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Research Article

Novel and Facile Synthesis of Biodegradable Plastic Films from Cornmeal by Using the Microwave Polymerization Technique

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Millions of tons of plastic are produced annually, but a major portion of plastic waste remains unrecycled. The uncycled plastic ultimately becomes a major source of solid trash and releases a variety of chemicals into our environment which can adversely affect the human health and marine life. In this study, a novel approach has been opted to synthesize a biodegradable plastic by using the microwave polymerization technique. In this novel approach, raw material (cornmeal), plasticizer (glycerin), and additive (vinegar) have been combined together to fabricate biodegradable plastic films from the microwave polymerization method. A number of rheological properties such as shear stress (Pa), shear rate (1/s), strain, and viscosity (Pa.s) of newly synthesized plastic were studied. These properties confirmed the presence of a shear thinning effect in the biodegradable plastic films on the basis of flow behavior of cornmeal. In order to check the water uptake ability and biodegradability of the cornmeal-based plastic films, water uptake and biodegradation tests were carried out. The fabricated films were neat, thin, and chewable and demonstrate promising characteristics. Therefore, these synthesized films can potentially become a suitable candidate in the packaging industry.

1. Introduction

Over the last few decades, an exponential increase in the demand of plastic has led the world towards some critical environment-related health issues based on the hazardous aspects of plastic wastes. Tons of plastic is produced annually, but a major portion of the plastic waste remains unrecycled at the end. In many countries, the uncycled plastic is considered solid trash. The smaller units such as polyvinyl chloride (PVC), polystyrene, and polyurethane, which are often used in producing plastics, are sometimes considered as highly toxic materials. Due to the non-biodegradability character of all these plastics, an extremely hazardous impact is being consistently observed on aquatic as well as human life [1]. Different organs and immune systems of aquatic animals are being badly affected due to the accumulation of low molecular weight plastic waste. In addition to the monomers, which are required to produce the plastic polymers, many chemicals are also required to accomplish the basic production criteria of making plastics. The plastics synthesized from these chemicals can stay in the environment for a longer time, thus making the plastic wastes extremely hazardous. In a nut shell, the presence of such conventional plastic wastes in the environment can adversely affect almost all kinds of organisms including humans and the aquatic animals [2, 3].

Due to potential hazardous effects of conventional plastics, researchers are working really hard to develop some environment friendly and easily biodegradable plastics on urgent basis. Luckachan and Pillai [4] reported various mechanisms to produce biodegradable plastic. In one of these appealing methods, a biodegradable component was added to the synthetic raw material to enhance the biodegradability of synthesized plastics. A number of studies have been reported in the literature on the production methods of plastics which show different advantages related to easier biodegradation through the micro-organisms' action leading towards an improvement in soil conditioning, recycling nature to reduce waste disposal problems, and more importantly the methods related to lowering the possibility of accumulation of high molecular weight plastic in the environment [5]. Plant-based synthesized biodegradable plastic is another important development in the plastic industry as an alternate to the conventional plastic. Green plants produce many biodegradable plastic-making reagents, e.g., starch and cellulose which can produce reliable and easily degradable environment friendly plastic [6]. Various materials such as soybean, rice starch, potato starch, corn starch, and cellulose have also been employed in a number of research works for the production of biodegradable plastics [7–12]. All the materials described above can be used for the synthesis of biodegradable plastic. Such materials are eco-friendly, cost effective, and easily available and are promising candidates to overcome the detrimental effects of conventional plastic. In addition, different methodologies can be applied to produce biodegradable plastic. Solvent casting is one of the most important methods to produce polylactic acid (PLA)-based biodegradable plastic [13]. Extrusion and injection molding are some additional techniques used in the production of biodegradable plastic [14]. Microwave heating is yet another important process to produce different kinds of biodegradable plastic and composites [15, 16].

