fibres and glass fibres is described in Table 4.

Although synthetic composites like glass fibres have high density with significantly high cost, natural fibre (flax fibres) exhibits fairly good density of 1.5 g/cm³ and cost between \$0.22 and \$1.10/kg [89]. In other words, the cost of glass fibres is nearly about 1200–1800 US\$/tonnes and density is around 2500 kg/m³ while natural fibres cost lies between 200 and 1000 US\$/tonnes and density varies from 1200 to 1500 kg/m³ [90].

TABLE 2: Chemical composition of natural fibres [41, 44].

Type of fibre	Cellulose	Lignin	Hemicellulose (%)	Pectin (%)	Ash (%)	Moisture content (%)	Waxes	Microfibrillar angle (deg)
Fibre flax	71	2.2	18.6–20.6	2.3	—	8–12	1.7	5–10
Seed flax	43–47	21–23	24–26	—	5	—	—	—
Kenaf	31–57	15–19	21.5–23	—	2–5	—	—	—
Jute	45–71.5	12–26	13.6–21	0.2	0.5–2	12.5–13.7	0.5	8.0
Hemp	57–77	3.7–13	14–22.4	0.9	0.8	6.2–12	0.8	2.62
Ramie	68.6–91	0.6–0.7	5–16.7	1.9	—	7.5–17	0.3	7.5
Kenaf	37–49	15–21	18–24	—	2–4	—	—	—
Jute	41–48	21–24	18–22	—	0.8	12.5–13.7	0.5	8
Abaca	56–63	7–9	15–17	—	3	5–10	—	—
Sisal	47–78	7–11	10–24	10	0.6–1	10–22	2	10–22
Henequen	77.6	13.1	4–8	—	—	—	—	—

TABLE 3: Mechanical properties of natural fibre [44, 45].

Fibre	Density (g/cm ³)	Elongation (%)	Tensile strength (MPa)	Moisture absorption	Young's modulus (GPa)
Cotton	1.5–1.6	3.0–10.0	287–597	8–25	5.5–12.6
Jute	1.3–1.46	1.5–1.8	393–800	12	10–30
Flax	1.4–1.5	1.2–3.2	345–1500	7	27.6–80
Hemp	1.48	1.6	550–900	8	70
Ramie	1.5	2.0–3.8	220–938	12–17	44–128
Sisal	1.33–1.5	2.0–14	400–700	11	9.0–38.0
Coir	1.2	15.0–30.0	175–220	10	4.0–6.0
Softwood kraft	1.5	—	1000	—	40.0
E-glass	2.5	2.5–3.0	2000–3500	—	70.0
S-glass	2.5	2.8	4570	—	86.0
Aramide (normal)	1.4	3.3–3.7	3000–3150	—	63.0–67.0
Carbon (standard)	1.4	1.4–1.8	4000	—	230.0–40.0

TABLE 4: Comparison between glass fibre and natural fibres [45].

Properties	Natural fibre	Glass fibre
Density	Low	Double
Cost	Low	High
Renewability	Yes	No
Recyclability	Yes	No
Energy consumption	Low	High
Distribution	Wide	Wide
CO ₂ neutral	Yes	No
Abrasion to the machine	No	Yes
Health risk when inhaled	No	Yes
Disposal	Biodegradable	Nonbiodegradable

3. Pineapple Plant

Pineapple is perennial herbaceous plant with 1-2 m for height and width belongs to family Bromeliaceae [91]. It is chiefly cultivated in coastal and tropical regions, mainly for its fruits purpose. In India, it is cultivated on about 2250 000 acres of land [92] and is continuously increasing its production. Figures 1(a) and 1(b) show a pineapple plant in the field; it is

a short stem with dark green colour. First sprout of leaf looks decorative; later it converts into 3 ft. long, 2 to 3 inch wide sword shaped and numerous spirally arranged fibrous leaves edges as well as curved towards the cross section to maintain the stiffness of the leaf [93].

Each pineapple fruit has equal number of hexagonal sections on outer shell and does not depend on the size or shape. Now Malaysia is one of large producers in Asia as much as Hawaii. It produces a huge amount of waste material, about 384,673 metric tonnes in year 2008 [2]. Productions of Pineapple leaf fibres are plentiful for industrial purpose without any supplementary addition and annually renewable and of easy availability [94]. Pineapple is known as Nanas in Malaysia; basically they use different varieties for different purpose; for commercial purpose they use red pineapple and green pineapple; for edible purpose, they prefer Sarawak pineapple and Morris pineapple. Pineapple fruits contain many major and minor elements. Table 5 shows the percentage of elemental found in pineapple fruit. It is source of bioactive compounds, particularly in proteolytic enzymes. Pineapple is very rich source of bromelain and other cysteine proteases are present in different part of pineapple [95, 96]. Commercially, bromelain has been used in many food industries, cosmetics, and dietary supplements [46, 97].

TABLE 5: Elemental composition of pineapple plant.

C	O	N	Ca	P	Fe	k	Mg	Cu	O/C ratio	Reference
73.13	24.17	2.70	0.00	—	—	—	—	0.00	0.33%	[46]
—	—	6.4–10	2.5–10	0.1–0.18	0.06–0.11	2.89	0.33	0.002–0.02	—	[47]

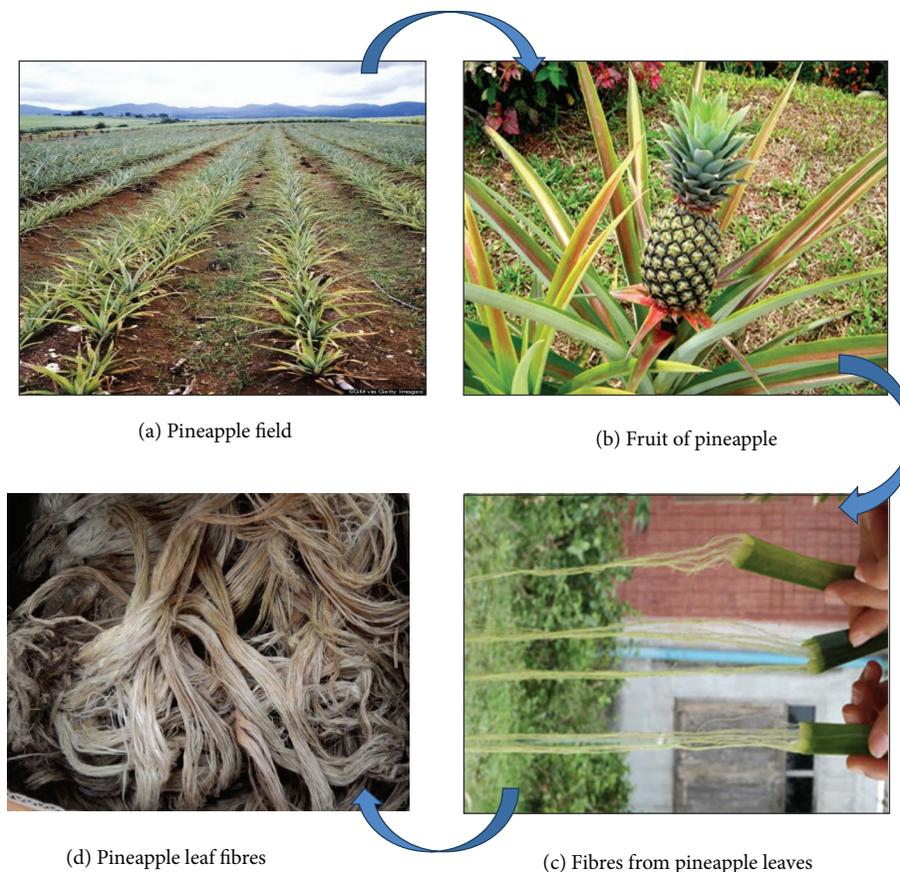


FIGURE 1: Production of pineapple leaf fibre, sequential (a) plantation of pineapple, (b) fruit of pineapple, (c) extraction of fibres from pineapple leaves, and (d) Indonesian PALF.

3.1. History. Pineapple is a native plant of America, first seen by Columbus and his companion in November 4, 1493, at an island of West Indies. When the new world was discovered, pineapple has been spread all over South America coastal region as well as in tropical regions. A Spanish government officer, De Oviedo, came to America in 1513; he handed over first written documents of some varieties of pineapple, and he added some Indies varieties also. The plant is called “pineapple” because of its fruit which look like pine cone. The native Tupi word for the fruit was *anana*, meaning “excellent fruit;” this is the source for words like *ananas*, common in many languages. The pineapple is an old emblem of welcome and can often be seen in stamped decorations. In 17th century Americans imported pineapple from Caribbean because of its apparently exotic features and rareness; pineapple began to be considered as an icon of wealthy people in America. The Portuguese contributed their important role in introducing the fruit throughout the whole tropical regions and major parts of world like south and east coast of Africa, Madagascar,

south India, China, Java, Philippines, and Malaysia [47]. Nowadays, varieties of pineapple plants are available which are used in various applications such as edible, medicinal, and industrial applications. For example, bromelain is an enzyme extracted from its leaves and helps in respiratory ailments. A mixture of pineapple juice and sand is powerful cleaner for boat decks. Dehydrated waste material of pineapple is used as bran feed for cattle, chicken, pigs, and so forth [98].

3.2. Pineapple Leaf Fibre. Every year tonnes of pineapple leaf fibres are being produced, though very small portions are being used in the field of feedstock and energy production. The expansion of biocomposites has amplified industrial usage that would release the possibilities to minimize the wastage of renewable materials. It promotes a non-food-based market for agricultural industry [99]. It is white in colour, smooth, and glossy as silk, medium length fibre with high tensile strength. It has a softer surface than other natural fibres and it absorbs and maintains a good colour [100].

However, PALF has high specific strength and stiffness; it is hydrophilic in nature due to high cellulose content [101–103]. Extraction of fibres from pineapple leaf fibre is carried out by mechanical method and retting method, exhibited in Figure 1(c). Fresh leaves yield about 2 to 3% of fibres [104]. Fibrous cell of PALF consists of vascular bundle system in the form of bunches which is obtained after mechanical removal of the entire upper layer after harvesting. PALF is composed of many chemicals constituents. It is multicellular lignocellulosic fibre containing polysaccharides, lignin in major amount, and some minor chemicals like fat, wax, pectin, uronic acid, anhydride, pentosan, colour pigment, inorganic substance, and so forth [105]. Fibre is collection of thin and small multicellular fibres which appears like a thread. These cells are tightly joined with the help of pectin [106]. PALF constitute cellulose (70–82%) and arrangement of fibres is the same as in cotton (82.7%) [55, 107, 108].

In all the collection, pineapple leaf fibre is more compatible natural fibre resource and constitutes a good chemical composition. PALF has better mechanical strength than the jute when it is used in making of fine yarn [109, 110]. The cellulosic molecules model of PALF is a three-dimensional structure and parallel to crystalline region of the fibre. Remaining parts of molecular structure are supposed to associate within amorphous regions. Pineapple leaf fibre (PALF) is vital natural fibre, which have high specific strength, rigidity, and flexural and torsional rigidity as much as jute fibres. Considering these exclusive properties of PALF, industries can use it as an outstanding alternative raw material in the prospect of reinforcing composite matrixes [30].

3.3. Extraction of Pineapple Leaf Fibres (PALF). Pineapple natural fibres have excellent mechanical strength but due to lack of knowledge it is still not utilised properly. It can be used in various applications like artificial fibres, as a sound absorber and thermal insulator, and so forth. There are various methods to extract the PALF from leaves of pineapple.

3.3.1. Scrapping Method of Extraction. Scrapping machine is the machine used for scrapping the pineapple leaf fibre [111]. The machine is the combination of three rollers: (a) feed roller, (b) leaf scratching roller, and (c) serrated roller [53]. Feed roller is used for the feeding of leaves into the machine; then leaves go through the second roller that is called scratching roller. It scratches upper layer of leaf and removes the waxy layer. And at last leaves come to the dense attached blade serrated roller, which crushes leaves and makes several breaks for the entry passage for the retting microbes [112].

3.3.2. Retting of Pineapple Leaves. In retting process, small bundles of scratched pineapple leaves are immersed in a water tank which contains substrate : liquor in 1 : 20 ratio, urea 0.5%, or diammonium phosphate (DAP) for fast retting reactions. Materials in water tank are regularly checked by using finger to ensure fibre are loosened and can extract many chemical constituents like pentosans, lignin, fat and wax, ash content, nitrogenous matter, and pectin. After retting process, fibres

are segregated mechanically, through washing in pond water. Extracted fibres are dried in hanging place by air. Both ball mill and disc mill can be used to extract PALF from chopped fresh pineapple leaf [113]. The methods not only are simple but also provide higher fibre yield and smaller fibre than the conventional methods. Among the two mechanical grinding methods studied, wet ball milling is much slower but provides PALF with a greater number of elementary fibre [114].

3.4. Chemical Composition. Technical Association of Pulp and Paper Industry (TAPPI) [115] standards reported that the chemical constituents and extractive like holocellulose, α -cellulose, lignin, and ash content of PALF were analysed from different source of fibres, age of fibres, and climatic conditions. The procedure to extract the fibres may attribute the factor of various types of chemical composition and cell wall structure [116]. In a transmission electron microscopy, PALF cell wall shows distinct different layers as primary (P), secondary, and tertiary (S1, S2, and S3) layers. The chemical composition of PALF is depicted in Table 6. Pineapple leaf fibres have many chemical constituents like α -cellulose, pentosans, lignin, fat and wax, pectin, nitrogenous matter, ash content, degree of polymerization, crystallinity of α -cellulose, and antioxidants [54, 117, 118]. PALF has a large quantity of α -cellulose (81.27), low quantities of hemicelluloses (12.31%), and lignin content (3.46%) [106]. PALF has higher cellulosic content as compared to other natural fibres like oil palm frond, coir, and banana stem fibres [116]. The higher quantity of cellulose in PALF supports the higher weight of the fruit [119]. The chemicals composition fibre directly affects performance of fibres [120].

3.5. Physical and Mechanical Properties. Reinforced natural fibres composite plays a huge share in biocomposite and material science. PALF has been proved as a good substitute of synthetic fibres, because of its economical and renewable nature. Specific strength of natural fibres supports in enhancing the physical and mechanical strength of polymer matrix without using any additional processing. The superiority of PALFs mechanical properties is related with the high content of alpha-cellulose content and low microfibrillar angle (14°). Due to extraordinary qualities of PALF, it can be used as reinforcing composite matrix [30]. The physicomaterial properties of any natural fibres depend on fibre-matrix adhesion, volume fraction of fibre, aspect ratio, orientation, and stress transfer efficiency at interface [60]. The result of PALF based polymer composites shows excellent stiffness and strength compared to other cellulose based composite materials [73]. Strange characteristics of PALF are noticed; that is, a wet PALF bundle exhibits lower strength by 50%, but when it converts into yarn, its strength increases up to 13%. Table 7 shows the physical and mechanical strength of PALF. The PALF exhibits a modulus range from 34.5 to 82.51 GN·m⁻², tensile strength ranges from 413 to 1627 MN·m⁻², and an elongation at breakpoint ranges from 0.8 to 1.6%. PALF can sustain abrasiveness [121]. Datta et al. [122] studied many different types of properties and behaviour like morphology of surface structure, tensile

TABLE 6: Chemicals composition of PALF.

Cellulose content (%)	Hemicellulose (wt.%)	Lignin content (%)	Pectin (wt.%)	Holocellulose	Moisture content (wt.%)	Extractives	Ash (%)	Fat & wax	PALF composition /reference
85	—	12	—	—	—	—	—	—	[48]
70–82	—	5–12	—	—	11.8	—	—	—	[49]
67.1–69.3	—	14.5–15.4	—	—	—	—	1.21	—	[50]
68.5	18.8	6.04	1.1	—	—	—	0.9	3.2	[51]
69.5	—	4.4	1.2	—	—	—	2.7	4.2	[52]
69.5	—	4.4	1.1	—	—	—	0.9	3.3	[53]
70–80	—	5.0–12.7	—	—	11.8	—	—	3.3	[14]
74.33	—	10.41	—	80.68	—	6.6 8	4.73	—	[54]

TABLE 7: Physical and mechanical strength of PALF.

Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Specific strength (GPa/g/cm ³)	Specific modulus (GPa/g/cm ³)	Elongation at break (%)	Dia. (μ m)	Microfibril angle	PALF fibre /reference
1.52	413–1627	34.5–82.51	0.3–1.1	22.7–54.3	1.6–3	20–80	—	[55]
1.526	170	62.10	1.1	40.70	3	—	—	[24]
1.44	413–1627	34.5–82.51	—	—	1.6	—	—	[56, 57]
1.526	413	62.10	—	—	1.6	50	—	[58]
1.07	126.60	4.405	—	—	2.2	—	—	[22]
	413–1627	34.5–82.5	—	—	1.6	20–80	14	[14]
1.526	170	6.260	—	—	3	—	—	[27]
1.52	170	6.21	—	—	3	—	—	[59]
1.07	126.60	4.405	—	—	2.2	—	—	[60]
1.526	413	6.5	—	—	1.6	30–60	—	[61]
1.526	170	62.10	—	—	3	—	—	[62]
1.44	413–1627	34.5–82.51	—	—	—	20–80	8–14	[63]
1.44	413–1627	34.5–82.51	—	—	1.6	20–80	—	[33]
1.44	170	6.26	—	—	1.6	5–30	12	[64]
1.526	413	4.2	—	—	3.0–4.0	50	14	[65]
1.440	—	—	—	—	—	1.56–4.5	8–15	[66]
—	293.08	18.934	—	—	1.41	150–300	—	[67]

behaviour, and dielectric property. PALF shows good elastic property in cellulose type I structure. In comparison to other natural fibres PALF has high strength. The electrical properties show high anisotropy.

3.6. FTIR Spectra. FTIR spectroscopy is used to observe functional groups in natural fibres, such as hydroxyl group, carbonyl groups and vinyl groups, ketone group, and many more. It helps to identify the changes in chemical compound of natural fibres before and after the chemical treatments [123]. Table 8 shows the typical FTIR spectra of various untreated natural fibres hemp, sisal, jute, kapok, kenaf, and oil palm fibre along with PALF. The characteristic of the O–H group is common for all, visible in between the intensity of 3338–3450 cm⁻¹. The untreated fibres show common peaks corresponding C–H stretching and C–O stretching at 2924.2 and 1741.1 cm⁻¹, respectively [69]. According to Jonoobi,

in kenaf, the broad peak at 3338 cm⁻¹ which appears in spectra is attributed to the O–H frequency, whereas the peaks at 2899 cm⁻¹ mainly take place from C–H stretching [124]. Sreekala noted that the untreated oil palm fibre shows peaks corresponding C–O stretching at 770 cm⁻¹ and C–H stretching at 2850 cm⁻¹, whereas oil palm fibre shows another peak at 3450 cm⁻¹ due to the –O–H stretching [69].

FTIR spectra of holocellulose and α -cellulose samples free from extractive of PALF are presented in Figure 2 [54]. The peak 3343 cm⁻¹ represents O–H groups in case of α -cellulose sample. In holocellulose and free-extractive samples, hydroxyl stretching frequency displayed at 3,296 cm⁻¹ and 3327 cm⁻¹, respectively. For α -cellulose sample, another peak frequency at 1725.25 cm⁻¹ shows C–O bending frequency. While, in case of holocellulose and free extractive, the peak frequency at 1728 and 1733 cm⁻¹ corresponds to the carbonyl peak frequencies, respectively. The sharp band

TABLE 8: Infrared transmittance peaks (cm^{-1}) of untreated natural fibres [28, 68–70].

Bond/stretching	PALF (cm^{-1})	Hemp (cm^{-1})	Sisal (cm^{-1})	Jute (cm^{-1})	Kapok (cm^{-1})	Kenaf (cm^{-1})	Oil palm fibre (cm^{-1})
–OH	3349.9	3448	3447.2	3447.9	3419.7	3338	3450
C–H	2903.8	2920.5	2924.2	2918.8	2918.1	2899	2850
C=O	1737.4	—	1736.5	1737.2	1741.1	1736	1735
C=C	1608.3	1654	1653.9	1653.8	1596.1	—	1606
C–H	1374.2	1384.1	1384.1	1384.1	1383.6	—	—
C–H	—	—	1259.9	1255.6	1245.5	—	—

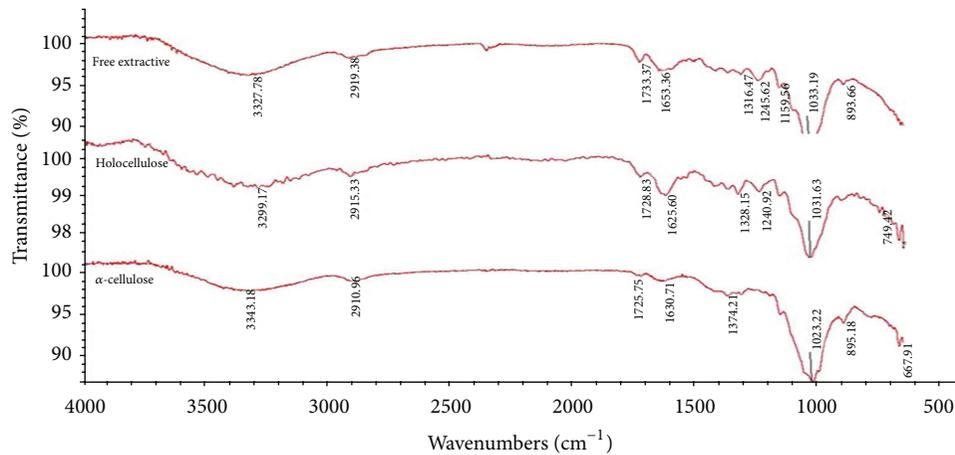


FIGURE 2: FTIR spectra of pineapple leaf fiber in various forms [54] (With Permission).

observed at 1733 cm^{-1} is due to the absorption of carbonyl stretching of ester and carboxyl groups which is most abundant in pineapple leaf hemicelluloses [54].

4. Challenges for PALF as Reinforcement

PALF shows lower degree of compatibility with hydrophobic polymers due to its hygroscopic nature. Existence of natural waxy substance on surface of fibre layer provides low surface tension, which does not allow a strong bond with polymer matrix. However, the literature suggests various methods to improve the fiber surface to make it suitable for good interfacial fibre/matrix bonding. Natural fibres reinforced polymers are susceptible to humidity and water absorption that causes a physical degradation of final product. High moisture content in fibre can cause swelling or dimensional defect at the time of composites preparing that affect the physical and mechanical property of the final product. [62]. At low temperature, water molecule faces obstacle by stiffness of polymer chain segments. Moisture diffusion into polymer depends on various factors such as molecule structure, polarity, crystallinity and the hardeners used in composite making [125].

5. PALF Based Composite

Natural fibres are focused study among researchers and industries, as a replacement of glass fibres to natural fibres. The rapid growth in research on environmental issues

is acceleration factors to utilise natural fibres in coming decades. Recently, PALF is being utilised effectively in polymer matrix to develop composites with improved mechanical strength [126]. The outstanding mechanical properties of individual PALF are reflected in its ultimate product. Various research has been done to reinforce PALF with thermoset [73], thermoplastic [64], biodegradable plastics [25, 26], and natural rubber [127].

5.1. Epoxy Based PALF Reinforced Composite. Epoxy resin has excellent properties like adhesion, strength, low shrinkage, corrosion protection, and many other properties [128]. Although it is expensive resin, its mechanical and chemical properties are very good. Natural fibres like jute, flax, sisal, and bamboo fibres with epoxy reinforced have been studied [129–133]. In case of PALF there is no work done yet. PALF has a major problem related to adhesion with many polymer matrices. PALF is hydrophilic in nature and it does not have good compatibility with hydrophobic polymer. PALF contains waxy substance on its surface causing low surface tension which negatively affects the bonding with polymer matrix. To overcome this issue PALF surface is modified to improve bonding. In surface modification process reagents make fibres hydrophobic in nature and graft the fibres surface with resin matrix and some compatible polymers [134]. A number of researches have been carried out to improve the adhesion between PALFs and matrix, for example, cyanoethylation, alkalization, dewaxing, and grafting of acrylonitrile monomer [135]. These methods have

been proved to be a very effective modification to enhance the adhesion property of PALFs with polymer matrix. Benzoylated PALF with alkali treatment are used to enhance the adhesion and tensile properties. The alkalization process makes the fibres surface rough and improved mechanical hold. A rough surface improves the affinity of epoxy matrix and interfacial adhesion made strong due to deposition of DGEBA resin on fibres surface. Furthermore PALF-epoxy composites will exhibit a positive result in interfacial bonding when combination of alkalization and DGEBA solution will be used. Such kinds of surface modification will enhance the flexural, tensile, and impact properties of epoxy composite [126].

5.2. Polyethylene Based PALF Reinforced Composites. A pineapple leaf fibre reinforced with polyethylene exhibits high performance composites [9]. In comparison to other natural fibres, pineapple leaf fibre (PALF) shows excellent mechanical and physical properties but the hydrophilic nature of PALF causes a negative impact. Thus, a chemical treatment such as alkali, isocyanate, saline, and permanganate was carried out to improve the water resistance. Peroxide modification is very helpful to reduce the hygroscopicity of fibres [136].

5.3. Polypropylene Based PALF Reinforced Composites. Pineapple leaf fibres (PALF) are renounced as possible and plentiful substitutes for the high-priced and nonrenewable synthetic fibres. PALF enhances the mechanical properties of the polymer matrix through its own high specific strength. PALF is multicellular, lignocellulosic and has very good mechanical properties. In study of stress behaviour of PALF reinforced polyethylene composite, stress is inversely proportional fibre content. Mechanical properties of polypropylene-pineapple leaf fibre reinforced composites are reported. The tensile and flexural properties of composites are depending on volume fraction [60]. The recent study showed very useful composites with high-quality strength. PALF is being used as a reinforced agent in polypropylene matrix in the place of pure resin, to improve the mechanical properties. Flexural modulus and flexural stress are directly related to the volume fraction. Though, value is insignificant due to fibre-to-fibre repulsion and dispersion problems. Researchers are mainly focused on improving the mechanical properties of PALF-PP composites and interfacial relation.

5.4. Vinyl Ester Based PALF Reinforced Composites. Now natural fibres are widely used in the research as a substitute of glass fibre (GF) in fibre reinforced plastics (FRP). In comparison to glass fibre, these natural fibres have lower densities, are economical, consume lesser energies during production, cause less or no abrasion to machines, and are not hazardous to health when inhaled [137]. In spite of these properties, pineapple leaf fibres are untouched in research areas especially for reinforcing plastics although this application is now becoming an important research area. Now polymers composite is focused on using pineapple leaf fibres for developing value added applications. Despite several merits, PALF possesses inherent demerits such as

poor interfacial fibre-matrix adhesion and absorbing water. In the last two decades, a lot of researches have been carried out to optimize the problem of the interfacial adhesion between natural fibres and polymer matrices [82]. There is not much literature available on PALF-vinyl composites. Vinyl esters are strong, flexible, and less hydrophilic in nature [138]. Moreover, interfacial shear stress (IFSS) is the measurement of fibre-matrix adhesion which is always higher for natural fibre-vinyl ester compared to those of other matrices [139]. Most of the work on PALF-reinforced thermoset composites used hand lay-up method in sample preparation and very few if any reported the use of liquid compression moulding process. As reinforced matrix, both untreated and bleached PALF are using in the form of random and unidirectional PALF mats. To evaluate the viability of PALF-vinyl ester eco-composites, there are many criteria of measurement, for instance, mechanical properties, water absorption, and thermal stability.

5.5. Polyester Based PALF Reinforced. PALF is obtained from the pineapple plant's leaves. Major compounds of PALF are cellulose (70–80%), lignin (5–12%), and ash (1.1) [140]. The recent study proved that by using different surface modified pineapple leaf fibres as reinforcing material can be used for polyester matrix. PALF fibre loading up to 30% by weight with polyester showed significant increment in flexural strength, tensile strength, and impact strength. Toughness of composite material is reached up to the benchmark of engineering materials. Surface modification by chemical treatment can enhance the strength of individual fibers and it can help to develop better mechanical strength PALF/polyester composite for commercial purpose [71].

5.6. Polycarbonate Based PALF Composite. A poor contact between PALF and matrix are prone to moisture intake and ultimately degradation through insects and pests [31, 141]. Thus, fibre surface modification is an important and necessary step to reduce the polarity of fibre. There are many methods like alkaline treatment [142], grafting with maleic anhydride copolymer [34], saline coupling agent such as *c*-aminopropyl trimethoxy silane (Z-6011) and *c* methacrylate propyl trimethoxy saline (Z-6030) [143, 144]. Polycarbonate (PC) is an amorphous thermoplastic resin. It provides numerous vital and important characteristics such as lucidity, dimensional strength, high impact strength, and high heat resistant and flame resistance. Though there are some limitations of using the PALF in some applications. At low temperatures, it becomes softer and easy to remove from mould [145]. There are very few research works published on the PALF reinforced with polymers [146].

5.7. Low Density Polyethylene Based PALF Composite. Melt mixing and solution mixing techniques have been used in preparation of PALF reinforced LDPE composites. Solution mixed technique shows a better tensile strength than melt mixed technique. Relation of fibre size, loading %, and orientation with mechanical properties has been studied. Through fibre distribution curve and scanning electron micrographs,

TABLE 9: PALF biocomposites and hybrid composites with thermosets and thermoplastics.

Natural fibre	Resin	References
PALF	Vinyl ester	[71]
PALF	Epoxy	[72]
PALF	Polycarbonate	[35]
PALF	Polypropylene	[60]
PALF	Polyester	[73]
PALF	Low density polyethylene	[74]
PALF	Polyethylene	[75]
PALF + banana	Epoxy resin	[76]
PALF + disposable chopstick hybrid fibre	PLA & polybutylene succinate (PBS)	[77]
PALF + kenaf	HDPE	[78]
PALF + glass fibre	Polyester	[79]

it is possible to analyse fibre rupture and damage during composite making. Fibre length of 6 mm length was found to be suitable for PALF reinforced with LDPE. Mechanical properties are found to be improved and elongation at break is inversely proportional to fibre loading. In comparison to random and transverse orientation, longitudinal orientation of fibres showed better mechanical properties of composites. PALF-LDPE composites are ecofriendly, biodegradable and exhibit superior performance than any other cellulose-fibre-reinforced LDPE systems [74].

6. PALF Based Hybrid Composites

Various combinations of natural lignocellulosic composite are promising interest of researchers. It provides wide range of results and properties which is very difficult to achieve through a single type of reinforcement. This type of matrix is generally used for the fibre having good interaction between matrix and fibres and together gives a better mechanical performance [147, 148]. Thus, hybrid composite is the mixture of two different types of fibres reinforced into a matrix. It has various improved qualities which help to make it best composite. Individual strength of fibres is combined to achieve improved composite with better efficiency. Many researches are in progress for partially or fully replacement to glass fibres (GF) by natural fibres. GF has very good quality of reinforcement along with natural fibres like sisal, jute, pineapple, hemp, and so forth [149, 150]. Composites and hybrid composites with PALF are shown in Table 9. Mechanical characteristic of hybrid composite and GF is studied by Thomas et al. [151, 152]. Idicula et al. studied the well mixed random orientation of banana/sisal hybrid fibre reinforcement with polyester composite [153]. Transformation maximum stress between fibres and matrix has been calculated for the composite of banana and sisal fibre ratio 3:1, showing lowest impact strength. There is another

composite of natural fibre reinforced with short carbon and kenaf fibre hybrid system [154]

On the basis of these studies, the aim of this research is to develop a high-performance, cost-effective, and lightweight pineapple leaf fibres and GF as the reinforcement based hybrid composites. Utilization of pineapple leaf with disposable chopsticks is very popular [155, 156]. Pineapple leaf fibre (2.3–3.9 mm) and recycled disposable chopstick fibres were integrated into PLA and PBS. The optimum ratio and content of the hybrid fibres were investigated in order to obtain the best thermal and mechanical properties.

7. PALF Applications and Future Prospects

PALF is generally used in making threads for textile fabrics from several decades. A future prospect of diversified application of PALF is presented in Figure 3. Present application of PALF for various purposes is textile, sports item, baggage, automobiles, cabinets, mats, and so forth. Surface modified PALF is introduced for making machinery parts like belt cord, conveyor belt cord, transmission cloth, air-bag tying cords, and some cloths for industry uses [157]. PALF is very good for carpet making because of its chemical processing, dyeing behaviour, and aesthetically pleasing fabric [158]. The use of pineapple leaf fibre can be considered relatively as new in the paper manufacturing industry in Malaysia [159]. PALF can be suitable for various other applications such as cosmetics, medicine, and biopolymers coating for chemicals [160–162].

The pineapple leave fibre is one of the natural fibres, having highest cellulosic content nearly 80%. Its density is similar to the other natural fibres while Young's modulus shows highest tensile strength when compared to other natural fibres. These properties are suitable for its application as building and construction materials, automotive components, and furniture. From this review it is clear that limited work has been done on thermal, electrical, dynamic, and mechanical properties. Till now, PALF has been studied as being reinforced with PP and unsaturated polyester only, so it is required to understand its behaviour with other resins also in relation to fabricated biocomposites and hybrid composites. PALF is widely accepted in textile sector and already used in our daily life materials but we attribute that further study will enhance the application in various other exiting products.

8. Conclusions

Pineapple leaf fibre is very common in tropical regions and very simple to extract fibres from its leaves. The utilization of pineapple leaf fibre in composite material is a new source of materials which can be economic, ecofriendly, and recyclable. However, the main issue of PALF is its hydroscopic nature, which makes a big hurdle for fibre utilization as a reinforced material in polymer composites. Surface modification of PALF is required to improve for good interfacial adhesion of PALF with polymers in fabrication of polymer composites. Synthetic fibres can be replaced or partially substituted with PALF in fabrication of composite

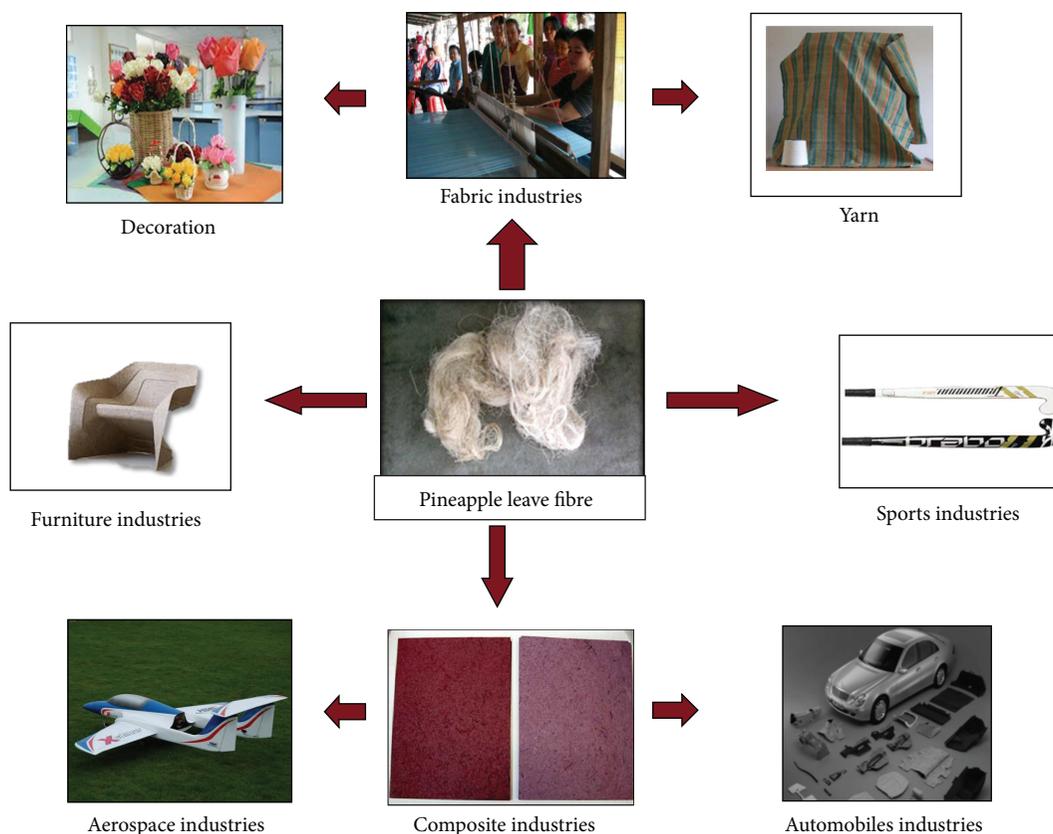


FIGURE 3: Various present and future applications of pineapple leaves.

products for different applications. The author concluded various recent works reported on chemical modification of PALF and physical and mechanical properties of PALF reinforced polymer composites and its hybrid. Pineapple is one of the natural fibres having highest cellulosic content nearly 80%. Density of PALF is similar to other natural fibres while Young's modulus is very high, and tensile strength is highest among the related natural fibres. These properties are suitable for its application as building and construction materials, automotive components, and furniture. From this review it is clear that limited work has been carried out on thermal properties such as, electrical properties, thermal conductivity, dynamic mechanical analysis, and modelling of mechanical properties of PALF reinforced polymer composites. In most of the examples, PALF fibres are reinforced with PP and unsaturated polyester only, so it is required to study the behaviour of PALF with other resins to get wider application in biocomposites and hybrid composites manufacturing. PALF is widely accepted in textile sector and already used in our daily life materials but we attributed that further study will enhance its application in development of various existing products.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Influence of Incorporation of Natural Fibers on the Physical, Mechanical, and Thermal Properties of Composites LDPE-Al Reinforced with Fique Fibers

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This study shows the effect of the incorporation of natural fique fibers in a matrix formed by low-density polyethylene and aluminum (LDPE-Al) obtained in the recycling process of long-life Tetra Pak packaging. The reinforcement content was 10, 20, and 30% fibers, manufactured by hot-press compression molding of composite boards (LDPE-Al/fique). From the thermogravimetric analysis (TGA) it was determined that the proportions of the LDPE-Al were 75 : 25 w/w. Likewise, it was found that the aluminum particles increased the rigidity of the LDPE-Al, reducing the impact strength compared to LDPE recycled from Tetra Pak without aluminum; besides this, the crystallinity in the LDPE-Al increased with the presence of aluminum, which was observed by differential scanning calorimetry (DSC). The maximum strength and Young's modulus to tensile and flexural properties increased with the incorporation of the fibers, this increase being a direct function of the amount of reinforcement contained in the material. Finally, a reduction in the density of the compound by the generation of voids at the interface between the LDPE-Al and fique fibers was identified, and there was also a greater water absorption due to weak interphase fiber-matrix and the hydrophilic fibers contained in the material.

1. Introduction

In industry, composite materials have attracted great interest due to their good specific properties. These are evaluated according to the materials' mechanical performance, which depends on the characteristics of each of their components, the arrangement of the reinforcement in the matrix, and interfacial quality. In recent years, interest has grown worldwide in the incorporation of cellulosic fibers such as sisal, fique, jute, henequen, and wood pulp, among others, in composites, because present studies show that for their good mechanical properties the fibers can act as reinforcing polymeric matrices [1–6].

Among natural fibers, it can be highlighted that fique has an average density of 1.47 g/cm³, a diameter (equivalent to the area) of around 0.24 μm, an ultimate strength of approximately 132.40 MPa, and Young's modulus between 8.20 and 9.10 GPa. This fiber is produced in different departments of

Colombia, mainly Cauca, Nariño, Santander, and Antioquia, which produce 98% of the fiber in the country [7–11].

Moreover, the trend in the state of the art tends to point toward polymeric matrices coming from renewable sources or recycling processes involving high turnover products. Amongst the latter class of materials are mixtures of low-density polyethylene and aluminum (LDPE-Al) obtained from the recycling of long-life Tetra Pak packaging, which are composed of 5% aluminum, 20% polyethylene, and 75% paperboard. Neves in 1999 reported the basic process to the industrial recycling of the Tetra Pak packaging, mainly based on the separation of the paperboard layer of the aluminum and polyethylene layers by hydropulping process for 35 min, where cellulosic fiber was obtained suitable for use in different papermaking process, while the LDPE-Al's residue could be used in power generation (through incineration) or in the manufacture of plastics elements, such as chipboards; also, it is possible to recover the aluminum by pyrolysis [9, 12].

Mourad et al., 2008 [13], analyzed the influence of recycling of the Tetra Pak packaging on the reduction of Global Warming Potential (GWP); they determined that an increase in recycling from 2% (2000) to 22% (2004) reduces the GWP in more than 14%, and a 48% could be reached if the recycling of Tetra Pak packaging increases to 70%.

Due to the global interest, particularly by the Tetra Pak company, in the recovery and reuse of LDPE-Al, in this work we studied the influence of incorporating fique fibers in a matrix based on a binary mixture of LDPE and aluminum (LDPE-Al) on some physical, thermal, and mechanical properties of composite LDPE-Al/fique. The material is manufactured by the hot-plate press molding process with fique contents of 10, 20, and 30% by volume; these values of contents were determined from previous works, where it was observed that using the same process implemented in this work it is difficult to achieve a good distribution of the fibers in the composite and complete wetting of the fibers with the matrix when content of fiber is above 30% [9]. The characterization focused primarily on the tensile, flexural, and impact mechanical performance of the material. Also, we evaluated the influence of the fibers on the heat stability, crystallinity, density, and water absorption of the material.

2. Materials

The LDPE-Al without cellulose used in this research as composite matrix, supplied by INNOPACK LTDA, was processed in order to reduce its particle size. The material has a LDPE/aluminum ratio of 89.75/10.25 v/v by volume and a density of 1.10 g/cm³. Fique fibers belonged to the (white) eagle claw variety of the *Furcraea* genus and were supplied by Compañia de Empaques de Medellin; these fibers were used without any treatment and were arranged in the compound as a two-dimensional mat with a random arrangement, as shown in Figure 1. The fique employed had an average length of 51.70 ± 33 mm, maximum tensile strength of 263.65 MPa, average Young's modulus of 8.64 ± 0.71 GPa (measured with fiber lengths of 50 mm), and true density of approximately 1.102 g/cm³ [11, 14].

3. Experimental Procedures

3.1. Preparation of Composite and Specimens. The composite material formed with the binary mixture LDPE-Al as a matrix and fique as reinforcing fibers (LDPE-Al/fique) was obtained as rectangular boards with dimensions of 290 × 290 × 2 mm, using for this purpose one hot-plate press and a forced water circulation cooling system (LabPro 400, Fontijne Presses). To shape the specimens, stainless steel close-up type molds were used, where layers of LDPE-Al and fique fiber mats (to reach the desired percentages of fibers of 10, 20, and 30% fiber volume) were alternately placed. The molding was conducted at a temperature of 170°C and a pressure of 3 MPa; the complete process was 15 min, comprising 11 min of heating and 4 min of cooling under pressure (Figure 2). Finally the boards were demolded and adjusted to the required dimensions in various

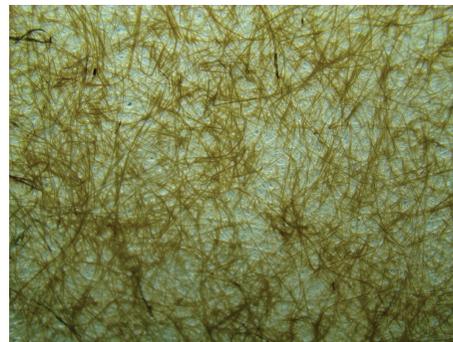


FIGURE 1: Dimensional randomization of fique mat used in the reinforcement of the LDPE-Al.

mechanical (tensile, flexural, and impact), physical (density, water absorption), and thermal (thermogravimetry and differential scanning calorimetry, DSC) tests using a numerical control router.

3.2. Mechanical Tests. Tensile mechanical properties were determined on samples of LDPE-Al matrix and the three LDPE-Al/fique composites with 10, 20, and 30% reinforcement. In all cases this characterization was performed after 48 hours of conditioning at a temperature of 25°C and relative humidity of 50%. The tests were conducted on an Instron 3366 mechanical universal testing machine fitted with a 10 kN load cell. Type I specimens were used and tested with a speed of displacement between clamps of 5 mm/min following the ASTM standard D638. All measurements were carried out on five test specimens and the analysis took into account the average of these ratings.

Through the flexural test, the mechanical flexural properties of LDPE-Al with and without reinforcement were measured. The materials were subjected to 48 hours of conditioning at a relative humidity of 50% and a temperature of 25°C. The tests were carried out on an Instron 3366 universal mechanical testing machine equipped with a 10 kN load cell. The specimens used had dimensions of 12.70 mm × 100 mm × thickness (thickness varied depending on the compound) and were evaluated at a speed within the range of 0.79–1.01 mm/min (the rate was determined based on the dimensions of the specimen). The distance between the supports was 16 times the thickness of the specimen and the test was conducted up to 5% strain, following the ASTM D790 standard. All measurements were carried out on five test specimens and the analysis took into account the average of these ratings.

The impact strength of LDPE-Al and LDPE-Al/fique for the three compounds was determined. Prior to the test, the materials were subjected to conditioning for 48 hours at 50% relative humidity and a temperature of 25°C. Trials were performed on an Izod Tinius Olsen impact pendulum equipped with a 4.53 N pendulum. The specimens were made following the standard ASTM D256, and the starting angle of the test was 55.80°. All measurements were carried out on five test specimens and the analysis took into account the average of these ratings.

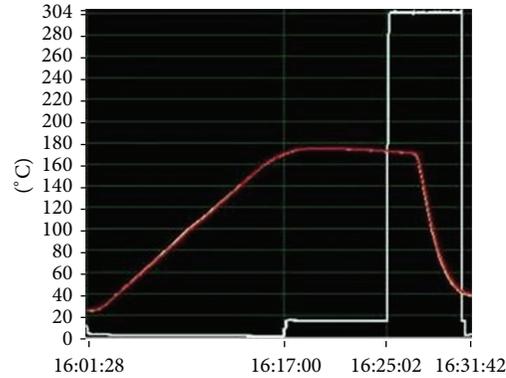


FIGURE 2: Manufacturing process of the boards produced from the LDPE-Al/fique compound.

3.3. Physical and Thermal Tests. The determination of the LDPE-Al and the three different compounds' (LDPE-Al/fique) density was performed according to the Archimedes method specified in ASTM D792. Due to the hydrophilic character of the fibers present in fique, the conventional density test consisting of immersion in distilled water was discarded; canola oil was used as the immersion liquid, which has a density of 0.911 g/cm^3 .

The water absorption test determined the ability of the LDPE-Al and the three compounds (LDPE-Al/fique) to absorb water at a set time. First, the materials were conditioned in an oven for 24 h at 50°C ; after this time had expired, conditioned specimens were weighed (conditioned weight) before being immersed in distilled water at a temperature of 25°C for 24 h. Finally, the water was removed, the specimens were surface-dried and weighed (wet weight), and the determination of the percentage of water absorbed was performed according to the model specified in the following:

$$\begin{aligned} &\text{Weight increment, \%} \\ &= \frac{\text{Wet Weight} - \text{Conditioned Weight}}{\text{Conditioned Weight}} * 100. \end{aligned} \quad (1)$$

The thermogravimetric analysis test (TGA) was carried out on TA Instruments TGA Q500 with a protective nitrogen atmosphere; the test was run at a heating rate of $10^\circ\text{C}/\text{min}$ in a temperature range between 25 and 550°C . The average weight of the samples tested was 6 mg.

Differential Scanning Calorimetry (DSC). The percentage crystallinity and the melting temperature of the LDPE-Al matrix, as well as the influence of the incorporation of fibers in the LDPE-Al/fique composite, were determined using a Q2000 DSC equipment from TA Instruments under a protective atmosphere of nitrogen, with a heating and cooling speed of $10^\circ\text{C}/\text{min}$. Tests were carried out in three steps: (1) first heating: -90°C to 150°C with an isotherm at 150°C for 4 min; (2) cooling: 150°C to -90°C with an isotherm at -90°C for 3 min; (3) second heating: -90°C to 150°C . The percentage

crystallinity was estimated using the model presented in the following:

$$X = \frac{\Delta H_f}{W_{pe} \Delta H_f^0}, \quad (2)$$

where X is the percentage crystallinity, ΔH_f is the compound's fusion enthalpy, ΔH_f^0 is the 100% crystalline polyethylene's fusion enthalpy (288.83 J/gr), and W_{pe} is the weight fraction of the polyethylene phase in the compound [15, 16].

4. Results and Discussion

4.1. Tensile Test. Figure 3 shows the maximum strength, Young's modulus, and maximum strain values for each material tested. Here it can be demonstrated that increasing the fiber content in the compound led to increases in the maximum strength and Young's modulus and a decrease in the strain of the material, revealing that the material undergoes a phenomenon of stiffening due to the inclusion of natural fibers. This behavior might be generated by the high aspect ratio of the embedded fibers (average of 247), which causes the fique properties to prevail over those of LDPE-Al. Accordingly, it is worth noting that Hidalgo et al. [9], in a similar work about a polyethylene-aluminum matrix reinforced with short fiber of fique, suggested the possible presence of mechanical anchors between the fibers and the matrix, which would restrict the strain capacity of LDPE-Al. Moreover, if one considers that the fibers of fique mats, which are used in this work, have a random distribution and could be tangled with each other, the possible mechanical anchorage between the fibers and the matrix could be even more important.

The best tensile mechanical performance was obtained by the 30% fique fiber compound, resulting in a maximum strength and Young's modulus of 21.22 MPa and 1.56 GPa, respectively. This implied increases of 97.80% in the maximum strength and 180.78% in Young's modulus relative to the material without reinforcement (LDPE-Al). It is important to remark that the maximum tensile strength was higher than that reported by Hidalgo et al. [9], who achieved a maximum tensile strength of 15.56 MPa for a composite of LDPE-Al matrix reinforced with 30% short fique fibers. However, the

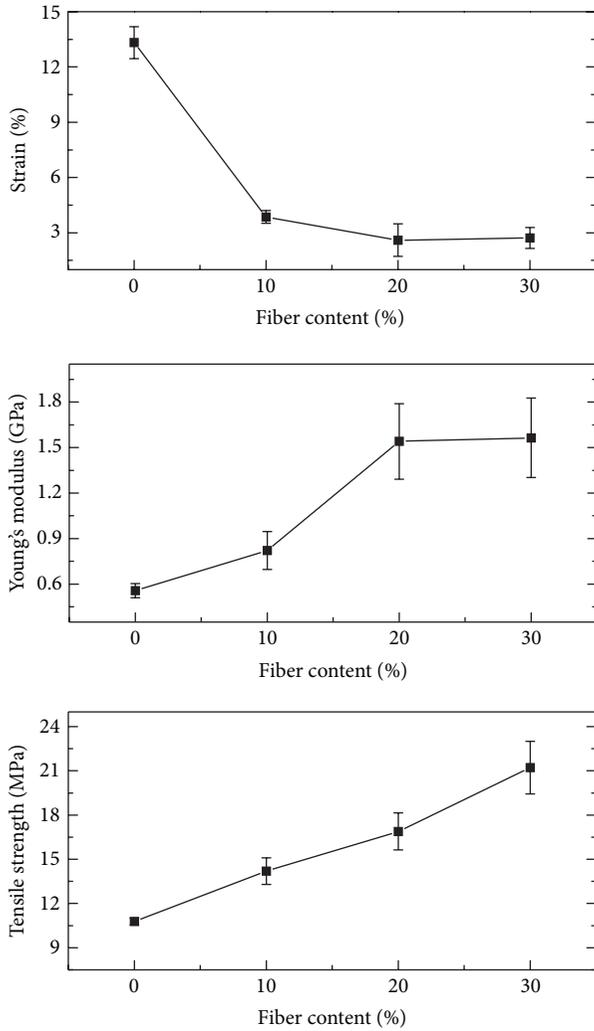


FIGURE 3: Tensile properties of the materials tested.

strain of this compound showed a decrease of 389.41% compared to the LDPE-Al.