In the present study, a novel approach has been opted to produce eco-friendly and biodegradable plastic which shows a considerable potential to replace the detrimental conventional plastic. In this novel approach, a microwave oven has been employed to yield the polymerization process. As compared to the conventional laboratory or vacuum oven-based polymerizations, a microwave oven-based polymerization is a modern, novel, cost effective, and eco-friendly technique to synthesize biodegradable plastic or plastic films [17–20]. In this method, the microwave oven was used in the rotational mode to heat the liquid, which is poured on a Teflon plate. The rotational heating of the liquid produces the process of polymerization to yield biodegradable plastic films. For this novel green synthesis of biodegradable plastic films, cornmeal was used as the raw material. To the best of our knowledge, the combination of raw material (cornmeal), plasticizer (glycerin), and additive (vinegar) is quite a new methodology to synthesize biodegradable plastic films from the microwave polymerization method.

2. Experimental

2.1. Materials. The raw materials (cornmeal, glycerin, acetic acid, distilled vinegar, and vinegar) were purchased from the local market of Lahore, Pakistan. Doubly distilled water (prepared in our own lab) was used to prepare all the dilutions. Sizing of the cornmeal was performed (to homogenize the particle size) with the help of a sieve shaker (MRC, Laboratory Instruments, UK), whereas Teflon plates were used for the casting of films. Preparation of the films was carried out using a microwave oven (Electron Microscopy Sciences, UK).

2.2. Preparation of Biodegradable Plastic Films. By using the mesh technique, cornmeal was passed twice through the mesh and collected in a bowl. 10 g of the finely prepared cornmeal obtained from the mesh was transferred into a blender to which 7.5 mL of vinegar, 10 mL of glycerin, and 15 mL of water were added. The mixture was then blended for 2 to 3 min to produce a homogenised slurry. The slurry was then evenly spread on the Teflon plate and placed in a microwave oven (Electron Microscopy Sciences, UK) for 1–2 min at 350°C after which the plate was removed from the microwave oven and cooled. A thin layer of film had formed on the Teflon plate which was then removed. The method was used to prepare high quality, fine, and clear biodegradable plastic films. Using the same procedure as described above, two additional composite films were prepared by substituting vinegar additive with the distilled vinegar and acetic acid (Figure 1). The tentative reaction mechanism of the formation of plastic films has been presented in Figure 2.

2.3. Characterization. The cornmeal-based films, synthesized by using vinegar, distilled vinegar, and acetic acid, were characterized by FTIR (Nicolet™ iS™ 10 FTIR Spectrometer—Thermo Fisher, UK) by employing the attenuated total reflectance (ATR) technique. All FTIR spectra were recorded at a resolution of 4 cm^{-1} within the frequency range of 4000–400 cm^{-1}. To obtain a clear spectrum, the number of scans was set to 32.

A rheometer (AR 1500ex TA instrument, USA) was used to measure the rheological properties such as shear stress (Pa), shear rate (1/s), and viscosity (Pa.s) of the cornmeal-based synthesized films. Rheological properties in terms of flow behaviour were examined to check the desired effect of shear stress on it. The dispersion was poured onto the plate which filled the gap between the rotor and the stator. Stress was then applied to it by moving the upper plate. As a result, different rheological properties were measured which demonstrated the flow behaviour of dispersion.

A scanning electron microscope (SEM, HITACHI S–3400N) was employed for the morphological investigation of newly synthesized biodegradable films. The SEM instrument was operated at an emission current of 60 μA, and acceleration voltage was kept at 10 kV.

The thermal stability of synthesized plastic films was checked using a thermogravimetric analyzer (TGA, Q500, TA Co., USA). The thermogravimetric analysis was performed at a rate of 10°C/min ranging from 25°C to 800°C under air atmosphere.