4.2. Flexural Test. The bending behavior of the materials studied is shown in Figure 4. Here it can be observed that the properties increased when the incorporation of fique fibers increased in the LDPE-Al matrix, corroborating the stiffness that was previously evidenced in the tensile tests.

Just as in the tensile tests, the best performance was observed in the material reinforced with 30% fique fibers, which reached values of 26.97 MPa to maximum strength and 1.37 GPa to Young's modulus, improving the properties of LDPE-Al matrix by 117.81 and 204.28%, respectively.

4.3. Impact Test. Figure 5 shows an impact strength of 10.47 kJ/m^2 (103.43 J/m) for the LDPE-Al; this value is less than that reported by Desiderá [17] for a LDPE recycled with Tetra Pak without aluminum (315 J/m). This made it clear that the 10.50% aluminum particulate content in the polyethylene used as a matrix in this investigation weakens the material,

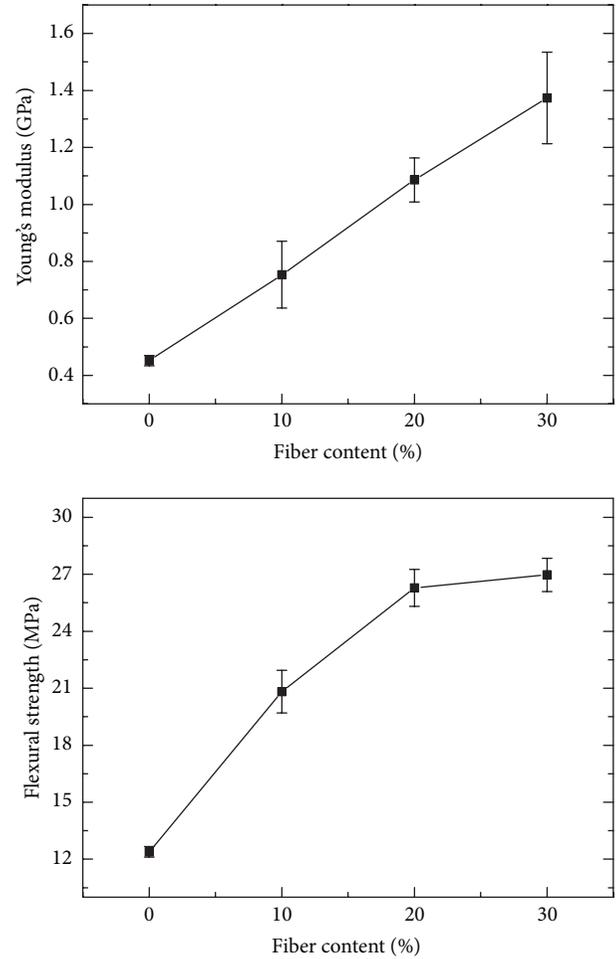


FIGURE 4: Flexural properties of the materials evaluated.

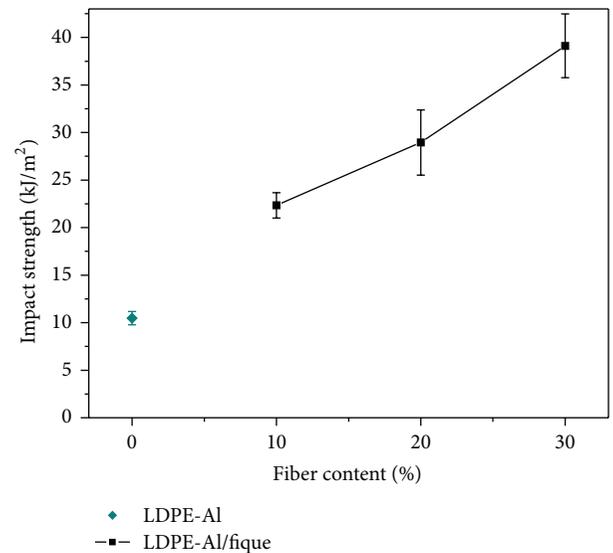


FIGURE 5: Impact strength of the composite depending on the fiber content.

generating a decrease in the ability of LDPE-Al to absorb energy; some authors that incorporated metal particles in

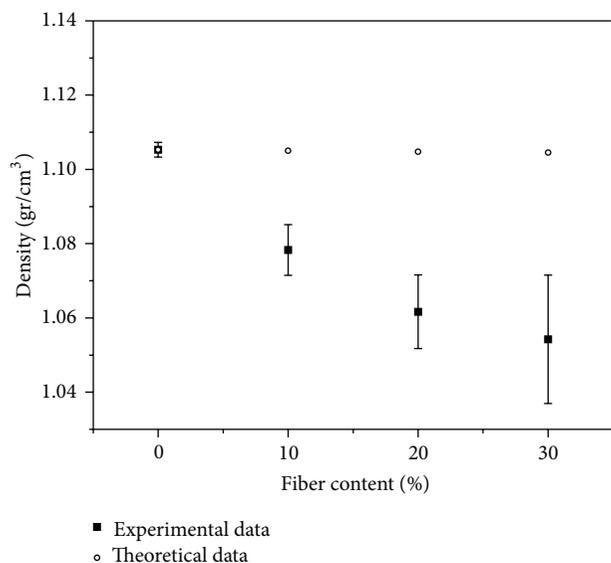


FIGURE 6: Density of LDPE-Al and 10, 20, and 30% fique fiber compounds.

polymeric matrices observed the same behaviour on impact strength and attributed it to weak interfacial adhesion in the composite, which generates that metallic particles behave as stress concentration points, facilitating the propagation of cracks in the material [17–19].

Moreover, it was found that, by incorporating fique fibers in the matrix, the material's impact strength increased. This phenomenon could be due to a possible energy absorption promoted by fracture mechanisms, which involve detachment, slippage, and fragmentation of the fiber and are not part of the unreinforced material fracture [20].

4.4. Density Test. Figure 6 shows the results obtained from the density tests of LDPE-Al and materials reinforced with 10, 20, and 30% fique fiber, and these results were compared with the density values estimated by the rule of mixtures.

By incorporating fique fibers, it was found that composite density decreased as the amount of fiber in the material increased. This occurred even though it was expected that the density of the compound would not undergo large variations with respect to the density of the LDPE-Al due to the similarity between the densities of LDPE-Al (1.100 g/cm^3) and fique (1.102 g/cm^3). This effect of the content of fique fibers on the composite density may be caused by the formation of a weak interface between the phases of the compound, which would affect the generation of voids and/or cavities between the fiber and the matrix; in Figure 7 a SEM micrograph can be observed, where the cavities present in the different materials evaluated are shown; hence the greater the amount of fibers in the material, the greater the difference between the experimental values and the value estimated by the rule of mixtures, as shown in the graphs presented in Figure 6. It is important to say that the standard deviations for the experimental values are higher when increasing the fique fiber content in the

composite; this is associated with an increase in the rate of the weak fiber-matrix interface.

4.5. Water Absorption Test. Figure 8 shows the response of the materials evaluated to the water absorption after being immersed in distilled water for 24 h at 23°C . The LDPE-Al without reinforcement had a water absorption percentage of 0.05%, which increased with the fiber content incorporated. This is attributed to the possible water absorption by diffusion and percolation mechanisms; the latter phenomenon is generated by microspaces present between the fiber and the matrix, as seen in Figure 7, which allow the filtration of water on the material and it becomes more important when the fiber content on the matrix is increased. Another reason for the observed trend is the hydrophilic character of the cellulosic fibers, especially promoted by the hemicellulose content, which is considered as the fiber component with the highest water absorption capacity, because it has a disordered intermolecular structure which prevents its hydroxyl groups which can establish hydrogen bonds with each other, thus allowing the formation of bonds with water molecules [21–23].

4.6. Thermogravimetric Analysis (TGA). TGA was performed on both the LDPE-Al and the material reinforced with 30% by volume of fique. Figure 9 shows the thermograms obtained in the materials evaluated. Here we can see an initial mass loss at a temperature close to 65°C in the reinforcement material, highlighting that this fall was not important in the LDPE-Al matrix. According to Monteiro et al. [24], the mass loss could be attributed to the loss of water in fique fibers (due to their hydrophilic state) contained in the composite. This reduction in mass was about 2.61%.

Likewise, the thermogram of LDPE-Al (Figure 9) demonstrates that the onset of degradation of the LDPE occurred from 350°C and a faster loss of mass of the polyethylene was present around 470°C , as the peak of the derivative curve DTG shows. These values were similar to those reported by Tajeddin et al. [25], who worked with a LDPE/kenaf composite. Moreover, one can see that the degradation of LDPE-Al reached a mass loss of around 75%, which is only associated with the polyethylene phase because the aluminum phase does not suffer any loss of mass by volatilization at a temperature of 500°C [26], implying that the remaining 25% is aluminum. Given that the LDPE (with which the Tetra Pak packaging is manufactured) has a density of 0.918 g/cm^3 [26] and that the aluminum has a density of 2.70 g/cm^3 , it was possible to confirm that the ratio 75/25 w/w that was determinate in the test is equivalent to the 89.75/10.25 v/v for LDPE/Al, previously established in Section 2.

Regarding the material reinforced with 30% fique fibers, it can be observed in thermogram (Figure 9) that before the LDPE thermal degradation occurred, thermal events associated with fique fibers occurred, which resulted in a loss of mass around 305°C , which has been attributed by some researchers [14, 24] to the degradation of hemicellulose. Furthermore, another important mass loss can be observed in the range of 325 to 400°C , corresponding to the thermal

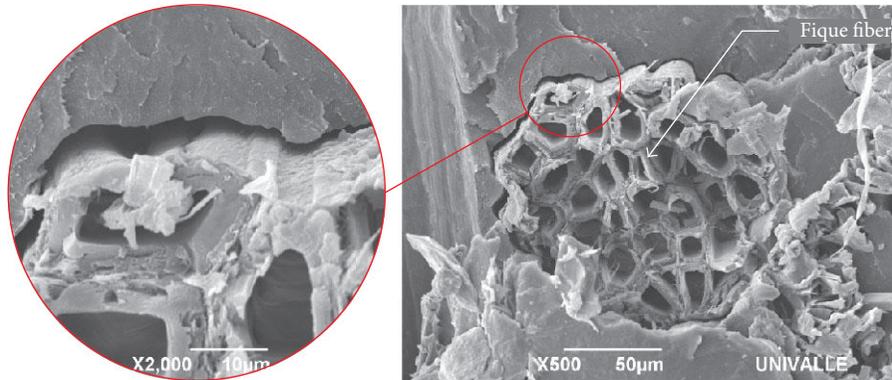


FIGURE 7: SEM micrograph. Cavities present in the fiber-matrix interface of the LDPE-Al/fique compound.

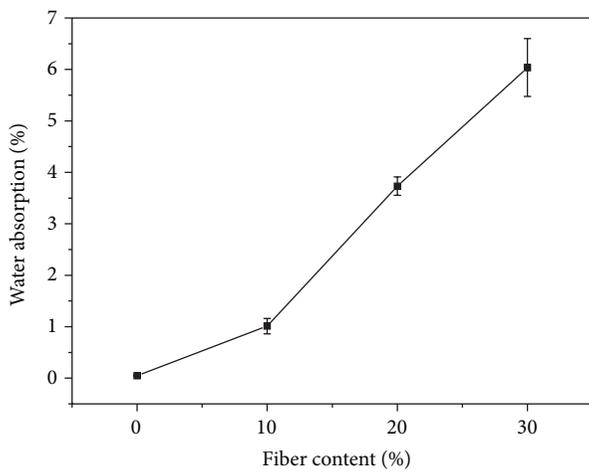


FIGURE 8: Water absorption by immersion of composite materials reinforced with fique fibers at 23°C.

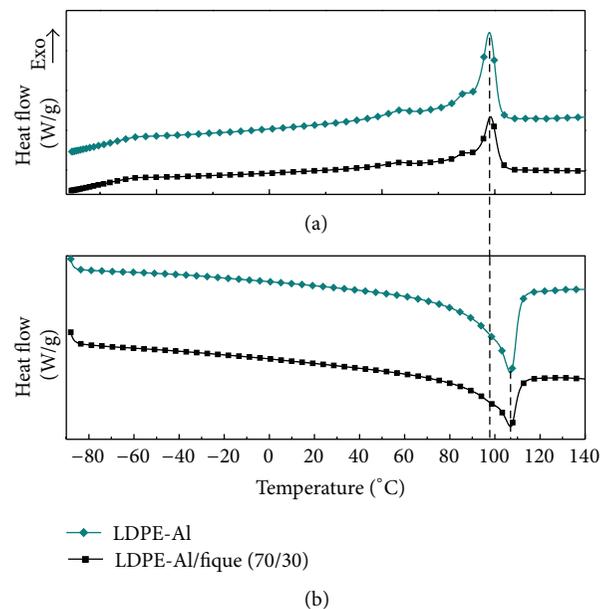


FIGURE 10: Heat flow versus temperature for LDPE-Al and 30% fique fiber compound: (a) cooling and (b) second heating.

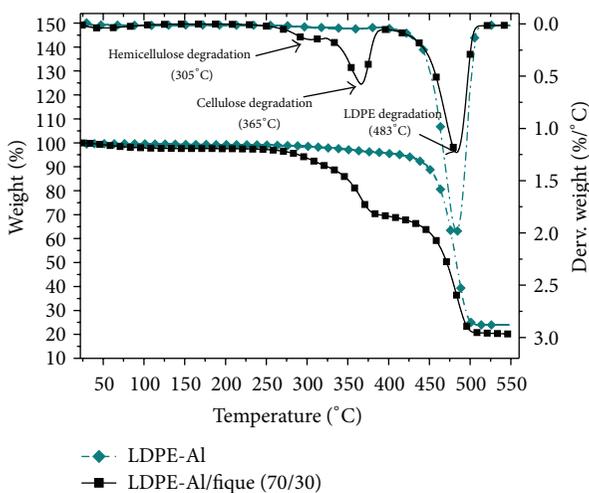


FIGURE 9: TGA thermogram for LDPE-Al compound and 30% fique fibers compound.

degradation of cellulose and thus the decomposition of the fiber. Moreover, the peak of the derivative associated with

the decomposition of LDPE shows a shift to about 483°C in the reinforcing material. The increase in the thermal stability of the compound has been previously reported in different studies [25, 27, 28], indicating that the incorporation of fibers in the material induces spherulite nucleation points, increasing the crystallinity of the polymer and, therefore, improving its thermal properties.

4.7. Differential Scanning Calorimetry (DSC). Just as with the TGA, the materials evaluated with this technique were 30% fique and LDPE-Al without reinforcement. Figure 10 shows the curves of heat flow as a function of temperature (cooling and second heating) for the materials tested. Here it can be observed that in the heating curves (Figure 10(b)) there is an apparent decrease in the enthalpy of fusion from 90.01 to 63.22 J/g with increasing fraction of the material components (fique fibers and aluminum), which do not present melt at the

TABLE 1: Degree of crystallinity (X) estimated for the polyethylene phase for each of the materials tested.

Material	Cooling			Second heating			$X_{\text{Phase LDPE}}$
	Onset point	T_c	ΔH_c	Onset point	T_f	ΔH_f	
		°C			Peak		
LDPE-Al	102.36	97.58	84.61	94.88	106.91	90.01	44.53
30	102.98	98.21	61.54	94.95	106.88	63.22	44.70

conditions of the test and are not miscible with the polyethylene phase; however, although the melting enthalpy of LDPE-Al/fique appears to be smaller than that shown by the LDPE-Al and the LDPE (98–115 J/g) [16, 17], when the melting enthalpy is corrected taking into account only the content of LDPE, the crystallinity of the polyethylene phase does not decrease (Table 1). This behavior was also observed by Aht-Ong and Charoenkongthum [29] in a biocomposite of LDPE/banana starch.

Table 1 shows the degree of crystallinity (X) estimated for the polyethylene phase for each of the materials tested. It was found that the crystallinity of the polyethylene phase within the LDPE-Al was 44.53%, which was greater than the value of 34% reported in various studies [16, 30] for low-density polyethylene, which was also determined by DSC tests. Desiderá [17], who studied a mixture of polyamide and polyethylene recycled from multilayer recycled packaging, attributed the increase in crystallinity to the effect of the presence of aluminum particles and/or impurities present in the recycled material, which act as nucleation points promoting the formation of spherulites. Similarly, when comparing the degree of crystallinity obtained in the phase of the LDPE-Al to that achieved in the fique-fiber-reinforced material, no significant difference can be seen. This crystalline phase content was maintained despite the decreasing fraction of aluminum in the composite owing to the incorporation of the fibrous material. The above shows that the fique fibers also promote the formation of crystalline phases in the polyethylene present in the matrix of the composite. In some studies [14, 21, 31] of fiber-reinforced related compounds, it has also been found that fibers act effectively as nucleation sites for the formation of spherulites.

Furthermore, the melting of the materials presented a well-defined peak whose base was found around 107°C. It is important to note that in some studies [25, 32, 33] melting temperatures of 102 to 105°C are reported for virgin and recycled LDPE, which could suggest further evidence of increased crystallinity in the polyethylene phase, since more energy is required to reach the melting point of the material, particularly regarding the fusion of the crystalline fraction.

5. Conclusions

In this work it was possible to develop a composite material comprising a matrix based on low-density polyethylene and aluminum (LDPE-Al) obtained from the recycling of post-consumer long-life Tetra Pak packaging and fique fibers as

reinforcement. Such material may be processed using a conventional processing method using hot compression molding.

With regard to the tensile and flexural properties, clear stiffening was observed with the addition of fique to LDPE-Al attributed to the good aspect ratio of the fibers used and their arrangement in the matrix. The impact strength of the material increased due to the generation of energy-absorbing mechanisms during fracture, such as detachment, slippage, and fiber fracture, which were absent in the material without reinforcement.

Thermal analysis techniques such as TGA and DSC, allowed determining that the aluminum particles (dispersed phase present in the LDPE-Al) and the incorporation of fique fiber on the composite induce nucleation points of spherulites which promote increased crystallinity on the polyethylene phase of the materials evaluated in 10.7% (with reference LDPE without fibers or aluminum), leading to improved thermal properties, as evidenced by the shifting of the decomposition temperature peak of the LDPE, which moved from 470 to 483°C when fique fibers were incorporated.

Furthermore, the incorporation of fique fibers on the LDPE-Al caused a decrease in density and an increase of water absorption; this is due to the hydrophilic character of natural fibers that also generates the formation of a weak interface with the matrix, which influence the generation of voids and/or cavities in the material.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Physical, Mechanical, and Morphological Properties of Woven Kenaf/Polymer Composites Produced Using a Vacuum Infusion Technique

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Nowadays, due to renewable issues, environmental concerns, and the financial problems of synthetic fibres, the development of high-performance engineering products made from natural resources is increasing all over the world. Lately, kenaf fibre has been used among many different types of natural resources in various shapes. Unidirectional long fibres or randomly oriented short fibre shapes are the most common type of kenaf fibres that have been investigated in previous works. This work characterises and evaluates the physical, mechanical, and morphological properties of plain woven kenaf fabric and its composites with three types of thermoset resin at 0°/90° and 45°/-45° orientation, in order to assess their suitability as lignocellulosic reinforced polymer composites. A vacuum infusion manufacturing technique was used to prepare the specimens with fibre weight content of 35% ± 2%. Eight specimens were prepared for each test, and five replications were adopted. A total of 78 samples were tested in this study. The results show that the composites with 0°/90° had the highest tensile, flexural strengths, and modulus. The morphological properties of composite samples were analysed through scanning electron microscopy (SEM) images and these clearly demonstrated the better interfacial adhesion between the woven kenaf and the epoxy matrix.

1. Introduction

In the past two decades a number of researchers have sought to use natural fibres with a polymer matrix composite (PMC); this has received considerable attention both in the literature and the industry. Although synthetic fibres such as Kevlar, glass, and carbon are extensively used for the reinforcement of plastics, these materials are expensive and are nonrenewable resources [1, 2]. Many of the woven natural fabrics are rising as a viable option to glass fibre reinforced composites in

industrial applications like packaging, paper making, and composite materials. One of the more popular natural fibres is kenaf fibre, which is an annual plant due to its rapid growth, and has an average yield of 1700 kg/ha [3, 4]. Kenaf fibre is produced from the bast of the stems of plants of genus *Hibiscus*, a family of Malvaceae, and species of *cannibinus*. It requires less water to grow. Kenaf fibres have the advantage that they are renewable resources, low cost, light, plentiful, nonabrasive, and nonhazardous. Therefore they can serve as an excellent reinforcing agent for plastics [5]. Kenaf fibre

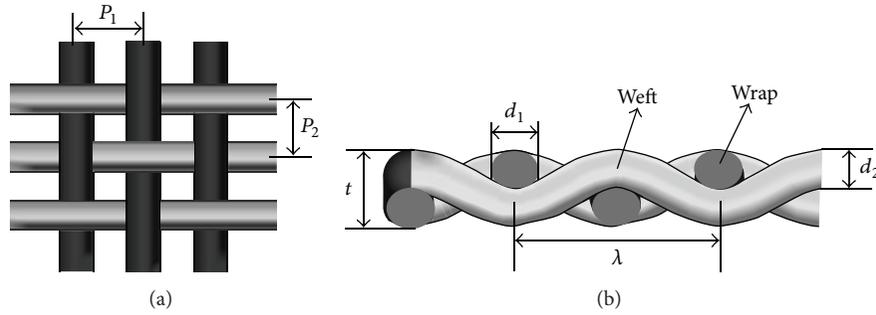


FIGURE 1: Plain woven fabric: (a) top view and (b) cross section view [7].

possesses moderately high specific strength and stiffness and can be utilised as a reinforcing material in polymeric resins to make a useful structural composite material. Kenaf has already been adopted in automobile parts due to its light weight and good mechanical properties [6].

Woven fabrics are formed, in particular, by the interlacing of fibre bundles (yarns) to form a fabric layer, which offers advantages in terms of good dimensional stability and high packing density [7]. The vertical yarn direction is called the warp while the horizontal yarn direction is called the weft as shown in Figure 1. The use of the plain weave technique can add structural strength to the material because it increases both the strength and the energy absorption capacity. Woven fabrics are used in a wide variety of defence and consumer products as the reinforcement phase of composites due to their flexibility, formability, and high specific strength because the interlocking increases strength better than fibre matrix adhesion [8]. Yarn slip, the relative sliding of the yarns composing the weave, is an important mode of deformation or failure, which leads to dramatic changes in the energy absorption and yarn density of the fabric. The use of a woven fabric pattern could add structural strength because it increases the strength and energy absorption capacity of the material.

Figure 1 illustrates a plain weave fabric. P_1 and P_2 represent the distance between warp and weft yarns, while d_1 and d_2 denote the warp and weft yarn circular diameter. t represents the fabric thickness (measured by a digital caliper), whilst λ indicates the fabric wavelength. The weave of the fabric is characterised by thickness, weight, density, wavelength, and interyarn fabric porosity (ϵ). Using (1), the interyarn fabric porosity (ϵ) was calculated. The ratio of the projected geometrical area of the opening across the material to the total area of the material is the definition of porosity [9, 10]:

$$\epsilon = \frac{(P_1 - d_1)(P_2 - d_2)}{(P_1 \times P_2)}. \quad (1)$$

The experimental investigation of the crashworthiness characteristics of kenaf fabric (mat) reinforced polyester (KFRP) circular tubes from the point of view of energy absorption, with different geometry, was carried out by Ibrahim [11]. It was found that geometry was an important factor to determine the ability of a material to absorb

energy. Furthermore, a thin-walled tube has a good geometry for a high strength to weight ratio and energy absorption capability. In another major study, the tensile and flexural strengths of the unidirectional kenaf fibre reinforced poly lactic acid (PLA) resin composites were investigated by Ochi [12] with different fibre content. Experimental results showed that the weight of composites increased linearly up to a fibre content of 50%.

In recent years, the effects of chemical treatments on the tensile and flexural properties of the short kenaf polypropylene composites were investigated by Asumani et al. [13]. Mechanical test results showed that the improvements in the tensile and flexural properties resulting from alkali silane treatment were due to the better bonding between the fibres and the polymer. Several attempts have been made to study the influence of fibre content on the mechanical and thermal properties of kenaf bast fibre reinforced thermoplastic polyurethane (TPU) composites with different fibre loadings (by El-Shekeil et al. [14, 15]). It was concluded that a 30% fibre loading displayed the best tensile strength, whilst the tensile modulus, thermal stability, hardness, and flexural strength increased with the increase of fibre content, but the strain value decreased with increasing of fibre content.

The mechanical properties of a nonwoven kenaf fibre composite and poly-L-lactic acid (PLLA) resin were investigated by Nishino et al. [16]. It was reported that kenaf fibre could be a good candidate for use as a reinforcing fibre for high performance polymer composites. In another study, Salleh et al. [17] found that processing at high temperature leads to an improvement in the tensile modulus of composites, in contrast with the diminished properties when processed at low temperatures especially with high fibre content. Furthermore, with the increased content of the fibre, the tensile strength and strain of the composite decreased when using low and high processing temperatures. It was also reported that a scale ratio between reinforcements of different aspect ratios may play a role as a controlling factor in optimising the mechanical properties of a composite material [18–20].

Another crucial factor is the kenaf fibre orientation, which has a significant effect on the mechanical behaviour of composite materials [21]. It was reported that the composite's properties were influenced by changing the fibre orientation. Chow et al. [22] studied the effect of weaving patterns and

TABLE 1: Physical and mechanical properties of polymers (manufacturer data sheet).

Polymer	Density (g/cm ³)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)	Hardener %
Epoxy LY556	1.14	73.3	3470	4.5	1:2 [HY951]
Unsaturated polyester	1.14	69	3800	2.3	0.2 [MEKP]
Vinyl ester	1.14	86	3200	5-6	0.2

random orientation on the mechanical properties of banana, kenaf, and banana/kenaf fibre-reinforced hybrid polyester composites. Plain and twill weaving patterns were used to fabricate the composite; the plain type showed improved tensile properties compared to the twill type. Moreover, the maximum increase in mechanical strength was observed in the plain woven hybrid composites rather than in randomly oriented composites, which lead to minimum stress development at the interface of composites because of the distribution of load transfer along the fibre direction.

Even though kenaf fibres have the potential to supplement synthetic fibres in polymer composites [23], limitations arise with respect to mechanical performance and moisture absorption when natural fibres are used [24, 25]. In this study, achieving the advantages of kenaf fibres and the woven pattern has been considered. Besides this, the prediction of the mechanical properties of composites has many advantages when components are changed in volume or type, as it does not need additional measurements in order to know their mechanical properties. Consequently, this paper aims to determine the physical, mechanical, and morphological properties. A discussion based on the data collected from the literature is also given in order to create a brief guideline for future development concerning the use of woven kenaf fibres.

2. Materials and Methods

In order to study the behaviour of woven kenaf fibres with three types of polymers on the mechanical properties of composites, the fibre density, fibre diameter, fibre length, moisture content, water absorption, and porosity of woven kenaf fibres are measured.

Kenaf fibre is the main fibre used in this study and was supplied by ZKK Sdn. Bhd., Malaysia (as shown in Figure 1). The physical and mechanical properties of kenaf yarn were measured according to the ASTM D3379-10 standard [26]. The plain woven kenaf fibre was prepared and cut to fabricate composite samples according to the ASTM standards. Three types of thermoset resins were used to fabricate the composite samples, namely, epoxy, unsaturated polyester, and vinyl ester resin. The properties of the three types of polymers are shown in Table 1 (manufacturer data sheet).

The kenaf fibre density was obtained using mathematical equation (2) by dividing the mass by the volume, according to the ASTM D 1895 standard [27]. Kenaf fibre was put into a container with a known volume (V_c). The weight of

the container was weighed and recorded as M_c and the kenaf filled container was weighed and labeled as M_k :

$$\text{Density } \rho \text{ (g/cm}^3\text{)} = \frac{M_k - M_c}{V_c}. \quad (2)$$

Both the diameter and the length of the kenaf fibre were measured using an optical microscope and digital caliper. Twenty kenaf fibre yarns were tested and the average value of the diameter and length was recorded.

All types of polymer composites will absorb moisture from the surrounding area to a certain extent when immersed in water or exposed to a humid environment [28]. It is not only the polymer matrix that absorbs moisture, but also the fibre, especially natural fibre, due to its hydrophilic nature. It is more sensitive towards water absorption, which causes instability in the properties of the composites [29].

The moisture content specimens were cut according to ASTM D 5229-04 [30] and weighed using an electronic balance of 0.00001 g accuracy to monitor the mass during the aging process. The specimen is $50 \times 50 \text{ mm}^3$, five specimens were tested, and the average was calculated. The moisture content of woven kenaf fibre was obtained by weighing the kenaf fabric, and the initial weight of the fibres was recorded as (M_1) before the samples were put in the oven at 105°C for 24 h. The kenaf fabric was weighed again and recorded as (M_2). The moisture content was determined using

$$\text{Moisture content} = \frac{M_1 - M_2}{M_1} \times 100. \quad (3)$$

In recent years, many research studies using a natural fibre and polymer matrix have been conducted. It has been demonstrated that the water absorption affects the performance of natural fibre reinforced composites negatively; therefore it is important to study their behaviour. The rate of the degradation is dependent on temperature and humidity [31], which lead to a significant loss in the mechanical properties of natural fibre based composites, especially kenaf fibre reinforced composites, in a humid environment [32]. In one of the largest longitudinal studies, Rassmann et al. [33] investigated the effect of water absorption on the mechanical properties of unwoven kenaf mat. It showed that the composite properties were influenced greatly by immersion in water.

In this study, plain woven kenaf fibre was immersed in water, and the water absorption behaviour was evaluated according to the ASTM D5229 standard [34]. Water absorption was measured after the immersion of the kenaf weave specimens in water at room temperature for 24 hours. Five specimens of kenaf fabric were weighed before and after

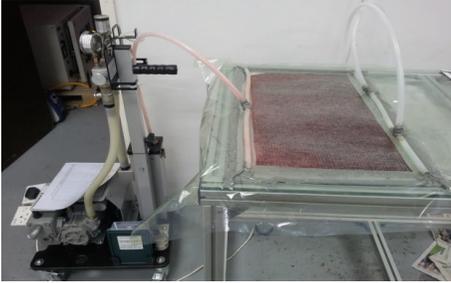


FIGURE 2: The composite specimen using vacuum infusion technique.

immersion, then the water absorption was determined using the following equation:

$$\text{Water absorption (\%)} = \frac{M_1 - M_0}{M_0} \times 100, \quad (4)$$

where M_1 is the mass of the sample after immersion (g) and M_0 is the mass of the sample before immersion (g) [35, 36].

The composite samples were made with 35% fibre weight content and the rest for any one of three types of polymers: woven kenaf fibre reinforced epoxy composite (KFRE), woven kenaf fibre reinforced polyester composite (KFRP), and woven kenaf fibre reinforced vinyl ester composite (KFRV). Eight specimens were fabricated for each group using the vacuum infusion technique. The vacuum infusion technique provides a number of improvements over traditional methods such as better fibre-to-resin ratio, less wasted resin, very consistent resin usage, and unlimited set-up time, and it is cleaner. The first step of the vacuum infusion technique was begun with polishing the glass surface by using wax (releasing agent), and the resin feed spiral was positioned. Thereafter, one layer of woven kenaf fibre was cut, weighed, and positioned on the surface. Then, both the resin feed connector and the vacuum connector were positioned. The first layer of the infusion, the peel-ply layer, was placed, and then the infusion mesh was added. Subsequently, the tape was applied down the vacuum bag, and the resin feed and vacuum hose were connected and sealed. The resin feed pot was set up and the vacuum pump and catch-pot were connected. The vacuum pump was switched on, the air was evacuated, and the vacuum bag was adjusted. Each polymer was mixed with the ratio of its hardener (resin: hardener by weight) according to the manufacturer's specifications. The vacuum pump was switched on, and the resin was infused and flowed evenly onto a distribution medium until it reached the end, as shown in Figure 2. The excess resin flowed into a resin trap. Demoulding the specimens was done after curing at room temperature for 24 hours; then the specimens were stored on a flat surface under room conditions.

In order to study the mechanical properties of the three types of woven kenaf reinforced polymers, tensile, flexural, and impact and scanning electron microscopy (SEM) tests are performed. Tensile tests of both the kenaf yarn and the plain woven kenaf composite for three types of polymers are investigated.

The strength of the kenaf yarn (weft and warp) was obtained using the universal testing machine with a capacity of 2.5 KN in accordance with ASTM D3379-10, [26]. The crosshead speed was 1 mm/min with a replication of 25 times. The fibre was randomly selected, then attached and glued to a tab shaped piece of cardboard, with a gauge length of 170 mm, and then tested.

Tensile testing was carried out in the composite laboratory of the Mechanical Department, Universiti Putra Malaysia, according to the ASTM D3039 standard [37]. All specimens were cut to the 250 mm × 25 mm × actual thickness in two angles 0°/90° and 45°/-45° for each composite and rectangular sectional area flat strip and gage length of 170 mm. Four-tab plates with a dimension of 40 × 25 mm were attached to the two sides of both ends of the specimens by an adhesion agent. The test was conducted using a universal testing machine with a capacity of 100 KN and crosshead speed 1 mm/min, with a replication of 8 times. The average value of the results for the five specimens was taken.

The flexural tests of the woven kenaf fibre composites were investigated using the three-point bending fixture according to the ASTM D-790 standard [38], with a crosshead speed of 1 mm/min. The rectangular shape three-point bending specimens were prepared with dimensions of 127 mm × 12.7 mm × actual thickness in two angles 0°/90° and 45°/-45° for each composite. The distance between the supports (span length) was calculated as per the standard, with a ratio of 16 : 1. For each case, eight specimens were tested and the average values of the five specimens were recorded.

The impact strength of the samples was measured using an Izod impact test machine, according to the ASTM 256 standard [39]. The standard specimens size was 63.5 mm × 12.7 mm × actual thickness in two angles 0°/90° and 45°/-45° for each composite and notched by motorised notchvis. All impact test samples were supported as a vertical cantilever beam and broken by a single swing of a pendulum, with hammer velocity 6 m/s. For each case, eight specimens were tested and the average value of five results was recorded.

Using the scanning electron microscope (SEM) instrument model ZEISS SUPRA 35VP, the fracture surface of the specimen after the tensile test was observed. All the fractured specimens were coated with a thin layer of gold, to avoid electron charge accumulation, and subjected to a voltage of 10–15 kv.

3. Results and Discussions

Not only the physical results of the woven kenaf fibres, but also the mechanical properties of the woven kenaf composites are reported and discussed. In addition, the scanning electron microscopy (SEM) images for the tensile specimens test are analysed.

The characteristics of individual fibres vary according to their shapes, sizes, and orientations, and the thickness of the cell walls. Some important physical elements must be known about each plantation fibre before it is used to reach the maximum potential [40]. The fibre length and diameter are the important parameters to determine the strength of natural fibre [41, 42]. The fibre's strength is an important

TABLE 2: (a) Properties of kenaf yarns. (b) Properties of plain weave kenaf fabric.

(a)	
Properties	Kenaf yarn
Yarn fineness (Tex)	942
Yarn type	1 ply spun
Twist direction	Z-twist
Fibre diameter (mm)	1 ± 0.1
Yarn breaking load (N)	79
Average breaking strength (MPa)	100.64
Average maximum strain (%)	17.3
(b)	
Characterisation	Woven kenaf
Thickness, t (mm)	2 ± 0.2
Weight (g/m ²)	890
Density (g/cm ³)	1.2
Warp density (warp/inch)	12
Weft density (weft/inch)	12
Wavelength, λ (mm)	4.2
Interyarn fabric porosity (ϵ)	0.274
Moisture content (%)	8.353
Water uptake (%)	148.86

factor when choosing a fibre that is specific for a certain usage. Table 2(a) shows the kenaf yarn properties while Table 2(b) shows the physical characterisation of plain woven kenaf. By weighing specified lengths of yarns and converting the data to the Tex unit (according to ASTM D 2260) [43], the yarn fineness was determined. In addition, yarn type and yarn twist direction was also observed. Tensile tests for randomly selected kenaf yarns were measured using the Universal Testing Machine Instron 5 KN, with speed 1 mm/min and a preload of 2 N. Breaking strength (MPa), breaking strain (%), and Young's modulus data were recorded.

One of the important parameters that should be considered when choosing natural fibre as a reinforcement in polymer composites is the moisture content. The dimensional stability, electrical resistivity, tensile strength, porosity, and swelling behaviour of natural fibre reinforced composites could be determined by the moisture content [44]. The average value of the moisture content of the woven kenaf was 8.353% for 5 specimens. While the average water uptake was 148.86% for 5 specimens after 24 hours. It can be observed that cellulose, which is a major component in kenaf fibre, influences water absorption highly [45, 46].

Figures 3 and 4 show the ultimate tensile strength and tensile modulus of woven kenaf composites with three types of polymers, at 0°/90° and 45°/-45°. Among these three types of polymers, epoxy resin shows the highest tensile strength, followed by polyester and vinyl ester, respectively. A similar trend has been reported in the study done by de Albuquerque et al. [47] on jute, where the strain development of the kenaf fibre reinforced composites varied according to the type of resins used. It was observed that there

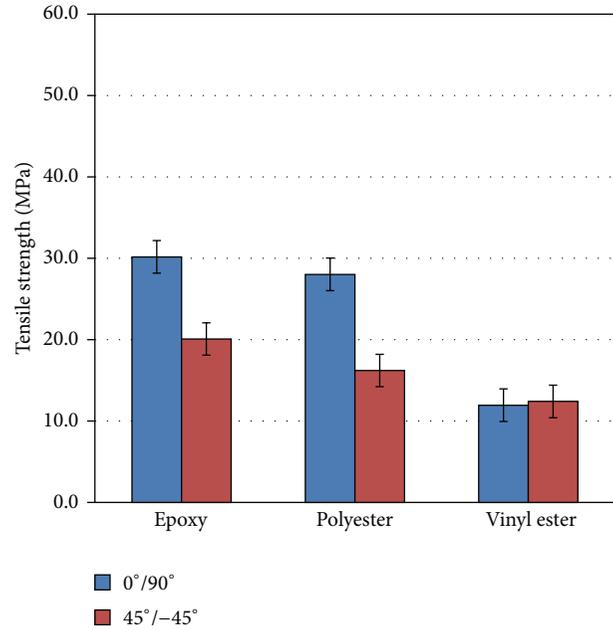


FIGURE 3: Tensile strength of three composites at 0°/90° and 45°/-45° orientation.

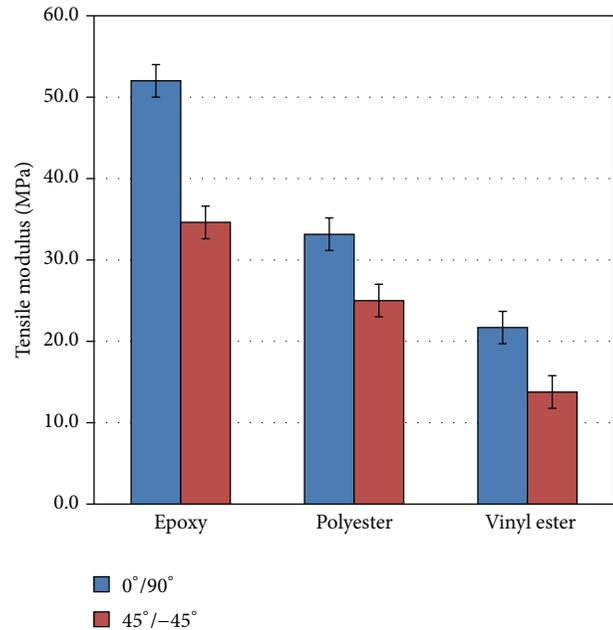


FIGURE 4: Tensile modulus of three composites at 0°/90° and 45°/-45° orientation.

was a decline in the tensile properties of the kenaf epoxy and unsaturated polyester composite samples with 45°/-45°, while, approximately, there were the same tensile properties for the kenaf vinyl ester composites. This could be due to a uniform distribution of stress transfer with the application of tensile load in both the longitudinal and transverse directions, whereas this is not found in the 45°/-45° orientation. Generally, the increase in the tensile strength and modulus of

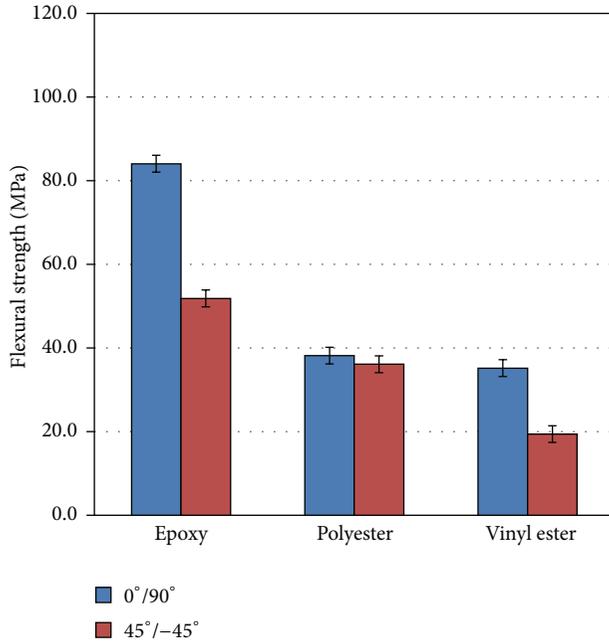


FIGURE 5: Flexural strength of three composites at 0°/90° and 45°/-45° orientation.

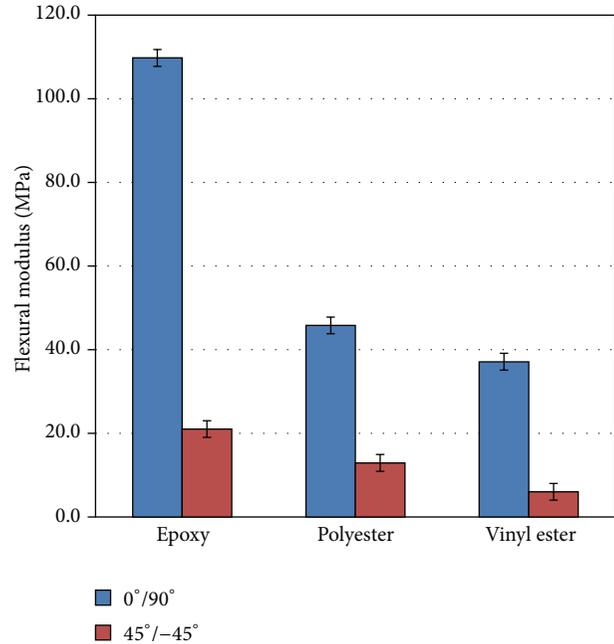


FIGURE 6: Flexural modulus of three composites at 0°/90° and 45°/-45° orientation.

kenaf composites with 0°/90° is attributed to the differences in the load-distribution properties of the kenaf fibres along the longitudinal and transverse directions. Thus, 0°/90° orientation could result in a capacity for greater stress uptake composites which leads to higher mechanical strength. In addition, it can be seen that the values of the tensile modulus of the 0°/90° orientation are higher than those of the 45°/-45° for the three types of polymers. Furthermore, the epoxy composites had a higher tensile modulus than either the polyester or vinyl ester composites in the 0°/90° and 45°/-45° orientation as a result of the epoxy bonds to the fibres being better than the polyester and vinyl ester resins. This is in agreement with the findings of Rouison et al. [48] who found similar trends for hemp fibres.

A similar finding was also observed in the flexural strength of the three types of polymers using a 3-point flexural test, as shown in Figures 5 and 6. Like the tensile modulus results, the resin type seems to have a significant influence on the flexural modulus for each of the three types of polymers. The ultimate flexural strength and flexural modulus of woven kenaf composites with epoxy and vinyl ester polymers decreased with 45°/-45°, whilst the ultimate flexural strength and modulus of woven kenaf composites with unsaturated polyester was almost the same. In different orientations, the flexural effect of both the fibre yarns in the warp and weft directions can create an interlocking structure which can result in constraints for the extension of the fibre yarns along the directions, resulting in fibres with a higher bending load capacity. As research studies have reported, the flexural properties depend on the type of polymer and fibre orientations are critical factors which have an important influence on the mechanical properties

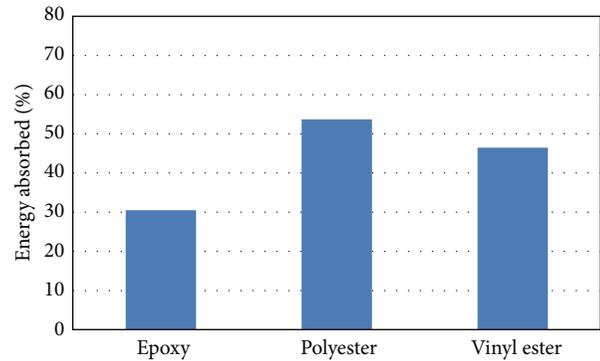


FIGURE 7: Impact strength of three composites at 0°/90° orientation.

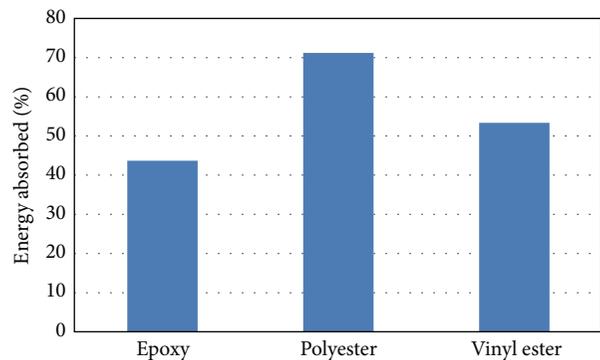


FIGURE 8: Impact strength of three composites at 45°/-45° orientation.

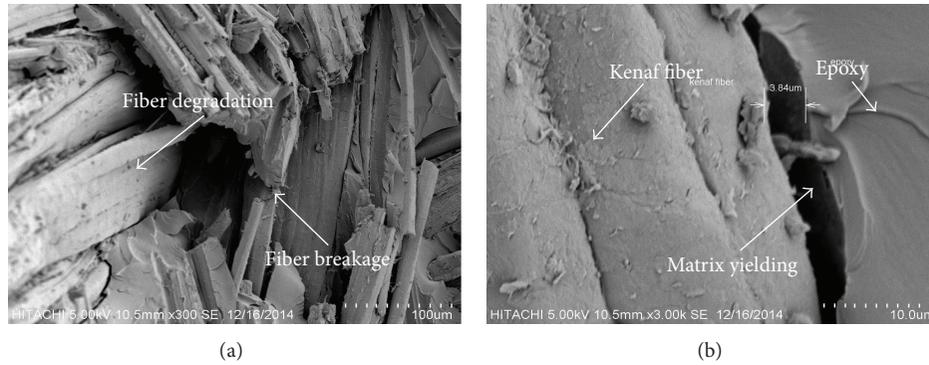


FIGURE 9: (a) The SEM micrographs of the tensile failure surfaces of KFRE. (b) The strong bonding of the kenaf fibre and the epoxy matrix.

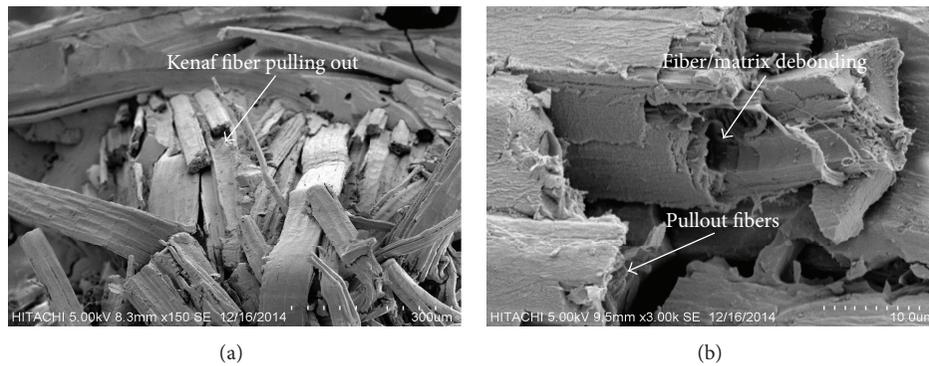


FIGURE 10: (a) The SEM micrographs of the tensile failure surfaces of KFRP. (b) Bonding area of the woven kenaf with the unsaturated polyester matrix.

of the composites [49, 50]. It is known that the flexural properties of the composites are also influenced by the composition and adhesion levels of the polymers, that is, the interfacial bonding. Epoxy composites have higher flexural strength and modulus properties compared to other resins, while vinyl ester composites exhibited lower strength values in the different orientations.

The impact strength of woven kenaf composites with three types of polymers, at $0^\circ/90^\circ$ and $45^\circ/-45^\circ$, is presented in Figures 7 and 8. For the same type of reinforcing fibres, the impact strength of composites differs with the type of polymers. As stated by others [51], the types of polymers, the fibre-matrix interface and the construction and geometry of composites are accountable for deciding the impact strength of composites. It may be observed that kenaf/polyester composites showed the highest energy absorption, while kenaf/epoxy composites exhibited the lowest. It can be concluded that the interfacial strength might have weakened the material causing it to absorb less energy than the other composition as indicated by a number of authors [17, 52]. The epoxy resin bonds better with the kenaf fibres than the other two polymers. This is an indication of the less fibre pullout and thus a better adhesion between the fibres and the matrix, thus causing a reduction in impact energy with increased fibre matrix adhesion. The kenaf/vinyl ester composites also absorbed a great amount of impact energy. It is clearly seen from Figure 8 that the composites with $45^\circ/-45^\circ$ orientation

have a greater impact strength than composites with $0^\circ/90^\circ$ orientation.

3.1. Morphological Properties of WKFC. SEM micrographs confirmed that the mode of failure of epoxy composites was due to fibre fracture, while that of the polyester and vinyl ester composites was due to fibre pullout failure modes. It can also be observed that the epoxy composites display a cleaner failure surface than those made with polyester or vinyl ester composites. This perhaps explains the relatively poor impact strength of epoxy composites, which is an indication of fibre pullout and good fibre matrix adhesion. Figures 9, 10, and 11 show examples of typical SEM micrographs where very few voids were found in the composites, and so a typical micrograph without voids is presented.

4. Conclusions

The woven kenaf composite material is fabricated with three types of thermoset matrix to study the mechanical properties with more emphasis. The matrix types used are epoxy, unsaturated polyester and vinyl ester. Plain woven kenaf possesses a good mechanical strength; therefore, it is a good possible candidate to be used as the reinforcement material in polymer composites. The stress-strain diagram of woven kenaf fibre reinforced thermoset composite is linear. The tensile, flexural, and impact strengths of the woven

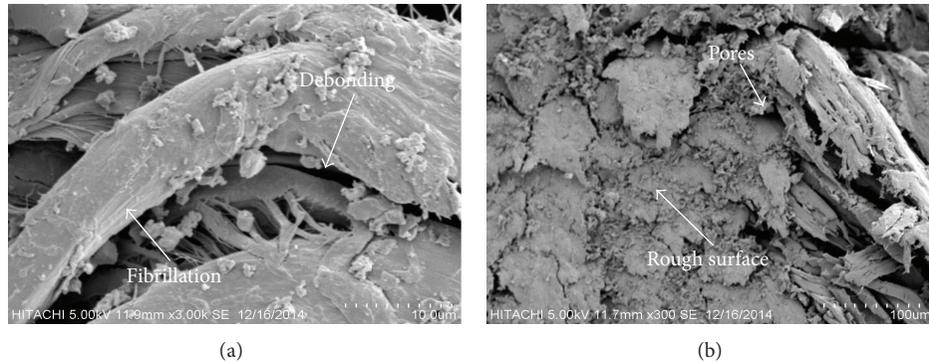


FIGURE 11: (a) The SEM micrographs of the tensile failure surfaces of KFRV. (b) Bonding area of the woven kenaf with the vinyl ester matrix.

kenaf/epoxy composite are superior to those of the others. Fractography studies of the fracture behaviour of the epoxy composite show that a better fibre-matrix adhesion exists (kenaf fibres were almost broken in the fracture plane). The variation of the mechanical properties, for the same type of thermoset, due to the variation of the fibre orientation, is significant. The results obtained from this study suggest that woven kenaf has higher properties for use as a reinforcement in the thermoset composites sector.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Mechanical Properties and Biodegradability of the Kenaf/Soy Protein Isolate-PVA Biocomposites

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The effective utilization of original natural fibers as indispensable components in natural resins for developing novel, low-cost, eco-friendly biocomposites is one of the most rapidly emerging fields of research in fiber-reinforced composite. The objective of this study is to investigate the interfacial adhesion properties, water absorption, biodegradation properties, and mechanical properties of the kenaf/soy protein isolate- (SPI-) PVA composite. Experimental results showed that 20 wt% poly (vinyl alcohol) (PVA) and 8 wt% glutaraldehyde (GA) created optimum conditions for the consolidation of the composite. The increase of interfacial shear strength enhanced the composites flexural and tensile strength of the kenaf/SPI-PVA composite. The kenaf/SPI-PVA mechanical properties of the composite also increased with the content of cross-linking agent. Results of the biodegradation test indicated that the degradation time of the composite could be controlled by the cross-linking agent. The degradation rate of the kenaf/SPI-PVA composite with the cross-linking agent was lower than that of the composite without the cross-linking agent.

1. Introduction

Biodegradable polymers that are derived from natural resources are potential substitutes for existing petroleum-based synthetic polymers, owing to their low cost, easy availability, and complete biodegradability [1]. Among various cellulose, starch, and protein materials, soy protein isolate (SPI) is used to form packaging and edible film because of its excellent film forming abilities, good biodegradable performance, and high barrier against oxygen and oil in low humidity conditions [2, 3]. However, the low mechanical properties and high moisture sensitivity of soy protein-based plastics have limited their usage [4]. These characteristics are attributed to the inherent hydrophilicity of natural proteins and the amount of hydrophilic plasticizer incorporated into them. Moreover, literature [5] has confirmed that SPI films that lack secondary components do not show good mechanical and barrier properties.

Soy protein is commercially available as SPI, soy protein concentrate (SPC), and soy flour (SF). Chemically, SPI contains 90% protein, while SPC contains 70% and 18% carbohydrates and 6% ash, with fiber and moisture making

up the remaining components. SF contains up to 55% protein and 32% carbohydrates. Soybean protein contains several amino acids, such as glutamic acid, arginine, lysine, cysteine, and aspartic acids, which have polar groups. These groups can act as useful cross-linking and/or hydrogen bonding sites to improve the mechanical properties of soy protein polymers. In the present research, SPI was modified with GA to increase its mechanical and physical properties and to improve thermal stability and processability as a matrix for composite fabrication. Several researchers have studied the cross-linking of GA with proteins and confirmed the reaction mechanisms [6]. Biswas et al. [7] and Gellerstedt and Gatenholm [8] have proposed that the GA reacts with the amino groups in protein to form cross-links. Zini et al. [9] used maleinized tung oil to cross-link the SPI and improve its tensile properties. A typical cross-linked structure of soy protein with the GA is shown in Figure 1 [6]. It was, however, difficult to assess the average degree of cross-linking because of the complexity of the chemistry. The cross-linking was judged based on the improved tensile strength and interfacial adhesion properties and decreased fracture strain and moisture absorption after the GA modification as well as

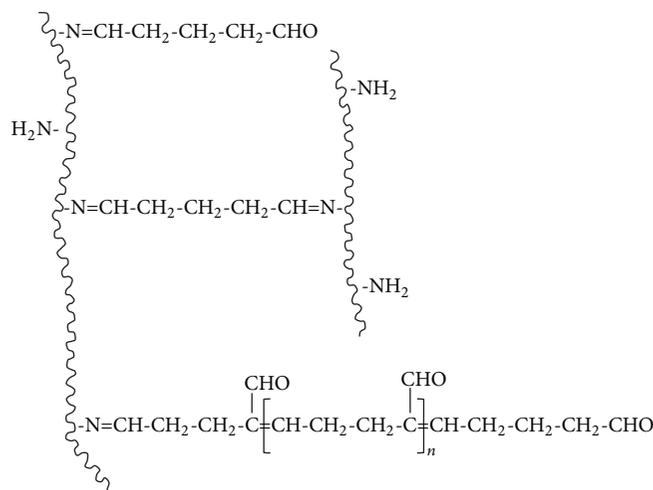


FIGURE 1: Schematic structure of the glutaraldehyde (GA) cross-linked soy flour.

the significant increase in the viscosity immediately following the addition of GA to the SPC solution [10].

Another approach to modify the moisture sensitivity of SPI films is to blend other natural or synthetic polymers with SPI materials [11]. Normally, biodegradable polymers such as gelatin, starch, cellulose, and protein are used as blend components to ensure that the final films can still be considered “green.” However, because natural polymers are inherently hydrophilic, these blends cannot solve the moisture sensitivity problem of SPI films. In addition to natural materials, PVA, the world’s most produced synthetic, water-soluble polymer, can be blended with natural polymers to form biodegradable composites. These PVA/natural polymer blends have promising industrial applications in many fields because of their biodegradability, biocompatibility, chemical resistance, and excellent physical properties [11].

Biocomposites composed of natural fibers and synthetic or natural polymer matrices have gained recent attention due to their cost effectiveness, low density, biodegradability, ready availability, energy recovery, and CO₂ sequestration [12]. The natural fibers commonly used to reinforce biocomposites are jute, flax, hemp, ramie, sisal, bamboo, and kenaf fiber [13]. The renewable and biodegradable characteristics of these natural fibers enable disposal processes, which are not possible with most industrial fibers.

Among others, kenaf offers the particular advantages of a fiber crop, including rapid growth in various climatic conditions and, subsequently, the prompt accumulation of carbon dioxide [14]. Kenaf fiber, obtained by processing the bark of the kenaf plant, exhibits low density and nonabrasiveness during processing, highly specific mechanical properties, and biodegradability. Due to their similarities, kenaf can be used either as an alternative to or in admixture with jute. In 1995, kenaf was priced at \$400 per tonne and from \$278 to \$302 per tonne in 2000 [15]. It takes 54 MJ to produce 1 kg of glass fiber, but only 15 MJ of energy to produce 1 kg of kenaf. Kenaf has been largely used to reinforce thermoplastic polymers [16, 17] and, recently, thermoset polymers [18]. Kenaf fibers

have also been used as nonwoven mats in the automotive, textile, fiberboard, civil, and electronic industries [19–21].

Until recently, studies on SPI/PVA blends reported the use of plasticizers and cross-linking agents to increase mechanical and physical properties, improve thermal stability, reduce moisture absorption, and improve processability as a resin for composite fabrication. Biocomposites reinforced with kenaf fiber that use a SPI/PVA blend have not been reported, despite their many advantages of biodegradability, biocompatibility, chemical resistance, and excellent physical properties. In this study kenaf nonwovens were used to fabricate environment friendly biocomposites using modified SPI-based resins. SPI was modified using PVA in order to improve the interfacial bonding of kenaf nonwoven/SPI and then cross-linked with GA to improve its mechanical properties and water resistance. The biodegradation of the biocomposites was analyzed to determine the effect of PVA and the cross-linking agent on the composting of the kenaf composites.

2. Experimentals

2.1. Materials. SPI with an approximate protein content of 90% was supplied by Solea Company, USA. GA (grade II, 25% solution), glycerol, and PVA (98% hydrolyzed, average molecular weight (Mw) of 89,000–98,000) were obtained from Sigma-Aldrich Chemical Company. Kenaf nonwovens with an areal density of 400 g/m² were obtained from KumHa Co. Ltd. (Korea).

2.2. Preparation of the SPI/PVA Film and Kenaf/SPI-PVA Composite. The SPI/PVA films were prepared using a casting method. First, the SPI (10 wt%) and PVA (5 wt%–20 wt%) were dissolved in water (pH 8) and cured at 70°C for 25 minutes. Second, 20 wt% glycerol was added according to the optimum condition [22]. Prepared solution was casted on a glass plate and dried at 40°C for 24 hours. Finally, the SPI/PVA film was cured at 140°C via hot pressing for 10 minutes, under a pressure of 7 MPa.

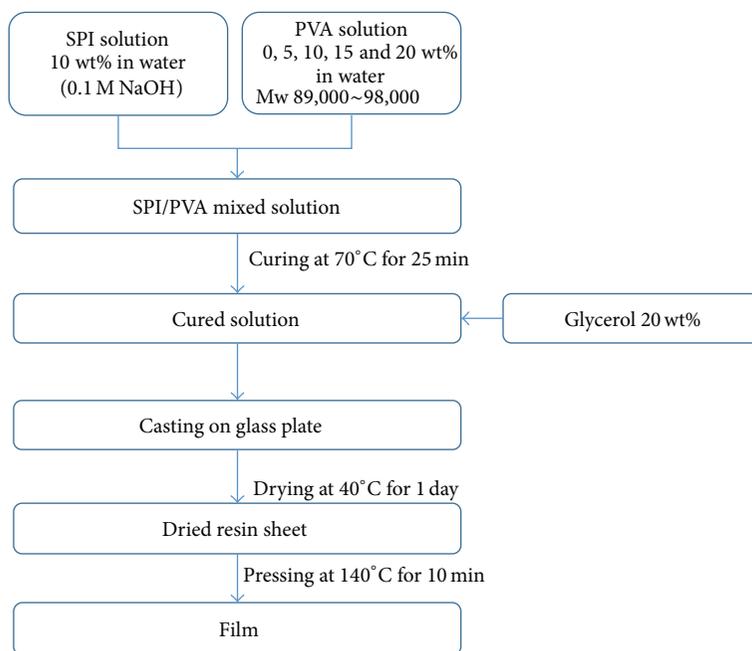


FIGURE 2: Manufacturing process of the SPI/PVA film.

Kenaf nonwovens were dewaxed by soaking them in a mixture of ethanol and benzene (1:2) at 50°C for 5 hours and then washed with distilled water and air dried. The dewaxed nonwovens were immersed in a 10 wt% aqueous sodium hydroxide solution at 30°C for 1 hour and then washed with distilled water and dried. To remove any remaining moisture, the pretreated kenaf nonwoven was cut into 20 cm by 20 cm pieces and dried at 100°C for 2 hours in a dryer and at 80°C for 3 hours in a vacuum oven. Kenaf nonwoven reinforced composites were fabricated using SPI (10 wt%)/PVA (15 wt%) resins added glycerol (20 wt%)/GA (0 wt%~25 wt%). The manufacturing process of the SPI/PVA film and kenaf/SPI-PVA composite are shown in Figures 2 and 3, respectively. The purposes of adding glycerol in kenaf/SPI-PVA composite were to improve the toughness and to make the kenaf/SPI-PVA composite more flexible.

2.3. Measurements

2.3.1. Water Absorption. The initial weight of the kenaf/SPI-PVA composite with the cross-linking agent was measured and the specimen submerged in distilled water at 25°C for 12 hours. Water absorption was calculated using (1), in which W_{wet} and W_{dry} represent weight of the sample after immersed in water and initial weight of the sample, respectively:

$$\text{Water absorption (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100. \quad (1)$$

2.3.2. Mechanical Properties. To investigate the effects of PVA and the cross-linking agent on the mechanical properties of SPI, tensile and flexural (three-point bending) tests were performed at a cross-head speed of 5 mm/min using an Instron

(model 4467), according to ASTM D638 and ASTM D790, respectively. The value of each mechanical property was determined by an average of ten specimens.

2.3.3. Interfacial Adhesion Test. The interfacial shear strength (IFSS) between the kenaf fiber and SPI was measured by a microdroplet debonding test using an Instron test system (model 4467) equipped with a 500 N load cell. The microdroplet test specimen of kenaf fiber with SPI was made to composite at 80°C for 24 hours. Figure 4 shows the test grip and microvises for the microdroplet debonding test. Tests were performed at a cross-head speed of 1 mm/min at room temperature. The maximum force (F_{max}) was recorded to calculate the interfacial shear strength (τ_{max}) using (2), in which D and L represent fiber diameter and fiber embedded length, respectively:

$$\tau_{\text{max}} = \frac{F_{\text{max}}}{\pi DL}. \quad (2)$$

2.3.4. Morphology. The surface and fracture morphologies of the kenaf/SPI-PVA composite were observed with a scanning electron microscope (SEM, S4700, HITACHI).

2.3.5. FTIR Analysis. A Fourier transform infrared spectrophotometer (FT-IR, Bruker Optic GmbH, ALPHA-P) equipped with an attenuated total reflectance (ATR) accessory was used to examine the surface composition of the uncross-linked and cross-linked kenaf/SPI-PVA composite. The spectra were recorded in the transmission mode in the range of 4000–500 cm^{-1} . FT-IR spectra were measured at a spectral resolution of 4 cm^{-1} , and the spectra were obtained with an accumulation of 128 scans for a high signal-to-noise ratio.

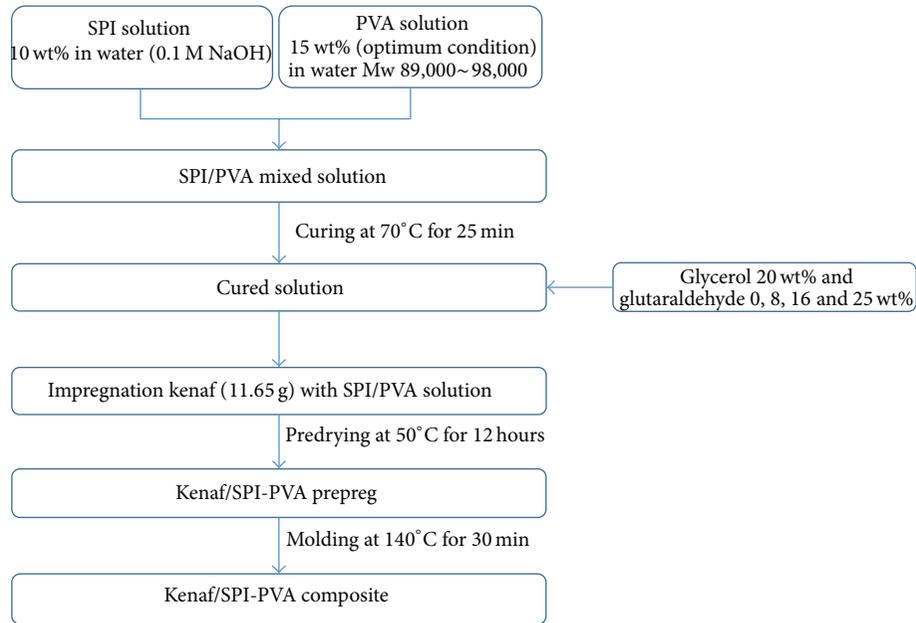


FIGURE 3: Manufacturing process of the kenaf/SPI-PVA composite.

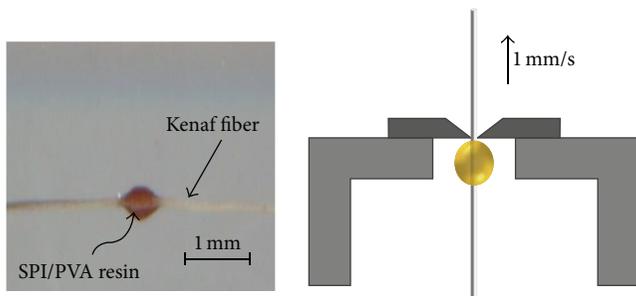


FIGURE 4: Photograph and schematic diagram of the microdroplet debonding test sample and test setup.

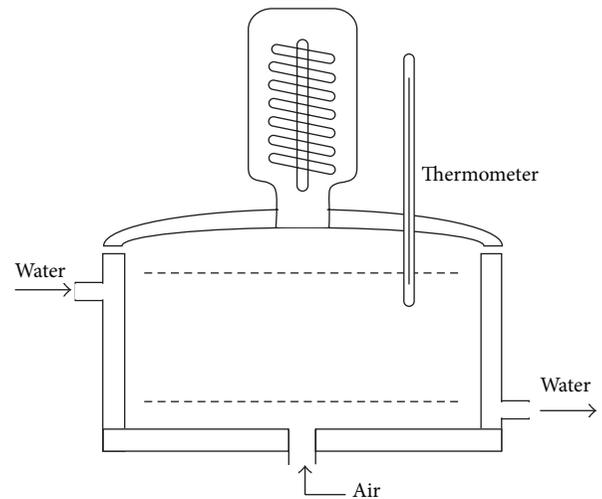


FIGURE 5: Schematic diagram of biodegradation test chamber.

2.3.6. Biodegradation. Test specimen of the kenaf/SPI-PVA composites containing the cross-linking agent was prepared in equal amounts of the size of 20 mm × 20 mm. They were dried in a vacuum oven for 2 hours. Specimens were mixed with the compost in a test bath (as shown in Figure 5) at $58 \pm 2^\circ\text{C}$, using a constant temperature bath. To maintain aerobic environment, air was injected continuously at 200 cc per minute during the test. Weight changes were measured after the specimen was dried in a vacuum oven for 12 hours at 50°C .

3. Results and Discussion

3.1. Effect of PVA Content on SPI/Glycerol Film

3.1.1. Tensile Properties. Figures 6 and 7 show the effect of PVA content on the tensile properties of SPI film without and with glycerol. The following results can be concluded from the data: (Figure 6) For the SPI/PVA films without glycerol, tensile strength decreased with the increase of PVA

content. (Figure 7) Comparing to the SPI/PVA films without glycerol, after adding glycerol (20 wt%), tensile strength of each SPI/PVA film increased and tensile modulus of it decreased with the content of glycerol. These behaviors are due to the plasticization effect of glycerol. Consequently, 15 wt% of PVA was chosen as an optimum condition. Enhancement of mechanical properties is attributed to the long-chain PVA molecules which contain many negative OH groups, forming strong intra- and intermolecule interactions with the protein molecules. These interactions may include hydrogen-bonding, dipole, and charge effects. In addition, blending long molecules in SPI could bring about molecular entanglements, which in turn will improve the mechanical properties of SPI [23].

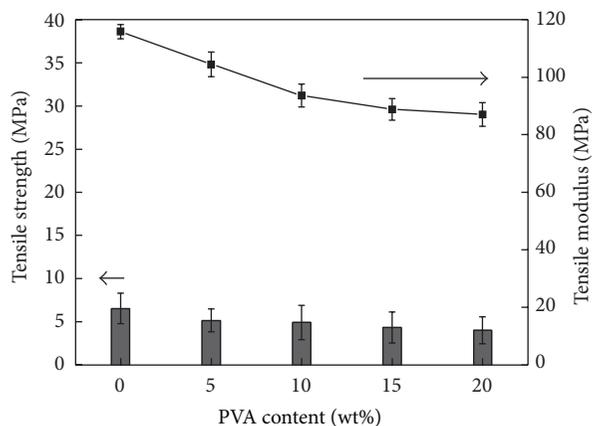


FIGURE 6: Tensile properties of the SPI film without PVA content.

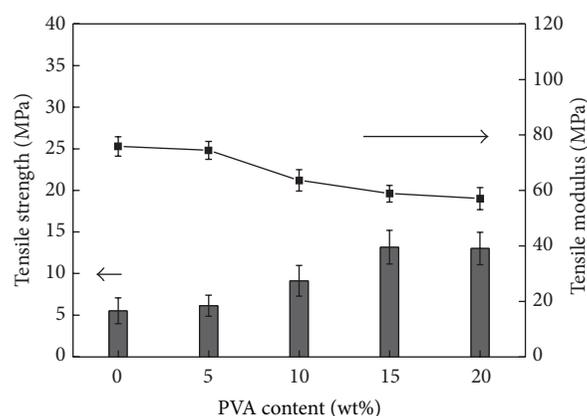


FIGURE 7: Tensile properties of the SPI/glycerol film with PVA content.

3.1.2. FTIR Analysis. The FTIR spectra of the SPI/glycerol film with and without PVA are shown in Figure 8(a). Pure glycerol is known to show absorption peaks corresponding to C-C and C-O groups in the fingerprint region from 800 cm^{-1} , 1150 cm^{-1} wavenumbers as reported by Lodha and Netravali [24]. The FTIR spectra of the SPI/glycerol without PVA show five peaks at 850 cm^{-1} , 900 cm^{-1} , 925 cm^{-1} (C-C skeletal vibrations), 1045 cm^{-1} (C-O stretch at C^1 and C^3), and 1117 cm^{-1} (C-O stretch at C^2) wavenumbers indicating the presence of glycerol on the specimen surface. Similar results for SPI/glycerol film have also been previously reported [24, 25]. Also, the absorption peak of 1480 cm^{-1} to 1570 cm^{-1} , 1600 cm^{-1} to 1700 cm^{-1} , and 3294 cm^{-1} in SPI refers to the hydrogen bond between protein chains and moisture in protein and carbonyl groups [23].

Figure 8(b) shows the FTIR spectra of SPI/glycerol film with PVA. The basic structure of the PVA molecule is -OH groups on carbon chains. The broad -OH absorption band was observed in the wavenumber range of 2918 cm^{-1} to 3565 cm^{-1} . As can be seen in spectra of the SPI/glycerol film with PVA, new absorption bands appeared in comparison

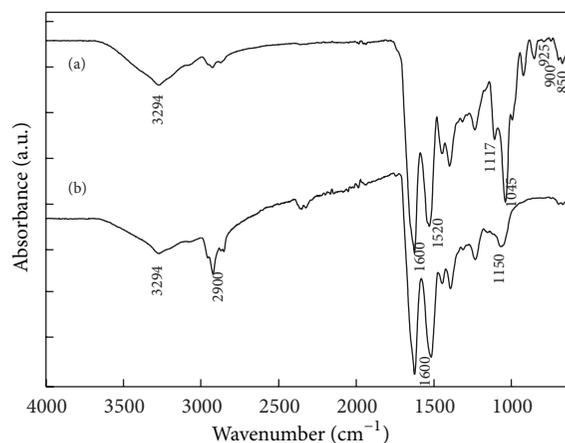
(a) SPI/glycerol without PVA
(b) SPI/glycerol with PVA

FIGURE 8: FTIR spectra of SPI/glycerol without and with PVA.

to the SPI/glycerol film without PVA. The absorption bands at 1600 to 1400 cm^{-1} and 1150 to 1250 cm^{-1} are attributable to -NH-, C-N stretching, and N-H bending (amide III) vibrations, respectively. A typical characterization of these spectra is the disappearance of the strong hydrogen bond appearing both in SPI and PVA spectra, whereas a new absorption band at 2900 to 3100 cm^{-1} appears. Normally, the absorption band of 2918 to 3565 cm^{-1} accords with the lapped characteristic band of -OH for moisture in SPI and PVA as mentioned earlier [23].

3.1.3. Morphology Observation. Figures 9(a) and 9(b) typically show the SEM photographs of SPI/glycerol film without and with PVA. Obviously, SPI/glycerol films can be fabricated smoothly without cracks and microholes. With the addition of PVA in SPI/glycerol, the surfaces have some ripples, which might owe to the toughening effect of little molecules.

SEM photographs of the fractured surface of the SPI/PVA film after the tensile test are shown in Figure 10(a). The SPI film without PVA showed a brittle fracture behavior and a shear fractured cross section due to fast crack propagation. With the increase of PVA content in the SPI, the blend materials become less brittle, as shown in Figures 10(b), 10(c), and 10(d).

3.2. Effect of GA Content on Kenaf/SPI-PVA Composites

3.2.1. FTIR Analysis. The FTIR spectra of the uncross-linked and cross-linked kenaf/SPI-PVA composite are shown in Figure 11. As can be seen in spectra of the cross-linked kenaf/SPI-PVA composite, most characteristic absorption bands appear with addition of SPI, PVA, and GA. As mentioned earlier in Section 3.1.2, the cross-linking of the kenaf/SPI-PVA composite was confirmed by strong hydrogen bond, -NH-, C-N stretching, and N-H bending vibrations after curing treatment, as compared to uncured kenaf/SPI-PVA composite.

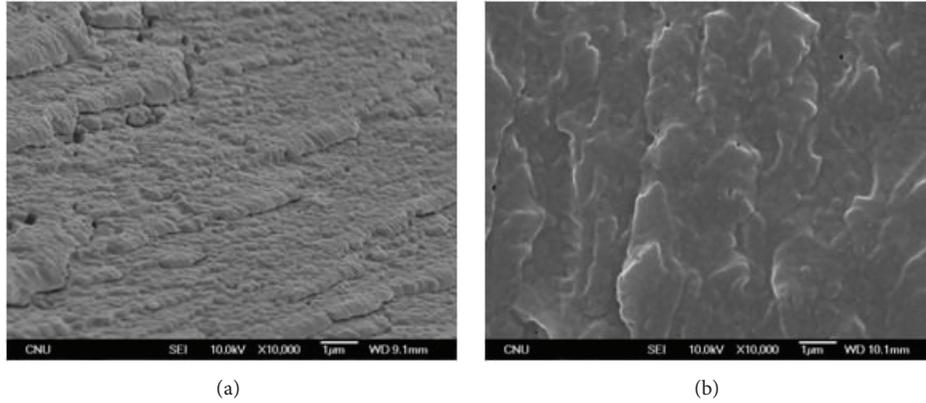


FIGURE 9: SEM photographs of surface of (a) SPI/glycerol without PVA, (b) SPI/glycerol film with PVA.

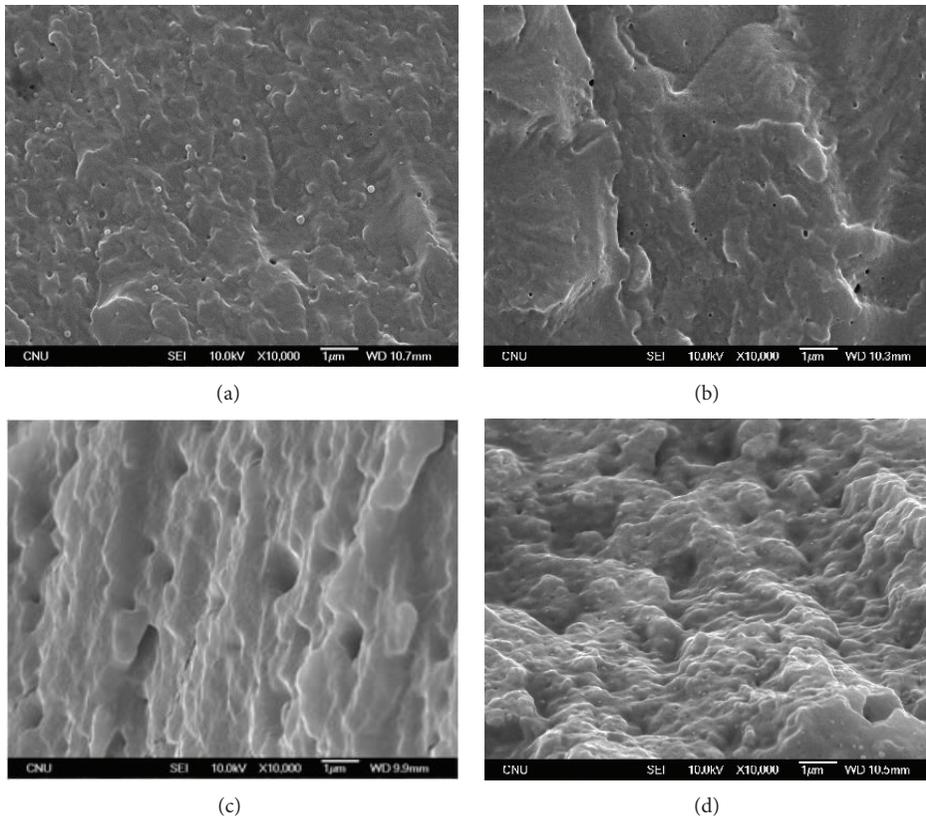


FIGURE 10: SEM photographs of tensile fracture surface of (a) neat SPI/glycerol film, (b) SPI/glycerol film with PVA (5 wt%), (c) SPI/glycerol film with PVA (15 wt%), and (d) SPI/glycerol film with PVA (20 wt%).

3.2.2. Interfacial Adhesion Properties. The interfacial adhesion strength was examined whether the addition of GA could improve adhesion between the kenaf fiber and the SPI. The average of thirty specimens was used to evaluate the IFSS as a manifestation of adhesion strength. The IFSS of the kenaf/SPI-PVA composite according to the added amount of GA is shown in Figure 12. The IFSS showed a maximum value of 15.03 MPa with the addition of 8 wt% GA. However, the IFSS of the kenaf/SPI-PVA composite with an added GA

of 16 wt% and 25 wt% decreased, indicating that the blend becomes brittle when highly cross-linked with GA.

The effect of the IFSS on tensile properties of the kenaf/SPI-PVA composites is shown in Figure 13. There is a proportional relationship between tensile strength and IFSS. Tensile strength of the kenaf/SPI-PVA composites increased from 17 MPa to 23 MPa when the IFSS was raised from 10.14 MPa to 15.03 MPa, as compared to 10.14 MPa IFSS. The increased tensile strength of the kenaf/SPI-PVA composites

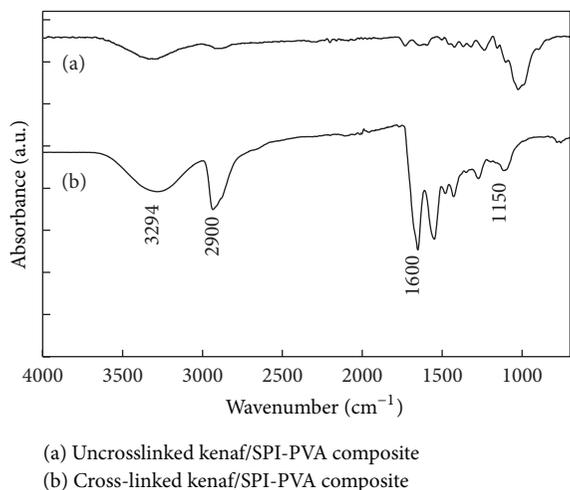


FIGURE 11: FTIR spectra of the uncross-linked and cross-linked kenaf/SPI-PVA composite.

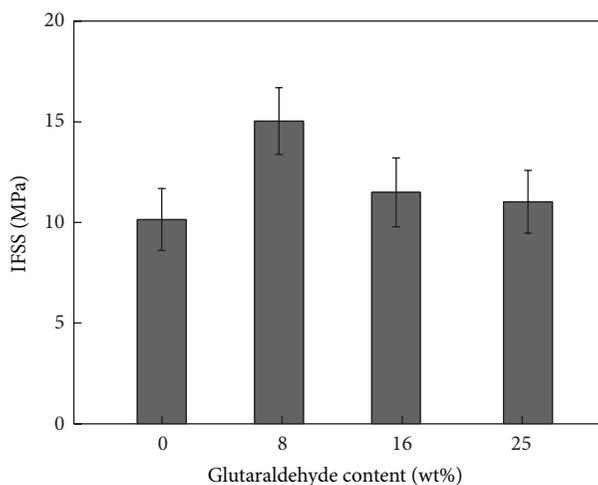


FIGURE 12: Interfacial adhesion properties of the kenaf/SPI-PVA composites with GA content.

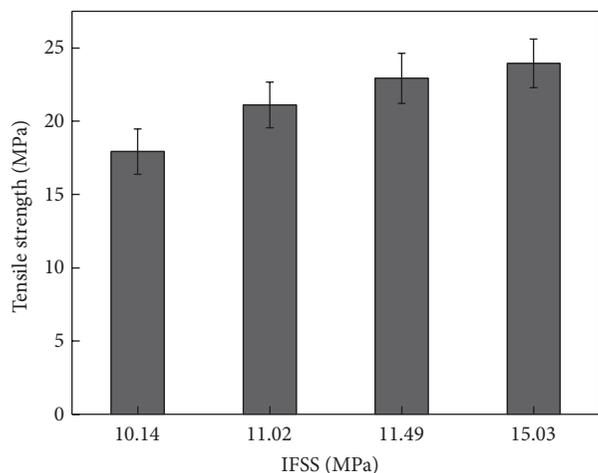


FIGURE 13: Relationship between tensile strength and IFSS of the kenaf/SPI-PVA composites.

indicates a good adhesion between kenaf fiber and SPI/PVA matrix when 8 wt% GA is added.

3.2.3. Mechanical Properties. Flexural and tensile properties of the kenaf/SPI-PVA composite with GA are shown in Figures 14 and 15. In cases of 16 wt% GA content, the flexural strength and modulus of the kenaf/SPI-PVA composite increased to 39 MPa and 2662 MPa, respectively. However, the flexural strength and modulus slightly decreased at the higher GA content, as shown in Figure 14. The slight decrease of flexural properties is well known such that internal stresses occur during the excessive cross-linking of thermosets and these residual stresses play an important role in flexural fracture. Residual stress build-up has been extensively studied in epoxy polymers and acrylate networks, and so forth [26]. It has to be noticed that excessive residual stresses in matrix and interface have been a reason of low compressive or flexural stress.

In Figure 15, while there appears to be little difference in tensile strengths of the kenaf/SPI-PVA composites with GA content, most of tensile strength is higher than those of the uncross-linked composite. Tensile modulus of the kenaf/SPI-PVA composite showed an increasing tendency with GA, while tensile strength did not show it. The increase in tensile modulus with GA addition can be attributed to the cross-links formed by GA with kenaf/SPI-PVA. Park et al. [27] showed that cross-linking SPI with GA increased the tensile properties from 8.3 to 14.9 MPa. They suggested that the covalent intermolecular and intramolecular cross-linking between soy protein and GA increased the mechanical properties of SPI/GA films.

3.2.4. Water Absorption. Water absorption properties of the cross-linked kenaf/SPI-PVA composite with the cross-linking agent after immersion in a water tank at 25°C for 12 hours are shown in Figure 16. Most of the water absorption of kenaf/SPI-PVA composite decreased with the cross-linking agents. As the GA content increased, water absorption decreased from 40.5% to 22.2%. Due to the cross-linking effect of GA, compact structure of the composite less absorbs the external moisture.

3.2.5. Fracture Surface. SEM photographs of the surface and fracture surface of the kenaf/SPI-PVA composites are shown in Figure 17. The surface and fracture surface of the composite without a cross-linking agent are shown in Figure 17(a), in which the kenaf fiber does not fully adhere to the SPI/PVA resin. The kenaf/SPI-PVA composites with a cross-linking agent were observed smooth interfacial bond between kenaf and SPI-PVA. As the interfacial bond mainly depended on the number of entangled chains forming connections across the interface, the strong bond indicated that the molecules of kenaf/SPI-PVA composites could yield more entanglement at 8 wt% GA. Obviously, many of cracks were observed in Figure 17(d) of the composite having 25 wt% of glutaraldehyde. These cracks might affect mechanical properties and fracture of the composite. Also, internal stresses in composites might occur during the excessive cross-linking as mentioned earlier.

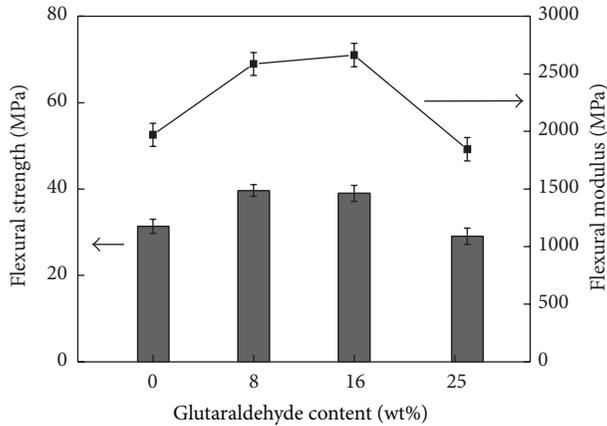


FIGURE 14: Flexural properties of the kenaf/SPI-PVA composites with GA content.

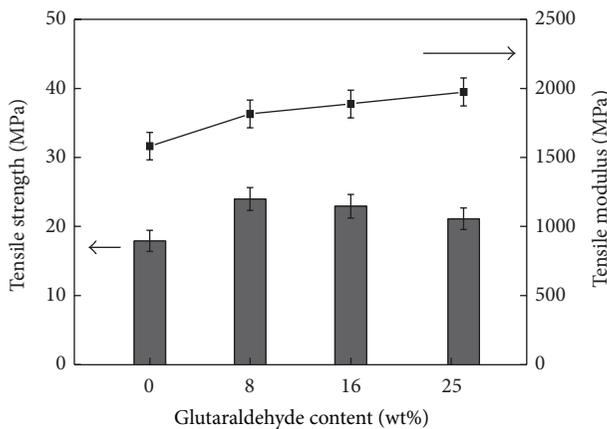


FIGURE 15: Tensile properties of the kenaf/SPI-PVA composites with GA content.

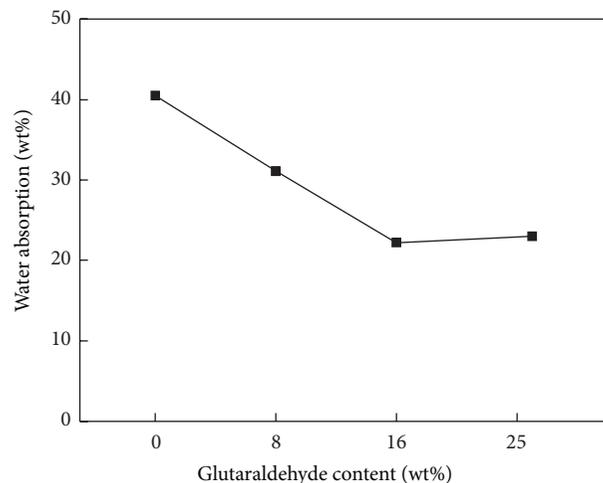


FIGURE 16: Water absorption of cross-linked kenaf/SPI-PVA composites with GA content.

3.2.6. Biodegradation Properties. The weight changes of the kenaf/SPI-PVA composite specimen, according to biodegradability, are shown in Figure 18. The weight of the kenaf/SPI-PVA composite without GA (a) decreased by approximately 22% after 5 days and approximately 43% after 20 days in a compost condition. The kenaf/SPI-PVA composite film with 8 wt% GA (b) showed a lower value of weight loss than the uncross-linked composite. Weight of the cross-linked kenaf/SPI-PVA composite decreased by approximately 12% after 5 days in a compost condition and 16% after 20 days. This indicated that the durability of the kenaf/SPI-PVA composite in a compost condition was enhanced by cross-linking with GA.

Photographs of the specimen under biodegradation conditions are shown in Figure 19. In the biodegradation test, moisture and temperature affected the biodegradation of the specimen. The kenaf/SPI-PVA composite without a cross-linking agent (a) was decomposed more in the compost than the cross-linked composite. In the kenaf/SPI-PVA composite with a cross-linking agent (b), however, biodegradability depended on the addition of GA rather than PVA [6, 20]. Considering biodegradation behavior, it can be concluded that the cross-linking of the kenaf/SPI-PVA composite with GA might govern the biodegradability. According to the biodegradation, by-products of microorganism appeared on the specimen's surface.

4. Conclusions

In this study, the kenaf/SPI-PVA composites were prepared with plasticizers and a cross-linking agent. Their interfacial adhesion properties, water absorption, biodegradation, and mechanical properties were analyzed. Results were as follows:

- (i) Increase of tensile strength in the kenaf/SPI-PVA composites indicated a good adhesion between kenaf fiber and SPI/PVA when GA of 8 wt% was added to the kenaf/SPI-PVA composites.
- (ii) Through the use of the cross-linking agent, the water absorption of the kenaf/SPI-PVA composite decreased. When GA 16 wt% was added, water absorption of the kenaf/SPI-PVA composite decreased significantly.
- (iii) The optimum preparation condition for the kenaf/SPI-PVA composite was established at PVA 15 wt% as a plasticizer and GA 8 wt% as a cross-linking agent.
- (iv) In the biodegradation test, degradation was controlled by the cross-linking agent GA. The degradation rate of the kenaf/SPI-PVA composite with GA was lower than the composite without GA, because the cross-linking between the kenaf fiber and SPI/PVA in the composite restricted its biodegradation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

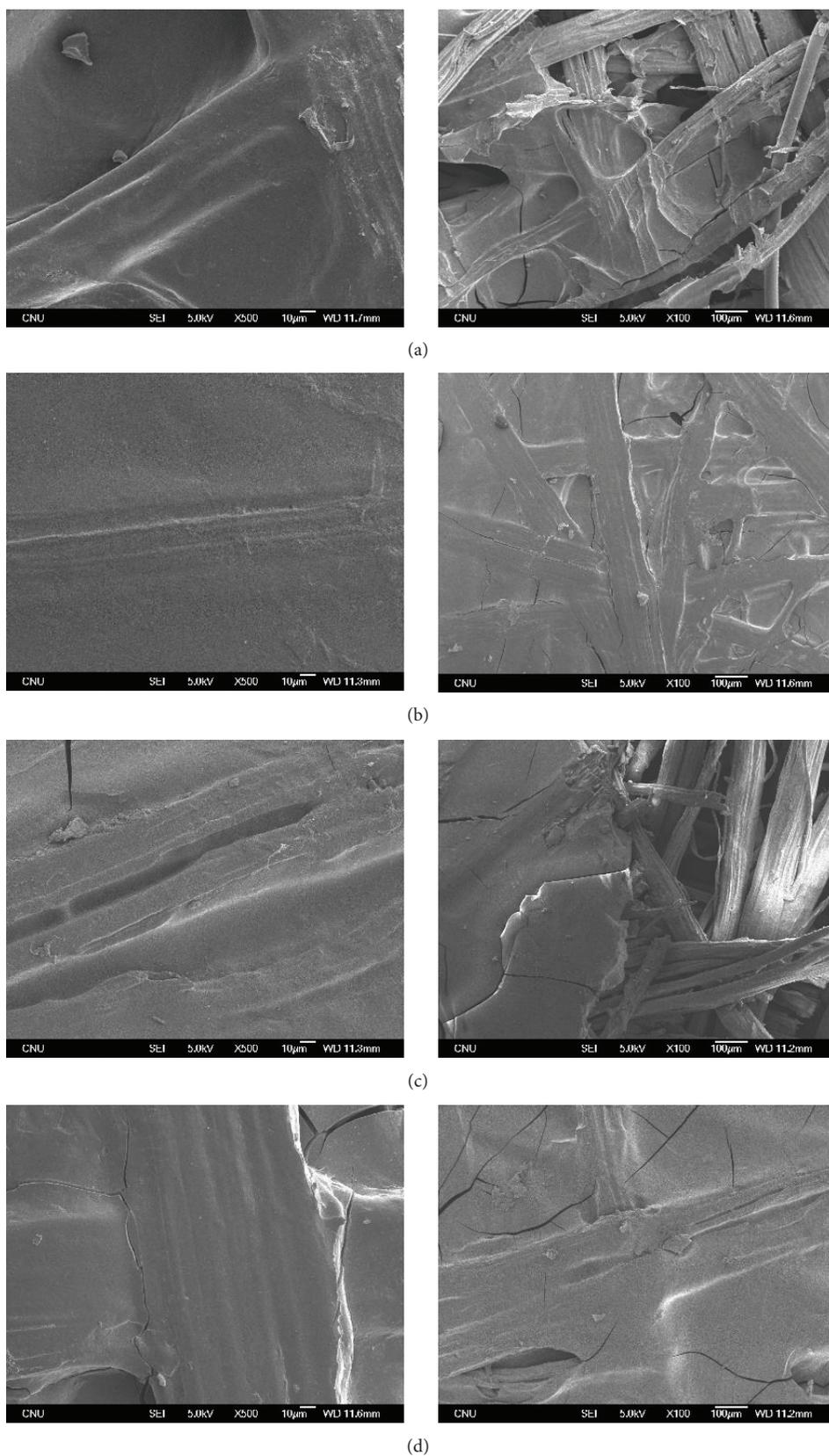


FIGURE 17: Surfaces (left, $\times 500$) and fracture surfaces (right, $\times 100$) of the kenaf/SPI-PVA composites with GA content: (a) 0 wt%, (b) 8 wt%, (c) 16 wt%, and (d) 25 wt%.

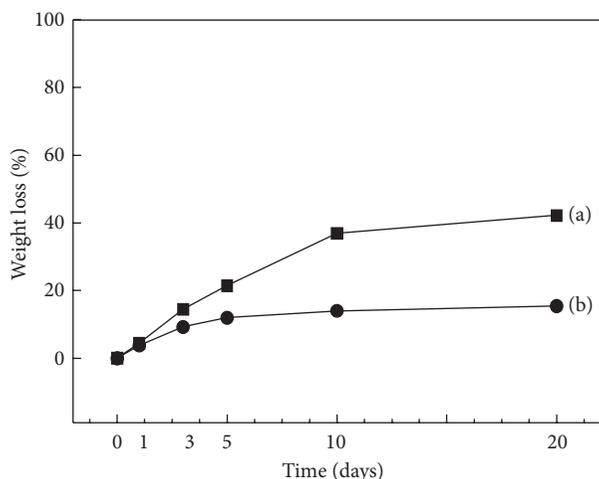


FIGURE 18: Weight loss (%) of (a) kenaf/SPI-PVA composite without GA and (b) kenaf/SPI-PVA composite having 8 wt% of GA with compost time.

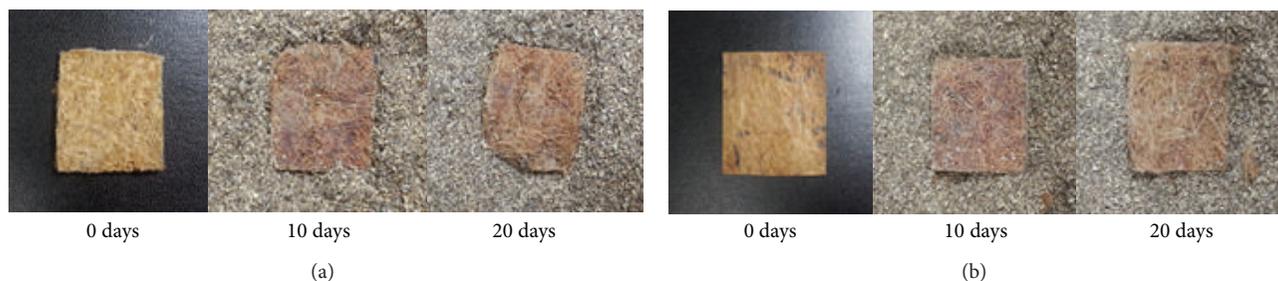


FIGURE 19: Photographs of the kenaf/SPI-PVA composite with compost time: (a) kenaf/SPI-PVA composites without GA, (b) kenaf/SPI-PVA composites with GA.

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Review Article

Rice Husk Filled Polymer Composites

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Natural fibers from agricultural wastes are finding their importance in the polymer industry due to the many advantages such as their light weight, low cost and being environmentally friendly. Rice husk (RH) is a natural sheath that forms around rice grains during their growth. As a type of natural fiber obtained from agroindustrial waste, RH can be used as filler in composites materials in various polymer matrices. This review paper is aimed at highlighting previous works of RH filled polymer composites to provide information for applications and further research in this area. Based on the information gathered, application of RH filled composites as alternative materials in building and construction is highly plausible with both light weight and low cost being their main driving forces. However, further investigations on physical and chemical treatment to further improve the interfacial adhesion with polymeric matrix are needed as fiber-polymer interaction is crucial in determining the final composite properties. Better understanding on how the used polymer blends as the matrix and secondary fillers may affect the properties would provide interesting areas to be explored.

1. Introduction

The increasing demand for eco-friendly materials, increasing depletion rate, and soaring prices of petroleum based plastics and pressing environmental regulations have all triggered a growing interest towards the field of composites [1, 2]. Composites materials are formed by combining two or more materials to improve properties of their original components. When one or more of the materials used are derived from biological origins, they are then defined as biocomposites (ASTM D7075-04) [3].