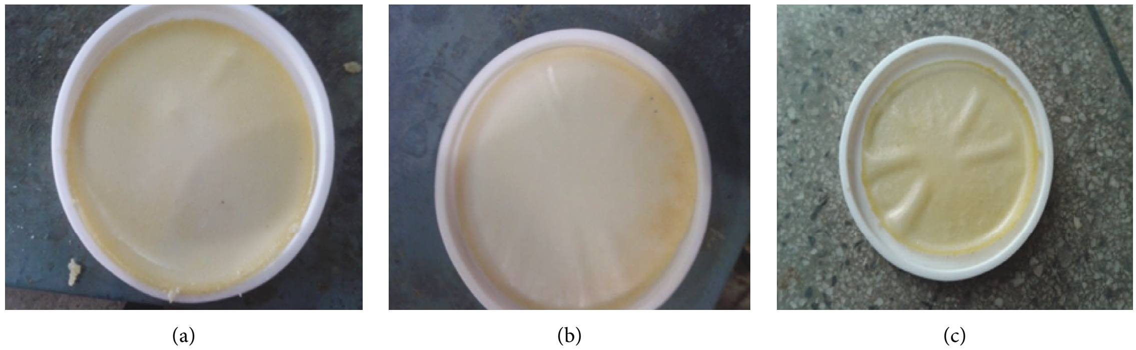

FIGURE 1: Biodegradable plastic films made from cornmeal in the presence of (a) vinegar, (b) distilled vinegar, and (c) acetic acid.

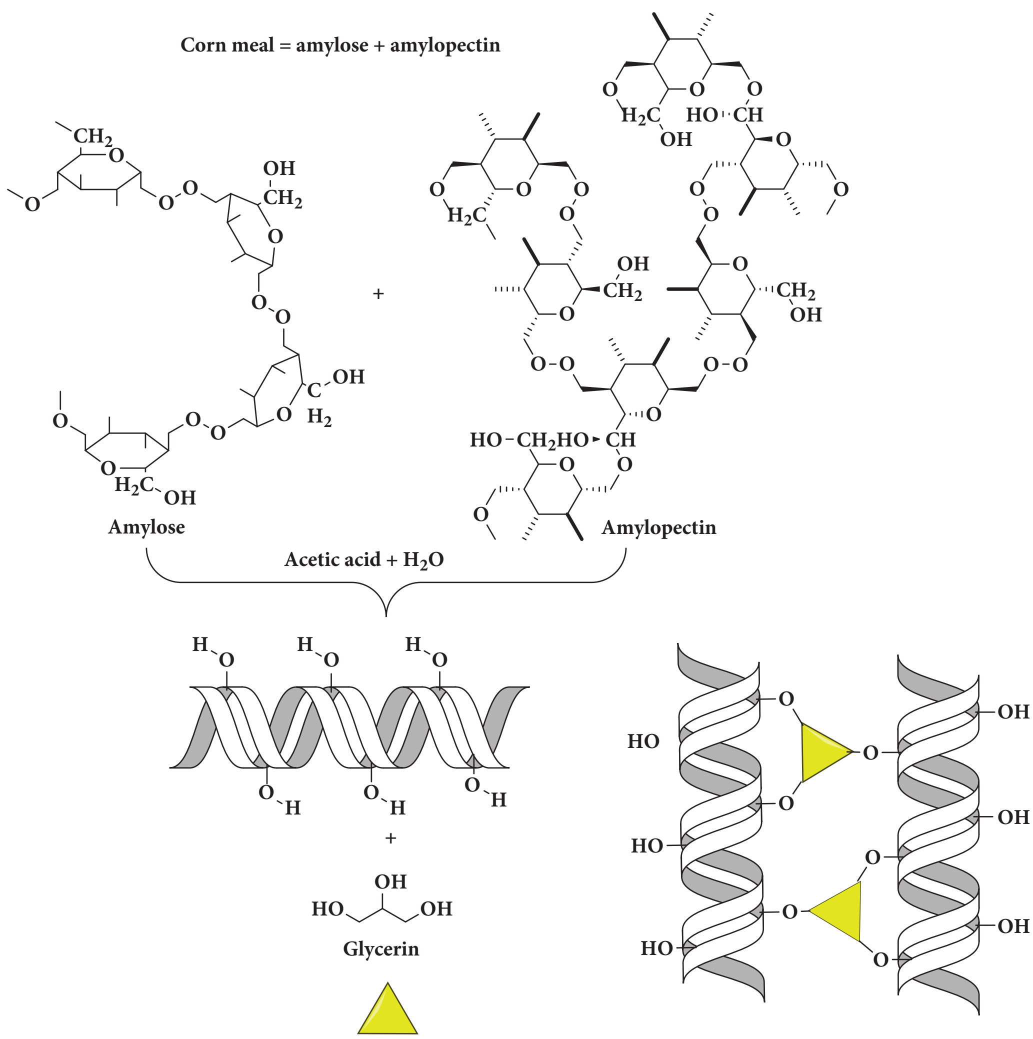

FIGURE 2: The tentative reaction mechanism.