In general, polymer composites consist of a polymer resin as the matrix and one or more fillers are added to serve specific objectives or requirements. For example, composites for aerospace and sports applications require high mechanical and thermal properties. Traditionally synthetic fibers such as carbon or glass fibers have been used to reinforce composites and are able to produce such properties. However, with the growing global environmental concerns, their slow biodegradability is a disadvantage. Therefore researchers are

finding other viable approaches to enhance or accelerate the biodegradability of polymeric composites. For this reason natural fibers provide good prospective as reinforcements fillers in thermosets, thermoplastics, and elastomers. Some main advantages of using natural fibers in composites are low cost, sustainability, light weight, and being nonabrasive and nonhazardous and more importantly they can accelerate biodegradability of the polymeric composites [4, 5].

Rice (*Oryza sativa* L.) is a primary source of food for billions of people and one of the major crops in the world. It covers around 1% of the earth's surface [6]. Statistics show that, during the period of 2010–2013, the average annual global production of rice was 725 million metric tons with Asia region alone producing over 90% of the total global rice production [7]. Rice husk (RH) is an inexpensive byproduct of rice processing and is separated from rice grain during the rice milling process. It is reported that, for every ton of rice produced, about 0.23 tons of RH is formed [8]. Rice milling is one of the most important industries in countries such as China, India, Indonesia, Malaysia, and Bangladesh [9].

TABLE 1: (a) Components and (b) physical properties of RH [21].

Property	RH
(a) Components (%)	
Cellulose	25–35
Hemicellulose	18–21
Lignin	26–31
SiO ₂ (silica)	15–17
Solubles	2–5
Moisture content	5–10
(b) Physical properties	
Particle size (μm)	26.64
Surface area (m^2/g)	0.92
Density (g/cm^3)	1.00

The incineration of RH is discouraged, which in turn produces ash, fumes, and toxic gases, leading to serious air pollution. Moreover, silica is intrinsic to RH and has been successfully used to enhance the mechanical properties of composites [10]. In the paddy plants of Malaysia, with a land area of approximately 680,000 hectares, a total of 840,000 tons of RH is produced every year [11, 12].

RH is a cellulose-based fibrous material with a wide range of aspect ratios [13]. The major components and physical properties of RH are tabulated in Table 1 [14–21]. Due to its high availability, low bulk density ($90\text{--}150 \text{ kg m}^{-3}$), toughness, abrasiveness in nature, resistance to weathering, and unique composition, a variety of applications have been proposed in the literature. RH has the potential to be utilized as an insulating material, in the production of organic chemicals [22], panel boards and activated carbon [23], and supplementary cementing material [9]. Potential of RH as source of power generation and its financial viabilities have also been studied and have produced encouraging results [24, 25]. Even though some of this husk is converted into the above-mentioned end products, however, like many other agricultural byproducts, the industrial applications of this biomass are still limited with little economic value. Therefore, it is very important to find pathways to fully utilize the RH and an intense research scrutiny is currently undertaken worldwide to identify potential applications and to develop economically feasible processes for these applications on a commercial scale.

Various researchers have reported on a variety of applications that involve RH. However, it has also been reported that, in the manufacture of composites panels with the use of RH, there is a poor interaction between the RH and matrix materials, which results in weak particle-matrix adhesion [26]. Although previous studies reported that RH particleboard could be used in the manufacture of furniture and interior fittings, the physical and mechanical properties of the particleboard were lower than those of the particleboards made from wood particles [27–29]. The main reasons for lower physical and mechanical properties of the RH particleboards are low aspect ratio and waxy/silica layer of the RH particles [18]. The incorporation of RH into polymer matrices provides advantageous characteristics, such as biodegradability, light

TABLE 2: (a) Chemical and (b) physical properties of typical RHA fillers [34].

Property	WRHA	BRHA
(a) Chemical composition (%)		
CaO	0.360	0.120
MgO	0.160	0.078
Fe ₂ O ₃	0.041	0.022
K ₂ O	0.690	0.950
Na ₂ O	0.034	0.018
Al ₂ O ₃	0.025	0.023
P ₂ O ₅	0.570	0.270
SiO ₂ (silica)	92.200	53.880
Loss of ignition (LOI)	1.620	44.480
(b) Physical properties		
Particle size (μm)	6.60	19.50
Surface area (m^2/g)	1.40	26.80
Density (g/cm^3)	2.20	1.80

weight, toughness, and resistance to weathering, and also makes the final products more economically competitive [30, 31]. Compared with wood-based composites, the RH filled polymer composites have higher resistance to termite and biological attack and also better dimensional stability upon exposure to moisture. Thus, these composites are increasingly being used in building construction, such as frames for windows and doors, slidings, decks, and interior panels, and in the automotive industry for interior parts like door panels and trims [32].

RH, when burnt in open air outside the rice mill, yields two types of ash that can serve as fillers in plastics materials, namely, white rice husk ash (WRHA) and black rice husk ash (BRHA). The upper layer of the RHA mound is subjected to open burning in air and yields BRHA in the form of a carbonized layer. On the other hand, the inner layer of the mound being subjected to a higher temperature profile results in the oxidation of the carbonized ash to yield WRHA that consists predominantly of silica [33]. Table 2 shows the chemical and physical properties of typical RHA fillers [34]. As can be seen in Table 2, WRHA has been analyzed and found to have approximately 95% silica content, while BRHA has typically only approximately 54% silica content and a substantial carbon content that is about 44%.

Compression molding, injection molding, and extrusion are the most commonly used processing techniques for natural fiber reinforced thermoplastic composites. Enhancement of processability of natural fiber reinforced thermoplastics is an important issue, as the addition of interphase modifiers reduces the flow properties of the composites considerably by increasing the interaction between the fiber and the matrix [19, 20]. On the other hand, incorporation of processing aid improves processability by reducing the viscosity of the molten composites. Processability enhancement, while retaining and/or improving the performance properties, is more economical and can be an added advantage for the natural fiber composites industry [20]. RH has been

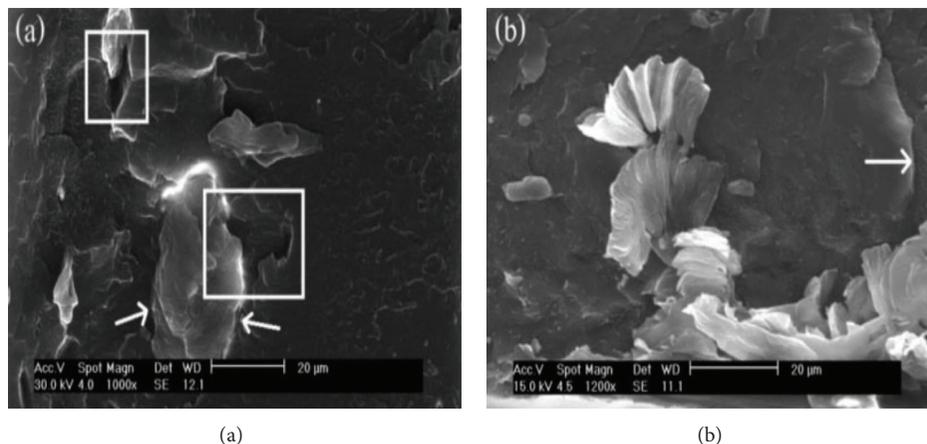


FIGURE 1: SEM micrographs of the fractured surface of composite films with varying MMT content: (a) 0 and (b) 6 wt% of MMT content [42].

incorporated into a wide variety of materials such as low-density polyethylene (LDPE) [18], high-density polyethylene (HDPE) [35], polylactic acid (PLA) [36], polypropylene (PP) [37], and polyvinyl chloride (PVC) [38]. In general, the resulting composites exhibit improved mechanical, thermal, chemical, physical, and other properties with the addition of RH. However, RH was shown to have varying degree of reinforcing effect on the different polymer matrices. In this respect, the aim of the present study is to describe the possibility for utilization of RH as fillers in the different polymer composites.

2. Rice Husk Composites

Many studies on the physical, mechanical, and thermal properties of RH filled polymeric composites and how these incorporation affects various thermosets, thermoplastics, and elastomers have been attempted [18, 35–38]. The composite properties are largely dependent on matrix properties and hence selection of the matrix is based on desired end properties of the composites. The literature review reveals that polyethylene (PE), PP, PVC, and PLA are among popular choices for RH filled polymer composites. The subsequent sections begin with some general characteristics of the polymers along with their particular applications and then report the influence of incorporating RH on the properties. In addition, properties of RH filled polymer composites are also summarized to gain a deep intuitive understanding on the subject of developing multifunctional material.

2.1. Rice Husk/Polyethylene Composites. PE is a synthetic thermoplastic polymer which is made from the monomer ethylene. It is an important family member of the polyolefin resins. It is the most widely used polymer in the world and predominates in plastics owing to a number of reasons such as high elongation at break, good chemical resistance, excellent water barrier and good oxygen barrier properties, light weight, and lower cost. PE has contributed greatly to the development of high performance materials and their

production and usage have been enormously increased [39]. PE is being made into products ranging from packaging films to bottles and automobile fuel tanks. PE is classified into different categories based mostly on its density and branching. It is worth mentioning that its mechanical and barrier properties are greatly influenced by the extent and type of branching. The long, chainlike molecules, in which hydrogen atoms are connected to a carbon backbone, can be produced in linear or branched forms. Branched versions are known as low-density polyethylene or linear low-density polyethylene; linear versions are known as high-density polyethylene and ultrahigh-molecular-weight polyethylene. Researchers have extensively studied the mechanical properties of RH filled PE and properties of some RH based composites are given in Table 3.

In our recent study [42], rice husk/maleic anhydride-modified polyethylene/montmorillonite (RH/MAPE/MMT) filled LDPE nanocomposites films (containing 0 to 6 wt% of MMT content) were prepared by extrusion blown film. The films were characterized by morphological, mechanical, oxygen (O_2) barrier, and thermal properties. The delamination of MMT layers evidenced from X-ray diffraction (XRD) results revealed the formation of intercalated nanocomposites, which was confirmed by the increase in the interlayer spacing and substantial reduction in their peak intensity of MMT. Scanning electron microscopy (SEM) confirmed that adding MMT did not alter the adhesion features between RH and LDPE (Figure 1). Furthermore, addition of RH/MAPE/MMT to the LDPE has improved the mechanical and O_2 barrier properties. Tensile and tear properties were improved with the addition of MMT and the maximum improvement of 8% in tensile strength and 5% in tear strength was observed at 3 wt% of MMT content. Concurrently, the modulus continues to increase while elongation at break decreases with increasing the MMT content. However, the most significant finding of this research was the large increase in O_2 barrier, in which the maximum barrier was observed at 4 wt% of MMT content (more than twofold). Additionally, thermogravimetric analysis (TGA) and differential scanning

TABLE 3: Mechanical properties of RH filled PE composites.

Matrix	RH (wt%)	Secondary filler (wt%)	Coupling agent or compatibilizer (wt%)	Tensile strength (MPa) (% incr.)	Tensile modulus (GPa) (% incr.)	Flexural strength (MPa) (% incr.)	Flexural modulus (GPa) (% incr.)	Impact strength (% incr.)	Reference
HDPE	65	—	—	13.5	2.39	33.5	2.90	26	[19]
HDPE	65	—	E-GMA (2.5)	22.5	2.37	49.06	3.32	28	[19]
HDPE	65	—	ethylene-acrylic ester-maleic anhydride (2.5)	20.9 (55)	2.42 (1.30)	40.2 (13.5)	2.81 (-3.1)	80 (111)	[20]
HDPE	30	—	Ultra-Plast TPI0 (1)	—	—	—	—	—	[40]
HDPE	50	—	MAPE (2)	25.64	2.5	—	—	18.39	[41]
HDPE	50	MMT* (2)	MAPE (2)	29.83	3.2	—	—	17.82	[41]
rHDPE	45	Sawdust (17.1)	MAPP (7.9)	7.5	0.6	—	—	15.20	[35]
rHDPE	44.5	Sawdust (17.1)	MAPP (7.9)	11.6	1.02	—	—	33.20	[35]
rHDPE/rPET (75/25)	60	—	MAPE* (3)/E-GMA (5)	23 (15)	1.55 (89)	35 (17)	3.5 (192)	25 (-69)	[12]

% incr. = percentage increase; not. = notched; unnot. = unnotched.

*phr.

TABLE 4: DSC results of the nanocomposites film [42].

Samples	T_{onset}	T_{pm}	T_m	T_c	X_c
LDC-0	511	551	107	95	19.1
LDC-2	519	553	107	96	19.5
LDC-3	524	559	108	95	19.8
LDC-4	525	559	108	95	20.7
LDC-5	520	557	107	96	20.3
LDC-6	514	552	108	95	19.6

LDC: LDPE/RH/MAPE (90:4:6 wt%) composites film reinforced with different MMT content (0–6 wt%); T_{onset} : onset temperature of degradation; T_{pm} : degradation temperature at peak maximum; T_m : melting temperature; T_c : crystalline temperature; and X_c : degree of crystallinity.

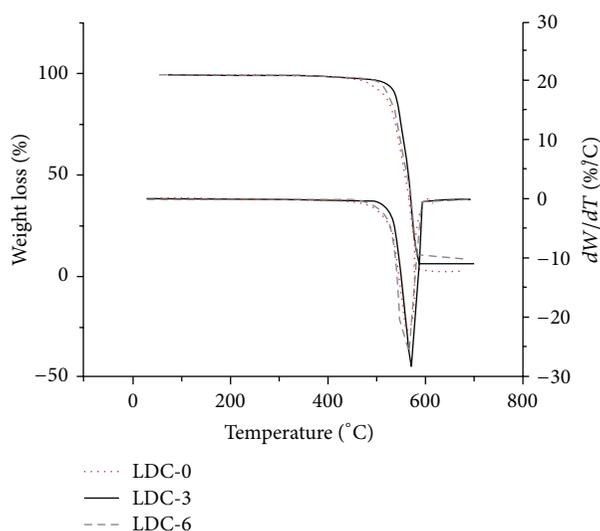


FIGURE 2: TGA and DTG thermograms of the nanocomposites film. LDC: LDPE/RH/MAPE (90:4:6 wt%) composites film reinforced with different MMT content (0, 3, and 6 wt%) [42].

calorimetry (DSC) results are shown in Figure 2 and Table 4, respectively. As can be seen, the degree of crystallinity (X_c) and thermal stability of LDPE/RH/MAPE/MMT nanocomposites are better than those of LDPE/RH/MAPE composites and the maximum improvement was at 4 wt% of MMT content. The unique combination of O_2 barrier, biodegradation, and mechanical properties for the LDPE/RH/MAPE/MMT nanocomposites films showed that these nanocomposites films provide potential candidates for a variety of food packaging.

The adhesion between the reinforcing fiber and the matrix plays an important role in the final mechanical properties of the materials. In another study by Majeed et al. [43], RH flour (having particle size of less than $75 \mu\text{m}$) and nanoclay filled LDPE composites were prepared by extrusion blown film. In this study, MAPE was used as compatibilizer in various concentrations ranging from 0 to 8 parts per hundred (PPH), and the effect of MAPE compatibilizer on the morphological, tensile, and oxygen barrier properties was examined. The XRD results showed the addition of 2, 4, 6, and 8 PPH of MAPE increased the interlayer spacing of MMT

by 20, 33, 36, and 38% compared to the uncompatibilized composites, respectively. From morphological observations, it can be concluded that the compatibilizer helps polymer molecules to penetrate and delaminate the clay platelets to realize large filler aspect ratio. In addition, it was found that adding compatibilizer enhances natural fiber dispersion in the continuous LDPE phase, and the RH aggregates started disappearing with increased compatibilizer concentration, which in turn improves homogeneity, as confirmed by SEM (Figure 3). Furthermore, the compatibilizer improved the tensile properties. It was observed that adding only 2 PPH of MAPE to the composites system improved the film tensile strength by approximately 22% compared to uncompatibilized films. The tensile properties of the composites films continued to increase as the MAPE concentration increased. This improvement in tensile properties is due to improved interfacial interactions between filler and matrix, owing to the MAPE. Therefore, composites films with high compatibilizer content showed better tensile strength. Moisture absorption usually deteriorates the mechanical properties of composites due to debonding of reinforcements from the polymer matrices. However, in this particular study, moisture absorption increased the tensile strength of uncompatibilized composites, and the authors attributed this increase in tensile strength to the fiber swelling, which could fill the gaps between fiber and polymer matrix and eventually could lead to an increased strength. It is notable that the increase in tensile strength is not significant for compatibilized composite samples with no significant change observed between the properties of dry and water aged samples. On the other hand, moisture absorption decreased the tensile properties for the compatibilized composites. Indeed, the most significant finding of this research was the large increase in oxygen barrier. Oxygen barrier property of the composite films improved remarkably by the presence of MAPE compatibilizer (more than twofold by 4 PPH MAPE). The decrease in permeability also confirms that the impermeable clay platelets are well dispersed as the extent of dispersion of clay platelets plays a major role in creating a tortuous path for the permeating molecules.

Recently, Kwon et al. [18] reported the effect of adhesive type and content on the dimensional stability and mechanical properties of three-layer particleboards. The composition layers were made by the mixture of wood particles (face layer, 30 wt%) and RH particles (core layer, 70 wt%) under laboratory conditions (Figure 4). Two types of thermosetting adhesives, liquid urea-formaldehyde (UF) and phenol-formaldehyde (PF), and thermoplastic adhesive (LDPE) powder were used as binder in the experiments. They found that the dimensional stability and mechanical properties of particleboards with RH core were significantly improved by the incorporation of LDPE into the core layer. It was studied that at the amounts of UF and PF adhesives decreased from 8 to 4 wt% at the same LDPE content (10 wt%); the thickness swelling (TS) and water absorption (WA) of the particleboards increased but were significantly lower than those of the control specimens. The reason was that a hydrophilic material (RH) was replaced by a hydrophobic material (LDPE). They explained that although the internal bond (IB) strength of particleboards containing 10 wt% LDPE

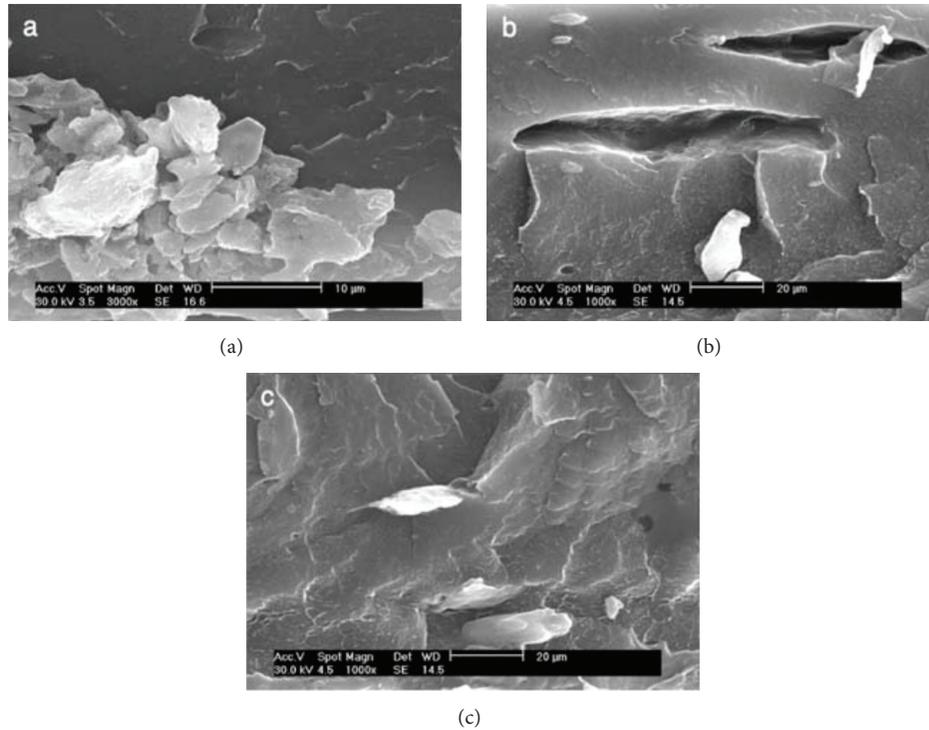


FIGURE 3: SEM micrographs of the fractured surface of composite films with varying compatibilizer concentrations: (a) 0, (b) 2, and (c) 6 PPH [42].

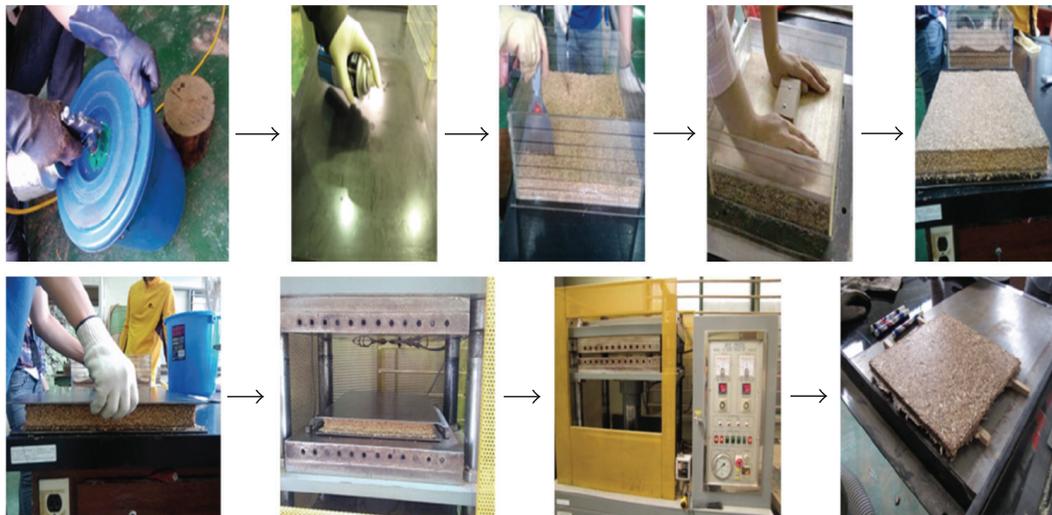


FIGURE 4: Laboratory-scale production of three-layer particleboards [18].

decreased with decreasing UF adhesive content in the core layer, it was higher than that of the control particleboards. Different fracture modes were observed during the IB tests. The fracture modes of particleboard samples with and without LDPE were presented in Figure 5 [18]. This study also demonstrated that the bending strength (MOR) and modulus of elasticity (MOE) of the particleboards containing 10 wt% LDPE decreased with decreasing the amounts of UF and PF adhesives. However, there were no statistically significant

differences in the MOR and MOE values of the particleboard types as the adhesive content decreased from 8 to 4 wt% in the core layer. Based on the findings obtained from Kwon et al.'s [18] study, it can be suggested that the RH particleboards containing LDPE (in particular above 20 wt% of LDPE) are suitable for use in damp places, such as bathrooms, toilets, kitchens, and laundries.

Chuayjuljit et al. [44] successfully obtained silica (SiO_2) from RHA. They explored the possibility of using silica

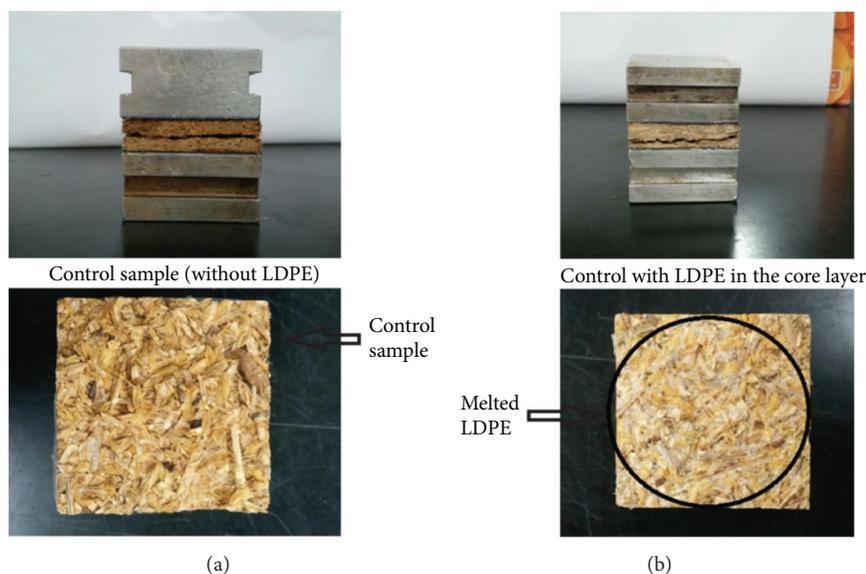


FIGURE 5: Fracture modes and fracture surface of the IB test samples without LDPE (a) and with LDPE (b) [18].

TABLE 5: Properties of RHA silica and commercial silica [44].

Properties	RHA silica	Commercial silica
Average particle size (micron)	4.27	6.61
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	131.35 ± 2.34	511.97 ± 4.70
Bulk density (g cm^{-3})	0.677	0.319
pH	5.7	6–8
Oil absorption (g g^{-1})	1.92	2
Silica content (% SiO_2)	99.6	99.0

from RHA (RHA silica) as antiblocking agent in LDPE film. Properties of RHA silica were compared with commercial silica, as can be seen in Table 5. In addition, the appropriate amount of silica to be used as an antiblocking agent in LDPE film was also investigated. The results indicated that silica prepared from RHA, although composed of finer particles, showed less porosity than that of commercial silica, resulting in a lower specific surface area. Nevertheless, it is possible to use the obtained RHA silica as an antiblocking agent for LDPE film. They found that the addition of RHA silica to LDPE film modifies the film blocking behavior by inducing film roughness. However, the blocking is reduced not as much as in the case of commercial silica. It is investigated that, to the same antiblocking capability, 2000–3000 ppm of RHA silica is needed as opposed to 500–1500 ppm of commercial silica normally used in the plastic film industry. It was found that, as the amount of silica increased, certain mechanical properties (tensile strength, elongation at break, and tear strength) were decreased markedly. This is probably because silica has a lower bulk density and larger average particle size.

Panthapulakkal et al. [19] explored the potential of extruded RH filled HDPE composites profiles for structural applications. In their study, four different coupling agents

based on ethylene-(acrylic ester)-(maleic anhydride) terpolymers and ethylene-(acrylic ester)-(glycidyl methacrylate) terpolymers were used to enhance the performance properties of the composites. The chemical composition and molecular weight of these coupling agents, and also tensile and flexural strength of HDPE/RH (32.5 : 65 wt%) composites are given in Table 6. They studied the effects of various coupling agents (2.5 wt%) on various performance properties of RH filled HDPE composites. The results indicated that these coupling agents significantly enhanced the tensile and flexural strength of the HDPE/RH composites, and the extent of the coupling effect depends on the nature of the interface formed. It is notable that the tensile and flexural strength of HDPE/RH composites without present of any coupling agent are 13.5 and 33.5 MPa, respectively. Their results showed that RH filled HDPE composites gain enough strength and rigidity by incorporating coupling agents and can be used for making structural materials. They found that incorporation of coupling agents enhanced the resistance to thermal deformation and the water absorption properties of the composites, whereas it reduced the extrusion rate significantly. Among the four coupling agents used, the coupling agent with a glycidyl methacrylate functional group and without any methyl acrylate pendant group on the polymer backbone (EGMA1) was found to be the best coupling agent for the RH filled HDPE composites. They concluded that the extrusion rate of these composites is reduced by the incorporation of the coupling agents and has to be enhanced by proper use of process aids.

In another study by Panthapulakkal et al. [20], the effect of coupling agent and processing aid on the performance properties of RH filled HDPE composites was studied. In their study, HDPE composites filled with 65% RH were extruded using a single screw extruder with die dimensions of 3×8 mm. They investigated the processability and performance properties of the HDPE composites, which were

TABLE 6: Interrelation between chemical compositions of coupling agents and mechanical strength of HDPE/RH (32.5 : 65 wt%) composites [19].

Coupling agent (2.5 wt%)	Butyl acrylate (wt%)	Maleic anhydride (wt%)	Methyl acrylate (wt%)	Glycidyl methacrylate (wt%)	Molecular weight (g mol ⁻¹)	Tensile strength MPa	Flexural strength MPa
EBMA1	6	3.1	—	—	120000	20.9	40.2
EBMA2	17.7	3.1	—	—	120000	19.3	42.7
EGMA1	—	—	—	8	100000	22.5	49.6
EGMA2	—	—	15	9	—	15.7	33.8
HDPE/RH*	—	—	—	—	—	13.5	33.5

*Without coupling agent.

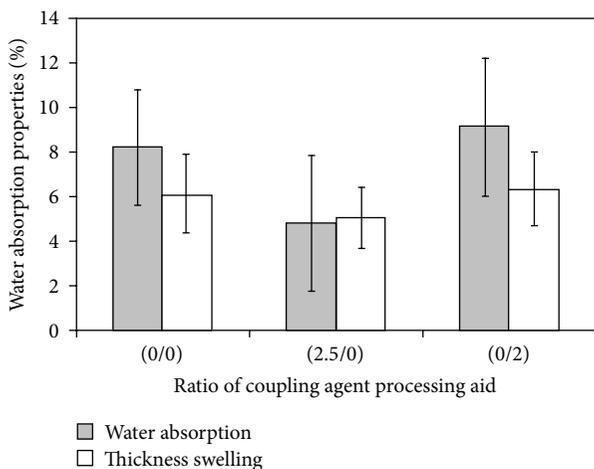


FIGURE 6: Tensile and flexural modulus of the composites with and without process additives [20].

highly dependent on the concentration of the coupling agent and processing aid in the composites formulation. In their study, attempt was made to optimize the composites formulation with respect to both coupling agent and processing aid to achieve optimum mechanical and water absorption properties with an optimum extrusion rate. It was observed that incorporation of a terpolymer (ethylene-acrylic ester-maleic anhydride) based coupling agent enhanced the tensile strength, flexural strength (Figure 6), and resistance to water absorption properties of the composites with a significant reduction in the processability. However, this study revealed that the addition of processing aid reduced the strength and stiffness of the composites and the effect was at a higher content of processing aid in the formulation. They found that the extrusion rate of the composites improved by the incorporation of processing aid and processing aid adversely affected water absorption resistance of the composites. They observed that the composites with a coupling agent to processing aid ratio of 0.73 : 0.59 by weight showed an optimum combination of performance properties and extrusion rate.

In an interesting study, the compounding of RH and HDPE was investigated using corotating twin-screw extruder [40]. Four sizes of RH were studied at various compositions. The size ranged from 500 μm and below, while the content

of RH in the composites varied from 30 to 50 wt%. Also, a fixed amount of Ultra-Plast TP10 as a compatibilizer and Ultra-Plast TP 01 as lubricant was added to the composites compound. It was noticed that among the four RH sizes (A, 250–500; B, 125–250; C, 63–125, and D, <63 μm), RH with the size of 250–500 μm which has the largest particle was considered to be the most appropriate size as the composites filler based on thermal stability test. The melt flow rate of RH/HDPE decreased with the increasing in RH filler and apparent viscosity also increased with composition for all fillers sizes. They found that, when RH was incorporated into the HDPE matrix, the melt flow rate of RH size A (250–500 μm) composites performed well above the control limit set. Although composites with RH size C and D had better melt flow at 30 wt%, the fillers tended to degrade at high processing temperature, such as 190°C or when longer residence time was used. Melt flow rate above 4 g 10 min⁻¹ was found to be the lower limit for injection molding process. It is observed that RH size A has the highest impact resistance among the other sizes. The large particles of RH have low agglomeration and dispersed better in the composites matrix. Filler incorporated at 30% of RH size A was found to be suitable for processing and to have optimum rheological properties with respect to impact strength compared to 40 and 50 wt% of RH.

Kord (2011) fabricated nanocomposites based on HDPE and rice husk flour (RHF) blend (ratio of 50 : 50 wt%) with different content of nanoclay using an internal mixer [41]. In his study, the influence of nanofiller at four levels, 0, 2, 4, and 6 parts per hundred compounds (phc), on the thermal and rheological behavior was studied. The morphology of nanoclay was determined by XRD, and the effect of morphology on the thermal and dynamic mechanical properties was also considered. It was indicated that the crystallization temperature, crystallization enthalpy, and crystallinity level increased with increasing of nanoclay up to 2 phc and then decreased. Additionally, the dynamic mechanical behavior of nanocomposites was improved by the addition of nanofiller and XRD patterns revealed that the nanocomposites formed were intercalated. It was also reported that the sample containing 2 phc of nanoclay had higher order of intercalation and better dispersion, as confirmed by XRD. It was found that with increasing of coupling agent (MAPE) a fully exfoliation morphology could be obtained. Therefore, he concluded

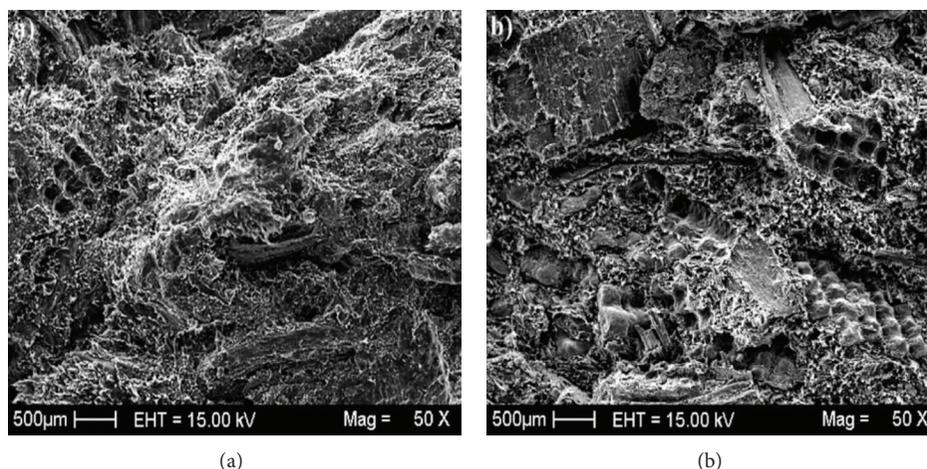


FIGURE 7: SEM micrographs of fracture surfaces of sample from composites at 50x: (a) 0.5% AOs and (b) 20% FRs [35].

that thermal and rheological properties of the HDPE/RHF nanocomposites were improved by increasing of MAPE content.

Hamid and coworkers [35] studied the physical and mechanical and thermal properties of recycled high-density polyethylene (rHDPE) reinforced with a high content of hybrid RH and sawdust. They also studied the effect of antioxidants (AOs) and fire retardants (FRs) as additives. The rHDPE and natural fibers were compounded into pellets by a compounder; then the pellets were extruded using a corotating twin-screw extruder and the test specimens were prepared using hot and cold press processes. Also, maleic anhydride-grafted polypropylene (MAPP) was used as a coupling agent to increase the adhesion of the fiber-matrix interface. Results showed that the samples with 0.5 wt% of AOs and 20 wt% of FRs produce the most reasonable strength and elasticity of composites. Furthermore, the effect of the presence of AOs and FRs on water uptake was minimal and microstructure analysis of the fractured surfaces of composites confirmed improved interfacial bonding. As can be seen in Figure 7, composites with (a) 0.5% AOs and (b) 20% FRs content show the good dispersion of hybrid fibers in the matrix. Therefore, good dispersion of fibers in composites leads to high performance on physical and mechanical properties. There is no clear gap between hybrid fibers and matrix (Figure 7), indicating the good interface bonding. The fibers were perfectly attached to the matrix and it is also evident that the fibers were strongly imbedded in the matrix, indicating the efficiency of the mixing, which was attributed to a good interfacial interaction between hybrid fibers and matrix. It was concluded from the results that the addition of AOs and FRs as mineral fillers improves not only the aging and fire resistance aspects but also the durability performance of rHDPE reinforced with a hybrid of RH and sawdust. As a result, various parameters influence the mechanical properties of fiber-reinforced composites: fiber aspect ratio, fiber-matrix adhesion, stress transfer at the interface, mixing temperatures, and the addition of a coupling agent.

More recently, Chen et al. [12] fabricated RHF composites based on uncompatibilized (UPB) and compatibilized (CPB) recycled high-density polyethylene/recycled polyethylene terephthalate (rHDPE/rPET) with ethylene-glycidyl methacrylate (E-GMA) copolymer by a two-step extrusion and hot pressing with fiber content of 40, 60, and 80 wt%. They noted that the tensile and flexural properties of the composites were significantly increased with increasing RHF content, especially the tensile and flexural modulus. In contrast, as expected, they observed that the addition of RHF to the polymer blends (PB) matrices decreased the elongation to break and impact strength of the composites. However, the results indicated that the compatibilization of PB matrices by E-GMA compatibilizer could further increase the overall mechanical properties of CPB-based composites. In their research, WA test was examined in distilled and seawater. In long-term water immersion test, Chen et al. [12] found that the WA and TS increase with RHF content and immersion time for all types of composites irrespective of the types of polymer matrix (UPB and CPB) and immersion conditions (distilled and seawater). They also observed that the diffusion coefficient, thermodynamic solubility, and permeability obtained from the Fickian model and the swelling rate parameter obtained from swelling model increased with the RHF content. However, all these parameters decreased with the compatibilization of rHDPE/rPET by E-GMA, especially at lower content matrix. SEM analysis of the compatibilized matrix composites confirmed the improved interfacial bonding of matrix-matrix and filler-matrix phases (Figure 8). As can be seen in Figures 8(a) and 8(a'), the UPB displayed an incompatibility morphology of an obvious phase segregation structure between rHDPE and rPET, whereas the CPB exhibited a finer dispersion of rPET component inside the HDPE matrix. Figures 8(b) and 8(c) show a coarse morphology in the polymer matrices. From Figure 8(b), it can be clearly observed that the larger particle size shows no evidence of interfacial interaction and adhesion within the matrix phase, which confirmed the incompatibility of the two matrix individual components. The black arrows in the

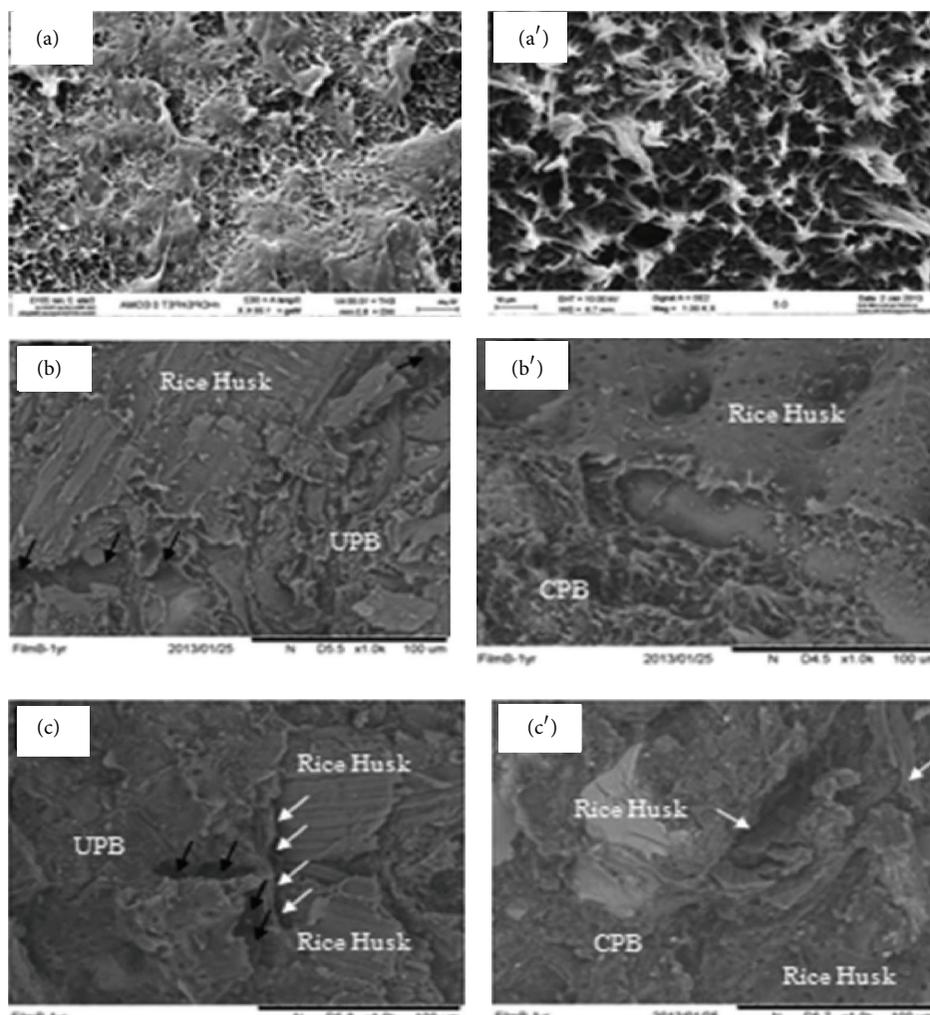


FIGURE 8: SEM micrographs of (a) 0 wt% UPB, (a') 0 wt% CPB, (b) 40 wt% RHF-UPB composite, (b') 40 wt% RHF-CPB composite, (c) 80 wt% RHF-UPB composite, and (c') 80 wt% RHF-CPB composite (magnification, 1000x) [12].

Figures 8(b) and 8(c) show that the available spaces or sites for the water molecules diffuse and form hydrogen bonds with the polar rPET by breaking the existing bonds between the hydroxyl groups of the rPET chain. However, RHF-reinforced composites with CPB matrices exhibited a finer surface morphology (Figures 8(b') and 8(c')) with smaller size matrix domains, which indicates the good dispersion or rPET particles inside the rHDPE matrix and the better interfacial adhesion within the matrix. By comparing Figures 8(b/b') and (c/c'), it can be observed that the RHF fillers at the concentration of 40 wt% were well embedded in the PB matrix, which indicates the relatively good interface adhesion between the fibers and matrix. Meanwhile, the white arrows in the latter figure show a clear gap between the polymer matrix and the RHF fillers, which enhances the water diffusion. This indicated the poor filler-matrix interfacial bonding, as a result of insufficient amount of coupling agent at high RHF content (80 wt%). Based on the results and findings in this work [12], they proposed that

the agrofiller/recycled plastics composites are suitable for outdoor applications in terms of low WA and TS.

2.2. Rice Husk/Poly(lactic Acid) Composites. PLA is a synthetic thermoplastic polymer and one of the most promising candidates for biodegradable polymers with excellent mechanical properties [45]. PLA is produced on a large scale from fermentation of cornstarch to lactic acid and subsequent chemical polymerization. As PLA is obtained from renewable resources, therefore, it represents a good candidate to produce disposable packaging in addition to its application in the textile and automotive industries and clinical uses [46]. Pure PLA can degrade to carbon dioxide, water, and methane in the environment over a period of several months to two years, compared to other petroleum plastics needing a very long period. Although PLA is an eco-friendly plastic with good biocompatibility, poor hardness, slow degradation, hydrophobicity, and lack of reactive side-chain groups limit

TABLE 7: Mechanical properties of RH filled PLA composites.

Matrix	RH (wt%)	Coupling agent or compatibilizer (wt%)	Tensile strength (MPa) (% incr.)	Tensile modulus (GPa) (% incr.)	Flexural strength (MPa) (% incr.)	Impact strength (Jm^{-1}) (% incr.) Unnot.	Reference
PLA	AT RHF (25)	—	7.35 (-82)	—	13.9 (-84)	—	[48]
PLA	WT RHF (25)	—	39.47 (-21)	—	52.4 (-39)	—	[48]
PLLA/starch (42/42)	5	TC/MDI (10/1)	8.58	0.062	—	35.23	[49]
PLLA/starch (37/37)	15	TC/MDI (10/1)	14.58	0.225	—	22.31	[49]

AT RHF = alkaline-treated rice husk fiber; WT RHF = water-treated rice husk fiber; TC = triethyl citrate; MDI = diphenyl-methane-4,4'-diisocyanate.

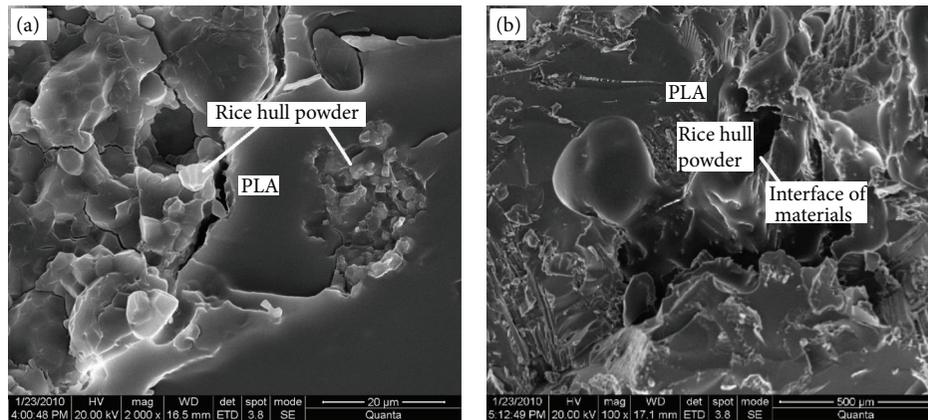


FIGURE 9: SEM micrographs of composites: (a) 20 g of RHP and (b) 20 g of RHP + 2 g of MAPP [50].

its application [47]. The mechanical properties of RH filled PLA composites are illustrated in Table 7.

In research by Hua et al. [50], the rice husk powder (RHP) was modified by PLA using melt-blending technique, and MAPP was used as coupling agent. The mechanical properties, water absorbability of RHP/PLA composites, and the relations between these properties and microscopic characteristics were investigated. Their result showed that, with the increasing content of RHP, the maximum tolerable tension and tensile strength increased. The water absorptivity of materials increased with the increasing of RHP content (after 24 hours). They also found that coupling agent could significantly reduce the water absorbability of composite materials. They observed that the hygroscopicity was slow in the beginning and it became strong after a certain period of time because the characteristics will change remarkably after the RHP soaking in the water for a long time. It is also reported that, with the increasing of RHP, the hardness of composite materials increased the tensile strength enhancement, and the maximum bearable tension increased too. As shown in Figure 9(b), there is no obvious change in the content density and the porosity of the RHP in the composites with MAPP compared to composites without MAPP (Figure 9(a)). But it shows that the pore becomes obviously small and smoother. In addition, when the adhesion between PLA and RHP became closer, the agglutination performance of materials enhanced, the composite materials had lower

water absorptivity, and the tensile strength and the most high tension all obtained enhancement obviously when the MAPP was added to RH composites. Therefore, the usage of coupling agent is one of the effective ways to strengthen the performance of composite materials.

Zawawi et al. [51] did a comparison study on microwave properties of natural fiber reinforced PLA composites in order to recognize their potential as alternatives to common printed circuit board (PCB) for electronic communication industries. Thus, they reported on measured dielectric properties for two composites (kenaf/PLA and RH/PLA) and their results were compared. The samples were prepared in equal wt% (50:50 wt%), and the complex dielectric permittivity ($\epsilon = \epsilon' - j\epsilon''$) and loss tangent ($\tan\delta$) of both composites have been studied in the frequency range of 500 MHz to 10 GHz. It was observed that, from 500 MHz to 3.32 GHz, real permittivity (ϵ') values are consistent throughout the wide frequency range, at approximately 3.3. However, the permittivity seems to decrease at higher frequencies starting from 3.35 GHz for both composites, down to 2.5 at 10 GHz. From their observation, real permittivity (ϵ') parameter has shown significant variation with frequency range. It is also observed that kenaf/PLA composites with the same weight content have higher permittivity (ϵ') value compared to RH/PLA composites. Meanwhile, they noticed that loss tangent ($\tan\delta$) is low and remains similar for both composites. The results showed that both kenaf/PLA and RH/PLA composites can

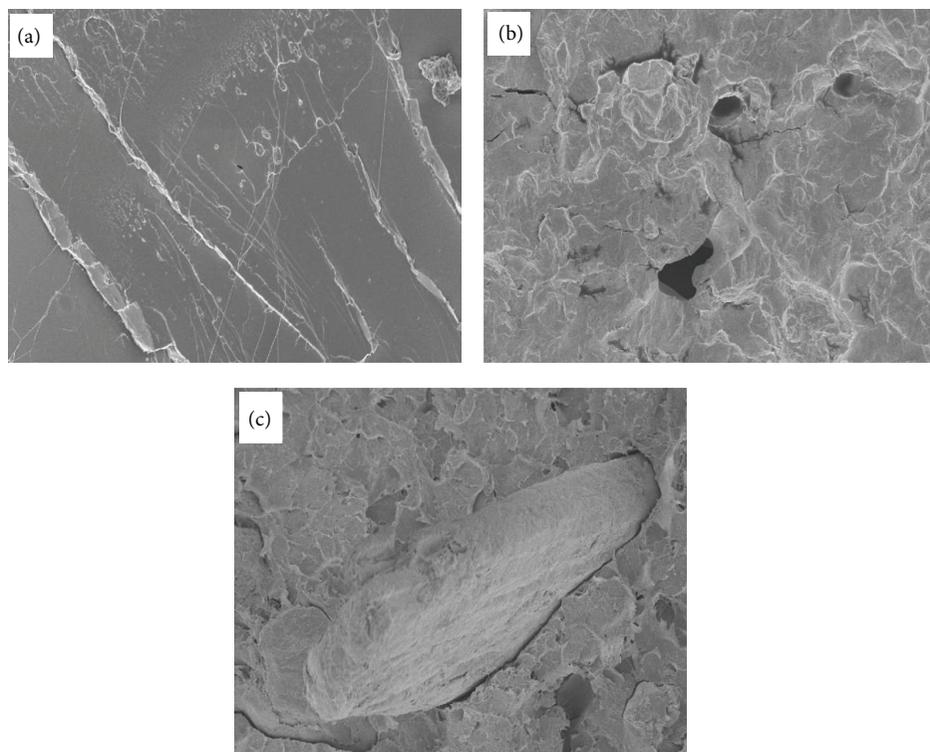


FIGURE 10: FESEM micrographs of flexural fractured surfaces of (a) pure PLA, (b) PLA/AT RHF, and (c) PLA/WT RHF composites [48].

be used for microwave applications due to their permittivity range and low loss tangent comparable to existing commercial substrates, such as epoxy-based dielectrics.

Most recently, a research group in (2014) focuses on the influence of surface treatment and fiber sizes on mechanical behavior, physical properties, and morphology of RH fiber reinforced PLA [48]. Modified RH fiber was prepared by using 6 wt% sodium hydroxide (NaOH) and distilled water. PLA composites reinforced with modified RH fiber (25 wt%) was mixed using the internal mixer and fabricated by the mini injection molding. Farah Dina et al. (2014) found that the tensile and flexural strength of PLA composites with 100, 200, and 500 μm particles sizes of water treated fiber are much higher than those of alkaline treated ones. DSC and TGA analyses were performed and indicated that the water and alkaline treatments reduced the thermal stability of the PLA composites (Table 8). The authors claimed that surface treatment by NaOH on RH fiber could not successfully improve the interfacial adhesion between fibers and PLA matrix. Field emission scanning electron microscopy (FESEM) micrographs of flexural fractured surfaces of composites are shown in Figure 10. Microcrack and pores are indicated by circle and arrow, respectively (Figure 10(b)). This behavior is due to the brittle fracture of PLA matrix adjacent to the alkaline treated RH fiber (AT RHF). The interface between the alkaline treated RH fiber and PLA is loose. It may be due to the loss of fiber-matrix interfacial adhesion and the failure of the fibers in the load distribution which are the evidence of poor fiber-matrix adhesion. From Figure 10(c), it is clear that the PLA/water treated RH fiber (WT RHF)

TABLE 8: DSC and TGA results of WT RHF and AT RHF filled PLA composites.