2.4. Biodegradation Studies of Plastic Films. To assess the biodegradation of the plastic films produced, each sample was buried in a beaker containing 625 g soil and 625 g sand at room temperature. The beakers were kept under observation for 24 days. Moisture content of the soil and sand was maintained by adding 400 mL of water into each beaker at the start of the process. This procedure was repeated every three days throughout the observation period. A similar approach has already been reported where biodegradation studies were performed on a biodegradable plastic synthesized from corn and rice starch [21]. Following the reported method, the specimen weight was determined before and after testing by employing equation (1). The specimen's mass was determined before and after testing. For visual inspection, SEM images of the specimens were taken before and after testing.

$$\text{Mass loss\%} = \left(\frac{M_O - M}{M}\right)100, \quad (1)$$

where M_O is the mass of the sample before the test and M is the mass of the sample after the test.

The typical pH value of the Pakistani soil ranged between 7 and 8, and soil that was selected for the experiment had a pH value of 7.8. After biodegradation of the film, pH of the soil was also determined.

The method described by Zhao et al. was opted to measure the pH of the soil [22]. Following this method, soil samples were air dried, and then 10 g of dried soil was mixed with 20 mL of doubly distilled water. The mixture was shaken vigorously for 30 min, and the suspensions were allowed to settle for 60 min. Next, 20 mL of each suspension was transferred to a 50 mL tube (Sarstedt AG & Co. KG, Nümbrecht, Germany) and centrifuged for 5 to 6 min at the rate of 3,000 rpm. After filtering the supernatants, a pH meter (HAnna Instrument, Italy) was used to measure the pH.

2.5. Water Uptake Test. A humidity chamber (desiccator) with 100% humidity was created by using silica as the bottom layer. The plastic films were dried at 60°C for 24 h, weighed, and then placed in the desiccator. The weight difference was measured on a daily basis until the weight of films was constant. The water uptake of the films was calculated by using a formula given in the following equation [23]:

$$\text{Water uptake\%} = \left(\frac{M_f - M_i}{M_i}\right)100, \quad (2)$$

where M_f is the final mass of the sample and M_i is the initial mass of the sample.

3. Results and Discussion

3.1. Characterization. Figure 3(a) illustrates the FTIR spectrum of the cornmeal. The hydroxyl group (O–H) peak appears at 3277 cm^{-1} in the spectrum. A peak of C–H group was observed at 2929 cm^{-1} along with a C–O group peak at 1151 cm^{-1}. The peak observed at 923 cm^{-1} indicates carbon-carbon stretching [24]. Figure 3(b) illustrates the spectrum of the film made from cornmeal in the presence of vinegar. It can be observed that there is a shift of reactant group peaks and an introduction of two new peaks, i.e., carboxyl group and glycerol. The spectrum clearly shows the hydroxyl group (O–H) peak at 3275 cm^{-1}. A peak for C–H group was observed at 2930 cm^{-1}. Two strong peaks of C–O and –COOH were observed at 1151 cm^{-1} and 1022 cm^{-1}, respectively. Carbon-carbon stretching showed a peak at 923 cm^{-1}, while a glycerol peak was observed at 1415 cm^{-1}. The introduction of two new peaks as desired confirmed the formation of the product. A similar spectrum of cornstarch-based thermoplastic gave peaks in the same range [10]. For the composites prepared from cornmeal in the presence of distilled vinegar and acetic acid, respectively, peaks were observed in the same spectral region as were seen in the case of the composite prepared from cornmeal and vinegar (Figures 3(c) and 3(d)). The similarity of all three spectra, based on the actual product and composite, shows that although the nature of additives is different, but they constitute similar chemical composition.

3.2. Rheological Measurement. The graphs were plotted between shear stress and the shear rate (Figure 4(a)) for dispersion in the presence of vinegar. Shear stress is the stress applied to the parallel cross-sectional area of the fluid, and the shear rate is the rate of change of viscosity. The obtained graph shows an inverse relationship between shear stress and the shear rate. With an increase in the shear stress, the shear rate decreases which ultimately decreases viscosity. The decrease in viscous behaviour with increasing stress proves the shear thinning effect, i.e., a decrease in the friction between the layers of fluid upon stress. The graph between viscosity (Pa.s) and the shear rate (1/s) for dispersion in the presence of vinegar is presented in Figure 4(b). The figure depicts a decrease in viscous behaviour to prove the shear thinning effect, i.e., the property of a non-Newtonian fluid. In the shear thinning effect, the frictional force reduces between the layers of fluid as stress is applied. A similar plot in which shear thinning effect had been shown was obtained for partially hydrolyzed polyacrylamide (PHPA) polymer [25]. In the case of both composite dispersions, the shear thinning effect has been observed which indicates a similar decrease in friction between the layers of fluid upon stress. The same rheological properties of dispersion in the presence of vinegar, distilled vinegar, and acetic acid produce the same type of a shear thinning effect when stress is applied on these dispersions.

3.3. Biodegradation Studies of Plastic Films. Biodegradation of cornmeal-based films as a result of microbial attack was determined by weight loss after burial in a mixture of sand and soil for 20 days. The weight of films, after burying in a mixture of sand and soil for 10 days, got reduced to some extent which shows the initiation of biodegradation phenomena. After 1 week, the rate of biodegradation of the films was noticed, and it was observed that the films had almost faded. After 3 weeks, the films had completely biodegraded which indicates that the plastic films are biodegradable. The complete biodegradability of cornmeal-based plastic films shows that these films are environment friendly and susceptible to degradation due to the action of bacteria or micro-organisms present in sand and soil (Figure 5).

We opted an approach similar to the one already been reported in the literature, where biodegradation studies were performed on biodegradable plastic synthesized from corn and rice starch [21]. Biodegradability of 99.8% (Figure 6) was achieved after 20 days, and the plastic film got broken into pieces on touching.

After complete degradation of the film, the pH of the soil was determined as well. The pH of the soil just changed slightly from 7.8 to 7.6. This slight change in pH is probably because of formation of carbonic acid from the combination of carbon dioxide and water, and this minimal change in pH will definitely not have any detrimental effect on the soil.