Samples	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	ΔH_m (J/g)	Decomposition temp. of the different weight loss (wt%)		
				5	50	75
PLA	64	171	99	364	395	407
PLA/WT RHF	66	169	77	347	382	400
PLA/AT RHF	57	160	52	296	339	—

fracture surface is rougher than the PLA/alkaline treated RH fiber (Figure 10(b)), which facilitates the mechanical interlocking. Additionally, two phases can be clearly seen and RH fibers were pulled out from the matrix in the fracture process, with large voids thereby being created, as indicated by arrow (Figure 8(c)).

Working in another direction, Battagazzore et al. [52] extracted silica powder from RH by a simple extraction procedure (Figure 11) for preparing PLA composites with differing filler contents (5, 10, 20, and 30 wt%) using melt compounding. The thermal, mechanical, and morphological properties have been investigated. Indeed, the presence of extracted silica has induced significant improvements of Young's modulus as well as a slight reduction of the oxygen permeability of PLA. The collected values at 10 and 30 wt% have been compared with prepared samples using a commercial silica and they found that the achieved mechanical properties turned out to be higher than those exhibited by the homologous samples prepared by using a commercial

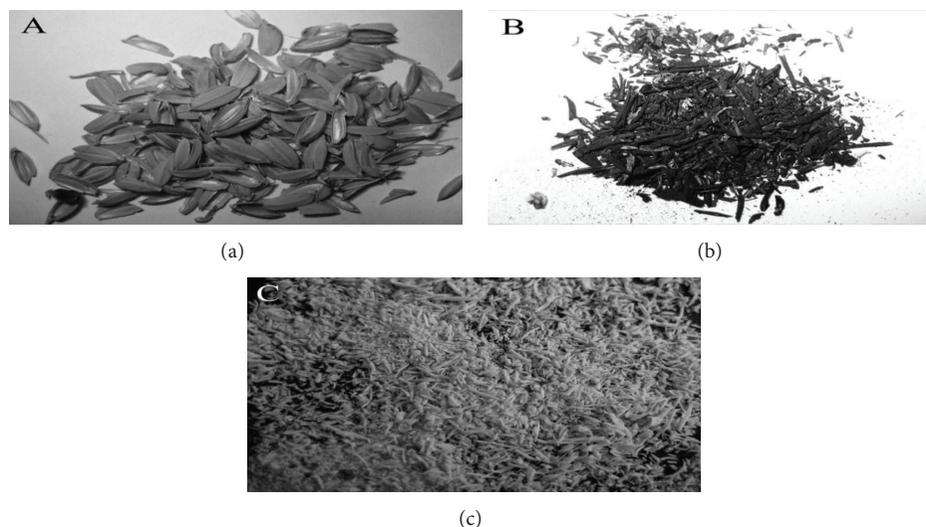


FIGURE 11: Typical images of (a) RH, (b) RHA, and (c) extracted silica [52].

silica, as can be seen in Figure 12. The economic analysis of the materials and whole process (silica extraction and composites preparation) highlighted that the production of a formulation containing 20 wt% silica can be considered economically sustainable, when the energy recovered from the RH burning is reused.

A group in France [53] investigated specific surface treatments, which aimed to improve the adhesion between PLA, RH, and Einkorn wheat husk. In the first part of their study, husks (RH and Einkorn wheat husk) were treated by alkaline solutions at three concentrations (2, 5, and 10%) at room temperature for different times between 6 and 48 hours. Results revealed that the alkaline treatment dissolved a fraction of waxes, lignin, and hemicellulose, so that the polarity of their surface was increased and therefore alkaline treated husks were more sensitive to moisture and had lower surface energies. Moreover, the alkaline treatments had more influence on wheat than on RH, as confirmed by chemical mechanism determination (Figure 13), FTIR (Figure 14), and SEM observations (Figure 15). In the second part of the Tran et al. (2014) study, different surface treatments including alkaline treatments with NaOH solutions at different concentrations and silane agents (γ -aminopropyltriethoxysilane (APS) and γ -glycidoxypropyltrimethoxysilane (GPS)) on the characteristics of RH and wheat husk were investigated. These silane treatments were applied either alone or on previously alkaline treated husks (NaOH 5% for 24 h). The results showed that silane treatments reduced the moisture sensitivity and raise the energy surface of the husks. In the last part of their study, treated husks were incorporated into PLA to produce composites. Nevertheless, alkaline treatments did not improve the mechanical properties of composites. However, an increase in the mechanical properties and the thermal stability of composites was obtained. Better results were obtained with APS agent compared to GPS agent because of a higher reactivity; the group amine of APS showed more effect on PLA than group epoxy of GPS. When

silane treatments were combined with an alkaline pretreatment, composites showed higher mechanical properties and thermal stability than composites with only silane treatment. Alkali treatment cleaned the surface of husk and activated the hydroxyl groups. They found that these active hydroxyl groups reacted with the silanes more easily than the hydroxyl group on the surface of untreated husks. It was also given in evidence that wheat husks (with higher cellulose content) lead to better performances when they are incorporated within PLA compared to RH. They proposed future works on the influence of the treatment surface on the aged resistance of composites.

In another work, Sareeladdanon and Potiyaraj [54] prepared polymer composites of PLA and linear low-density polyethylene (LLDPE) with the addition of different amount of rice husk silica (RHS), 0.5 and 1 wt%, using melt-mixing in a twin-screw extruder and processed into film by a chill roll cast extruder. The mechanical properties of PLA/RHS and LLDPE/RHS composites were investigated through tensile testing and tear testing. The results showed that the tensile modulus and tensile strength of PLA increased with the addition of 0.5 wt% RHS and dropped with further addition of RHS (1 wt%); this may arise from the agglomerates of silica particles in the PLA matrix. However, the elongation at break of PLA increased with the addition of silica at the higher content. On the other hand, the tensile modulus of LLDPE decreased with the addition of silica because of nonuniform dispersion of silica particles.

In a recent publication, Mohammadi-Rovshandeh et al. [49] investigated the use of RH and bleached rice husk (BRH) in the form of powder and the effect of lignin removal on mechanical and thermal properties of prepared composites with PLA and starch. They confirmed that the lignin has been removed from RH using FTIR technique, as indicated by disappearing of lignin aromatic C=O peak (1648 cm^{-1}) in the FTIR spectra of BRH (Figure 16). The tensile, Charpy impact, and hardness tests were implemented to study the

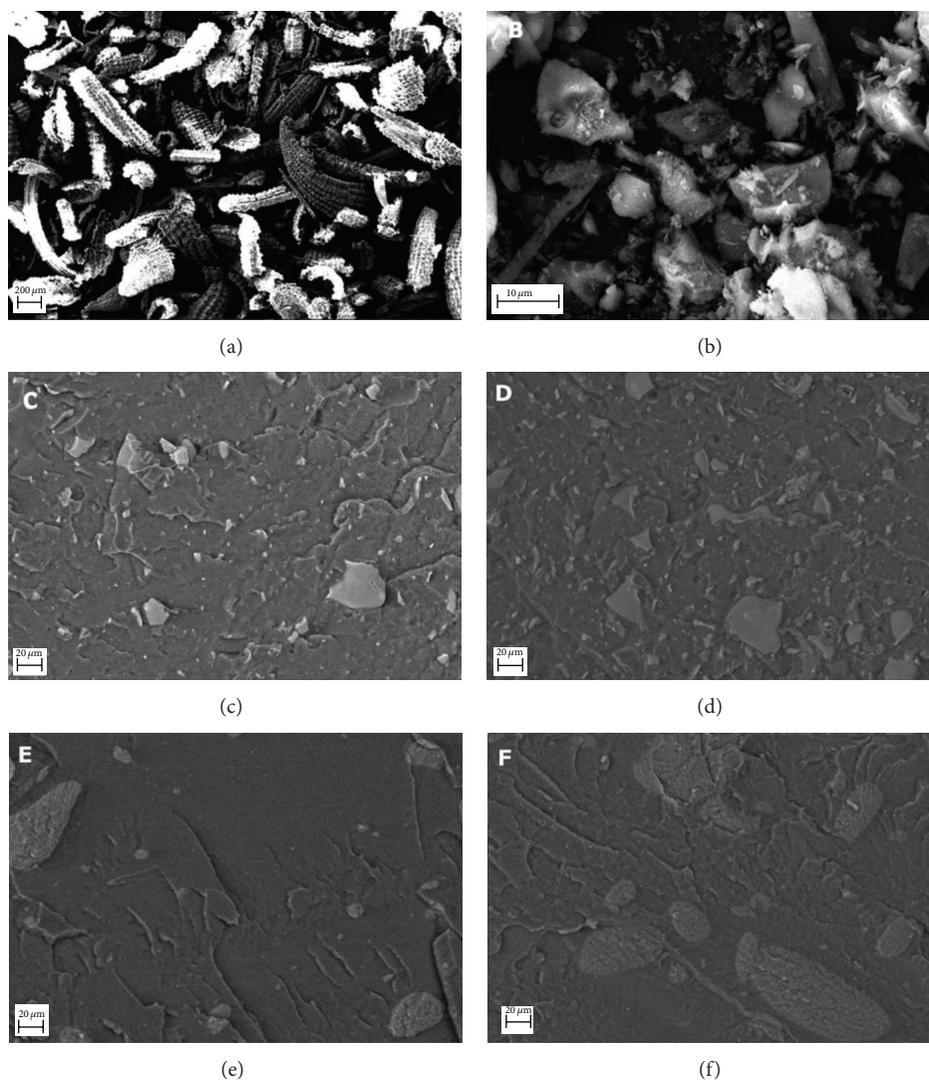


FIGURE 12: SEM micrographs of silica powder (a and b) and composites containing 10 and 30 wt% of extracted (c and d) and of commercial silica (e and f) [52].

mechanical properties. It was shown that the filler content in PLA/starch blends could improve the mechanical properties of composites. It was concluded that filler caused an increase in the toughness and Young's modulus of composites. It was also found that filler improved the tensile strength and hardness of PLA/starch blend. The mechanical properties revealed that 5–10% of BRH or RH may be used in composites which result in improvement of the tensile properties as well as hardness. It was clearly observed that the BRH samples show larger modulus, Charpy impact strength, and hardness compared to those composites filled with RH. Despite larger values for the elongations at break of RH composites, the mechanical properties showed a significant improvement (25–50%) on lignin removal. In addition, the differential scanning calorimetry thermograms revealed an improvement in crystallization behavior and reduction of T_g from 47 to 31°C in the case of BRH filled polymer composites. Finally, they reported that, due to the removal of lignin in the

samples and modification of mechanical properties, the BRH could have the ability of wide use in the bioplastics and food packaging industries.

In an interesting research in Italy, Battagazzore et al. [36] focused on the extraction of cellulose from RH through a multistep process (Figure 17) and used different extracted cellulose contents (5, 10, 20, and 30 wt%) to fill PLA composites by melt-blending. The crystalline structure and morphology of the extracted cellulose have been investigated by using XRD and SEM, as can be seen in Figure 18. Four main peaks have been found at 16°, 17°, 22°, and 34° (Figure 18(a)). Indeed, the extracted cellulose has a crystalline structure with respect to hemicellulose and lignin, which are amorphous in nature. More specifically, cellulose has a crystalline structure due to the hydrogen bond interactions and Van der Waals forces between adjacent macromolecules. The thermal, mechanical, and oxygen barrier properties of the resulted PLA composites have been investigated and correlated with the observed

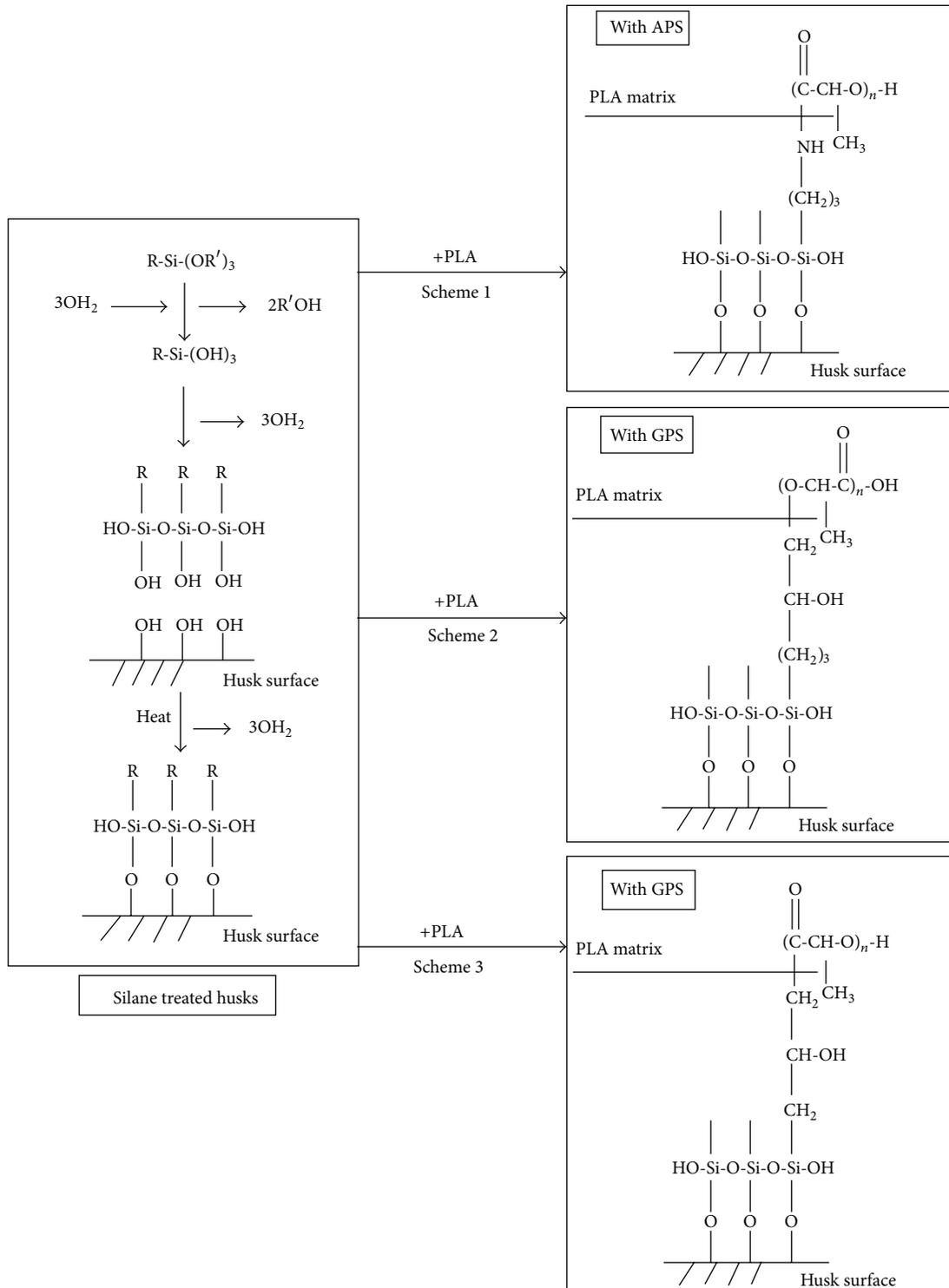


FIGURE 13: Chemical mechanisms at the interfacial area between silane (Scheme 1: APS and Schemes 2 and 3: GPS) treated natural fibers and PLA matrix [53].

morphologies (Figure 19). They reported that, in spite of a broad micrometric distribution of the cellulose particle size (as indicated by arrow in Figures 19(b) and 19(d)), the mechanical properties turned out to be strongly improved

and the oxygen permeability properties have proven to be slightly reduced as well. The most interesting aspect of this work was that similar mechanical and oxygen permeability properties have been achieved for both commercial cellulose

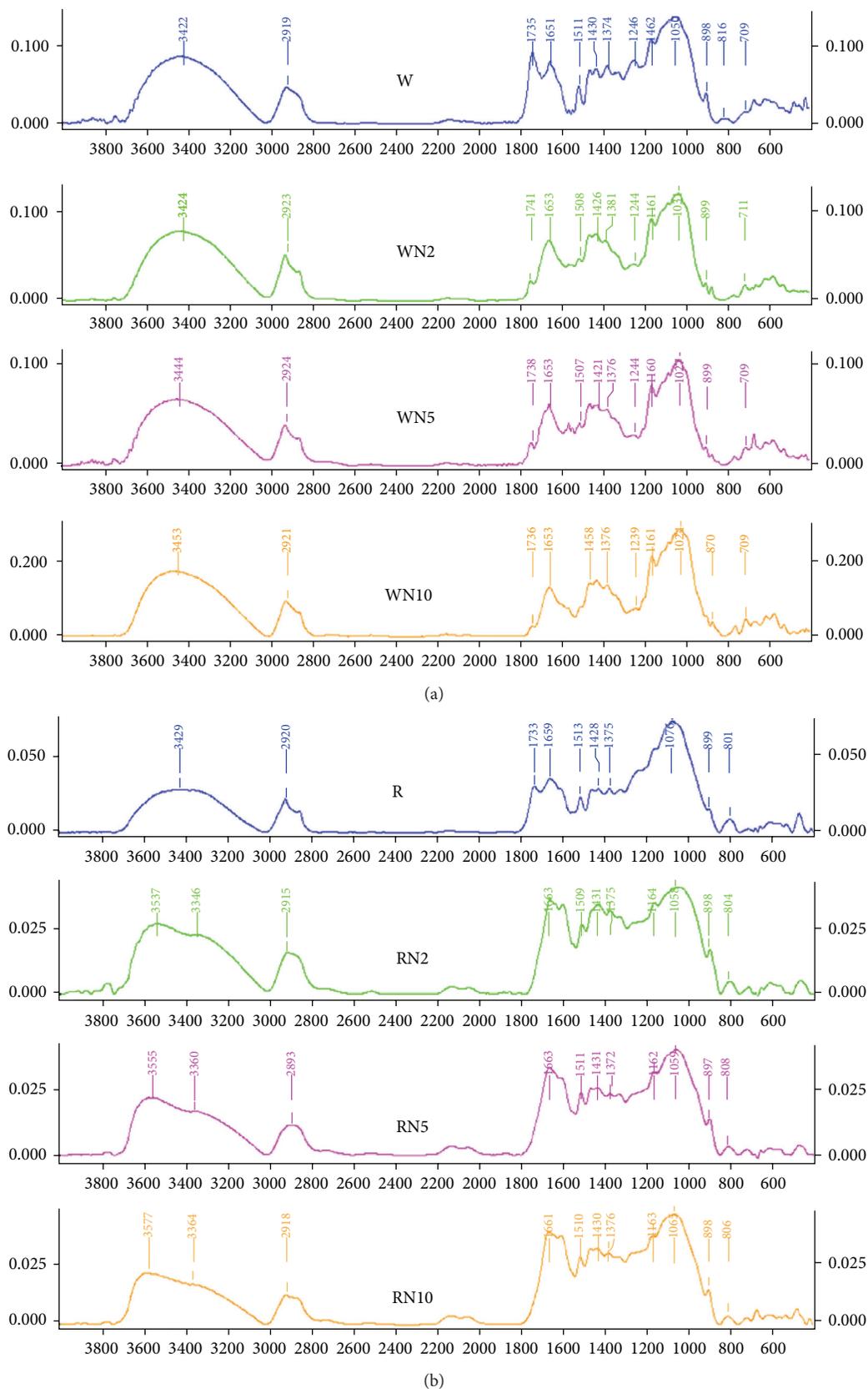


FIGURE 14: FTIR spectra of untreated and alkaline treated (a) wheat husk and (b) RH at different NaOH concentrations (2, 5, and 10%). Einkorn wheat husk (W), einkorn wheat husk + NaOH (WN), long-grain RH (R), and long-grain RH + NaOH (RN) [53].

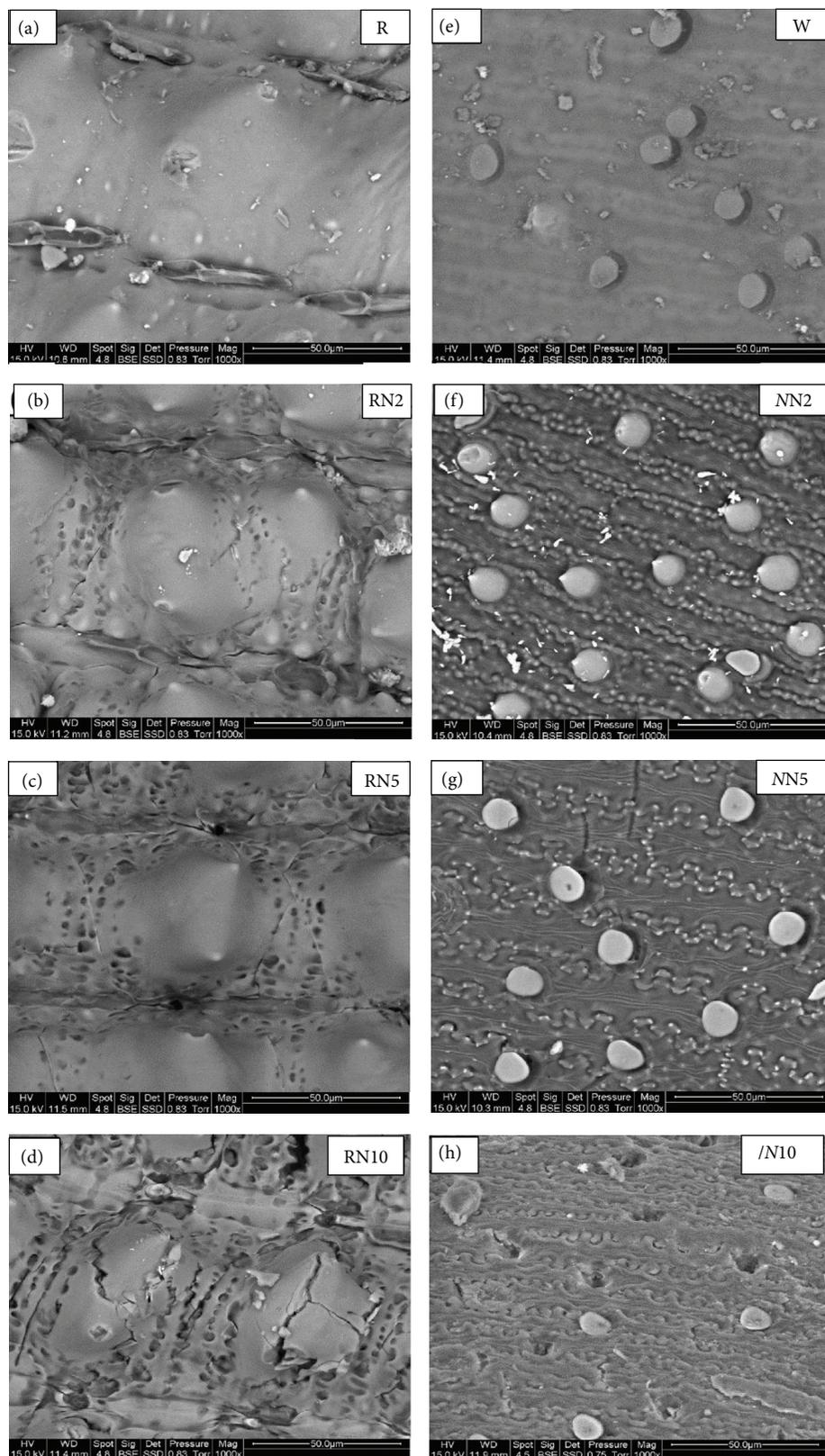


FIGURE 15: SEM micrographs of husks before and after treatment by NaOH: (a) untreated RH; (b–d) treated RH with NaOH concentration of 2%, 5%, and 10%, respectively; (e) untreated wheat husk; and (f–h) treated wheat husk with NaOH concentration of 2%, 5%, and 10%, respectively [53].

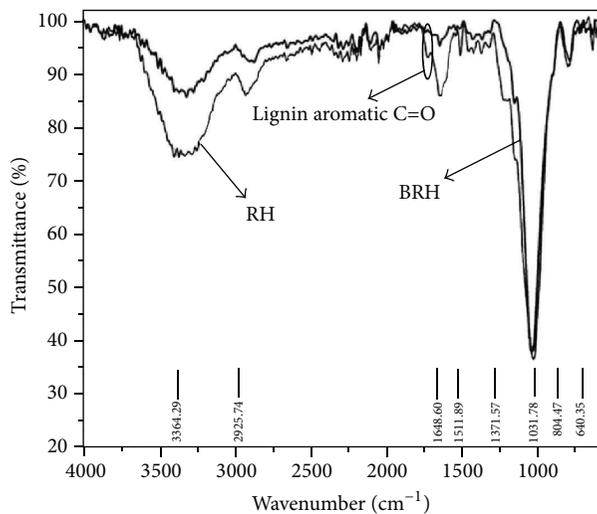


FIGURE 16: FTIR spectra of RH and BRH [49].

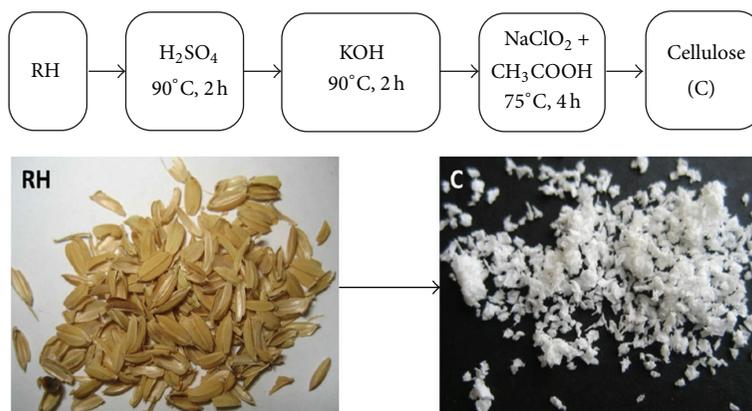


FIGURE 17: Schematic representation of the cellulose extraction from RH [36].

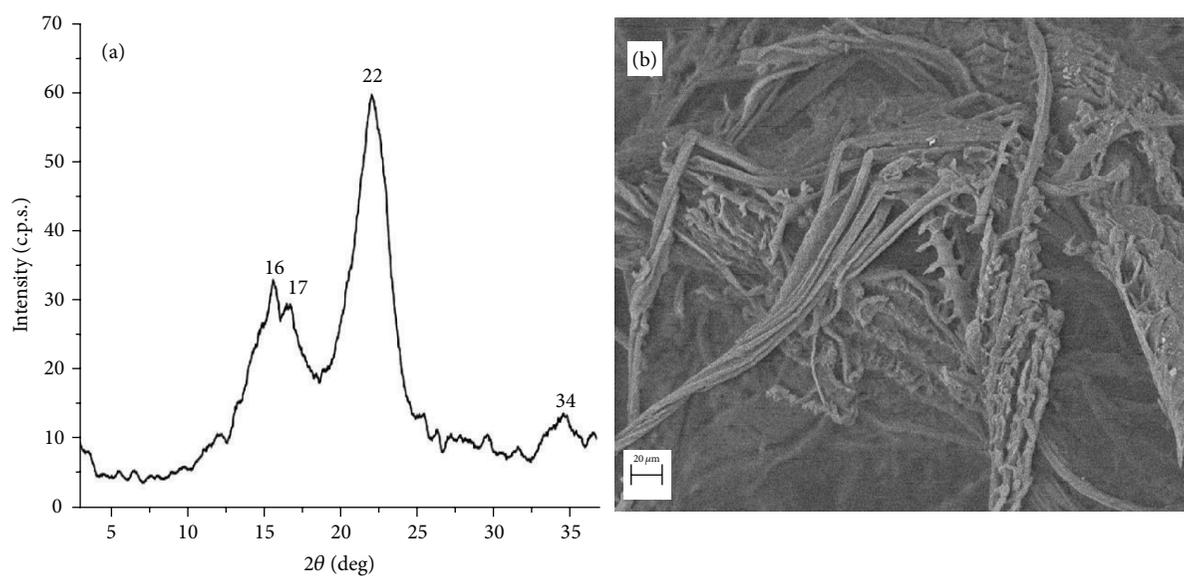


FIGURE 18: (a) XRD patterns and (b) SEM micrograph of the extracted cellulose [36].

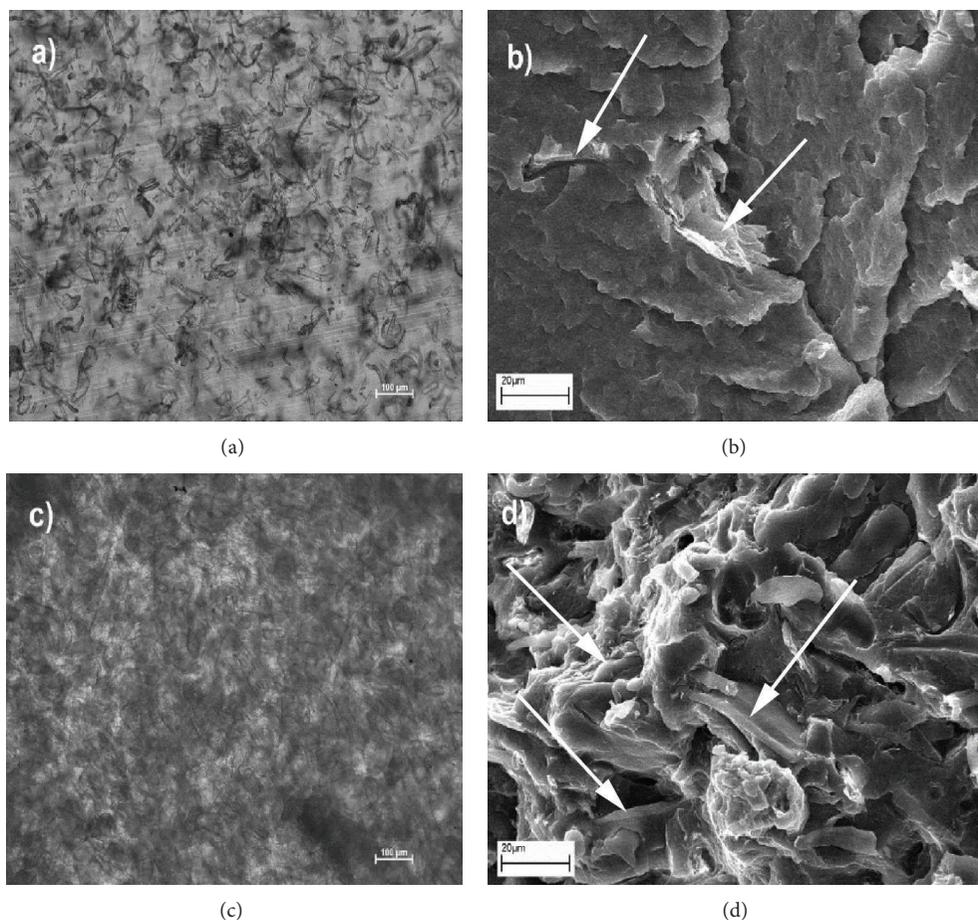


FIGURE 19: Optical and SEM macrographs of PLA filled with 5 wt% cellulose (a and b) and PLA filled with 30 wt% cellulose (c and d), respectively [36].

and cellulose derived from RH. Above all, Battagazzore et al. [36] demonstrated that an industrial waste as RH can be recycled for conferring enhanced final properties to PLA.

2.3. Rice Husk/Polypropylene Composites. PP is an addition polymer chemically synthesized from the monomer propylene. It is a thermoplastic polymer mainly used in packaging, laboratory equipment, automotive components, yogurt containers, and margarine tubs. Its transparency and resistance to heat and chemicals nature make it suitable for a variety of applications. Melt processing of PP can be achieved through extrusion and molding. However, the most common shaping technique used is injection molding. Table 9 shows experimental results from different researches in terms of mechanical properties of RH composites by employing PP as matrix material.

Many researchers have reported comparative studies on different fibers based composites. Premalal et al. [21] compared two types of fillers (RHP and talc) to prepare PP composites using a Brabender Plasti-Corder internal mixer at 180°C, which contained 0, 15, 30, 45, and 60 parts per hundred parts of polymer (php) of fillers. The processability and mechanical properties of the composites with respect

to the filler type and filler content were investigated. It was found that talc composites are easier to process than RHP filled polymer composites. They reported that, in terms of mechanical properties, Young's modulus and flexural modulus increased, whereas yield strength and elongation at break decreased with the increasing in filler contents for both types of composites. They observed that the PP/RHP composites have lower yield strength, Young's modulus, flexural modulus, and higher elongation at break than PP/talc composites. SEM studies of tensile fracture surfaces of the composites are shown in Figure 20. The voids which can be seen in Figures 20(a) and 20(b) clearly indicated the poor interaction between RHP and matrix. As reported by Premalal et al. (2002), the polar nature of RHP and nonpolar nature of the matrix can be cited as one of the possible causes for this observation. By increasing the RHP content (Figure 20(b)), significant filler aggregation has also appeared, which contributed to the poor stress transfer from matrix to filler resulting in poor properties. On the other hand, the talc filled polymer composites (Figures 20(c) and 20(d)) show brittle-type failure. They do not exhibit a tendency towards formation of large agglomerates. Compared to the RHP composites, a stronger talc-matrix interface is

TABLE 9: Mechanical properties of RH filled PP composites.

Matrix	RH (wt%)	Coupling agent or compatibilizer (wt%)	Tensile strength (MPa) (% incr.)	Tensile modulus (GPa) (% incr.)	Flexural strength (MPa) (% incr.)	Flexural modulus (GPa) (% incr.)	Impact strength (Jm ⁻¹) (% incr.)	Reference
PP	30*	—	24 (-21)	2.1 (80)	—	1.9 (27)	13 (-64)	[21]
PP	WRHA* 40	—	23	1.18	—	2.48	—	[33]
PP	10	—	29 (-15)	—	—	—	15 (-21)	[55]
PP	30	—	—	—	26	1.6	40	[56]
PP/NBRr (70/30)	10*	—	13 (-33)	1.1 (2)	—	—	—	[57]
PP	50	MAPP (4)	37.5 (5)	0.8 (78)	34 (143)	2.28 (61)	—	[37]

* phr.

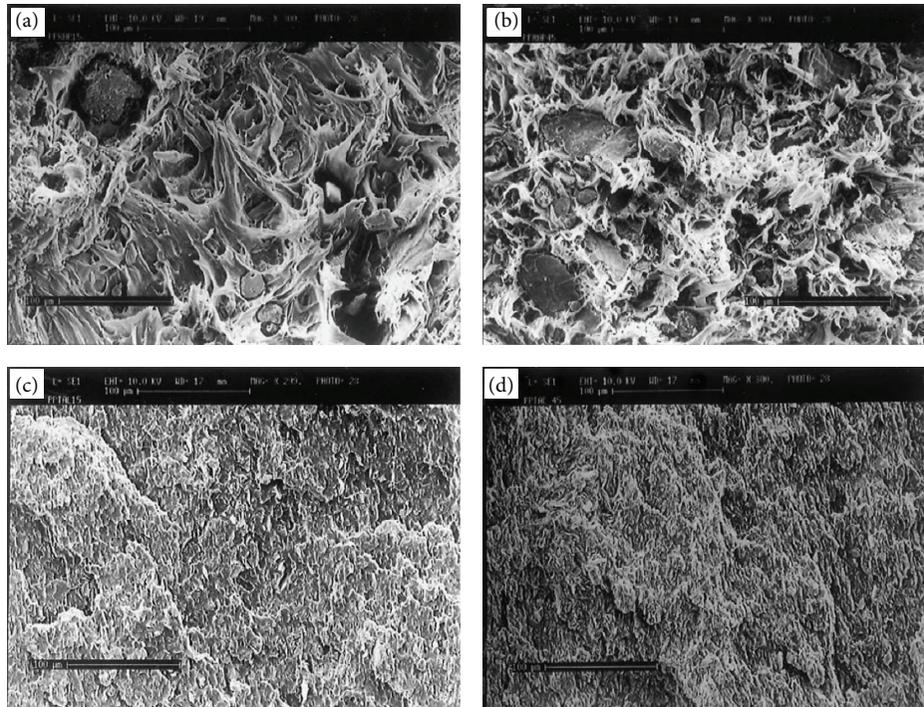


FIGURE 20: SEM micrographs of the tensile fracture surface of (a) and (b) PP/RHP composites and (b) and (c) PP/talc composite at 15 and 45 php of fillers content, respectively (mag. $\times 300$) [21].

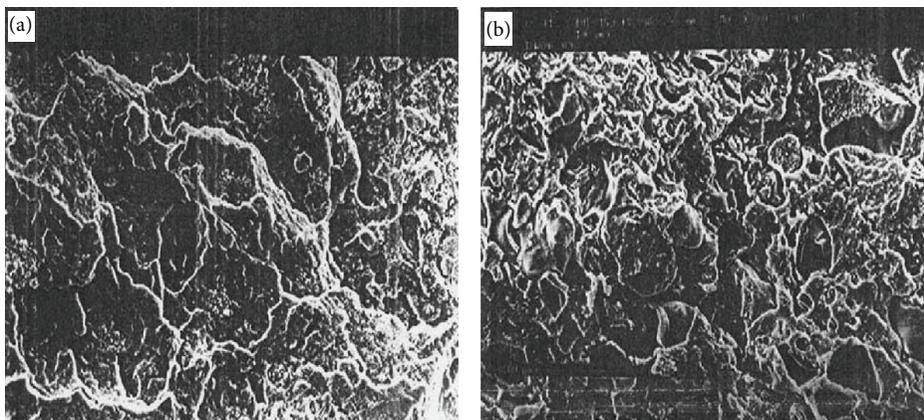


FIGURE 21: SEM micrographs of tensile fracture surface of (a) 40/0 and (b) 20/20 silica/WRHA (wt/wt) of PP/silica/WRHA hybrid composites, respectively (mag. $\times 300$) [33].

evident from the SEM micrographs. Furthermore, it seems that better filler distribution is achieved in talc composites than RHP composites.

As reported by Ismail et al. [33], PP hybrid composites were prepared using silica and WRHA fillers as reinforcing agents. In their study, both fillers were used at the similar total filler content (40 wt%). Ismail et al. (2003) found that the flexural modulus and tensile modulus of the composites increased with increasing of WRHA content in silica/WRHA weight ratio of PP/silica/WRHA hybrid composites, which was attributed to the higher aspect ratio of WRHA compared to silica. However, they noted that the tensile strength,

elongation at break, stress at yield, and water absorption of the composites increased with increasing of silica content in silica/WRHA weight ratio of PP/silica/WRHA hybrid composites. It was reported that the smaller particle size of silica could affect on the interfacial adhesion between silica and PP matrix. Degradation study showed that percentage loss of above properties increases with increasing of WRHA content in silica/WRHA weight ratio of composites. SEM micrographs of tensile fracture surfaces of composites are shown in Figure 21. It can be observed from Figure 21(a) that the fracture surface is rough with many tear lines. The rougher surface structure indicates that failure occurred with

higher tensile strength. Silica fillers were well embedded in PP matrix and good adhesion occurred between silica and PP matrix. In contrast, Figure 21(b) shows the filler agglomerates pull-out, which is responsible for the poor tensile strength and poor dispersion of WRHA in the PP matrix. It can be concluded that the silica has better adhesion with PP matrix compared to WRHA.

Another study presented by Yang et al. [55] showed that RHF-reinforced PP composites were prepared using twin-screw extruder and physical, mechanical, and morphological properties of PP/RHF were investigated. In their study, four levels of filler contents (10, 20, 30, and 40 wt%), six levels of test temperature (-30 , 0, 20, 50, 80, and 110°C), and five levels of crosshead speed (2, 10, 100, 500, and 1500 mm min^{-1}) were designed. By increasing the RHF loading and crosshead speed of test samples, the composite became more brittle. The authors attributed this increase in brittleness with increasing filler loading to the decrease in fraction of thermoplastic polymer and increased interfacial area. Concerning increase in brittleness with increasing crosshead speed, the frictional resistance between filler and matrix polymer decreased at higher crosshead speeds, and this increased the brittleness. The tensile strengths according to the filler loadings presented the same tendency at each test temperature. At the lower test temperatures (-30 and 0°C), the composites exhibited strong and brittle properties like glass, but the tensile strength drastically decreased as the test temperature was increased from (0 to 20°C) due to the glass transition of the polymer matrix. The matrix polymer became more ductile and softened as the test temperature increased. Therefore, they suggested that this problem could be reduced by using a compatibilizing or coupling agent. In this experiment, Yang et al. described that by increasing of test temperature the thermoplastic polymer was softened and the composites showed plastic matrix deformation, which decreased the tensile strength and modulus. They reported that, by increasing of filler contents, morphological study revealed more filler particles and increased the numbers of holes where filler particles have pulled out traces (Figure 22).

In the past ten years (2005), our research group [56] reported on the effects of coupling agent and impact modifier on the mechanical properties of PP/RH composites. In our study, as suggested by Yang et al. [55], ethylene 1-octene copolymers (EOC) and MAPP were used as the impact modifier and coupling agent, respectively. These compounds were melt blended using twin-screw extruder and then injection-molded into standard test samples. An improvement of 35% in flexural strength with the addition of 4 wt% of MAPP into the composites with 30 wt% of RH was observed. However, the flexural modulus and impact strength were decreased. Significant enhancement was also found in the impact properties by the incorporation of 20 wt% of EOC into the composites, but the flexural modulus reduced.

In a research by Santiagoo et al. [57], the properties of RHP filled PP/recycled acrylonitrile butadiene rubber (NBRr) composites with and without coupling agent (APS) were investigated. The composites with different RHP filler content (0 to 30 phr) were prepared using a Haake internal mixer. They studied the mechanical properties,

swelling behavior, and water absorption of PP/NBRr/RHP composites. They demonstrated that the addition of RHP to PP/NBRr/RHP composites increased processing torque, tensile modulus, water absorption, and swelling in oil but decreased the tensile strength and elongation at break of the composites. It was also found that, due to the strong bonding between APS treated RHP filler and PP/NBRr matrices, the APS treated RHP composites have higher processing torque, tensile strength, tensile modulus, and lower elongation at break when compared to untreated RHP composites. Furthermore, the APS treatments on RHP improved the adhesion between hydrophilic RHP fiber and the hydrophobic PP/NBRr polymer matrices, which led to reduction of water and oil absorption into PP/NBRr/RHP composites.

Recently, Duy Tran et al. [37] focused on preparation of composites based on PP and Vietnamese RHF (size distribution, $100\text{--}125\ \mu\text{m}$) with the presence of MAPP as a compatibilizer. The researchers have investigated the effect of RHF and MAPP content on properties of PP composites. The results showed that the addition of MAPP to PLA/RHF composites not only did improve tensile and flexural strength but also improved toughness of composites, as confirmed by SEM micrographs (Figure 23). In the absence of MAPP, the composites displayed a rough morphology with appearance of the phase separation between the RHF particles and PP matrix (Figure 23(a)), which clearly showed the poor interaction between filler and matrix. However, in the presence of 4 wt% MAPP (Figure 23(b)), the morphological observation demonstrates that the compatibilizer reduces the separating positions and covered the free spaces between filler and the matrix, which indicated improve adhesion at the interfacial region between filler and matrix. Besides, they found that the thermal stability of composites was also enhanced in the presence of compatibilizer. Their results showed that MAPP acted as the effective factor to improve interfacial adhesion between RHF filler and PP matrix. Duy Tran et al. [37] claimed that Vietnamese RHF is a promising renewable resource to be applied for polymer composites.

2.4. Rice Husk/Polyvinyl Chloride Composites. PVC is a thermoplastic polymer. It is a vinyl polymer constructed of repeating vinyl groups having one of their hydrogens replaced with a chloride group. It is the third most widely produced plastic after polyolefin and is medium strong and transparent material, resistant to chemicals, grease, and oil. It is used for sewage pipe lines and other pipe line applications owing to its biologically and chemically resistant characteristics. It is also used for windows, door frames, and such other building materials by adding impact modifiers and stabilizers. It becomes flexible on addition of plasticizers and can be used in cabling applications as wire insulator. Mechanical properties of RH/PVC composites have been studied by various researchers to understand the effect of RH content on strength of the resulting composites and their ability to resist deformation and are shown in Table 10.

In one set of our experiments [62], RHA fillers were added to acrylonitrile butadiene styrene (ABS) impact modified unplasticised PVC (PVC-U) in order to reduce the cost and

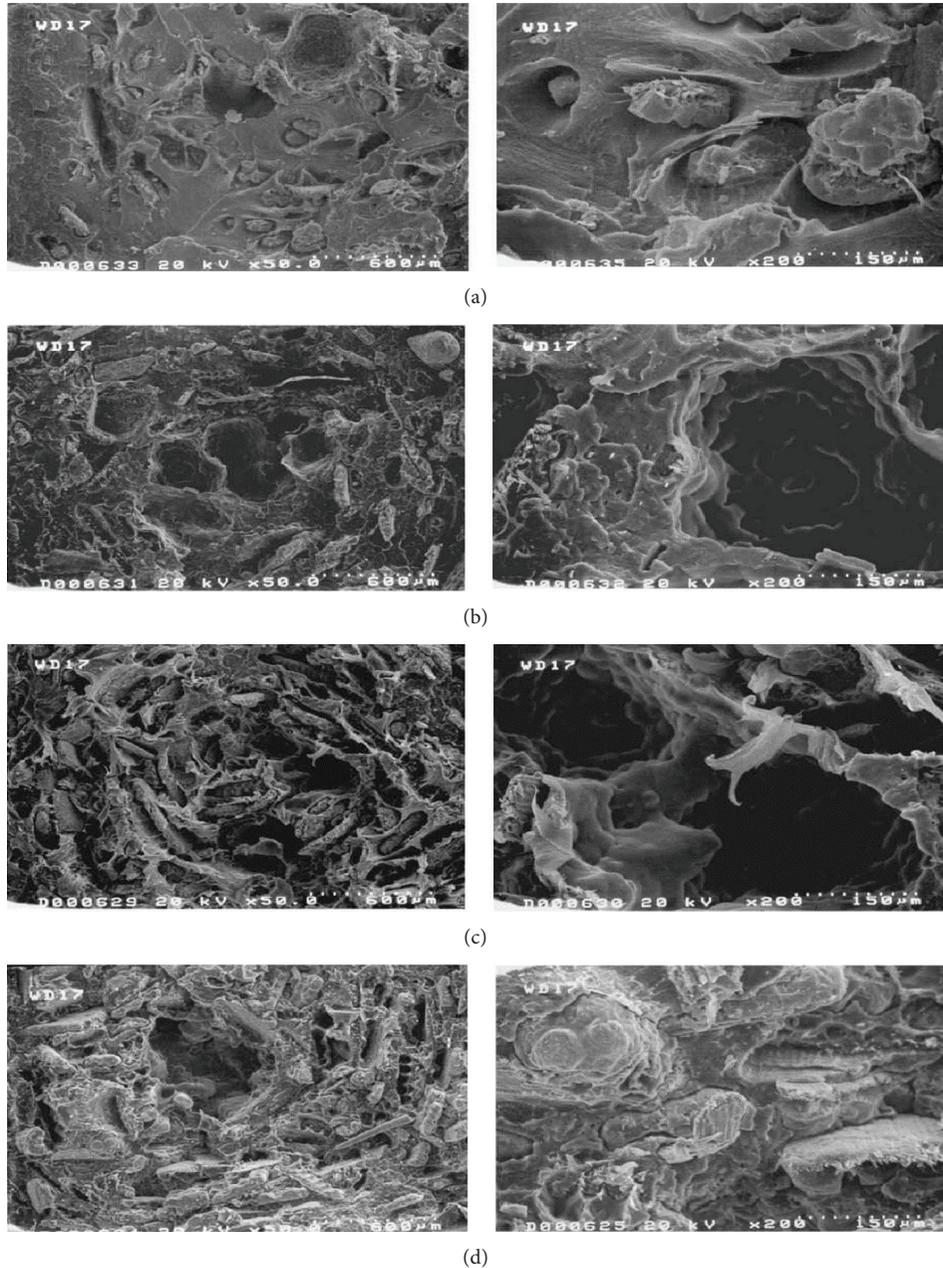


FIGURE 22: SEM micrographs of the tensile fracture surfaces of the PP/RHF composites with different filler contents: (a) 10, (b) 20, (c) 30, and (d) 40 wt% of RHF contents [55].

maintain or improve properties. A processability study was conducted to investigate the fusion behavior of filled impact modified PVC-U using Brabender Plasti-Corder with fitted mixing head. The processability study showed that as the RHA content increased the fusion time increases. In such cases, attempts to analyze and compare the effect of RHA content and various types of coupling agents on the fusion behavior of impact modified PVC-U were carried out. Our work was carried out on the preprepared RHA, with different content levels. It was found that 10 phr RHA filled impact

modified PVC-U samples has shorter fusion time and higher fusion torque compared to other levels of filler contents. Upon the addition of 20 phr RHA, the end torque value decreased compared to unfilled sample. It was also found that the zirconate-treated samples have longer fusion time and lower processing torque compared to other types of coupling agents. Our experimental results also showed that the low contents of the filler have the faster fusion during processing.

Unmodified and modified RHP filled PVC composites with different amounts of RHP content (0, 10, 20, 30,

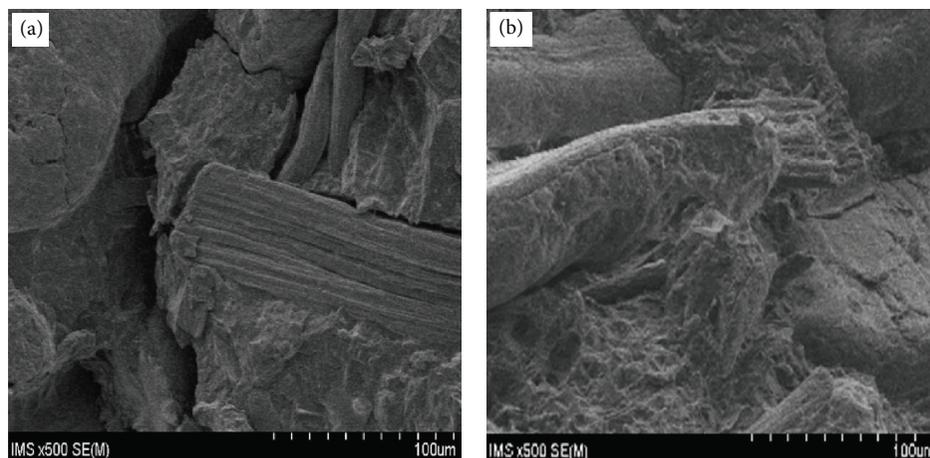


FIGURE 23: SEM micrographs of (a) PP/RHF and (b) PP/RHF with 4 wt% of MAPP [37].

and 40 wt%) were developed by Chand and Jhod [58]. Mechanical, thermal, and electrical properties of these composites were determined. Density of PVC/RHP composites decreased with increasing RHP content in the PVC composites. The tensile strength of PVC/RHP composites was found to decrease with increasing of RHP in the composites (from 33.9 to 19.5 MPa). However, adding of MAPP modified RHP improved the tensile strength of PVC/RHP composites. In addition, the researchers found that the flexural strength and flexural modulus of composites also increased on treatment of RHP due to the improved bonding between RHP and PVC matrix. They reported that Arc-resistance of PVC/RHP composites decreased with increasing of RHP content in the composites. Furthermore, they found that, due to the presence of impurities and water molecules, volume resistivity and surface resistivity decreased with increasing of RHP content in the composites. They confirmed that Vicat softening temperature of PVC/RHP composites increased in both treated and untreated RHP filled PVC composites.

In an intensive study, Xu et al. [59] fabricated PVC and natural fiber composites by melt compounding and compression molding. The influence of fiber type (i.e., bagasse, rice straw, RH, and pine fiber) and content level of styrene-ethylene-butylene-styrene (SEBS) block copolymer on composites properties were investigated. Mechanical analysis showed that storage modulus and tensile strength increased with fiber contents at the 30 wt% level for all composites. SEBS showed moderate effect on tensile strength of PVC/natural fiber composites, but no obvious contributions to impact strength of the composites were observed. However, among the four natural fibers used, rice straw offered better mechanical properties than bagasse, RH, and pine fiber. They reported that the addition of natural fibers decreases the thermal stability of neat PVC but also weakened the self-accelerating effect during degradation of PVC. The researchers also found that the SEBS had little effect on the thermal stability of the composites. After being immersed in water for four weeks, PVC/RH composites showed lower water absorption rate and better dimensional stability in water compared to the other three types of composites. The

results showed that the addition of SEBS increased the water absorption rate of PVC/natural fiber composites. They concluded that PVC composites filled with agricultural fibers had properties comparable with those of PVC/wood composites. They proposed future work with effective coupling agents for PVC (virgin and recycled) and natural fibers.

In the study by Crespo et al. at Polytechnic University of Valencia [60], new composites materials were fabricated, based on lignocellulosic fillers filled thermoplastic composites. In their study, carboxylate plasticizer-di-isononyl-cyclohexane-1,2-dicarboxylate were used as a plasticizer. Filler amount influenced the PVC/RH composites regardless of particle size (150, 500, or 1000 µm). Mechanical properties and SEM analysis of composites were investigated. They found that although the mechanical properties decreased, the resulted composites became more rigid with increasing filler content in all of the particle formulations. They reported that the behavior of the composites at different plasticizer concentrations was very similar to that of plasticized PVC without filler and also resistance values decreased as plasticizer concentration increased regardless of particle size or filler amount. They concluded that the particle distribution had a considerable influence on the properties of the PVC/RH composites, and it was seen that smaller particles equipped the material with improved mechanical properties due to the better dispersion and alignment of the particles within the PVC polymer matrix, as indicated by SEM micrographs (Figure 24).

In 2010, our research group [38] investigated the effects of RH and acrylic impact modifiers on the mechanical properties of PVC-U composites. The composites were prepared using a two-roll mill at 165°C before being hot-pressed at 185°C. In our study, it was found that the incorporation of RH fillers from 10 to 40 per hundred resins (phr) has increased the flexural and tensile modulus of the unmodified and modified (8 phr impact modifier) PVC-U composites. The flexural strength for both unmodified and modified PVC-U composite was observed to increase until 20 phr of RH content. However, the tensile and impact strength of PVC-U composite decreased with increasing RH content. The SEM

TABLE 10: Mechanical properties of RH filled PVC composites.

Matrix	RH (wt%)	Coupling agent or compatibilizer (wt%)	Tensile strength (MPa) (% incr.)	Tensile modulus (GPa) (% incr.)	Flexural strength (MPa) (% incr.)	Flexural modulus (GPa) (% incr.)	Impact strength (% incr.)	Reference
PVC	10	—	19.5 (-43)	—	95 (-12)	3.1 (-16)	—	[58]
PVC	30	SEBS (2.5)	33 (61)	—	—	—	15.5 (-38)	[59]
PVC	20	Carboxylate plasticizer* (40)	6.2 (-63)	0.035 (335)	—	—	—	[60]
PVC	20	Acrylic impact modifier* (4)	58 (-2)	1.8 (20)	83 (-8)	4.1 (2.5)	—	[38]
PVC	10	—	19.4 (-43)	—	92.4 (-13)	3.07 (-16)	116 (-30)	[13]
PVC	TRH (10)	—	27.6 (-19)	—	102.2 (-4)	3.52 (-3.5)	140 (-15)	[13]
rPVC	35	—	12.84 (-15)	1.55 (25)	—	—	—	[61]

THR = treated RH using maleic anhydride and benzylperoxide.

* phr.

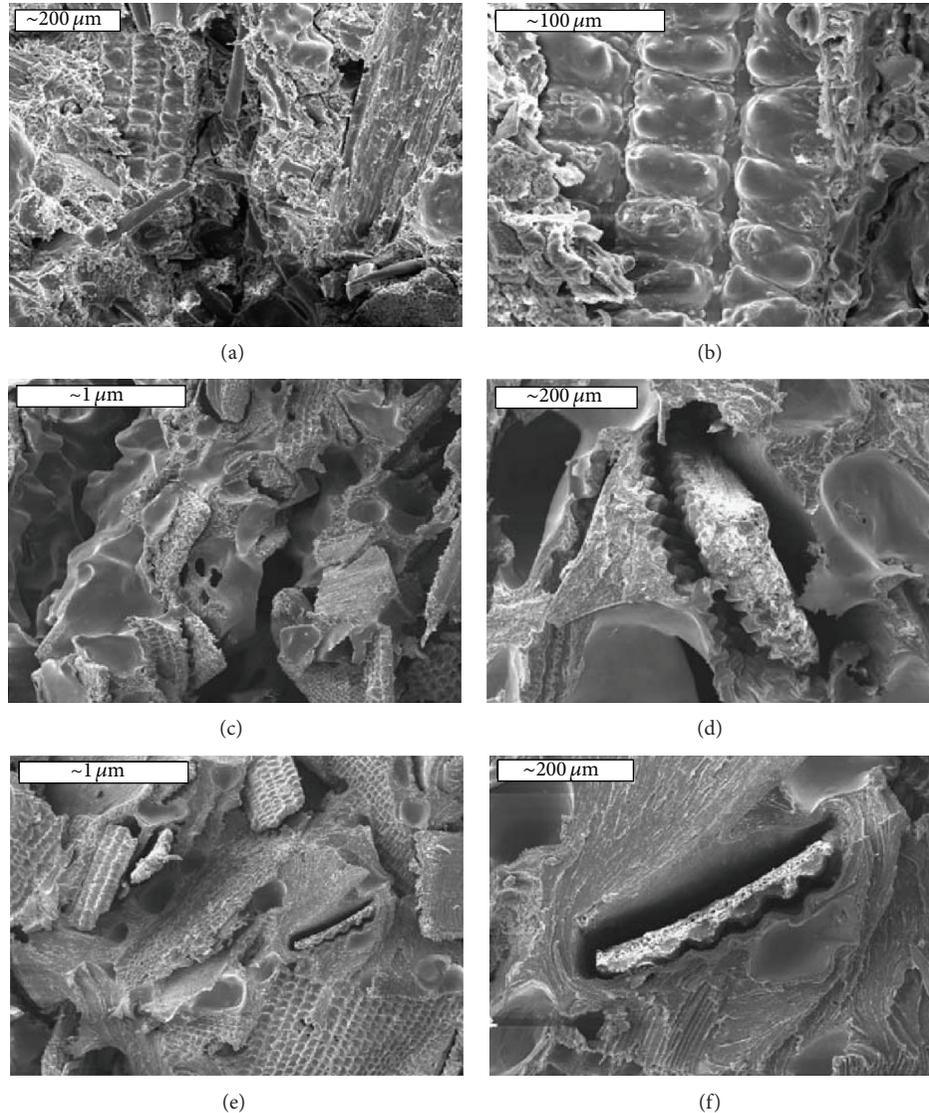


FIGURE 24: SEM micrographs of plasticized PVC containing 20 wt% RH filler with different plasticizer and particle size: (a) 40 phr, 150 μm , $\times 150$; (b) 40 phr, 150 μm , $\times 500$; (c) 60 phr, 500 μm , $\times 50$; (d) 60 phr, 500 μm , $\times 150$; (e) 60 phr, 1000 μm , $\times 50$; and (f) 60 phr, 1000 μm , $\times 150$ [60].

micrographs showed that the RH fillers agglomerated and unevenly distributed throughout the matrix, as indicated by circles (Figure 25). The result showed that the impact strength of the filled PVC-U composites (20 phr filler) increased, but the tensile and flexural properties decreased with increasing impact modifier content from 0 to 8 phr. It was also found that the formulation containing 8 phr of acrylic impact modifier and 20 phr of RH content has the best balance of stiffness and toughness properties.

In the study by Chand et al. [13], a good interfacial interaction between RH and PVC has been achieved by modifying the surface of the former using MAPP as a compatibilizing agent. In their study, the positive effect of RH reinforcement as well as surface treatment has been reflected in the improved tribological and mechanical properties of the resulted PVC composites. According to Chand et al.

[13], the filler concentration should be kept to a minimum if optimum improvement is desired. Therefore, low filler concentration of RH (10 wt%) was proved to be the optimum concentration to achieve maximum strength as well as tribological properties. However, they reported that the larger filler concentration results in larger filler-filler interaction, inhomogeneous dispersion, and inadequate wetting of filler by polymer resin. They noted that the wear resistance of RH filled PVC composites can be increased if the surface of RH is treated suitably with a coupling agent. They observed that, by increasing abrasive grit size, the wear rate increased. SEM micrographs were used to understand the wear resistance of MAPP modified RH filled PVC composites (Figure 26). It is also reported that, with increasing sliding distance, wear rate gradually decreased and attains an almost steady state in multipass condition. Size effect was also observed

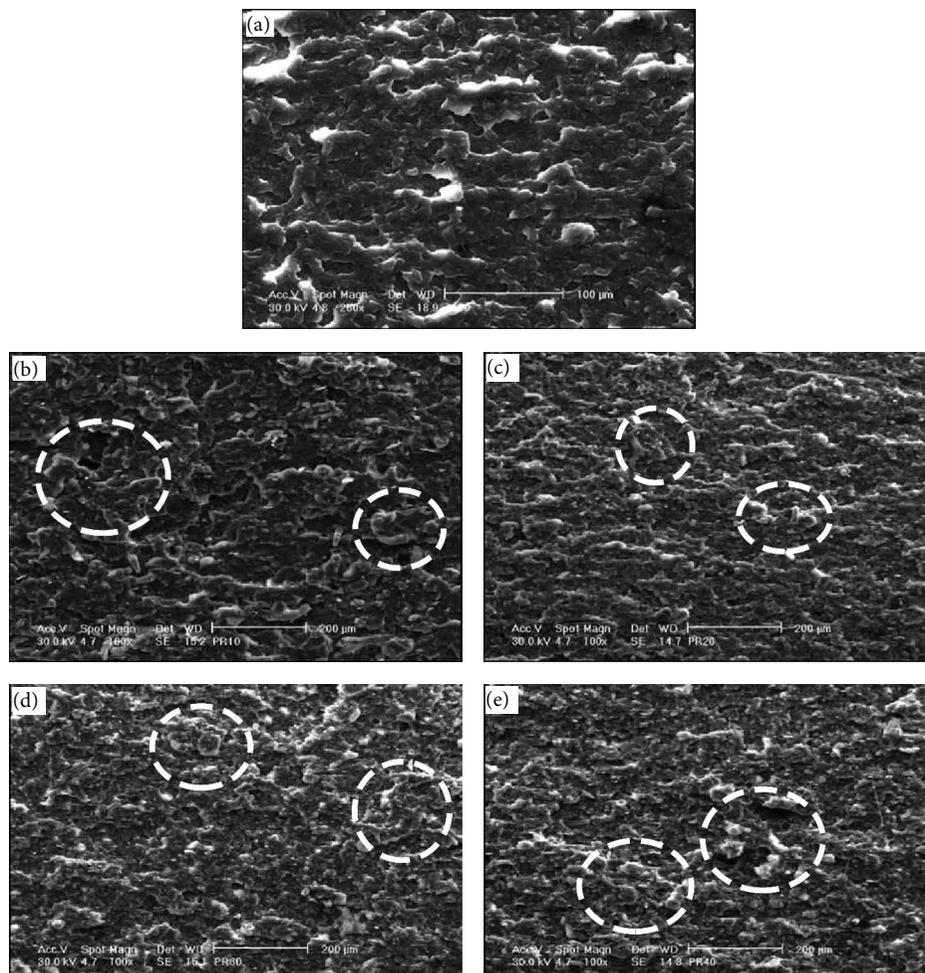


FIGURE 25: SEM micrographs of impact fracture surfaces of (a) unfilled unmodified PVC-U; (b) RH filled impact modified PVC-U composites at 10, (c) 20, (d) 30, and (e) 40 phr of RH content [38].

for composites having 40 wt% of modified filler. Lancaster-Ratner correlation was found to be more linear for MAPP-treated RH filled PVC composites compared to untreated RH/PVC composites. They concluded that probably this is due to increased filler-matrix adhesion upon treatment in the case of the former.

In another study by Chand et al. [63], the influence of a foaming agent on the mechanical and wear behavior of surface modified RH filled PVC composites has been studied. In their study, the surface of RH was modified using MAPP and benzylperoxide for better coupling with the PVC polymer. In Chand et al.'s [63] research, six composites having 10, 20, and 30 wt% of unmodified and surface modified RH having a small percent of a foaming agent have been investigated and compared with foamed PVC. It was observed that with an increase in RH content wear resistance as well as compressive strength of composites increased. They found that wear resistance of PVC foamed composites further improved with surface treatment of RH by MAPP, due to improvement in compatibility between RH and PVC compound, as confirmed by SEM analysis (Figure 27). They proposed a correlation

between compressive strength and wear resistance and also they reported that foaming agent reduces the density of composites.

In another work by Chand and coworkers [64], the effect of addition of RH in PVC composites on the dielectric properties at different frequency and temperature has been investigated. Measurements have been performed in the frequency range of 1–10 kHz and temperature range of 32–80°C. Chand et al. [64] proposed a new reasonable model based on existing equations which was experimentally verified. In their investigation, frequency and temperature dependent parameters were experimentally obtained and taken as contribution to the proposed model. The dielectric constant for composites with various fibers to matrix ratio was determined with this model. They reported that dielectric constant of the composite was highly influenced by the fiber composition. The experimental results showed that dielectric constant (ϵ') increased with the addition of RH in PVC and decreased with increasing frequency, which indicated that the major contribution to the polarization came from orientation polarization. Additionally, they demonstrated that the

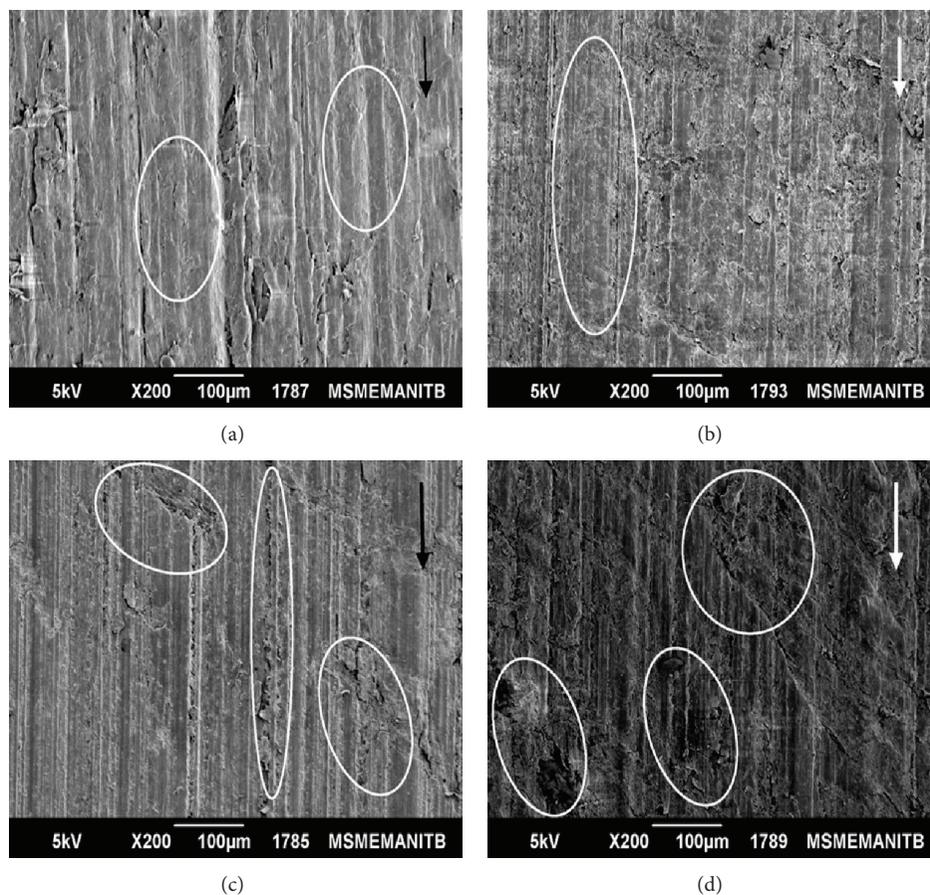


FIGURE 26: SEM micrographs of maleic anhydride modified RH filled PVC composites: (a) PTRH10 and (b) PTRH30; unmodified RH filled PVC composites: (c) PRH20 and (d) PRH40; with the sliding speed of 10 s, sliding distance of 6.28, and applied load of 10 N. (P = PVC; T = treated (modified) and downward arrow shows sliding direction) [13].

dielectric constant (ϵ') increases with increasing RH content temperature due to greater freedom of movement of dipoles within PVC at higher temperatures. Researchers reported that the proposed frequency and temperature dependent model to calculate the dielectric constant (ϵ') of the RH filled PVC composites matches the experimental results. They also found that $\tan \delta$ peaks at different frequencies are dominant in case of 30 and 40 wt. % of RH composite.

A recent study by Ramle et al. [61] demonstrated good interfacial interactions between RH and recycled PVC (rPVC) by incorporation of aminosilane as coupling agent. The aminosilane-treated rPVC was mixed with RH and then fabricated using hot compression molding. Three different ratios of RH:rPVC (65:35, 55:45, and 45:55) were used to prepare RH/rPVC composites. The positive effect of RH reinforcement as well as surface treatment has been reflected in the improved tensile properties of the resulted rPVC composite. However, the tensile properties of RH/rPVC composites decreased with the increasing RH content. They claimed that this is due to the poor adhesion between RH and rPVC matrix. Ramle et al. (2013) reported that the flexural stress of the treated composite decreased with increasing

RH content. However, the incorporation of aminosilane as coupling agent caused to significantly increase the tensile stress of RH/rPVC composites with 45 wt% of RH content. SEM micrographs of RH/rPVC composites are shown in Figure 28. The incompatibility between RH and PVC can be clearly observed, as indicated by the circle (Figure 28(a)), resulting in low tensile strength. However, better adhesion and bonding between the RH and PVC were achieved after the addition of aminosilane, as indicated by the circle (Figure 28(b)). Based on these findings, it is beneficial to carry out further study in the development of RH filled rPVC waste composites.

3. Conclusion and Future Prospects

This review aims to highlight previous works on RH filled polymer composites and provides relevant data for several applications as well as further research areas. RH has been used in combination with various polymeric matrices including PE, PP, PVC, and PLA to form polymer composites. RH filled polymer composites were prepared by different

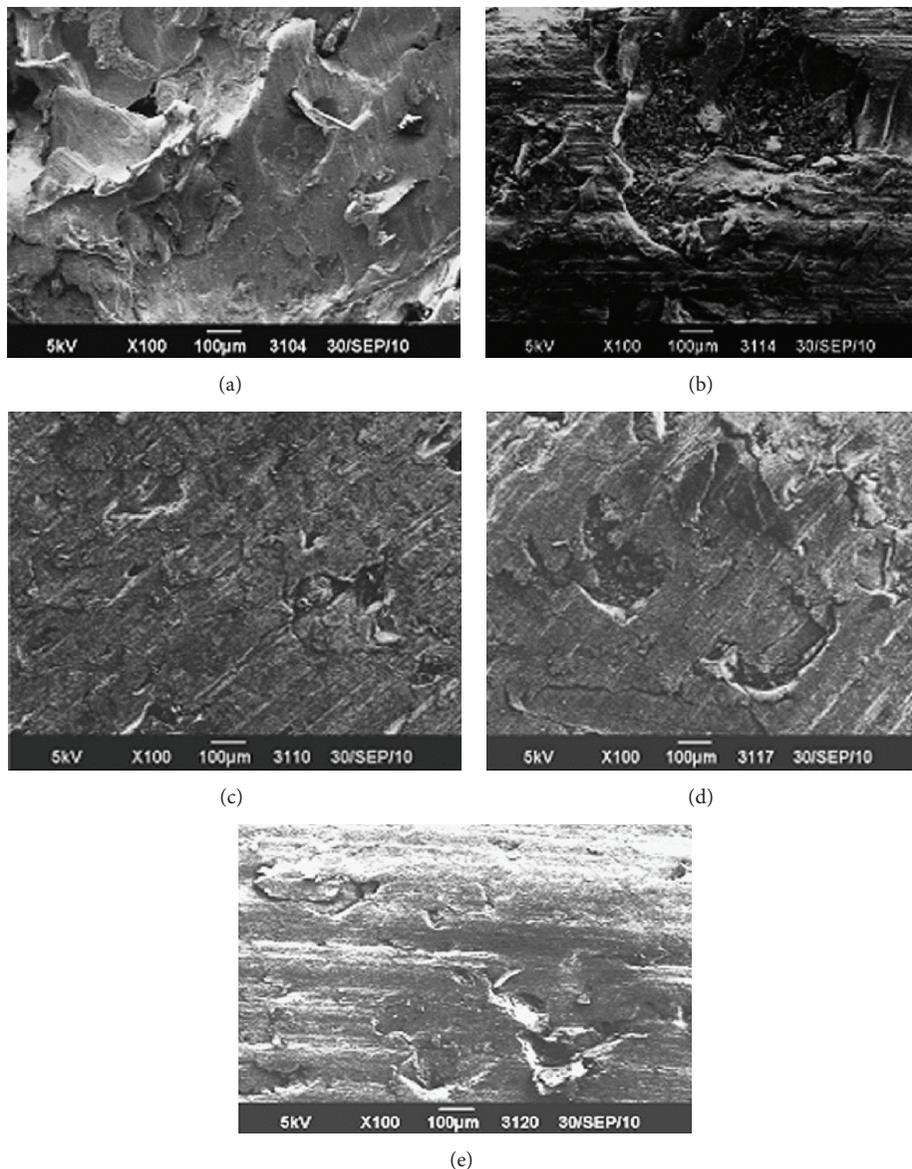


FIGURE 27: SEM micrographs of worn surfaces of foamed PVC without RH: (a) FPRH0; RH filled foamed PVC: (b) FPRH2 and (c) FPRH3; MAPP modified RH filled PVC composites: (d) FPTRH2 and (e) FPTRH3. (P = PVC; T = treated; F = foaming agent) [63].

methods, for example, single screw extruder, corotating twin-screw extruder, internal mixer, and compression molding. The different preparation methods have resulted in composites with different mechanical, physical, thermal, and morphological properties. The addition of RH resulted in reduced tensile strength of composites. Therefore, the use of various types and amount of coupling agent/compatibilizer (approximately ≤ 5 wt%) have been reported in order to improve the mechanical properties of composites. Furthermore secondary fillers such as MMT along with compatibilizers have been used to improve mechanical properties of composites. Interestingly, RH filled PE composites have been found to possess better overall mechanical properties compared to other composites such as PLA, PP, and PVC.

Based on this review, the application of RH filled polymer composites as alternative composites materials in building and construction is highly plausible with both lightweight and low cost as its main driving forces. For such applications, biodegradability and weathering properties of the composites need to be evaluated. Although many studies have reported on the use of coupling agent and compatibilizers, further investigations on physical and chemical treatment to further improve the interfacial adhesion with polymeric matrix are needed. The reason is that fiber-polymer interaction is important in determining the final composite properties. So far only single polymer has been used as the matrix in RH filled composites. Limited work has been reported on the use of secondary fillers. Therefore, better understanding of the

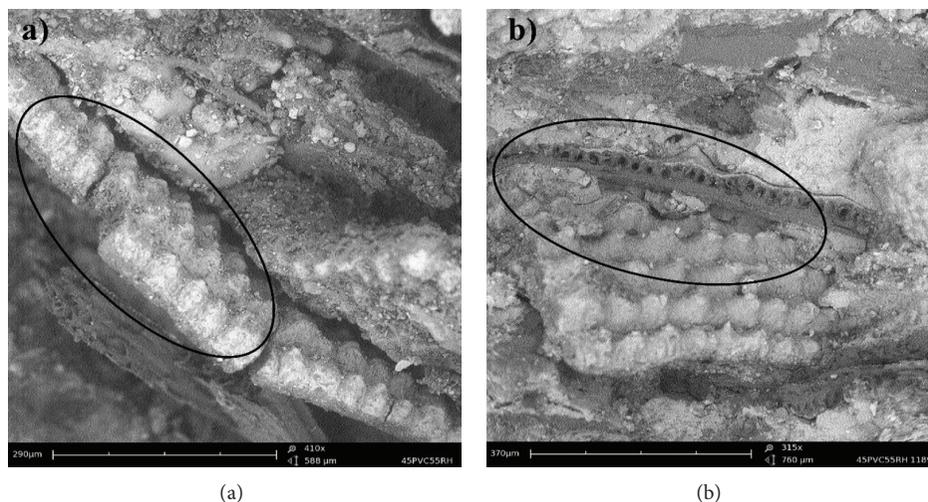


FIGURE 28: SEM micrographs of RH/rPVC composites (55% RH + 45% rPVC) (a) without the addition of aminosilane and (b) with addition of aminosilane [61].

use of polymer blends as the matrix and secondary fillers in controlling the properties of polymer composites would provide interesting areas to be investigated.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Kenaf Fibre Reinforced Polypropylene Composites: Effect of Cyclic Immersion on Tensile Properties

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This research studied the degradation of tensile properties of kenaf fibre reinforced polypropylene composites due to cyclic immersion into two different solutions, as well as comparison of the developed composites' tensile properties under continuous and cyclic immersion. Composites with 40% and 60% fibre loadings were immersed in tap water and bleach for 4 cycles. Each cycle consisted of 3 days of immersion and 4 days of conditioning in room temperature (28°C and 55% humidity). The tensile strength and modulus of composites were affected by fibre composition, type of liquid of immersion, and number of cycles. The number of immersion cycles and conditioning caused degradation to tensile strength and modulus of kenaf fibre reinforced polypropylene composites. Continuous and cyclic immersion in bleach caused tensile strength of the composites to differ significantly whereas, for tensile modulus, the difference was insignificant in any immersion and fibre loadings. However, continuous immersion in the bleach reduced the tensile strength of composites more compared to cyclic immersion. These preliminary results suggest further evaluation of the suitability of kenaf fibre reinforced polypropylene composites for potential bathroom application where the composites will be exposed to water/liquid in cyclic manner due to discontinuous usage of bathroom.

1. Introduction

Polymeric composites with various natural reinforcements (e.g., natural fibres, woods, and hybrid fibres) received significant attention in numerous applications including automotive and construction industries [1, 2]. However, the application of natural fibre composites usually intended for interior application; one of the main reasons is degradation of mechanical properties of natural fibre composites in the presence of water. Recent studies [3–8] have reported that the effect of water uptake in natural fiber composites limits their outdoor applications. In general, there are three ways to understand the term “water absorption” such as water diffusing (1) directly into the matrix, (2) through interphase matrix/reinforcements, and (3) by imperfections, like pores and cracks. Once it enters the polymers, it can

exist in several ways: as bound water, characterized by strong interaction of the molecule with matrix and free water, present in capillaries and micro cavities within the polymer [9]. When moisture diffuses into composites, it degrades fiber-matrix interfacial bonding, lowers the glass transition temperature, swells, plasticizes, hydrolyzes, and sometimes microcracks the matrix [10]. Although water absorption can cause degradation of mechanical properties, redrying process can help the materials in regaining certain percentages of their mechanical properties [11, 12]. Generally, the moisture diffusion in composite depends on factors such as fiber weight fraction, void volume, viscosity of matrix, chemical treatment of natural fiber, humidity, and temperature [13].

Haniffah et al. reported that, under cyclic immersion, longer duration of immersion and shorter drying exhibit the greatest amount of water retained in kenaf/PP

composites [14]. The tensile properties were also affected by increasing temperature of water immersion. Generally, it is reported that the tensile properties decreased with increasing immersion time [15–18]. Moreover, the mechanical degradation increased as the number of cyclic immersions increased. However, lesser degree of degradation occurred in composites with fibres modified using coupling agents [19, 20]. Similar studies on natural fiber reinforced polymeric composites have shown that the sensitivity of certain mechanical and thermal properties to moisture uptake can be significantly reduced by using coupling agents and fiber surface treatments [21, 22].

Besides soap, bleach is one of the common chemicals used in bathroom causing physical (e.g., colour) and mechanical changes to the composites that affect the perception of durability of the composites. Kenaf/PP composites experienced degradation by the chemical reagent, bleach [23]. The degradation of kenaf PP composites in bleach solution mostly occurs on kenaf fibres because PP was resistant to bleach attack [24]. The aim of this study is to compare the effect of bleach and water under cyclic immersion on tensile properties of kenaf/polypropylene (PP) composites for potential bathroom application.

2. Materials and Methods

2.1. Materials. Kenaf plant (variety V36) used in this study was supplied by National Kenaf and Tobacco Board's (NKTB), Malaysia. Polypropylene, grade TitanPro 6331, was purchased from Titan Chemicals Corp. Sdn., Bhd Johor, Malaysia. Liquids for immersion used in this treatment were tap water (pH 7.67) and domestic bleach (Clorox Regular, Malaysia) with active ingredient, for example, sodium hypochlorite 5.25%. Prior to treatment, bleach solution (pH 11.64) was prepared with 200 mL of bleach diluted in 1 L of tap water (16.17% v/v).

2.2. Measurement of Liquid Content. Liquid content in the composite was measured using the following:

$$\text{Liquid content (\%)} = \left(\frac{\text{Weight (g)} - \text{Initial Weight (g)}}{\text{Initial Weight (g)}} \right) \times 100\%. \quad (1)$$

Negative value might occur if composites are immersed in bleach especially for longer cycle. This indicates that the bleach causes some parts of composites to dissolve and to be lost in the liquid during conditioning.

2.3. Composite Preparation. The processing of kenaf/PP composites was done at Institute of Tropical Forestry and Forest Product (INTROP), Universiti Putra Malaysia (UPM). The composites were prepared with 40% and 60% fibre loadings using corotating extruder (Micromac, Micromagna, Perak, Malaysia). Then, the produced pellets were injected into tensile specimen mould using JSW 85-ton injection moulding machine model J85EM 110H using injection pressure of 78.72 MPa and injection speed of 48 mm/s. The temperatures

of injection moulding barrel were 195 and 210°C for 40 and 60% fibre loading, respectively. The specimen was prepared following type I of ASTM D638 standard and four replicas were tested for each parameter of treatment.

2.4. Methods of Treatment. All samples underwent 4 cycles of immersion and conditioning with each cycle consisting of 3 days of immersion and 4 days of conditioning. After the fourth day of conditioning, the specimens were tested using universal testing machine (Instron). The other set of specimens underwent immersion for 12 days and was conditioned for 4 days in order to evaluate the tensile properties of the composites under cyclic and continuous immersion. Three determined factors in this study were composition (40% and 60% fibre loadings), liquid of immersion (water and bleach), and cycle of immersion (the 0th, the 1st, the 2nd, the 3rd, and the 4th cycle). Two statistical analysis methods, ANOVA *F*-Test and Fisher's least significant difference (LSD), were used to determine the significant difference between experimental results.

3. Results and Discussion

3.1. Liquid Content in Composite. Liquid content in composite was the general term used in this study to describe the amount of liquid in composite at certain time regardless of whether composite was in immersion or conditioning stage. Liquid absorption was the amount of liquid absorbed by composite during immersion stage, while liquid retention was amount of liquid retained by composites during conditioning stage. The results of sorption pattern are presented in Figure 1 with all factors included in the graph. Composites were immersed in liquid and conditioned at room temperature for 4 cycles. During the first cycle of immersion, two distinguishable patterns were observed for composites with 40 and 60% fibre loading. Liquid of immersion (bleach and water) caused the patterns of liquid content to differentiate from each other with increase in cycle. The difference in pattern of liquid content was more apparent at the end of last cycle in composites with 60% fibre loading than composites with 40% fibre loading. It is clear that, even after the conditioning, some of the water absorbed by the fibers could not be removed from the composites and the amount of liquid retained inside the composite also increased with increase in immersion cycle. On the other hand, the amount of liquid retained by the composite during bleach immersion was lower as compared to water. Moreover, the highest uptake of the solution was nearly constant for immersion cycles 3 and 4.

3.2. Effect of Cyclic Immersion on Tensile Strength. Tensile strength of the composite influenced by combined effect of material composition, liquid of immersion, cycle of immersion, and conditioning is shown in Figure 2. It is seen that the fibre loading clearly influenced tensile properties of the composites; increase in fibre loading caused reduction in tensile strength at all immersion cycle. The liquid absorbed caused fibre to become more ductile during pull-out due to Poisson's effect; that is, fibre length increased with decrease in diameter.

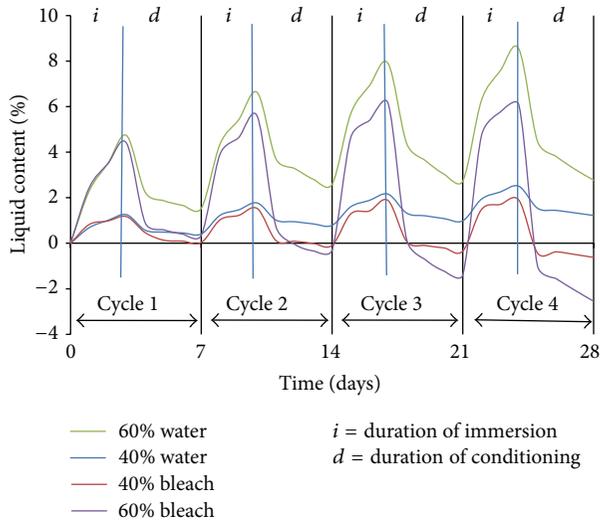


FIGURE 1: Pattern of liquid content during immersion and conditioning of kenaf/PP composites.

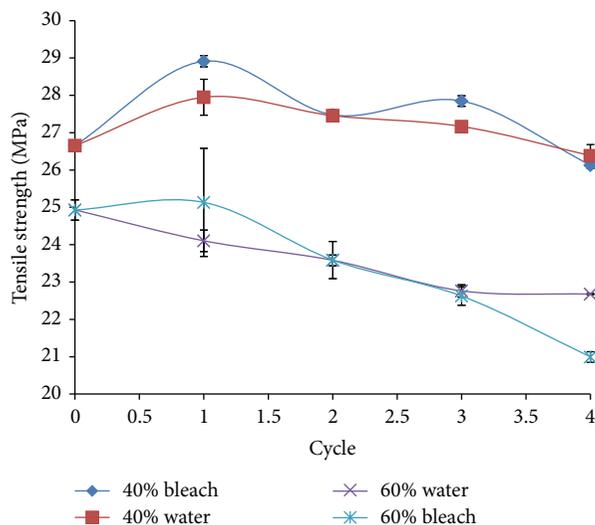


FIGURE 2: Tensile strength of PP composites with 40% and 60% of kenaf fibres loadings due to repeated immersion and drying.

The liquid also filled the gap between fibre and matrix and acted as lubricant during fibre pull-out. Residual stress might be produced due to uneven cooling or compaction during injection moulding. The early penetration of liquid, during dimensional expansion of fibre, might cause the fibre to release the residual stress exerted on it. However, the liquid could act as a lubricant when the amount of penetrated liquid increased.

3.3. Statistical Analysis on Tensile Strength. Statistical analysis is presented in Table 1. *F*-Test on three factors has been carried out to confirm the significance difference on tensile strength caused by compositions (composites with 40% and 60% fibre loadings), types of immersion liquid immersed into (water and bleach), and cycles (cycle 0, cycle 1, cycle 2,

cycle 3, and cycle 4). The differences between parameters of composition and cycle were also significant. Thus, it was confirmed that fibre loading in the composites affected tensile strength of composites.

Although the *F*-Test indicated that the difference between cycles was significant, the actual difference between cycles was shown by Fisher's least significant difference (LSD) method as presented in Table 2. The significant increase in tensile strength during the first cycle of immersion was verified by statistical analysis (Table 2). Then, tensile strength dropped to a value similar to cycle 0 and cycle 3. Possibly the residual stress, originating from processing of the composites, was released at early stage of immersion and thus improved tensile strength of the composite. However, as the immersions repeated, the liquid seeped between matrix and fibre and reduced the efficiency of loads transferred from matrix to the fibre that resulted in lower tensile strength of the composites.

In the analysis of liquid, *F*-Test in Table 3 shows that liquids of immersion (bleach and water) did not give significant difference regarding tensile strength of the composite, but there was significant interaction in *F*-Test between liquid and cycle (noted by Liquid * Cycle in Table 1). Therefore, each cycle underwent *F*-Test to isolate the interaction effect. *F*-Tests results showed that liquid of immersion significantly affected tensile strength of composites only on cycle 4. LSD analysis as shown in Table 3 reconfirmed significant difference between water and bleach in cycle 4. Therefore, the degradation in cycles 2 to 3 was observed to be higher due to the effect of water whereas only on the fourth cycle the bleach affected tensile properties of kenaf/PP composites.

3.4. Effect of Repeated Immersion on Tensile Modulus. Modulus (stiffness) is another basic property of composites; the primary intention of filler incorporation is usually to increase the stiffness of the resultant material. However, moisture absorption could significantly reduce the modulus of the composites. Clear differences amongst the effects of fibre loading, immersion cycles, and liquid of immersion on tensile modulus of the composites are observed (Figure 3). As the immersion cycle was increased, a reduction in modulus with both liquid immersions was observed. However, this reduction in tensile modulus was drastic and significantly higher in composites with 60% fibre loading as compared to 40% fibre loading. The moisture uptake, due to the immersion process, changes the structure and properties of fibers and matrix and the interface between them [18]. Moreover, as fiber content was increased, water absorption was expected to be increased [25, 26]. High fiber content in the composite leads to more water penetration into the interface through the micro cracks induced by swelling of fibers creating swelling stresses that led to composites failure [18]. The extent of strength and stiffness loss depends upon aging time and temperature also. Thwe and Liao [27] reported on bamboo-fiber composites that both the tensile strength and modulus decreased after aging in water at 25 and 75°C for prolonged period.

The composites immersed in bleach solution had lower modulus compared to water immersed composite samples.

TABLE 1: ANOVA for tensile strength of kenaf/PP composite with 40% and 60% fibre loadings immersed in water and bleach.

Source	DF	Sum of squares	Mean square	F value	Pr > F
Composition	1	242.32	242.328	384.28	<0.0001
Liquid	1	0.7029	0.70291	1.11	0.2953
Composition * Liquid	1	0.0183	0.01831	0.03	0.8653
Cycle	4	64.168	16.0421	25.44	<0.0001
Composition * Cycle	4	17.019	4.25486	6.75	0.0001
Liquid * Cycle	4	11.245	2.81119	4.46	0.0032
Composition * Liquid * Cycle	4	0.5062	0.12656	0.20	0.9370
Error	60	37.836	0.63061		
Corrected total	79	373.82			

TABLE 2: Means comparison among cycles for tensile strength.

t grouping	Mean	N	Cycle
A	26.4623	16	Cycle 0
B	25.7923	16	Cycle 1
B C	25.4007	16	Cycle 2
C	24.9134	16	Cycle 3
D	23.7962	16	Cycle 4

TABLE 3: Compilation of mean comparison among liquid at each cycle.

Cycle	Liquid		Significant (Y/N)
	Water (MPa)	Bleach (MPa)	
0	25.7923	25.7923	N
1	26.026	26.8985	N
2	25.5191	25.2822	N
3	24.9653	24.8616	N
4	24.5308	23.0616	Y

This is perhaps due to degradation of the natural fibers by bleach solution, which might have caused the fiber-matrix interfacial debonding. The potential for fiber/matrix debonding and microcracking at the interface during wet/dry cycling of composites is dependent upon (among other factors) the dimensional stability of the fiber reinforcement in response to moisture fluctuations. Mohr et al. [28] showed that composites produced with fibers, which were wetted and dried prior to the mixing, exhibited superior dimensional stability compared to composites produced with fibers, which had never been dried. The bleached (i.e., low-lignin) composites exhibited accelerated progression of fiber mineralization as compared to unbleached fibers. Unbleached composites exhibited greater toughness, particularly for low numbers of wet/dry cycles. Without exposure, unbleached fiber composites exhibit greater flexural properties than bleached fiber composites.

3.5. Statistical Analysis on Tensile Modulus. Statistical analysis with *F*-Test in Table 4 showed that the difference between parameters of composition, liquid, and cycle was significant.

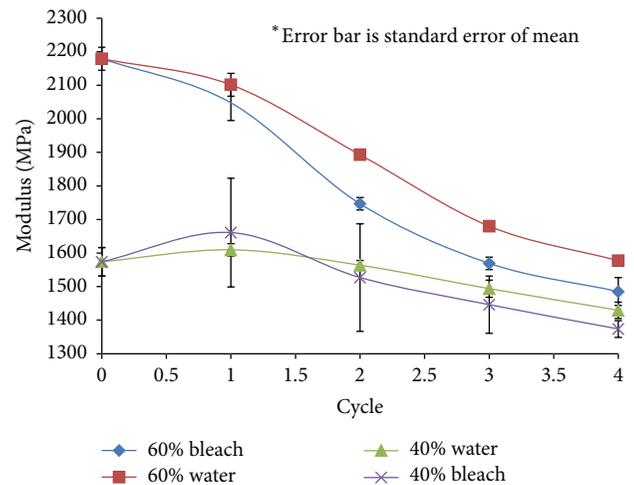


FIGURE 3: Tensile modulus of kenaf/PP composites with 40% and 60% fibre loadings due to repeated immersion and drying.

Since all the factors are significant, the interaction between the factors does not influence the results of ANOVA *F*-Test.

Both composition and liquid of immersion had only two parameters; the significant difference in Table 4 referred to composites with 40% and 60% fibre loadings and also water and bleach, respectively. On the other hand, cycle had five parameters and LSD test was used to compare which parameters were different. Table 5 showed that cycles 2, 3, and 4 differ from all cycles but cycles 0 and 1 do not differ from each other. This proved that significant degradation only started on cycle 2 onward.

The experiment confirmed that cycle of immersion, composition, and liquid of immersion had effects on tensile modulus of kenaf/PP composites. However, the cycle of immersion only affected tensile modulus of the composites on the second cycle onward.

3.6. Difference in Tensile Strength between Cyclic and Continuous Immersion. Result of tensile strength of composites with 40 and 60% fibre loading immersed in water and bleach is presented in Figure 4. Both types of immersion had caused degradation in composites with 60% fibre loading immersed in bleach. Tensile strength of composite with 40%

TABLE 4: ANOVA for tensile modulus of 40 and 60% fibre loading kenaf/PP composites immersed in water and bleach.

Source	DF	Sum of squares	Mean square	F value	Pr > F
Composition	1	2057626	2057626	535.48	<0.0001
Liquid	1	48306	48306	12.57	0.0008
Composition * Liquid	1	19701	19701	5.13	0.0272
Cycle	4	2117627	529407	137.77	<0.0001
Composition * Cycle	4	644814	161203	41.95	<0.0001
Liquid * Cycle	4	32139	8035	2.09	0.0931
Composition * Liquid * Cycle	4	8649	2162	0.56	0.6906
Error	60	230554	3843		
Corrected total	79	5159415			

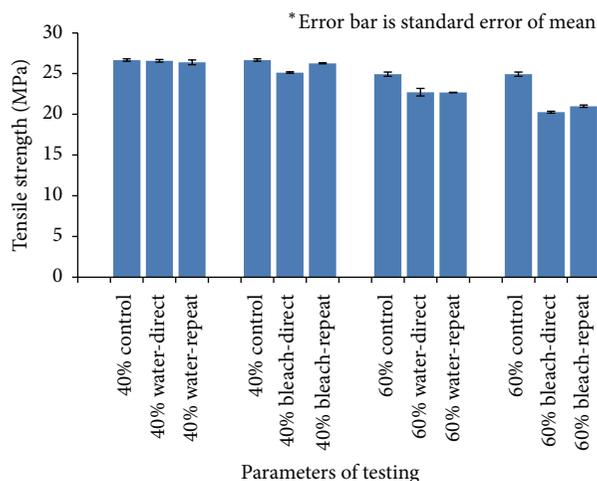


FIGURE 4: Difference of tensile strength between control, continuous (direct), and cyclic (repeat) immersion for 40 and 60% fibre loading of kenaf/PP composites.

TABLE 5: Means comparison between cycles for tensile modulus.

t grouping	Mean	N	Cycle
A	1876.53	16	Cycle 0
A	1854.93	16	Cycle 1
B	1682.55	16	Cycle 2
C	1547.28	16	Cycle 3
D	1466.32	16	Cycle 4

fibre loading immersed in water under continuous and cyclic immersion did not significantly differ. Tensile strength of composite with 40% fibre loading immersed in bleach was degraded under continuous immersion but, under cyclic immersion, tensile strength remains almost the same as composite without any immersion. It might be possible that conditioning process in cyclic immersion reduced the activity of bleach on the composites.

3.7. Differences in Tensile Modulus between Cyclic and Continuous Immersion. Both continuous and cyclic immersions had reduced tensile modulus of composites (refer to Figure 5). Composites with 40% fibre loading had loss around

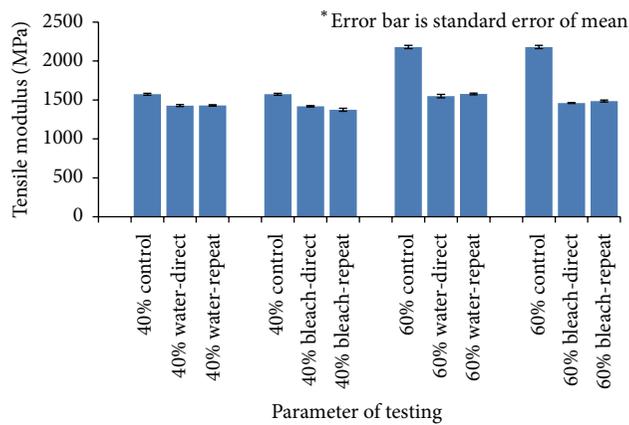


FIGURE 5: Difference of tensile modulus between control, continuous (direct), and cyclic (repeat) immersion for 40% and 60% fibre loading of kenaf/PP composite.

100 MPa of tensile modulus while composites with 60% fibre loading had loss around 600 MPa of tensile modulus due to 12 days of immersion. Furthermore, composites under continuous and cyclic immersion had similar value of tensile modulus. Therefore, the reduction of tensile modulus is not influenced by type of immersions.

4. Conclusions

Both continuous and cyclic immersions in bleach affected the tensile strength of the kenaf fibre reinforced polypropylene composites. Increased number of cycles of immersion and conditioning caused degradation of tensile strength and modulus. However, continuous immersion in the bleach reduced the tensile strength of composites more compared to cyclic immersion.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Study of Surface Roughness of Machined Polymer Composite Material

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The aim of this paper is to evaluate the influence of selected cutting parameters (speed of rotation and feed rate) on the surface topography of drilled WPC material. Objective of the study is to establish dependence of the surface roughness of borehole walls (parameter R_z —average maximum height) on the speed of rotation and feed rate of a drill bit. Technological parameters of experimental drilling were feed rate of 100–300 mm·min⁻¹ and speed of rotation of 2000–6000 rpm.

1. Introduction

In the field of composite materials reinforced with natural fibers the following ways of machining are preferred.

- (i) *Milling*. Study [1] is one of the first published works, which are focused on wear of milling tools in technology of circumferential milling of commercially acquired WPC materials and comparative samples (classic wood). The author registered higher wear of tools when machining WPCs in comparison to machining of wood. He assumes that the increased wear of tools for machining WPCs was due to their composition and modified properties. Type of a matrix used in the production of composites represents an important factor affecting the quality of machined surfaces.
- (ii) *Cutting*. The publication [2] describes the relationship between the speed of cutting when sawing and the quality of machined surfaces of three samples of WPCs with a different matrix (PE/PP/PVC) + rice hull flour. The experimental results show that the spindle speed has a significant effect on the surface quality of the machined samples. The advantage of using a high cutting speed in sawing WPCs is evident.
- (iii) *Turning*. The publications [3, 4] describe the quality of machined surfaces after turning with a monolithic HSS tool when changing the feed rate of machining (at a constant cutting speed and depth of cut). It is recommended to use the tools with a large radius of curvature and lower feed rates.
- (iv) *Drilling*. In recent years there have been a large number of studies focused on evaluation of the effects that input cutting parameters have on achieved quality of holes. Study [5] assessed the quality of boreholes in composite material with PE matrix and hemp fiber reinforcement (density of 1350 kg·m⁻³ and module of 3.25 GPa, prepared with a use of hand lay-up process). The authors recommend the use of higher cutting speeds and lower values of feeds for achieving minimal damage to the holes (regarding maintaining the roundness of the holes).
In [6] the so-called “green” materials are machined (composites reinforced by bamboo and Japanese cedar fibers). The thrust force (its effect on quality of the holes), chip forming, and tool wear are evaluated in this study.