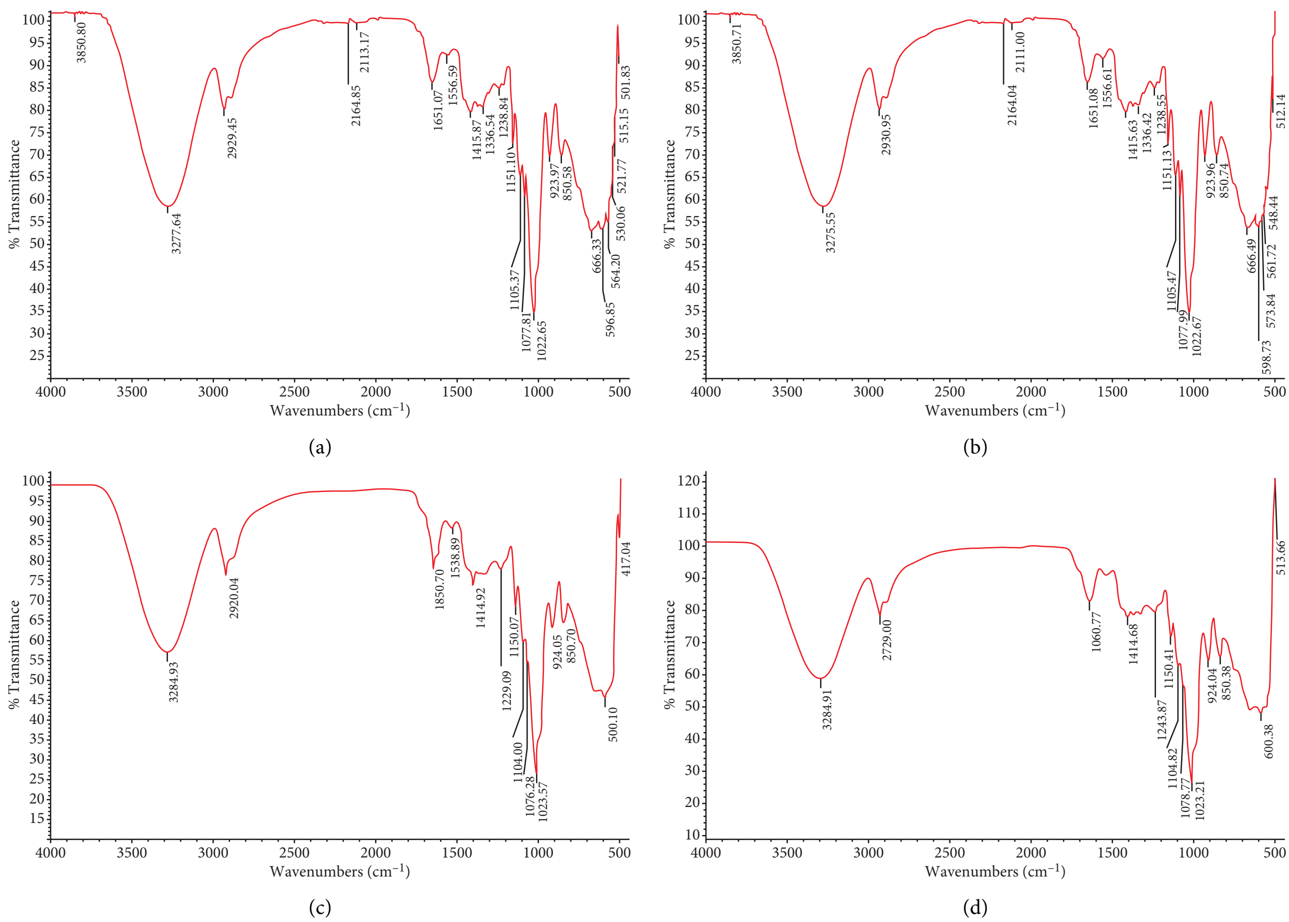

FIGURE 3: FTIR spectra of (a) cornmeal, (b) the film made from cornmeal in the presence of vinegar, (c) the film made from cornmeal in the presence of distilled vinegar, and (d) the film made from cornmeal in the presence of acetic acid.

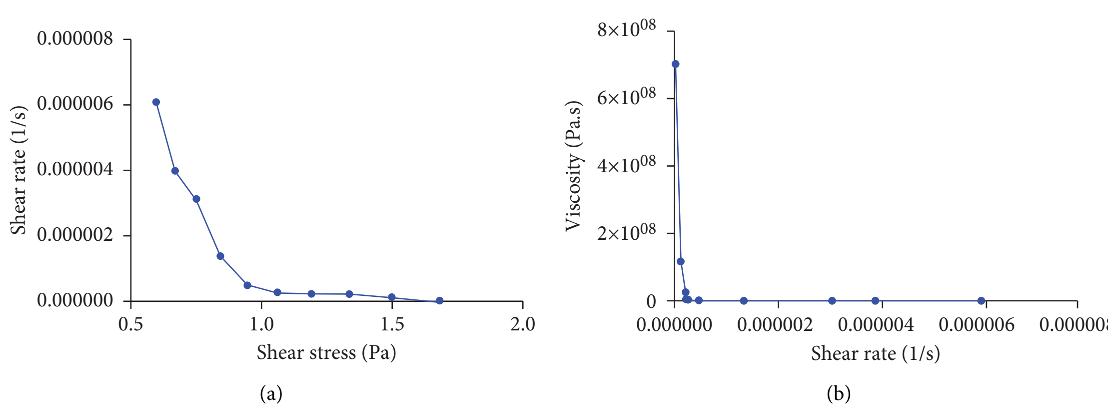

FIGURE 4: Relation between (a) shear stress and the shear rate (b) the shear rate and viscosity.