Based on analysis of present state of the problematic and study of research and scientific publications, it can be stated

TABLE 1: Mechanical properties of tested material (tensile strength test).

Number of samples	Ultimate tensile strength [Mpa]	Relative elongation [%]	Reduction [%]
1	24	2.8	2.0
2	15	2.9	0.4
3	24	3.4	0.8
4	15	5.1	0.4
5	Defect		

TABLE 2: Mechanical properties of tested material (three-point bending test).

Number of samples	Ultimate bending strength [Mpa]
1	18.76
2	15.69
3	16.71
4	15.44
5	17.13

that nowadays there are no available quality and relevant scientific outputs from the area of monitoring the topography of machined wood plastic composites. In the light of this, this paper is presented focusing on experimental study of surface topography after machining-drilling at exactly designed experimental conditions (technological parameters such as feed rate and spindle speed, which are regarded in whole experiment as variable and other influences on the experiment are considered as constant because experiment was carried out at the same conditions and with the same tools, machines, and devices).

2. Materials and Methods

In the experiment samples of natural fiber reinforced composite were used. The material consists of HDPE matrix reinforced with wood fibers or chips (more than 75% vol.). Machined profile (with dimensions of $60 \times 40 \times 3600$ mm) was manufactured by extrusion technology. Mechanical properties of the composite are given in Tables 1 and 2. The ultimate tensile strength (Table 1) was determined according to ISO 6892-1, with a constant load speed of $0.015 \text{ mm}\cdot\text{s}^{-1}$. The ultimate bending strength was determined using the three-point bending test (Table 2) according to ISO 178-1, with a constant load speed of $0.08 \text{ mm}\cdot\text{s}^{-1}$. The test samples were cut out from the middle part of the profile in direction parallel to the axis of extrusion. A microscopic image of the material structure before machining is shown in Figure 1. The material contains microcracks mostly localized in the contact area of wood and plastic. The length of microcracks ranges from $20 \mu\text{m}$ to 4 mm. Some cracks pass even through the wood chips in the direction of their longitudinal axis. Cracks are unevenly distributed throughout the volume of the material. Orientation of wood particles follows the flow of the polymer.



FIGURE 1: Microscopic structure of the tested WPC material (optical microscope Nikon Eclipse 80i, reflected light).



FIGURE 2: Holes with required diameter drilled into the material.

Two types of drill bits made of high-speed steel (HSS) without any unusual additives of alloy components (DIN 338) were used for drilling of tested samples:

- (i) drill bit number 1—with TiN coating;
- (ii) drill bit number 2—without coating, with surface finish—blackening.

The drill bits had the same diameter of 9.0 mm, working length of $l_t = 125$ mm, apical angle of the point of $\varepsilon_r = 118^\circ$, and helix angle of $\lambda = 30^\circ$.

The three-axis vertical machining centre Pinnacle VMC650S was used as a working machine. The frame saw ERGONOMIC 275.230 DG was used to cut samples with required dimensions of 230 mm. The process of cutting and drilling was realized without using process fluids (drilled holes—passable, deep drill strategy). Technological parameters of the cutting process are shown in Table 3.

3. Results and Discussion

For each configuration of the drilling system, three boreholes were made (Figure 2). To measure the parameter of surface roughness the MITUTOYO SJ-400 device was used with contact operation with the automatic compensation of radius and inclination, with an evaluation length of $l_r = 4.0$ mm (filter profile $\lambda_c = 2.5$ mm). Before the measurement, the samples were cut in the axis parallel to holes (Figure 3). The surface roughness was measured at the distance of

TABLE 3: Technological parameters of the cutting process and marking of holes.

Hole number	1	2	3	4	5	6	7	8	9
Spindle speed [rpm]	2000	4000	6000	2000	4000	6000	2000	4000	6000
Feed rate [mm·min ⁻¹]	100	100	100	200	200	200	300	300	300

TABLE 4: Dependence equations Rz on changing conditions of the cutting process (the first equation is for the HSS tool with TiN coating— with *; the second equation is for the HSS tool without coating).

	Dependence equations $Rz = f(f)$		Dependence equations $Rz = f(n)$
$f = 100 \text{ mm} \cdot \text{min}^{-1}$	$Rz = 5.6667f + 5.5139 R^2 = 0.8824^*$ $Rz = 10.508f + 0.8111 R^2 = 0.9116$	$n = 2000 \text{ rpm}$	$Rz = 2.6875n + 11.153 R^2 = 0.5286^*$ $Rz = 4.9917n + 7.7222 R^2 = 0.9714$
$f = 200 \text{ mm} \cdot \text{min}^{-1}$	$Rz = 1.7375f + 16.267 R^2 = 0.3224^*$ $Rz = 8.7875f + 4.6972 R^2 = 0.7113$	$n = 4000 \text{ rpm}$	$Rz = 5.6708n + 7.6889 R^2 = 0.8988^*$ $Rz = -0.5458n + 18.031 R^2 = 0.2371$
$f = 300 \text{ mm} \cdot \text{min}^{-1}$	$Rz = 3.0375f + 16.383 R^2 = 0.7113^*$ $Rz = -1.725f + 23.414 R^2 = 0.3052$	$n = 6000 \text{ rpm}$	$Rz = 0.0583n + 23.372 R^2 = 0.0145^*$ $Rz = -7.2417n + 43.903 R^2 = 0.7465$



FIGURE 3: Sample before surface roughness measurement (inner hole and marginal hole).

20 mm from the beginning of the hole on the right and left sides, with repeating 3 times. The values used in graphs in Figures 4 and 5 represent arithmetic averages of 3 measurements of the right and left sides of marginal and inner holes.

The following is description of graphic representations and linear dependence equations.

- (i) *HSS Drill Bit with TiN Coating (Tool 1)*. At the constant feed rate of $f = 100 \text{ mm} \cdot \text{min}^{-1}$ the values of Rz parameter rise with increasing revolution. At the feed rate of $f = 200 \text{ mm} \cdot \text{min}^{-1}$ the Rz values decrease at $n = 4000 \text{ rpm}$ and then they subsequently go up (by $6.1 \mu\text{m}$). At the maximum feed rate of $300 \text{ mm} \cdot \text{min}^{-1}$ the values of Rz parameter act oppositely to the previous case (Figure 4(a)). Based on linear dependency equations the increasing tendency is visible in case of all three feed rates (Table 4, highlighted lines). However, the coefficient of determination is not greater than 0.90 in any of the cases and therefore the equations are not statistically important. Figure 4(b) shows the graphic dependence of Rz on increasing feed rate. At the minimal revolution the Rz values increase at the feed rate of $200 \text{ mm} \cdot \text{min}^{-1}$ and then they subsequently decrease under $1.7 \mu\text{m}$. At the revolution of 4000 rpm there is an evident increase of Rz values in the whole

range of feed rates. At the maximum revolution the course is almost constant even at the change of the feed rate. Linear equations confirm these courses, but when the statistical significance is concerned, however, none meets the criterion $R^2 > 0.90$.

- (ii) *HSS Drill Bit without Coating (Tool 2)*. The Rz values rise with increasing revolution at the feed rates of 100 and $200 \text{ mm} \cdot \text{min}^{-1}$. A significant increase is visible when the revolution is changed from 4000 rpm to 6000 rpm . Maximum reached values are almost identical (at $n = 4000 \text{ rpm} \rightarrow Rz_{\text{max}} = 34.225 \mu\text{m}$; at $n = 6000 \text{ rpm} \rightarrow Rz_{\text{max}} = 34.292 \mu\text{m}$). At the maximum feed rate of $300 \text{ mm} \cdot \text{min}^{-1}$ the Rz value decreases and then subsequently increases at the maximum revolution of 6000 rpm (Figure 5(a)). Linear dependence equations show evident increasing course, but only the dependence of Rz on the revolution at the minimum feed rate of $100 \text{ mm} \cdot \text{min}^{-1}$ ($R^2 = 0.9116$) is statistically significant. Figure 5(b) shows the visible change in course of Rz depending on increasing feed rate. At the minimum revolution the values of Rz parameter rise with the increasing feed rate. The opposite course is evident at maximum revolution. At the revolution of 4000 rpm the values range in a narrow interval— from less than $17 \mu\text{m}$ up to $18.05 \mu\text{m}$. Statistically important is the course at the revolution of 2000 rpm . Coefficient of determination is greater than 0.97. In case of higher revolution the equations are statistically insignificant and they have a decreasing tendency.
- (iii) Graphic dependencies differ depending on the use of tools with the same diameters but different surface finish (tools with/without coating). Using the tool with TiN coating the better quality of the surface (lower values of Rz parameter) was achieved. Use of a drill bit with surface finish improves the quality of the surface by more than 20%. On the other side, the differences in obtained values are minimal at the feed

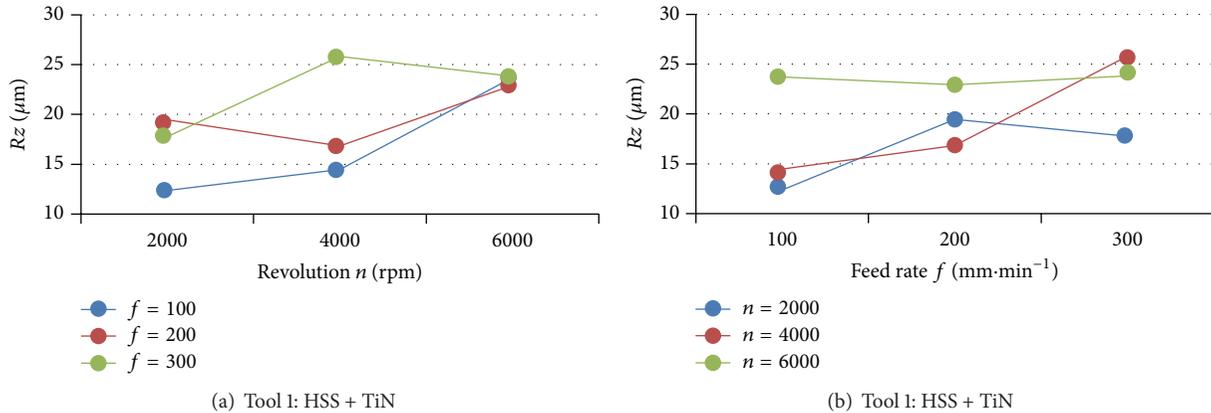


FIGURE 4: (a) Dependence of surface roughness parameter Rz on revolution; (b) dependence of surface roughness parameter Rz on feed rate (HSS tool with TiN coating).

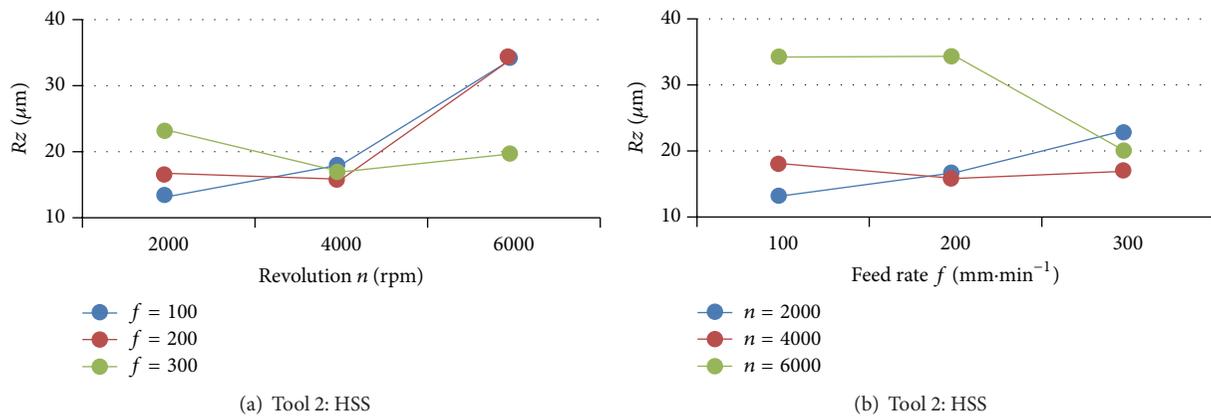


FIGURE 5: (a) Dependence of surface roughness parameter Rz on revolution; (b) dependence of surface roughness parameter Rz on feed rate (HSS tool without coating).

rate of 100 and 200 mm·min⁻¹ and at the minimal revolution.

Figures 6(a)–6(f) show the images obtained using a digital camera. Chips were removed from the place of a cut by a groove in the tool. Some melting of plastic and its sticking to the adjacent back part of a drill bit occurred during the process of cutting. In the case of coated tool the sticking of material matrix was even more apparent. When using a tool without coating the sticking of polymer does not occur in such extent. With regard to heterogeneity of the material it is not possible to categorize the formed chips into groups in more detail; the particular section of chips has different shapes (alongside the inner volume there is a different ratio of plastic and wood and the wooden parts are of different sizes). The edge of a hole is without damage in the part where a drill bit enters the material. In the area where a drill bit exits the material deformation occurs and a part of chip is fixed to the edge of a hole (see Figures 6(e) and 6(f)).

It is necessary to note that experimental results are valid only for presented technological conditions and tools, so in the future it is recommended to study other tools and technological parameters of machining and also to determine

the most suitable conditions to achieve surface with highest quality.

4. Conclusion

Topography of the surface is prescribed by interaction between tool and machined material and its properties. Along the extruded profile the mechanical properties of the studied material are different, which was proved by mechanical testing. The microscopic observation of the material structure showed the heterogeneity of the composite and also presence of microcracks located on contacts between wood particles and the polymer matrix. Graphical dependencies of studied parameters were constructed using values calculated as arithmetic average of Rz values measured on the surface of inner and marginal bore holes, which in the light of inhomogeneity of material are correlation coefficients at low values, which show statistical significance of described dependencies $Rz = f(f)$ and $Rz = f(n)$, respectively. In relation to changing characteristic along the profile it is not able to predict course of roughness parameters for variable parameters (depending on conditions of cutting process). Inhomogeneity can be

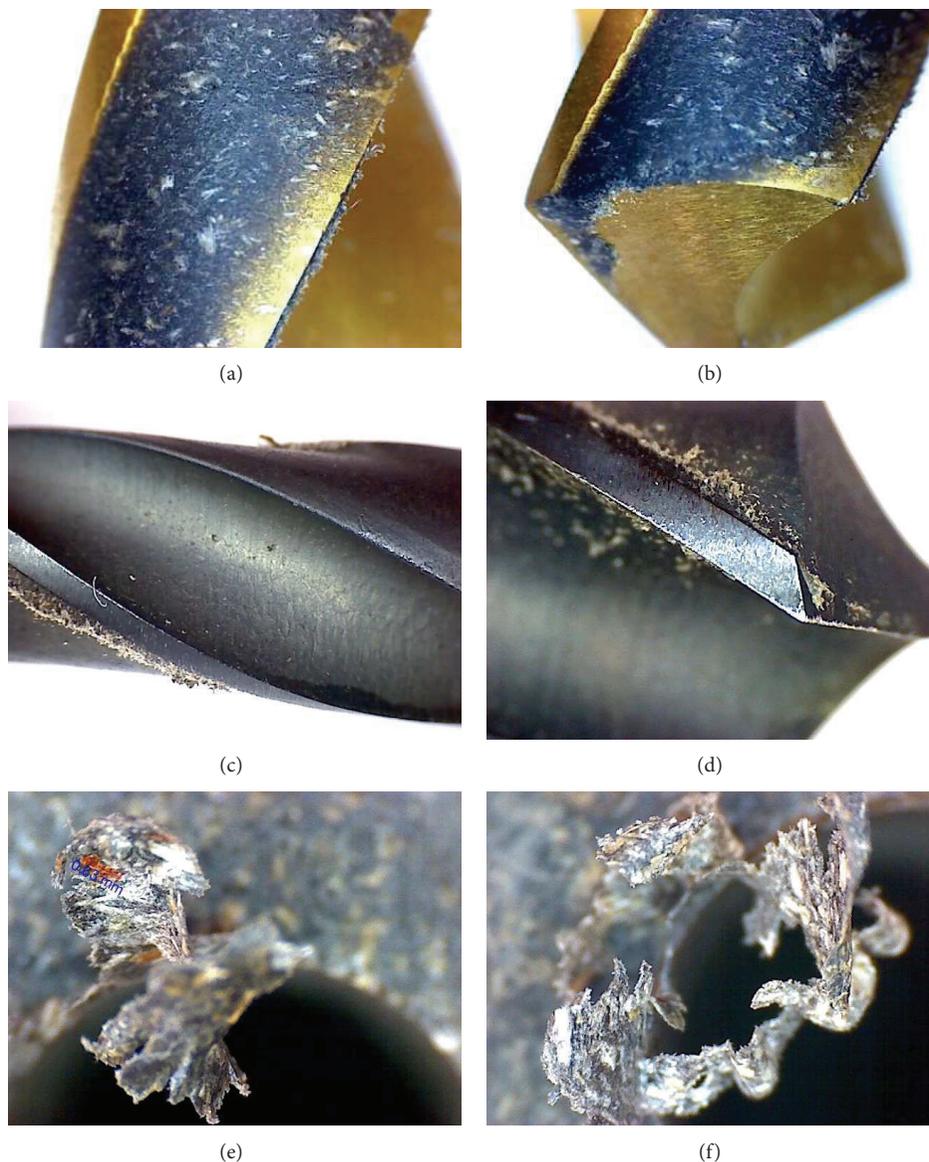


FIGURE 6: Macroscopic images obtained using a digital microscopic camera Digi Micro 2.0: (a) and (b) details of tool with TiN coating after drilling, (c) and (d) details of tool without coating after drilling, and (e) and (f) details of bored hole.

partially reduced by adding of coupling substance in production process of profile (reduction of cracks on borders wood-plastics). Further research can be possible pointed on material area—exactly to increase homogeneity of material.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Research Article

Numerical Simulation Analysis of Unfilled and Filled Reinforced Polypropylene on Thin-Walled Parts Formed Using the Injection-Moulding Process

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Thin-walled moulding technology has attracted increasing attention, particularly in electronic packing applications. The injection moulding of shallow, thin-walled parts with a thickness of 0.7 mm was performed using three types of materials from polypropylene, PP (PP, PP + 50 wt% wood composite, and PP + 10 wt% glass fibre composite). The highest deflection resulting from PP + 50 wt% wood does not occur in the critical area of the thin-walled part compared with PP + 10 wt% glass fibre. In addition, the results revealed that the warpage at the midpoint of the part surface injected using PP + 50 wt% wood is 0.04 mm lower than the value of 0.08 mm obtained when injected using PP + 10 wt% glass fibre. The warpage was hypothesised to result from the residual stress caused by nonuniform volumetric shrinkages formed during the solidification phase.

1. Introduction

Recently, the thin-walled moulding technology has attracted increasing attention for some applications specifically in electronic packaging. These industries tend towards the production of products that possess characteristics such as thinness, light weights, small dimensions, environmental friendliness, and good structural strength. Therefore, manufacturer concerns regarding the research and development of creating 3C (computer, communication, and consumer) products indicate that the products should have the properties such as light weights, thinness, short lengths, and small dimensions. In 2014, some companies, such as Roctool, Ju Teng, and Xiaomi Inc., demonstrated the capability of producing thin-walled electronic housings for smartphones and tablets with thicknesses of less than 1 mm [1, 2].

Shen et al. [3] investigated the optimum number of gates used during the filling stage by taking into account the

moulding conditions. The analysed geometrical model was a battery cover with a wall thickness at the four sides of 1.0 mm and a thickness at the base central region of 0.2 mm. Ozcelik and Sonat [4] also investigated the optimisation of the warpage and structural strength of a cell phone cover measuring 0.9 mm, 1 mm, and 1.1 mm in thickness using carbon fibre-reinforced PC/ABS composite materials. Azaman et al. [5–7] demonstrated that the lignocellulosic polymer composite is suitable for moulding thin-walled parts with thicknesses of 0.7 mm, as confirmed via simulation analysis using the MoldFlow software.

However, reducing the thicknesses of parts to less than 1 mm is extremely challenging in terms of filling and often leads to an inconsistent distribution of residual stresses, volumetric shrinkages, and warpage in moulded products. Cheng et al. [8] reported the influence of nonuniform stress and shrinkage distributions on warpage deformation. The distribution of residual stresses caused by nonuniform shrinkages

ultimately generated the most significant warpage problems, particularly in thin-walled parts. Oktem et al. [9] also reported that warpage and shrinkage were the most frequently involved factors in the defects of thin-walled plastic parts in terms of quality. The primary cause of warpage is commonly known to be variations in shrinkage during the injection processing of thin-walled plastic parts.

Subramanian et al. [10] reported that the geometry and mechanical properties of a material also play a critical role in the warpage and that the final warpage of a part strongly depends on its mechanical stiffness, which is a function of the geometrical configuration and of the material's mechanical properties. Azaman et al. [5] determined that the use of shallow, thin-walled parts is preferable for moulding composite materials with lignocellulosic polymers because of the resulting low residual stress and warpage. Shallow, thin-walled parts are more structurally rigid than flat, thin-walled parts, and they can be processed more economically with the use of less material.

The structural rigidity of a thin-walled part is greatly reduced relative to its thick-walled counterpart due to the reduction in its section modulus. The maximum deflection is inversely proportional to the thickness (high deflection occurs with thin parts). Therefore, a potential solution for moulding thin-walled parts is to use a fibre-filled polymer composite, which typically increases the material modulus of the moulded part compared with an unfilled moulded part. Shen et al. [12] performed a numerical analysis on a thin-walled part with a fibre-reinforced thermoplastic material. The MoldFlow software was used for the analysis. Different injection parameters (injection pressure, melt temperature, mould temperature, and injection time), different fibres (short glass and long glass fibres), different fibre ratios (40% and 50%), and different thickness values (0.9 mm and 1 mm) were used. The outer shell of a notebook computer was used as the analysis model. Ozcelik and Erzurumlu [13] found that the addition of glass fibre is the most significant factor for PA66 composites in minimising the occurrence of warpage in the moulded part.

Furthermore, Kwiatkowski et al. [14] reported several important factors that influence the deformation of an injection-moulded part, including the structure of the polymer used for the matrix of the composite, the sizes and types of fillers, and the percentage content of the filler. Hakimian and Sulong [15] found that loading glass fibres in the polymer provides a valuable effect on the formation of warpage and the shrinkage properties in moulded microgear parts. These phenomena are due to the orientation of fibres along the direction of the injection flow during the moulding process.

This literature review reveals that limited research has been conducted on the comparison of filled and unfilled thermoplastic composite in moulded thin-walled parts, specifically using neat polypropylene (PP), PP + 10 wt% glass fibre, and PP + 50 wt% wood composite. Hence, this study investigated the processability and identified the interactions among behaviours with respect to residual stresses, volumetric shrinkages, and warpage in moulded thin-walled parts.

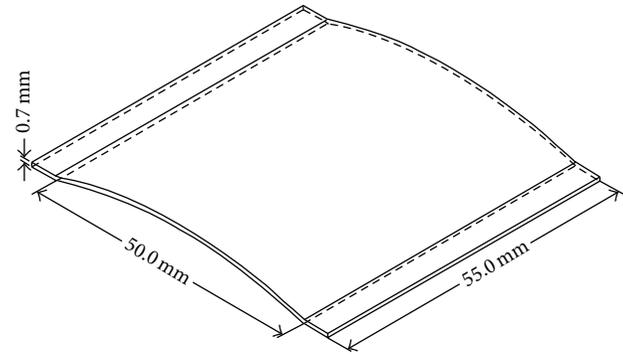


FIGURE 1: A shallow, thin-walled part [5–7].

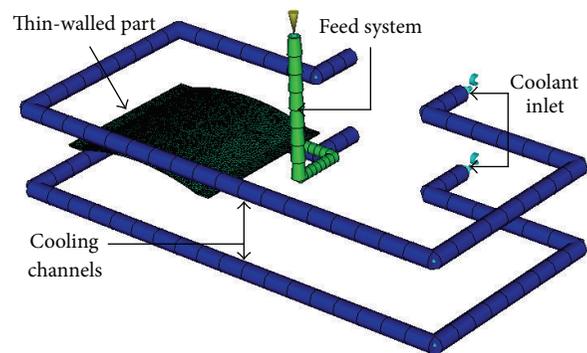


FIGURE 2: A mesh model for simulation [5–7].

2. Methodology

2.1. Part Design. Autodesk Inventor Professional was used to model the moulded thin-walled parts, as shown in Figure 1. A shallow, thin-walled part was created as a 3D design. The general dimensions of the part were 55 mm × 50 mm × 0.7 mm.

2.2. Numerical Simulation. Autodesk MoldFlow Insight was used to simulate and analyse the injection-moulding process. A mesh model was developed, as shown in Figure 2. The injection-moulding machine and the materials used in the simulation adhered to the following specifications: Arburg Allrounder 370c 88-ton injection-moulding machine (screw diameter of 30 mm); neat PP from SABIC PP PHC27; SABIC Europe B.V.; PP + 50 wt% wood composite from Isoform Lip CPCW 50, Isokon; and PP + 10 wt% glass fibre composite from Polypro R200G; Idemitsu Kosan Co. Ltd. Table 1 presents the specifications of the injection-moulding machine. Table 2 presents the material properties of the PP, PP + 50 wt% wood composite, and PP + 10 wt% glass fibre composite. The simulation was performed using a set analysis (fill + cool + fill + pack + warp) for these models. The processing parameters for the simulations are shown in Table 3.

TABLE 1: Specifications of injection-moulding machine.

Parameters	Units	Value
Maximum machine injection stroke	mm	176.8
Maximum machine injection rate	cm ³ /s	112.1
Machine screw diameter	mm	30
Maximum machine injection pressure	MPa	247
Maximum machine clamp force	MPa	79.80

2.3. Measurement of In-Cavity Residual Stresses, Volumetric Shrinkage, and Warpage. The results indicate that the in-cavity residual stresses lie along the first principal direction (plotted at the centre of the surface). Similarly, the volumetric shrinkage and warpage were measured at the centre of the surface.

3. Results and Discussion

3.1. Filling Simulation. Figure 3 presents the results of the filling simulations for the materials containing PP without and with fillers. The results of the filling simulations for the thin-walled parts show that PP is more rapidly filled than that PP with fillers (10 wt% glass fibre and 50 wt% wood). The fill time of PP without filler is 1.139 sec, whereas for PP + 15 wt% glass fibre and PP + 50 wt% wood it is 1.171 sec and 1.269 sec, respectively. The properties of the wood fillers, the inconsistency in the shapes of the wood powders, and the possibility of weak interfacial bonding between the polymer and wood fillers cause difficulties for the filler to mix with the melted polymer compared with glass fibre fillers. These findings were similarly reported by Rozman and Wan Daud [16]. However, all materials appear to be ideal for moulding thin-walled parts without the short shot problem.

As shown in Figure 4, the unfilled PP material fills in thin-walled parts faster than the filled PP compound. According to the filling simulation results, with an injection time of 1.1 sec, the melted polymer composites containing PP + 10 wt% glass fibre and PP + 50 wt% wood still did not completely fill the cavity of the thin-walled parts. However, the difference in fill time, which is approximately 0.1 sec, is sufficiently small and demonstrates that the thin-walled part is capable of being moulded using all three materials. Azaman et al. [5] reported the potential processability of moulded thin-walled parts using lignocellulosic polymer composites in different types of thin-walled part designs, such as shallow and flat structural parts. Shen et al. [12] also conducted numerical analyses on thin-walled parts using different types of fibres (short and long), different fibre ratios (40 wt% and 50 wt%), and different thickness values (0.9 mm and 1 mm).

3.2. In-Cavity Residual Stresses Distribution. The in-cavity residual stresses in the first principal direction describe the inherent stress along the orientation direction before a part is ejected from a mould. These residual stresses occur inside a mould and will be altered after the part is ejected. However, the results obtained in this study are sufficient for relating and describing the quality of the final part in terms of the

predicted shrinkage and warpage [17, 18]. In addition, Altan and Yurci [19] noted that the critical stresses should be determined at or near the surface region because high tensile stresses near the region of the injection-moulded parts are known to result in environmental stress cracking and to be sensitive to chemical diffusion. However, the formation of residual stresses must be taken into account to distinguish the formation of residual stresses among unfilled and filled reinforced polymer composites.

Figure 5 presents the simulated residual stresses in the thickness direction at the centre of the thin-walled part surface for all three materials (i.e., PP, PP + 50 wt% wood, and PP + 10 wt% glass fibre). The thickness in the plot was normalised from -1 to 1 according to the core and cavity sides of the mould. The maximum residual tensile stresses occur near the wall in the core and cavity mould. The maximum residual stresses decrease when approaching the subsurface, at approximately 0.175 mm. However, the core region exhibits a parabolic tensile peak near a thickness of 0.35 mm for both sides of the parts. The distribution pattern of the residual stresses through the thickness of the part is consistent with the patterns reported in previous studies [20–22]; the only difference exists at the subsurface region where the residual compressive stress is normally formed. This difference occurred because these simulation results are based on the residual stress formed before ejection, which means that the results are almost always positive because the part is still constrained within the mould.

The widths of the core regions in the parabolic profile of the residual stresses on thin-walled parts for PP polymer wider than fibre/filler-reinforced polymers follow the sequence PP + 10 wt% glass fibre and PP + 50 wt% wood. This residual stress distribution profile is caused by thermal contraction (i.e., sources from the melt temperature, mould temperature, and shearing polymer melt), affecting the crystallisation process. This is explained by the different values of the coefficient of thermal expansion (CTE) of the compound, which influences the level of inner stresses in the crystallisation process, as shown in Table 2. The high CTE value of the compound is able to increase the crystallisation time, which consequently induces slower crystallisation with lower stresses that become frozen with sufficient relaxation. Ziran et al. [23] also reported that the crystallinity process, coefficient of thermal expansion, and elastic modulus have important effects on the development of internal stresses. With decreasing crystallinity, the internal stresses diminish.

As shown in Figure 5, the residual stress in the reinforced polymer composite is greater than that in the unfilled polymer. For filler-reinforced polymers, the orientation of the fillers has a greater effect than does the molecular orientation (neat polymer resin without fillers) [24]. Thus, the orientation of the fillers influenced the distribution of residual stresses in the through-thickness direction along the part surface. The results revealed that the residual tensile stress formed by PP + 50 wt% wood is approximately 25 MPa higher than the values of 20.2 MPa and 17.2 MPa for PP + 10 wt% glass fibre and PP, respectively, which occurred near the wall at both sides of the parts. However, the residual tensile stress of PP + 50 wt% wood was low (15.8 MPa) compared to that of PP + 10 wt%

TABLE 2: The material properties of PP, PP + 50 wt% wood, and PP + 10 wt% glass fibre.

	PP	PP + 50 wt% wood	PP + 10 wt% glass fibre
Trade name	SABIC PP PHC27	Isoform Lip CPCW 50	Polypro R200G
Filler content (wt%)	0	50	10
Material structure	Semicrystalline	Semicrystalline	Semicrystalline
Coefficient of thermal expansion, CTE ($1/^\circ\text{C}$)	$1.45E - 4$	$6.81E - 5$	$5.43E - 5$

TABLE 3: The processing parameter settings.

	PP	PP + 50 wt% wood	PP + 10 wt% glass fibre
Melt temperature ($^\circ\text{C}$)	230	185	230
Injection time (sec)	1	1	1
Mould temperature ($^\circ\text{C}$)	40	45	50
Cooling time (sec)	20	20	20
Packing pressure (MPa)	$0.8P_{\text{inject}}$	$0.8P_{\text{inject}}$	$0.8P_{\text{inject}}$
Packing time (sec)	10	10	10

Remarks: parameter setting refers to material database recommendation [11].

glass fibre (17.2 MPa) near the core region along the thickness direction, while the pure PP is 14.0 MPa lower than both of the filler-reinforced polymer composites.

Due to the characteristic of the chain structure of the polymer material, its molecular chains are easily oriented as a result of flow shear stress during the filling process and thermal contraction after the filling process. Therefore, for the unfilled polymer, PP exhibits the lowest residual stresses, which occurred near both the walls and core region of the thin-walled part. In contrast, the orientation of molecular chains in the filler-reinforced polymer in the through-thickness direction can be quite complex. The orientations of the fillers significantly influence the formation of residual stresses inside the moulded part. In particular, discussing the orientation of the particulate powder about the PP + 50 wt% wood fibre orientation compared to PP + 10 wt% glass fibre is more complicated. During the cooling phase, the possibility of wood powder orientation occurred with a random arrangement. According to Khalina et al. [25], the orientation distribution of the particulate powder is not the same as the arrangement of the fibre orientation in the moulded part, but the powder form dispersed more uniformly, as reported by Rozman et al. [26]. The simulation results show the expected high orientation of wood near the wall surface due to the value of the residual tensile stresses being high, and the opposite occurs in the core regions.

Similarly, the glass fibres oriented inside the polymer composite melt in the moulded thin-walled part during the crystallisation process. However, the arrangement of the oriented glass fibres differs, with the fibres on the wall surface being scattered parallel to the flow direction, whereas the orientation in the core regions is perpendicular to the flow direction. The arrangement of this orientation is more easily explained with the statement from Xu and Yu [24]. During

the cooling of the melt, the chains with frozen orientations always have a tendency to develop from a high energy state to lower energy state. This means that recrystallisation occurred, which will lead to an inconsistent alignment direction and further generate internal stresses. Therefore, filled polymers cause the melt flow rate to decrease and the cooling rate to increase because glass fibres impart a lower coefficient of thermal expansion to the reinforcement relative to the surrounding polymer [27]. Then, the frozen in orientation will be more critical; thus, the residual stress of the moulded part will be larger.

3.3. Volumetric Shrinkage Simulation. Figure 6 shows the value of percentage volumetric shrinkage change during the solidification process between the cavity and core sides, which was measured at the centre of the thin-walled part surface. The value of the volumetric shrinkage change (%VS max – %VS min) of PP + 10 wt% glass fibre was low (4.32%) compared to PP + 50 wt% wood and PP (4.7% and 6.48%, resp.).

Unfilled polymers, such as PP, exhibit isotropic linear shrinkage behaviour, meaning that the properties of the moulded part are similar, following the direction of flow, either parallel or perpendicular, as well as across the thickness. It is widely accepted that semicrystalline plastics shrink more than amorphous ones because of the closer packing in the crystalline structure [28]. In detail, during the filling stage, semicrystalline polymers such as PP can exhibit significantly higher shrinkage rates. There is a significant change in the specific volume when the polymer transitions from a closely packed semicrystalline solid to a loosely packed amorphous melt. This increase in the specific volume can give rise to significant volumetric shrinkage and high shrinkage rates. Moulding applications with such high shrinkage rates tend to be more difficult to control to tight tolerances due to their sensitivity to the processing conditions.

In contrast, glass/wood-filled polymer composites can be used to influence the amount of shrinkage that a material exhibits for thin-walled part moulding. The presence of these fillers is capable of changing the material properties, which primarily depend on the flow direction. Kwiatkowski et al. [14] reported that one factor that influences the shrinkage deformation is the percentage content of the filler. The shrinkage deformation of moulded parts is influenced by the difference in fibre orientation either parallel or transverse to the polymer flow direction, which resulted in the shrinkage measured parallel being 50% greater than that in the transverse direction [14].

For anisotropic materials, the glass or wood fillers can become highly aligned in the flow field during the filling,

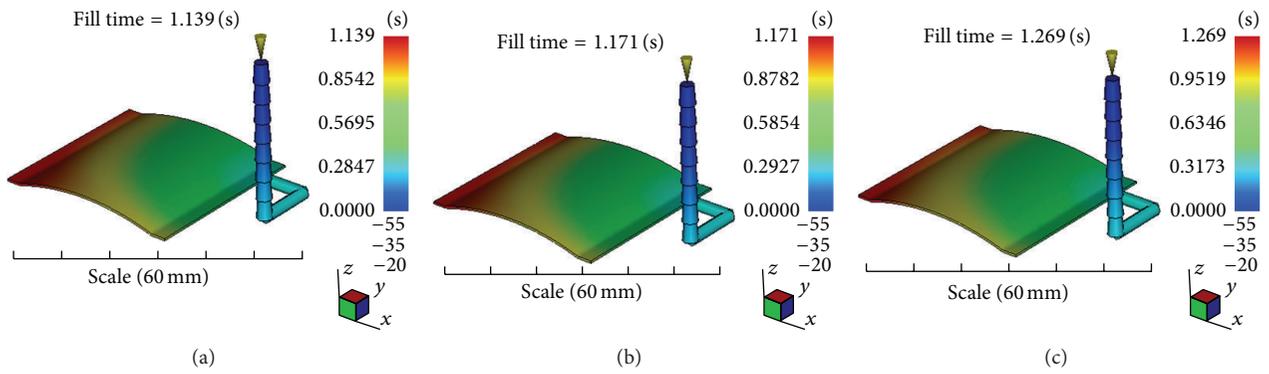


FIGURE 3: Fill times for (a) PP, (b) PP + 10 wt% glass fibre, and (c) PP + 50 wt% wood.

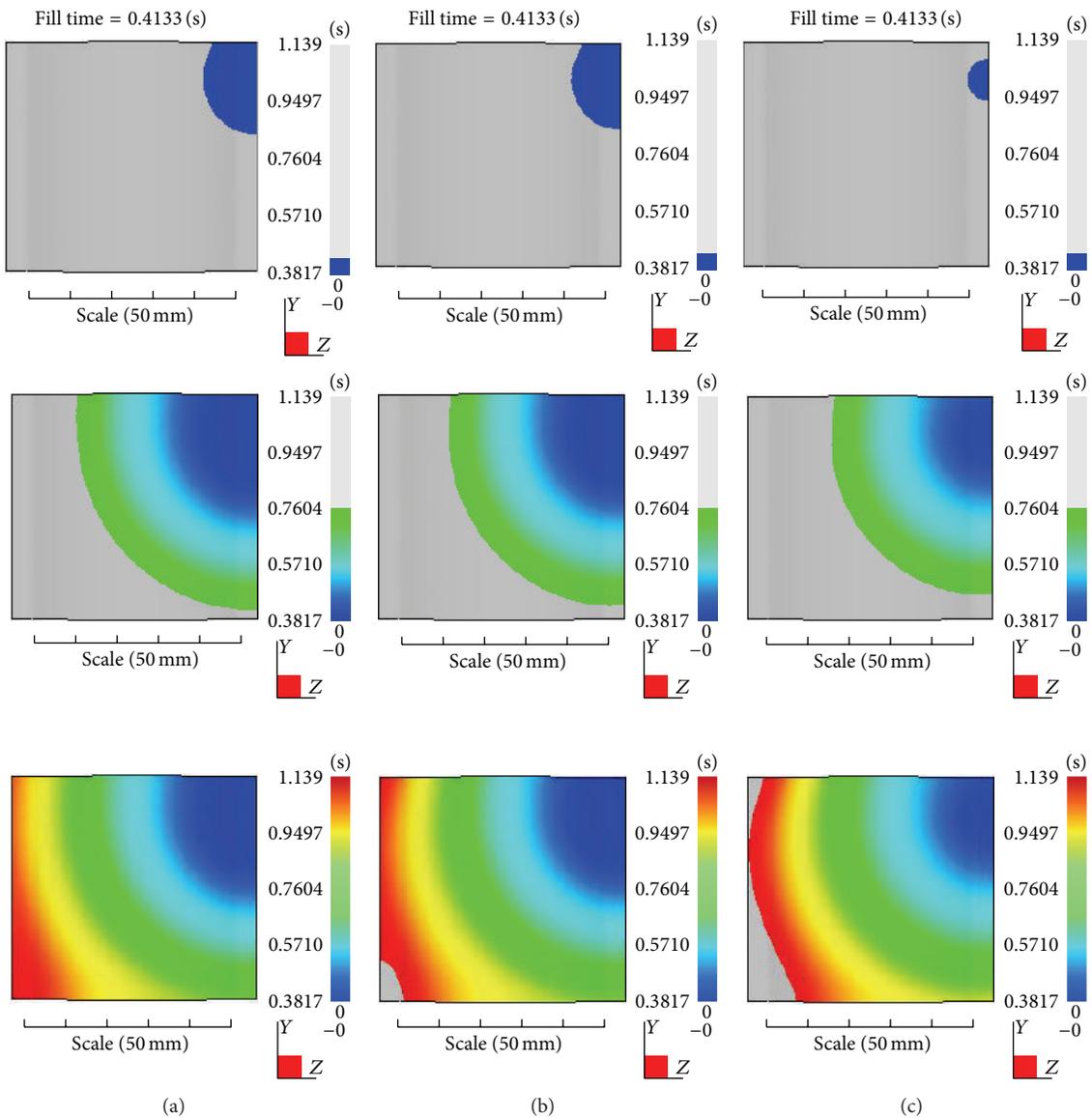


FIGURE 4: Filling phase for (a) PP, (b) PP + 10 wt% glass fibre, and (c) PP + 50 wt% wood.

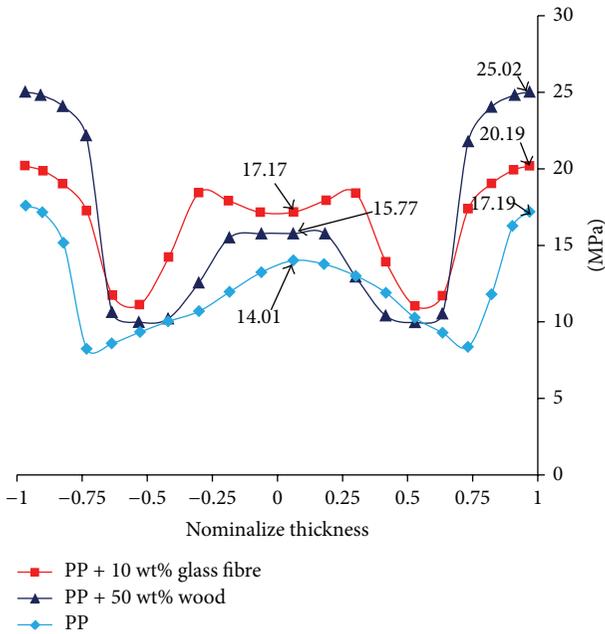


FIGURE 5: The residual tensile stress distribution occurs at the centre of the surface of the thin-walled parts for PP, PP + 10 wt% glass fibre, and PP + 50 wt% wood.

packing, and cooling stages. The orientation of the glass or wood filler through the thickness can be quite complex depending on the flow direction, which influences the determination of the arrangement of filler: either random, parallel, or perpendicular. In addition, anisotropic materials exhibit different properties in their principal shrinkage directions compared to isotropic materials.

The results show that the glass fibre-filled polymer composite exhibits less shrinkage changes. Because glass fibre has a lower coefficient of thermal expansion, the polymer compound also tends to have lower shrinkage as a result of the glass fibre having predominant alignment in the parallel direction that is dependent on the flow direction between wall surface and core regions. Filled polymer composites, such as PP + 10 wt% glass fibre and PP + 50 wt% wood, possess lower coefficients of thermal expansion, which will be reflected in lower changes in volumetric shrinkages during the solidification process compared to the PP polymer. Therefore, the addition of one or more fillers to a neat resin can be used to reduce the volumetric shrinkages of polymers and to increase the dimensions of the moulded parts, particularly in moulded thin-walled parts.

3.4. Warpage Simulation. The structural rigidity of a thin-walled part is greatly reduced due to the reduction in the section modulus. There are several potential solutions to increase the structural rigidity, such as using a glass- or wood-reinforced polymer compound, determining behaviour of residual stresses and volumetric shrinkage, optimising the moulding parameters, and emphasising the design process. When a moulded part distorts or deflects out of plane, warpage is occurring. In reality, the warpage problem can be

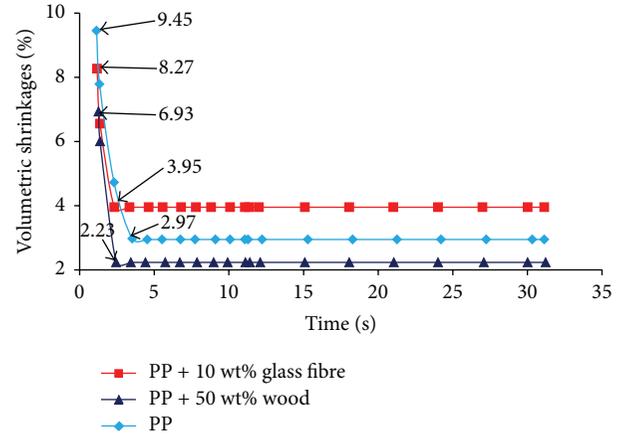


FIGURE 6: The residual volumetric shrinkages distribution occurs at the centre of the surface of the thin-walled parts for PP, PP + 10 wt% glass fibre, and PP + 50 wt% wood.

more difficult to predict and correct. Timothy [29] noted that the rigidity of a thin-walled part will still depend on the wall thickness and design specification, both of which dominate over the effect of fibre reinforcement or the resin used. Nevertheless, the results show that the warpage problem has a dependence on the residual stresses and volumetric shrinkage distribution behaviours, particularly for thin-walled parts.

The results in Figure 7 show that the maximum warpage on a thin-walled part is 0.43 mm for PP + 50 wt% wood, which is higher than PP and PP + 10 wt% glass fibre (0.36 mm and 0.29 mm, resp.). However, this high deflection resulting from PP + 50 wt% wood does not occur in the critical area of the thin-walled part compared with PP + 10 wt% glass fibre, as shown in Figure 7. Taking into account the structural rigidity of thin-walled parts, the high deflection should be prevented from forming along the curved surface of the part.

Visualisation of the simulation results shows that the minimum warpage distribution appears more uniform for the moulded thin-walled part using PP + 50 wt% wood than for that using PP + 10 wt% glass fibre and PP. The filler with fine powder form type results in dispersion with uniformity in moulding a thin-walled part. This was consistent with the finding of Rozman et al. [26], in which the enforcement of natural ingredients in fine powder form type can provide more uniform dispersion in a polymer matrix and provide an improvement in mechanical properties compared with the filler in the coarse fibre form type. Furthermore, the fillers materials in the coarse fibre form type tend to cluster or aggregate, specifically in moulded thin-walled parts.

The discussion will be focused in terms of improving the structural rigidity of thin-walled parts. The results reveal that the warpage at the midpoint of the part surface injected using PP + 50 wt% wood is 0.04 mm lower than that value of 0.08 mm using PP + 10 wt% glass fibre. This phenomenon can be attributed to changes in the distribution of residual stresses that occur in the core regions: PP + 50 wt% wood is 15.77 MPa lower than PP + 10 wt% glass fibre (17.17 MPa). Furthermore, the volumetric shrinkages of PP + 10 wt% of glass fibre are

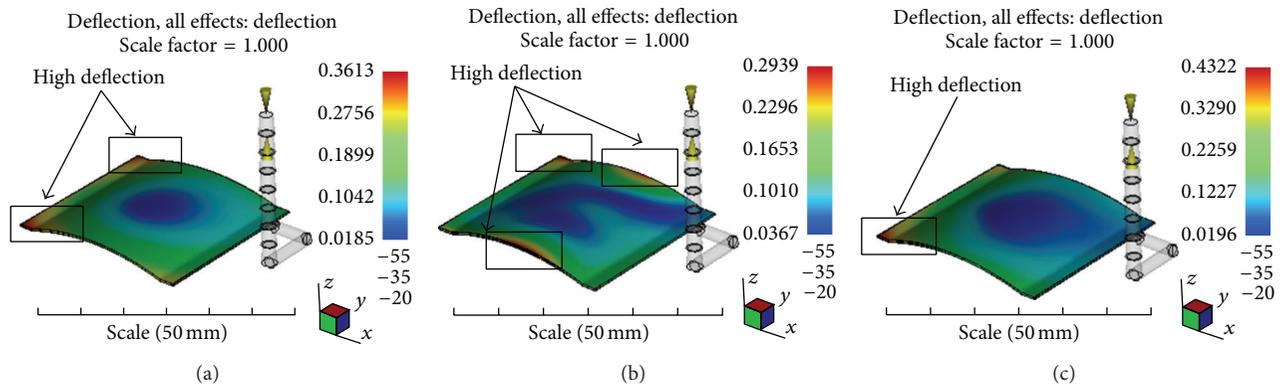


FIGURE 7: The distribution of warpages on the thin-walled parts for (a) PP, (b) PP + 10 wt% glass fibre, and (c) PP + 50 wt% wood.

observed to begin to become uniform at 3.95% from 2.3 sec, which is faster than that of PP + 50 wt% wood at 2.23% from 2.5 sec take longer or more time. More time required for the solidification process tends to minimise warpages occurring at the regions. Therefore, the results of constant volumetric shrinkage for PP + 50 wt% wood are lower than PP + 10 wt% glass fibre, which significantly affect the value of warpage at that location.

4. Conclusions

In conclusion, this study shows that unfilled and filled polymer PP composites are suitable for moulding thin-walled parts. The PP without filler filled the fastest, with a fill time of 1.139 sec. In contrast, the residual stress results show that the polymer composite has higher stress than the unfilled one. The residual tensile stress formed by PP + 50 wt% wood is approximately 25 MPa higher than the values of 20.2 MPa and 17.2 MPa for PP + 10 wt% glass fibre and PP, respectively, which occurred near the wall at both sides of the parts. However, the residual tensile stress of PP + 50 wt% wood was low (15.8 MPa) compared to that of PP + 10 wt% glass fibre (17.2 MPa) near the core of the thickness direction. Furthermore, some fillers in PP can be used to influence the amount of shrinkage that a material exhibits for the moulding of thin-walled parts. The value of the volumetric shrinkage change (%VS max – %VS min) of PP + 10 wt% of glass fibre was low (4.32%) compared to those of PP + 50 wt% wood and PP (4.7% and 6.48%, resp.). Visualisation of the simulation results revealed that the minimum warpage distribution appears to be more uniform for moulded thin-walled parts using PP + 50 wt% wood than for those using PP + 10 wt% glass fibre and PP. The high deflection resulting from PP + 50 wt% wood does not occur in the critical area of the thin-walled part compared with PP + 10 wt% glass fibre. In addition, the results revealed that the warpage at the midpoint of the part surface injected using PP + 50 wt% wood is 0.04 mm lower than the value of 0.08 when using PP + 10 wt% glass fibre. Finally, the results revealed that the existing warpage has a close relationship with the formation of residual stresses and volumetric shrinkages in moulded thin-walled parts.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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Review Article

A Review on Natural Fiber Reinforced Polymer Composite and Its Applications

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Natural fibers are getting attention from researchers and academician to utilize in polymer composites due to their ecofriendly nature and sustainability. The aim of this review article is to provide a comprehensive review of the foremost appropriate as well as widely used natural fiber reinforced polymer composites (NFPCs) and their applications. In addition, it presents summary of various surface treatments applied to natural fibers and their effect on NFPCs properties. The properties of NFPCs vary with fiber type and fiber source as well as fiber structure. The effects of various chemical treatments on the mechanical and thermal properties of natural fibers reinforcements thermosetting and thermoplastics composites were studied. A number of drawbacks of NFPCs like higher water absorption, inferior fire resistance, and lower mechanical properties limited its applications. Impacts of chemical treatment on the water absorption, tribology, viscoelastic behavior, relaxation behavior, energy absorption flames retardancy, and biodegradability properties of NFPCs were also highlighted. The applications of NFPCs in automobile and construction industry and other applications are demonstrated. It concluded that chemical treatment of the natural fiber improved adhesion between the fiber surface and the polymer matrix which ultimately enhanced physicochemical and thermochemical properties of the NFPCs.

1. Introduction

The increase in environmental consciousness and community interest, the new environmental regulations and unsustainable consumption of petroleum, led to thinking of the use of environmentally friendly materials. Natural fiber is considered one of the environmentally friendly materials which have good properties compared to synthetic fiber [1].

A late current industry research identified that the worldwide natural fiber reinforced polymer composites industry sector reached U\$2.1 billion in 2010. Current pointers are that interest in NFPCs industry will keep on growing quickly around the world. The utilization of NFPCs has expanded considerably in the shopper merchandise as developing industry sectors throughout the last few years. As indicated by evaluations, over 5 years (2011–2016), the NFPCs industry is estimated to grow 10% worldwide [2].

Natural fibers in simple definition are fibers that are not synthetic or manmade. They can be sourced from plants or animals [3]. The use of natural fiber from both resources, renewable and nonrenewable such as oil palm, sisal, flax, and jute to produce composite materials, gained considerable attention in the last decades, so far. The plants, which produce cellulose fibers can be classified into bast fibers (jute, flax, ramie, hemp, and kenaf), seed fibers (cotton, coir, and kapok), leaf fibers (sisal, pineapple, and abaca), grass and reed fibers (rice, corn, and wheat), and core fibers (hemp, kenaf, and jute) as well as all other kinds (wood and roots) [4]. The most common and commercially natural fibers in the world and world production have been shown in Table 1.

Fiber reinforced polymer matrix got considerable attention in numerous applications because of the good properties and superior advantages of natural fiber over synthetic fibers in term of its relatively low weight, low cost, less

TABLE 1: Natural fibers in the world and their world production [4].

Fiber source	World production (10^3 ton)
Bamboo	30.000
Sugar cane bagasse	75.000
Jute	2300
Kenaf	970
Flax	830
Grass	700
Sisal	375
Hemp	214
Coir	100
Ramie	100
Abaca	70

damage to processing equipment, good relative mechanical properties such as tensile modulus and flexural modulus, improved surface finish of molded parts composite, renewable resources, being abundant [5], flexibility during processing, biodegradability, and minimal health hazards. NFPCs with a high specific stiffness and strength can be produced by adding the tough and light-weight natural fiber into polymer (thermoplastic and thermoset) [6]. On the other hand, natural fibers are not free from problems and they have notable deficits in properties. The natural fibers structure consists of (cellulose, hemicelluloses, lignin, pectin, and waxy substances) and permits moisture absorption from the surroundings which causes weak bindings between the fiber and polymer. Furthermore, the couplings between natural fiber and polymer are considered a challenge because the chemical structures of both fibers and matrix are various. These reasons for ineffectual stress transfer during the interface of the produced composites. Accordingly, natural fiber modifications using specific treatments are certainly necessary. These modifications are generally centered on the utilization of reagent functional groups which have ability for responding of the fiber structures and changing their composition. As a result, fiber modifications cause reduction of moisture absorption of the natural fibers which lead to an excellent enhancement incompatibility between the fiber and polymer matrix [7].

The wide applications of NFPCs are growing rapidly in numerous engineering fields. The different kinds of natural fibers reinforced polymer composite have received a great importance in different automotive applications by many automotive companies such as German auto companies (BMW, Audi Group, Ford, Opel, Volkswagen, Daimler Chrysler, and Mercedes), Proton company (Malaysian national carmaker), and Cambridge industry (an auto industry in USA). Beside the auto industry, the applications of natural fiber composites have also been found in building and construction industry, sports, aerospace, and others, for example, panels, window frame, decking, and bicycle frame [8].

In a review of chemical treatments of natural fibers, Kabir and coworkers [9] concurred that treatment is an important factor that has to be considered when processing natural

fibers. They observed that fibers loose hydroxyl groups due to different chemical treatments, thereby reducing the hydrophilic behavior of the fibers and causing enhancement in mechanical strength as well as dimensional stability of natural fiber reinforced polymer composites. Their general conclusion was that chemical treatment of natural fibers results in a remarkable improvement of the NFPCs.

2. Natural Fiber Reinforced Composites (NFPCs)

Natural fiber polymer composites (NFPC) are a composite material consisting of a polymer matrix embedded with high-strength natural fibers, like jute, oil palm, sisal, kenaf, and flax [10]. Usually, polymers can be categorized into two categories, thermoplastics and thermosets. The structure of thermoplastic matrix materials consists of one or two dimensional moleculars, so these polymers have a tendency to make softer at an raised heat range and roll back their properties throughout cooling. On the other hand, thermosets polymer can be defined as highly cross-linked polymers which cured using only heat, or using heat and pressure, and/or light irradiation. This structure gives to thermoset polymer good properties such as high flexibility for tailoring desired ultimate properties, great strength, and modulus [3, 4]. Thermoplastics widely used for biofibers are polyethylene [11], polypropylene (PP) [12], and poly vinyl chloride (PVC); hereas phenolic, polyester, and epoxy resins are mostly utilized thermosetting matrices [10]. Different factors can affect the characteristics and performance of NFPCs. The hydrophilic nature of the natural fiber [5] and the fiber loading also have impacts on the composite properties [13]. Usually, high fiber loading is needed to attain good properties of NFPCs [14]. Generally, notice that the rise in fiber content causes improving in the tensile properties of the composites [8]. Another vital factor that considerably impacts the properties and surface characteristics of the composites is the process parameters utilized. For that reason, appropriate process techniques and parameters should be rigorously chosen in order to get the best characteristics of producing composite [10]. The chemical composition of natural fibers also has a big effect on the characteristics of the composite represented by the percentage of cellulose, hemicellulose, lignin, and waxes. Table 2 shows the chemical composition of some common natural fibers [4].

Many researchers [8, 11, 15–17] have examined and researched the suitability, competitiveness, and capabilities of natural fibers embedded in polymeric matrices. The researchers [4, 18, 19] concentrated on the effect of the fiber surface modifications as well as manufacturing processes in improving fiber/polymer compatibility. On the other hand, some researchers studied and compared between different natural fiber composites and their stability in various applications [20]. Al-Oqla and Sapuan [20] investigated the properties of jute/plastic composites such as crystallinity, fiber modification, thermal stability, weathering resistance, durability, in addition to their suitability to the automotive industry throughout ecodesign components. while Mohanty et al. [21] studied the effects of jute fiber on the mechanical properties

TABLE 2: Chemical composition of some common natural fibers [4].

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Ligning (wt%)	Waxes (wt%)
Bagasse	55.2	16.8	25.3	—
Bamboo	26–43	30	21–31	—
Flax	71	18.6–20.6	2.2	1.5
Kenaf	72	20.3	9	—
Jute	61–71	14–20	12–13	0.5
Hemp	68	15	10	0.8
Ramie	68.6–76.2	13–16	0.6–0.7	0.3
Abaca	56–63	20–25	7–9	3
Sisal	65	12	9.9	2
Coir	32–43	0.15–0.25	40–45	—
Oil palm	65	—	29	—
Pineapple	81	—	12.7	—
Curaua	73.6	9.9	7.5	—
Wheat straw	38–45	15–31	12–20	—
Rice husk	35–45	19–25	20	—
Rice straw	41–57	33	8–19	8–38

of pure biodegradable polymer (Biopol), the mechanical properties of the resulted composites, impact strength, tensile strength, and bending strength, showed an increase when compared with pure Biopol. The tensile strength of jute Biopol was enhanced by 50%, while bending strength and impact strength of the composites were enhanced by 30% and 90% in comparison to pure Biopol.

3. General Characteristics of NFPCs

The properties of natural fiber composite are different to each other according to previous studies, because of different kinds of fibers, sources, and moisture conditions. The performance of NFPCs relies on some factors, like mechanical composition, microfibrillar angle [20], structure [10], defects [22], cell dimensions [23], physical properties [4], chemical properties [24], and also the interaction of a fiber with the matrix [25]. Since every product in market has drawbacks, similarly, natural fiber reinforced polymer composites also have drawbacks. The couplings between natural fiber and polymer matrix are problem taken into consideration, as a result of the difference in chemical structure between these two phases. This leads to ineffective stress transfer during the interface of the NFPCs. Thus, the chemical treatments for the natural fiber are necessary to achieve good interface properties. The reagent functional groups in the chemical treatments have ability to react on the fiber structures and alter the fiber composition [9]. Natural fibers include a functional group named as hydroxyl group which makes the fibers hydrophilic. During manufacturing of NFPCs, weaker interfacial bonding occurs between hydrophilic natural fibre and hydrophobic polymer matrices due to hydroxyl group in natural fibres. This could produce NFPCs with weak mechanical and physical properties [8].

3.1. Mechanical Properties of the NFPCs. There are considerable enhancement and suggestions for the natural fibers that

can be implemented in order to enhance their mechanical properties resulting in high strength and structure. Once the base structures are made strong, the polymers can be easily strengthened and improved [26]. There are number of aspects that effects of composite are performance level or activities, of which to name a few are the following;

- (a) orientation of fiber [5],
- (b) strength of fibers [8],
- (c) physical properties of fibers [27],
- (d) interfacial adhesion property of fibers [28] and many more.

NFPCs are such composites whose mechanical efficiency is dependent upon the interface provided by fiber-matrix along with the stress transfer function in which stress is transferred to fiber from matrix. This has been reported by many investigators in several researches [1, 23, 29]. Characteristic components of natural fibers such as orientation [30], moisture absorption [31], impurities [32], physical properties [33], and volume fraction [34] are such features that play a constitutive role in the determination of NFPCs mechanical properties. Mechanical properties of PLA, epoxy, PP, and polyester matrices can be affected by many types of natural fibers and to show some of them, Figure 1 is included.

NFPCs show even better mechanical properties than a pure matrix in cases where jute fibers are added in PLA (polylactic-acid); in this case, 75.8% of PLA's tensile strength was improved; however, introduction or incorporation of flax fibers showed a negative impact on this addition. The addition of flax fibers resulted in 16% reduced tensile strength of the composites. Conversely, composites of PP were improved with the incorporation of hemp, kenaf, and cotton [5]. By far, maximum improvement is only seen in such composites where jute or polyester has been incorporated where a total of 121% improvement is evident compared to pure polyester [5].

TABLE 3: Physicomechanical properties of natural fibers [38].

Fiber	Density (g/cm ³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
OPEFB	0.7–1.55	248	3.2	2.5
Flax	1.4	88–1500	60–80	1.2–1.6
Hemp	1.48	550–900	70	1.6
Jute	1.46	400–800	10–30	1.8
Ramie	1.5	500	44	2
Coir	1.25	220	6	15–25
Sisal	1.33	600–700	38	2–3
Abaca	1.5	980	—	—
Cotton	1.51	400	12	3–10
Kenaf (bast)	1.2	295	—	2.7–6.9
Kenaf (core)	0.21	—	—	—
Bagasse	1.2	20–290	19.7–27.1	1.1
Henequen	1.4	430–580	—	3–4.7
pineapple	1.5	170–1672	82	1–3
Banana	1.35	355	33.8	53

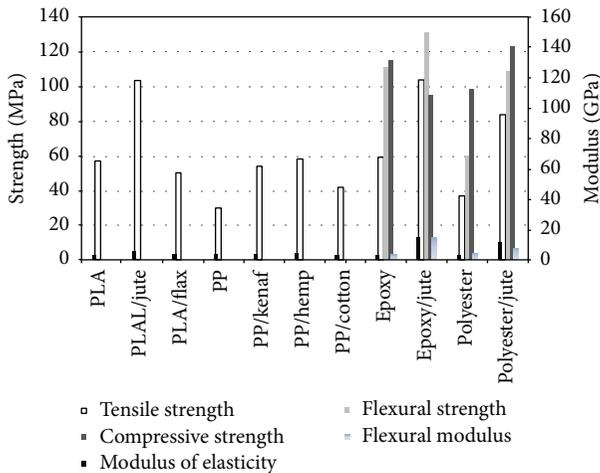


FIGURE 1: Some of mechanical properties of natural fiber reinforced polymer composite [5].

However, due to the rubber phase present in gum compound, a greater range of flexibility is present in such materials which results in reduced stiffness and storage modulus.

It is also known that stiffness and stress transfer in composites increases with an increased or excessive addition of fiber which provides a better loss modulus and also a better storage modulus. The loss modulus is also considered to be increased with fiber addition up to 756 MPa at 50 phr fiber loading compared to the loss modulus of gum that is 415 MPa [8].

A group of researchers led by Ismail et al. [37] studied the effect of size and filler content on fiber characteristics that cures a wound or any part of the body. Along with this, mechanical properties of Oil Palm Wood Flour (OPWF) was also examined which is reinforced with (ENR) epoxidized natural rubber composites. When the fiber content is increased, torque of the fibers is also increased and with smallest possible particle size of OPWF, highest torque

was noticed. However, increasing the factor of OPWF in ENR compounds showed reduced tensile strength and while reaching the break point a considerable elongation is evident. It also evident increase in elongation, tear strength, tensile modulus and hardness due to higher loading of OPWF. A higher tensile strength and tear strength as tensile modulus were identified in composites that were filled with even smallest proportion of OPWF [10]. The fracture behavior of composites is also affected due to the nonlinear mechanical behavior of natural fibers, under the influence of tensile-shear loads [1]. Table 3 shows the mechanical properties for common types of natural fiber in the world [38].

The bonding strength between fiber and polymer matrix in the composite is consider a major factor in order to get superior fiber reinforcement composites properties. Because of pendant hydroxyl and polar groups in fiber, this leads to extremely high moisture absorption of fiber, resulting in weak interfacial bonding between the fiber and the hydrophobic matrix polymers. To develop composites with good mechanical properties, chemical modification of fibre carried out to reduce the hydrophilic behavior of fibers and the absorption of moisture [15, 39].

The different surface treatments of advanced composites applications were reviewed by several researchers [40–42]. The effects of different chemical treatments on cellulosic fibers that were employed as reinforcements for thermoplastics and thermoset were also examined. For the treatments, the different kinds of chemical treatment include silane [43], alkali [44], acrylation [45], benzoylation [46], maleated coupling agents [47], permanganate [48], acrylonitrile and acetylation grafting [49], stearic acid [50], peroxide [51], isocyanate [52], triazine [53], fatty acid derivate (oleoyl chloride), sodium chloride, and fungal [9]. The main purpose of surface treatments of natural fibers to enhanced fibre/matrix interfacial bonding and stress transferability of the composites.

The impact of alkaline treatment on surface properties of Iranian cultivated natural fibers was studied by

Cordeiroa et al. [54]. The research revealed that alkaline treatment gets rid of some chemical components on the surface of the fibers, comprising uranic acid (hemicellulose), aromatic moieties (extractives), and nonpolar molecules from the partial lignin depolymerisation. There is a stronger effect on chemical components of nonwood fibers. Improving the crystallinity of nonwood fibers, in the softwood fibers result in only a minor increase. Hence, alkaline treatment can result in a remarkable improvement in the specific interaction of the fibers as well as improving the fibers' wettability.

Le Troedec et al. [55] revealed the effects of some chemical treatments, comprising ethylenediaminetetraacetic acid (EDTA), NaOH, polyethylene imine (PEI), CaCl_2 , and $\text{Ca}(\text{OH})_2$. The effects were on the mechanical properties of the composite materials from mixtures of hemp fiber and lime by differential thermal evaluation and tests. The observation was that every treatment had a direct effect on the fiber surface. The treatment was with 6% NaOH and led to cleaning fibers by removing the amorphous compounds, and the increase of the crystallinity index of fiber bundles, while the EDTA treatment led to separates fibers and complex calcium ions related to pectins. In brief, PEI treatment shows all studied properties an intermediate character and lime water treatment depicts calcium ions' fixation at the surface of fibers in comparison to a calcium chloride treatment which does not.

May-Pat et al. [1] reported on the impact of the interphase properties from well controlled surface treatment in the case of natural fibers. The fracture behavior and the mechanical properties of a NFPC depend on the properties of constituents and region of the fiber surface, or interphase, where the stress transfer occurs. Furthermore, the tailoring of the interphase by different kinds of surface treatments and carefully characterizing it provides a better knowledge of the behavior of the NFPCs. Moreover, different fiber surface treatments modify the natural fiber microstructure specifically under high loading rates.

Venkateshwaran et al. [35] studied the effect of alkali (NaOH) treatments of various concentrations (0.5%, 1%, 2%, 5%, 10%, 15%, and 20%) on the mechanical properties of banana/epoxy composite. The results reported that as compared to other treated and untreated fiber composites, 1% NaOH treated fiber reinforced composites have a better properties. The alkali concentration on the fiber surfaces results in better mechanical properties of the resulted composite. However, the rising of alkali concentration maybe causes fiber surface damage, leading to a decrease of mechanical properties. The effect of different chemical treatment on the mechanical properties and characteristic of sisal-oil palm hybrid fiber reinforced natural rubber composites have been studied by John et al. [56]. With chemical treatment, the torque values increased which lead to greater crosslinking. Similarly, alkali treatment showed a rise in the composites' tensile strength in comparison to untreated composites and with 4% NaOH treated fibers, optimum tensile strength was seen for resulted composites. In contrast, for composites treated with 4% NaOH a strong interface is apparent because of a more superior adhesion between rubber and fiber is present which avoids solvent entry and a little swelling occurs.

Van de Weyenberg et al. [24] examined the impact of flax processing parameters, and the fiber treatment, on the mechanical properties of flax fiber reinforced epoxy composites. It was discovered that the employment of long flax slivers may not necessarily lead to more superior composite properties. The highest enhancement of the flexural properties of the flax fiber reinforced epoxy composites can be gotten by chemical treatments. There was an increase of transverse strength of up to 250% and transverse modulus, of up to 500%. In addition, the longitudinal properties of the UD composites (both modulus and strength) showed improvements with 40% or more.

Some modifications in the chemical and physical properties of the lignocellulosic fibers can be observed after the treatment of the fiber of rubber wood with laccase enzymes. These chemical treatments lead to the amorphous lignin content, changing the hemicellulose content and ultimately the natural crystallinity [57]. The fiber has treatment effect on morphological and single fiber tensile strength of EFB fiber. The EFB fiber treated with boiling water, 2% sodium hydroxide (NaOH), and mixing of boiling water and NaOH was examined by Norul Izani et al. [13]. It was revealed that it changed the properties of the fiber surface topography after the treatment. Compared to untreated EFB fiber, the treated EFB fibers with the two types of treatment were more thermal stability. On the other hand, the tensile strength and Young's modulus of the treated fiber showed a rise in comparison to untreated fibers. For tensile modulus, the alkaline treatment has enhanced the tensile properties of sugar palm fiber reinforced epoxy composites at better soaking times and concentrations of alkaline. On the other hand, the increase the alkaline concentration may lead to fiber damage [58].

Acrylonitrile Butadiene Styrene (ABS) with the coating effect of OPEFB fibers was tested BT. The coated process enhanced the mechanical and physical properties and also improved the fiber performance. The ABS treatment led to reducing the water absorption and also decreased the biodegradation potential of the fiber in contact with soil. With the coating, the tensile strength and elasticity moduli of the OPEFB fibers became better than what they were in the past. The surface area between fiber and soil particles increased by coating fiber, which led to improving the shear strength parameters of the fiber reinforced soils [66].

3.2. Flame Retardant Properties of the NFPCs. Due to eco-friendly and sustainability nature, natural fiber composites prefers as compared to conventional synthetic fibre based composites. They are applied in diversified domains [9, 18, 20, 38, 67] such as building materials [68], aerospace industry, and automotive industry [69]. Natural fibers and polymers are organic materials and are very sensitive to alter any features if flame is introduced to them. Flame retardancy is another aspect that has become greatly significant in order to fulfill safety measures taken while developing natural fiber composites.

In the presence of flame, burning of composites takes place in five different steps as shown below:

(a) Heating.

- (b) Decomposition.
- (c) Ignition.
- (d) Combustion.
- (e) Propagation [70].

If flame retardancy has been achieved in the aforementioned steps, no matter whether ignition step has been conducted or not, the procedure will be terminated before an actual ignition is set up. There are two forms of products that are obtained upon burning of composites; these two include high cellulose content and high lignin content. High cellulose provides chances of higher flammability whereas higher values of lignin show there is a greater chance of char formation [71]. Thermal resistance is provided by flax fibers [72]; however, silica or ash is another important feature that is helpful in extinguishing fire [73].

In order to enhance fire resistance of various NFPCs, different procedures are undertaken. Fire barriers are kind of barriers that can be applied to phenolics, ceramics, intumescent, glass mats, silicone, ablatives, and chemical additives too. Coatings and additives used in the system of intumescent are found to be very promising fire barrier treatments in which these barriers are expanded upon heating resulting in a cellular surface that is charred even. However, with the help of this charred surface, internal or underlying components and protected against flux and heat.

One of the well-known or profound flame retardants for reinforced polymers (natural fibers) is used with the combination of char developing cellulose material [74]. The only method of reducing combustion in this scenario is through increasing stability and char formation in the polymer. This will result in reduced flammability, decrease visible smoke, and restrict the volume of products produced due to combustions [72]. Fire retardant coating is another method that helps in enhancement of fire resistance property of composites. This coating is done at the end or finishing stage or impregnation. Due to changes in the fibers and lingo-cellulosic particles, fire resistance is altered during the process of manufacturing [75].

The two most widely used metal hydroxide flame retardants are known to be aluminum hydroxide $[\text{Al}(\text{OH})_3]$ and magnesium hydroxide $[\text{Mg}(\text{OH})_2]$ which are purposefully added to polymers. The chemical reaction through which these two flame retardants decompose are as follows:



Out of these two flame retardants, magnesium hydroxide display better thermal stability as compared to aluminum hydroxide since the temperature range given off by the decomposition of magnesium hydroxide is nearly 300–320 degrees centigrade ($^{\circ}\text{C}$) which is much higher than the temperature range offered by aluminum hydroxide that is only 200°C . For this reason, aluminum hydroxide is not considered to be thermally stable as it cannot be used for polyamides, polypropylene, or others whereas magnesium hydroxide can be used.

It was also shown in a research that the addition of expandable graphite (EG) and ammonium polyphosphate (APP) in composite polymer as a source of flame retardant (FR) helps in enhancing flax fiber reinforced PP composite's property of fire retardancy. It was also shown that heat release rate (HRR) in a composite additive of 30 wt% of flax fiber and 25 wt% of EG (expandable graphite) was decreased to 35 from 167 kW/m^2 [76].

Spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine (SPDPM) is a type of intumescent flame retardant for PLA that was studied by Zhan et al. [77]. Char formation that is a result of spirocyclic pentaerythritol bisphosphorate disphosphoryl melamine (SPDPM), an active component of flame retardancy, enhances antidripping performance of PLA and flame retardancy too with an addition of 25 wt%. Flame retardancy is not an easy thing to be imparted and it is only possible if there is an extensive high loading of inorganic filler.

Hapuarachchi and Peijs [78] studied the development of fully bio-based natural fiber composite that has enhanced features of fire or flame retardancy. This natural fiber composite was developed with the help of PLA polymers that were derived from crops accompanied with 2 kinds of nanofillers which are able to produce synergy corresponding to flame retardancy. Upon analysis, after incorporating hemp fiber mat in PLA resin, decrease in PHRR (peak heat release) in calorimeter will be shown.

3.3. Biodegradability of the NFPCs. High strength composites are resultant products of natural fiber reinforcement in polymers which also provide extra or improved biodegradability, low cost, light weight, and enhanced properties related to mechanical structure [29]. At temperatures as high as 240°C , natural fibers start degrading whereas constituents of fiber, such as hemicelluloses, cellulose, lignin, and others, start degrading at different levels of temperature; for example, at 200°C lignin starts to decompose whereas at temperatures higher than this other constituents will also degrade [9].

Since thermal stability of the fibers is dependent on the structural constituents of fibers, it can be improved if the concentration levels or the structural constituents are completely removed, such as lignin and hemicelluloses. This can be achieved with the help of chemical treatments. Development of fibers and materials that provide services are two important aspects which should be considered while degrading natural fibers [9]. Natural fibers have a short lifetime with minimum environmental damage upon degradation whereas synthetic ones affect environment due to pollution caused by degradation. Lignin, hemicelluloses, and cellulose concentrations or composition affect thermal degradation features of lingo-cellulosic materials [13]. More than fifty percent weight of jute or Biopol composite is lost after exactly 1500 days of burial [21].

3.4. Energy Absorption of the NFPCs. High strength, energy absorption, and stiffness are obtained by composite materials which are widely used in automotive and motorsport sectors of industry mainly due to the property of mass reduction [79].

Enhanced energy absorption is evident from the increased volume fraction that is only possible in the presence of low speed such as 2.5 m/s [80]. On the other hand, at high speeds, such as 300 m/s, similar performance is shown by flax, jute, and hemp, but jute showed brittleness and low strength of fibers [81]. Potential of NFPCs that is required for application in providing sustainable energy absorption was investigated by Meredith et al. While keeping focus on motorsport [80]. Vacuum Assisted Resin Transfer Molding (VARTM) technique is used to test conical specimens of flax, jute, and hemp for their properties and features. Various values exhibited by different kinds of materials were recorded to analyze specific energy absorption (SEA).

3.5. Tribology Properties of NFPCs. Since every material has some wear and friction properties that degrade with respect to time, the tribological loadings are important to consider for an improved mechanical part design [5]. Around 90% failure is obtained due to differences in tribological loading conditions which alters their wear and friction properties [82]. Reinforcement is a method with which fiber's or polymers tribological properties are altered (either positively or negatively) [83]. Studies on different kinds of tribological analysis have been conducted on fibers including kenaf/epoxy [84], betelnut fiber reinforced polyester [85], sisal/phenolic resin [86], sugarcane fiber reinforced polyester (SCR) [87], and cotton/polyester [88]. Improvement in wear performance of PLA was evident due to the addition of natural fibers in which wear rate of composites was quite low in comparison to wear rate at higher loads on neat PLA [82].

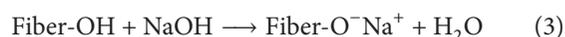
Kenaf fibers reinforced with epoxy composite were used by Chin and Yousif [84] for a kind of bearing application, in which they showed an 85% enhancement of wear performance and normal orientation in composites. Wear and friction features of glass fiber/polyester (GRP) and sugarcane fiber/polyester (SCR) were studied by El-Tayeb with different parameters including speed, the time taken for test, and load [87]. The research results concluded SCR as a competitor of GRP composite. The same characteristics were studied by Xin et al. [86] for sisal fiber reinforced resin brake composites which showed sisal fiber can be used instead of asbestos in brake pads [89, 90].

Laminated composites were developed with the help of three different natural fibers such as grevia, nettle, optiva, and sisal. This connection of natural fibers was studied by Bajpai et al. in which a hot compression procedure was used to incorporate three different materials in a PLA polymer [82]. Friction and wear features of composites were examined under different situations such as dry contact condition with varying operating parameters. Due to an option of variable operating parameters, applied load was varied in between range of 10 to 30 N with a speed ranging from 1 to 3 m/s and sliding distance of thousand to three thousand meters. The research results showed infusion of natural fiber mats, in PLA matrix, is capable of enhancing wear and frictional behavior of neat polymers. An approximate reduction of 10–44% in the coefficient of friction with a greater reduction of 70% seen in developed composites for specific wear rate is visualized in comparison to neat PLA [82].

3.6. Water Absorption Characteristics of the NFPCs. Natural fibers work well as reinforcement in polymers. However, the main weakness of the application of natural fibers is their susceptibility to moisture [91]. Mechanical properties of polymeric composites have a strong dependence on the interface adhesion between the fiber and the polymer matrix [15]. The natural fibers are rich of cellulose, hemicelluloses, lignin, and pectins, all of which are hydroxy 1 groups; that is, they are usually hydrophilic sources and strong polar whilst polymers show considerable hydrophobicity. Thus, there are major challenges of suitability between the matrix and fiber that weakens interface region between matrices and natural fibers [5]. At the composite materials' outer layers, water absorption happens and decreases gradually into the bulk of the matrix. A generally high water intake by composite materials results in an increased weight of wet profiles, a conceivable decline in their strength, and increment in their deflection, swelling, and causing pressure on nearby structures. These can cause warping, buckling, bigger possibility of their microbial inhabitation, freeze, and unfreeze caused destruction of mechanical characteristics of composite materials [92].

Oil palm fiber natural rubber (OPF-NR) composites increased in the water absorption percentage corresponding to an increase in fiber loading because of the fibers' hydrophilicity. The absorption behavior of NR showed modifications from Fickian to non-Fickian with additional OPF because of the microcracks and the viscoelastic nature of the polymer [8]. In the woven pandanus/banana fabric composites tests, woven pandanus fabric composites increased the water uptake compared to woven banana fabric composites because of higher lignin content and hemicellulose, as well as the presence of defects in the composite system [93]. Furthermore, temperature can affect the percentage of water absorption of the composites. At 65% humidity at 21°C, the equilibrium moisture content of some natural fiber can be observed in Table 4 [4]. It was revealed that the water absorption of OPF-NR composite was less than of OPF-sisal fiber-NR hybrid biocomposite. The incorporation of sisal fiber that contains relatively more holocellulose (23%), which is exceptionally hydrophilic brought on more water intake. Besides, the lignin content material of OPF (19%) was bigger than sisal fiber (9%). Lignin being hydrophobic reduces the water absorption [8].

Many researchers [8, 56] showed the effect of coupling agent such as maleic anhydride polyethylene and chemical treatments such as bleaching, acetylation, and alkali treatment on reduction moisture absorption of NFPCs. The surface of the fibers is cleaned during the chemical treatments to ensure there are no impurities which increases the fiber surface roughness and preventing the moisture absorption via the removal of the coat of OH groups of fiber as seen in equation below [5, 9]:



Sreekala and Thomas [91] investigated the moisture absorption properties of OPEFB fiber in different temperature condition. They also studied the effect of different modification

TABLE 4: The equilibrium moisture content of different natural fiber at 65% relative humidity (RH) and 21°C [4].

Fiber	Equilibrium moisture content (%)
Sisal	11
Hemp	9.0
Jute	12
Flax	7
Abaca	15
Ramie	9
Pineapple	13
Coir	10
Bagasse	8.8
Bamboo	8.9

on OPEFB fiber, such as silane treatment, gamma irradiation, latex coating, mercerization, acetylation, peroxide treatment, and isocyanate treatment on moisture absorption properties. They concluded that all the treatment causes the seduction in moisture absorption properties in all temperatures.

The mercerization of OPF-sisal fiber-NR hybrid composites led to reducing water adsorption of the composite by improving the adhesive characteristics of fiber surface and also providing a large surface area which causes better mechanical interlocking [94]. Shinoj et al. [8] conducted the effect of chemical treatment for agave fibers on moisture adsorption before blending in a polymer matrix. The chemical treatment is achieved using four types of reagents, acetic anhydride (Ac), maleic anhydride (MA), styrene (S), and acrylic acid (AA). This paper concludes that the chemical treatment causes decrease in the global diffusivity of water and also concludes that the water mobility in the fiber core is more than at the surface.

3.7. Viscoelastic Behavior of the NFPCs. Dynamic mechanical measurements or the viscoelastic behavior over a range of temperatures provides valuable insight into the structure, morphology, and determination of the interface characteristics of natural fiber composite materials [95]. Storage modulus gives an insight into the load bearing capability and the stiffness behavior of natural fiber composite materials. Storage modulus is a measure of the maximum energy stored in the material during one cycle of oscillation. The mechanical damping coefficient is the ratio of the loss modulus to the storage modulus and is related to the degree of molecular mobility in the polymeric material. On the other hand, loss modulus is proportional to the amount of energy dissipated as heat by the sample [96].

The viscoelastic behavior of novel commingled biocomposites based on polypropylene/jute yarns is reported by [96]. By using commingling method, jute yarn reinforced polypropylene commingled composites were prepared. The viscoelastic behavior or dynamic mechanical properties of the result commingled composites were studied according to the fiber content and different kinds of chemical treatments such as potassium permanganate (KMnO_4), maleic anhydride modified polypropylene (MAPP), toluene diisocyanate

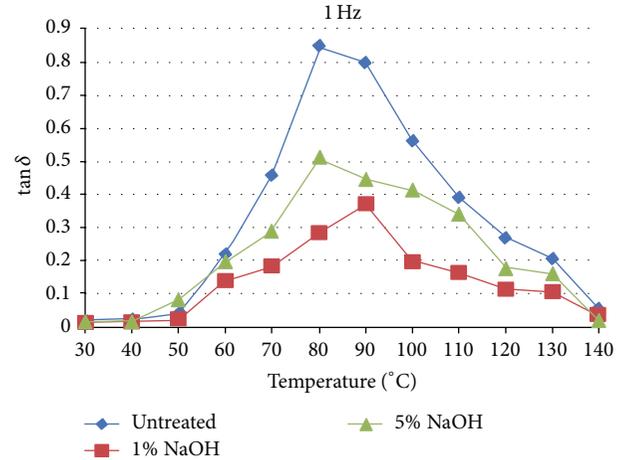


FIGURE 2: $\tan \delta$ versus temperature curves of the alkali treated and untreated composites at 1 Hz frequency [35].

(TDI), and stearic acid (ST). This study concluded that increasing of fiber content leads to increasing the storage and loss modulus of the composite. On the other hand, at all temperatures, the chemical treatment by KMnO_4 and MAPP leads to increasing the storage modulus and loss modulus of the respective treated composites than the untreated ones.

By using the dynamic mechanical analyzer, Venkateshwaran et al. [35] studied the impact of alkali treatments on the viscoelastic behavior of natural fiber composite. The corresponding viscoelastic properties were determined as a function of temperature and frequency when the measurements were executed in the tensile mode of the used equipment. At the temperature range of 30–140°C at 0.1, 1, and 10 Hz frequencies, respectively, the experiments executed the graphs plotted, as storage modulus (E') versus temperature and $\tan \delta$ versus temperature, as shown in Figures 2 and 3 [35].

3.8. Relaxation Behavior of the NFPCs. Natural fiber possesses an intrinsic relaxation behavior which has a main function in the stress relaxation of NFPCs. Thus, the tensile stress relaxation of the reinforcing fiber needs to be studied in detail [38]. Sreekala et al. [29], for instance, did such a study focusing on the character of individual OPEFB fiber and, in addition, examined the fiber surface modification effects, ageing, and strain level on the fiber relaxation behavior. The fibers stress relaxation was lessened significantly with surface treatments, like latex modification, and thus decreasing resulting physical interaction between the latex particles and fiber surface. Also, water and thermal ageing reduce the rate of relaxation for the oil palm fiber; the rate of stress relaxation of the OPEFB fiber was optimized at 10% strain level which is shown in Figure 4, while the relaxation modulus values for the fiber show similar trends as in the case of stress relaxation as shown in Figure 5. On the other hand, the stress relaxation rate of OPF-sisal fiber-NR hybrid composites showed a reduction with an increase in fiber percentage [97].

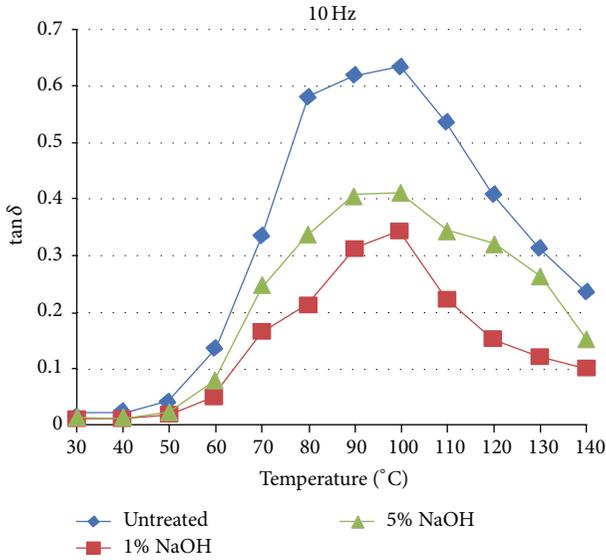


FIGURE 3: $\tan \delta$ versus temperature curves of alkali treated and untreated composites [35].

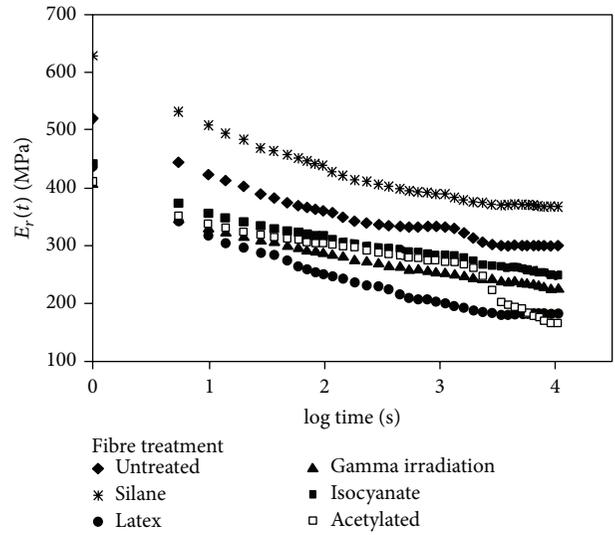


FIGURE 5: Relaxation modulus curves of untreated and treated OPEFB fiber at 10% strain [29].

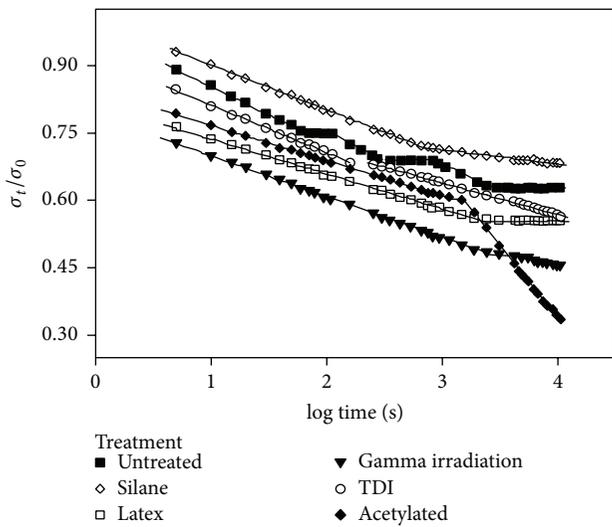


FIGURE 4: Stress relaxation curves of untreated and treated OPEFB fiber at 10% strain [29].

3.9. *Thermal Properties of NFPCs.* The untreated OPFs are thermally more stable when compared with treated ones, while OPF is considered thermally more stable compared to flax fibers and hemp fibers. Increase of temperatures from 20°C to 150°C causes increase of the heat capability of OPFs particularly from 1.083 J g⁻¹ °C⁻¹ to 3.317 J g⁻¹ °C⁻¹ [98]. The thermal diffusivity, thermal conductivity, and specific heat of the flax/HDPE composites lessened with a rise in fiber composition. However, the thermal conductivity and thermal diffusivity showed no significant changes in the range of 170–200°C. The biocomposites' specific heat showed gradual increase with temperature [4]. By using polycarbonate to generate functional composites, pineapple leaf fiber was the support. The changed pineapple leaf fibers composite,

treated with silane, showed the impact strengths and highest tensile. The composites' thermal stability is lower than the neat polycarbonate resin according to the thermogravimetric examination. Besides that, the thermal stability lessened with a rise in pineapple leaf fiber composition [4].

Enzymatic treatment for many natural fibers such as flax and hemp often natural fibers can lead to improvement in surface and thermal properties [56]. Hemicellulose and pectinase are the treatments which can improve the thermal properties of the fibers mentioned. The enzymes possess an attractive state for the improvement of the natural fibers' surfaces for natural fiber composite application [67].

Norul Izani et al. [13] studied the effect of chemical treatment on the morphological and tensile strength of the EFB fiber. The treatments were by the types of treatments, 2% sodium hydroxide (NaOH) and combination of both NaOH and boiling water. The chemical treatment by NaOH led to enhancing the fiber surface topography, thermal stability, and tensile strength of the fiber, while the chemical treatment using NaOH and water boiling caused the higher thermal properties of the EFB fibers compared to untreated fibers.

4. Natural Fiber Polymer Composites Application

The applications of NFPCs are growing rapidly in numerous engineering fields. The different kinds of natural fibers such as jute, hemp, kenaf, oil palm, and bamboo reinforced polymer composite have received a great importance in different automotive applications, structural components, packing, and construction [5, 99]. NFPCs are finding in electrical and electronic industries, aerospace, sports, recreation equipment, boats, machinery office products, and so forth. The widespread application of NFPCs in polymer composites due to its low specific weight, relatively high strength, relatively low production cost, resistance to corrosion and fatigue,

TABLE 5: The application of natural fiber composites in automotive industry [59–62].

Manufacturer	Model	Application
Rover	2000 and others	Rear storage shelf/panel, and insulations
Opel	Vectra, Astra, Zafira	Door panels, pillar cover panel, head-liner panel, and instrumental panel
Volkswagen	Passat Variant, Golf, A4, Bora	Seat back, door panel, boot-lid finish panel, and boot-liner
Audi	A2, A3, A4, A4 Avant, A6, A8, Roadstar, Coupe	Boot-liner, spare tire-lining, side and back door panel, seat back, and hat rack
Daimler Chrysler	A, C, E, and S class, EvoBus (exterior)	Pillar cover panel, door panels, car windshield/car dashboard, and business table
BMW	3, 5 and 7 series and other Pilot	Seat back, headliner panel, boot-lining, door panels, noise insulation panels, and moulded foot well linings
Peugeot	406	Front and rear door panels, seat backs, and parcel shelf
Fiat	Punto, Brava, Marea, Alfa Romeo 146, 156, 159	Door panel
General Motors	Cadillac De Ville, Chevrolet Trail Blazer	Seat backs, cargo area floor mat
Toyota	ES3	Pillar garnish and other interior parts
Saturn	L300	Package trays and door panel
Volvo	V70, C70	Seat padding, natural foams, and cargo floor tray
Ford	Mondeo CD 162, Focus	Floor trays, door inserts, door panels, B-pillar, and boot-liner
Saab	9S	Door panels
Renault	Clio, Twingo	Rear parcel shelf
Toyota	Raum, Brevis, Harrier, Celsior,	Floor mats, spare tire cover, door panels, and seat backs
Mitsubishi		Cargo area floor, door panels, and instrumental panel
Mercedes Benz	C, S, E, and A classes	Door panels (flax/sisal/wood fibers with epoxy resin/UP matrix), glove box (cotton fibers/wood molded, flax/sisal), instrument panel support, insulation (cotton fiber), molding rod/apertures, seat backrest panel (cotton fiber), trunk panel (cotton with PP/PET fibers), and seat surface/backrest (coconut fiber/natural rubber)
	Trucks	Internal engine cover, engine insulation, sun visor, interior insulation, bumper, wheel box, and roof cover
Citroen	C5	Interior door panelling
Lotus	Eco Elise (July 2008)	Body panels, spoiler, seats, and interior carpets
Rover	2000 and others	Insulation, rear storage shelf/panel
VAUXHALL	Corsa, Astra, Vectra, Zafira	Headliner panel, interior door panels, pillar cover panel, and instrument panel

totally biodegradable, improving the surface finish of molded part composites, relatively good mechanical properties, available and renewable sources as compared to synthetic fibers [5, 98]. On the other hand, there is a physical disadvantage of the NFPCs such as moisture absorption, restricted processing temperature, and variable quality and this disadvantage led to limiting their performance [73].

4.1. Natural Fiber Composites Applications in the Interior Car.

Most of the car companies in the world have done a lot of investigation in order to insert the NFPCs in their products. The car manufacture in Europe has done various researches to increase the applications of NFPCs in automotive industry, especially in car interior such as seat backs, parcel shelves, boot linens, front and rear door linens, truck linens, and door-trim panels [89]. Beside the use for car interior parts in automobile industry, natural fiber embedded in polymers

has been used for high requirement applications for exterior auto body components, such as the middle section between the headlights above the fender of a passenger bus [18].

German auto companies (BMW, Audi Group, Ford, Opel, Volkswagen, Daimler Chrysler, and Mercedes) utilize the cellulose fibers composites in various automobile part, shown in Figure 6, such as using coco nut fibers rubber latex composites for the seats of the Mercedes Benz A-class model and using fax-sisal fiber mat reinforced epoxy door panels of Mercedes Benz E-class model [8]. Audi company uses flax/sisal mat reinforced polyurethane composite with a mix to make door trim panels [60]. Ford is using kenaf fibers imported from Bangladesh in their “Mondeo” model and the door panels of the Mondeo are manufactured from kenaf reinforced PP composites while using flax in floor trays [61]. Kenaf and flax mixture has gone into package trays and door panel inserts for Opel Vectras. Volkswagen company used

TABLE 6: Natural fiber composite applications in industry [3, 63–65].

Fiber	Application in building, construction, and others
Hemp fiber	Construction products, textiles, cordage, geotextiles, paper & packaging, furniture, electrical, manufacture bank notes, and manufacture of pipes
Oil palm fiber	Building materials such as windows, door frames, structural insulated panel building systems, siding, fencing, roofing, decking, and other building materials [14]
Wood fiber	Window frame, panels, door shutters, decking, railing systems, and fencing
Flax fiber	Window frame, panels, decking, railing systems, fencing, tennis racket, bicycle frame, fork, seat post, snowboarding, and laptop cases
Rice husk fiber	Building materials such as building panels, bricks, window frame, panels, decking, railing systems, and fencing
Bagasse fiber	Window frame, panels, decking, railing systems, and fencing
Sisal fiber	In construction industry such as panels, doors, shutting plate, and roofing sheets; also, manufacturing of paper and pulp
Stalk fiber	Building panel, furniture panels, bricks, and constructing drains and pipelines
Kenaf fiber	Packing material, mobile cases, bags, insulations, clothing-grade cloth, soilless potting mixes, animal bedding, and material that absorbs oil and liquids
Cotton fiber	Furniture industry, textile and yarn, goods, and cordage
Coir fibers	Building panels, flush door shutters, roofing sheets, storage tank, packing material, helmets and postboxes, mirror casing, paper weights, projector cover, voltage stabilizer cover, a filling material for the seat upholstery, brushes and brooms, ropes and yarns for nets, bags, and mats, as well as padding for mattresses, seat cushions
Ramie fiber	Use in products as industrial sewing thread, packing materials, fishing nets, and filter cloths. It is also made into fabrics for household furnishings (upholstery, canvas) and clothing, paper manufacture.
Jute fiber	Building panels, roofing sheets, door frames, door shutters, transport, packaging, geotextiles, and chip boards.



FIGURE 6: Automobile components made of natural fiber composites [36].

cellulose fiber to make Seatback, door panel, boot-lid finish panel, boot-liner in Passat Variant, Golf, A4, and Bora model.

BMW Group has a lot of NFPCs into its automobiles. BMW Group used about 10 000 tonnes of natural fiber in 2004 [100]. Each BMW 7 series car boats 24 kg of renewable raw materials, with flax and sisal in the interior door lining panels. Also use cotton in the soundproofing, wool in the upholstery, and wood fiber in the seat back. Daimler-Benz in Germany is also working with a range of natural fibers \pm sisal, jute, coconut, European hemp, and flax \pm as reinforcing fibers in high-quality polypropylene components in order to replace glass fibers. Daimler-Benz has developed the dashboards and center armrest consoles along with seat shells and paneling on seat backs. Moreover, it increased the utilization of NFPCs in some automobiles by approximately 98% over earlier models by utilizing natural fibers, for example, abaca and flax. On the other hand, the Cambridge industry made rear shelf trim

panels of the 2000 model Chevrolet Impala using flax fiber polypropylene composite [8, 101]. Toyota, Proton, Volvo, and other automobile companies used cellulose fiber to make car parts as shown in Table 5.

4.2. The Natural Fiber Applications in the Industry. Other than the car industry, the applications of NFPCs are found in building and construction, aerospace, sports, and more, such as partition boards, ceilings, boats, office products, and machinery. The most applications of NFPCs are concentrated on nonload bearing indoor components in civil engineering because of their vulnerability to environmental attack [72]. Green buildings are wanted to be ecologically mindful, suitable, and healthy place to live and work. Biocomposites is consider one of the major materials utilized as a part of green materials at this time. It could be categorized, with regard to their application in the building market, into two principle products: firstly, structural biocomposites, which include bridge as well as roof structure, and secondly, nonstructural biocomposites which include window, exterior construction, composites panels, and door frame [2].

The wide advantages of natural fibers reinforced composites such as high stiffness to weight ratio, lightweight, and biodegradability give them suitability in different application in building industries [102]. Van de Weyenberg et al. [24] have shown that good properties of thin walled elements such as high strength in tension and compression, made of sisal fiber reinforced composite, give it a wide area of application, for instance, structural building members, permanent formwork, tanks, facades, long span roofing elements, and pipes strengthening of existing structures. On the other hand,

bamboo fiber can be used in structural concrete elements as reinforcement, while sisal fiber and coir fiber composites have been used in roofing components in order to replace asbestos [15]. Natural fiber reinforced concretes products in construction applications like sheets (both plain and corrugated) and boards are light in weight and are ideal for use in roofing, ceiling, and walling for the construction of low cost houses [103]. Table 6 shows the various applications of cellulose fiber in industry, construction, and other industries.

5. Conclusions

Natural fiber reinforced polymer composites have beneficial properties such as low density, less expensive, and reduced solidity when compared to synthetic composite products, thus providing advantages for utilization in commercial applications (automotive industry, buildings, and constructions). Using natural fibers as reinforcement for polymeric composites introduces positive effect on the mechanical behavior of polymers. This paper evaluates the characteristics and properties of natural fiber reinforced polymer composites: mechanical, thermal, energy absorption, moisture absorption, biodegradability, flame retardancy, tribology properties. Viscoelastic behavior and relaxation behavior of NFPCs are researched. Also the application of NFPCs in automobile and industry is reported. The effects of chemical treatment of the natural fiber properties were also addressed. The physical and mechanical properties of these NFPCs can be further enhanced through the chemical treatment, while moisture absorption of the NFPCs can be reduced through surface modification of fibers such as alkalization and addition of coupling agents.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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