The deterioration of bioplastic samples due to microbial activity was examined using SEM studies. The SEM image shown in Figure 7(a) is of the newly synthesized biodegradable film, whereas the SEM image shown in Figure 7(b) is of the decomposed sample due to a 20-day long microbial activity on the film after its burial in soil and the sand. Flaws on the surface of structure are quite obvious, and the material's surface had lost its evenness. Big variations in the sample's structure can easily be seen in the SEM images. The biodegradation over the plastic film due to the presence of flaws and filmy loss can also be proven using SEM images.

Thermal degradation analysis was performed to examine the stability of the polymer film (Figure 8). In the first regime of degradation, a small weight loss of ~7–8% was found in the temperature range of 100°C to 110°C. Such a small weight loss in the mentioned temperature range indicates an evaporation of the moisture contents of the film. However, a major weight loss was observed in the temperature range of

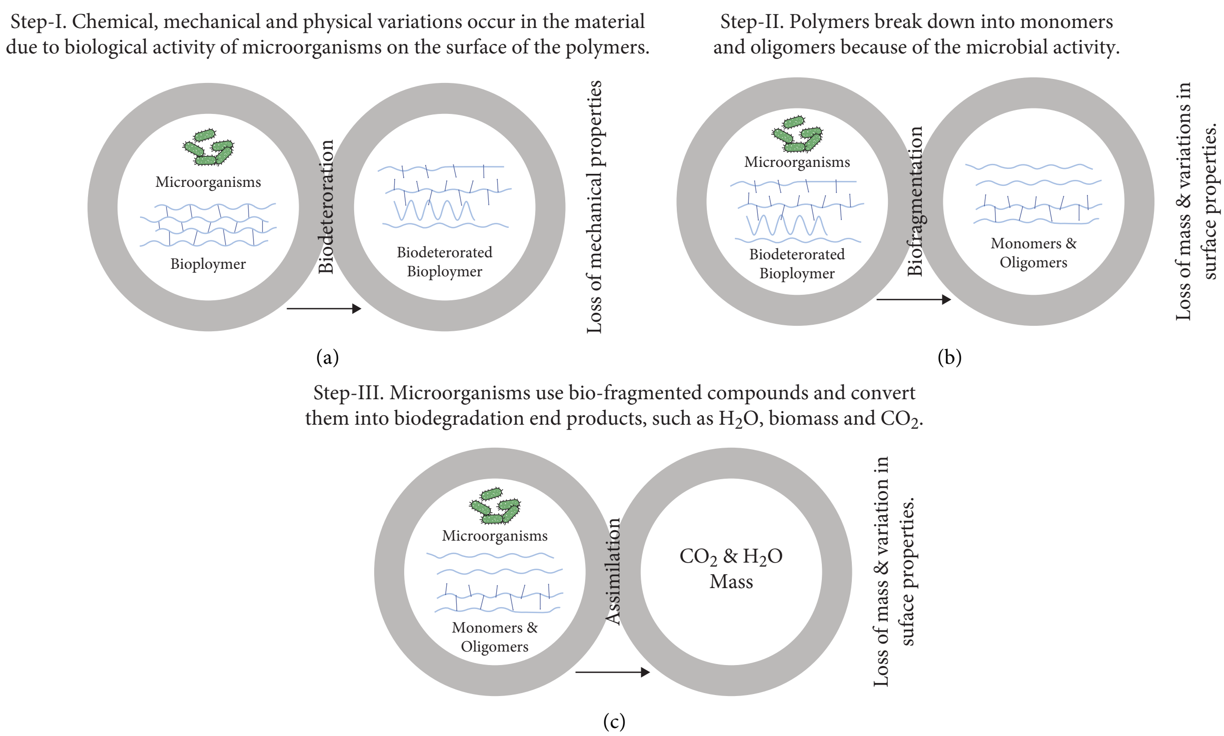

Figure 5: (a) Biodeterioration, (b) biofragmentation, and (c) assimilation are the three major steps which describe the biodegradation phenomenon of a polymer.

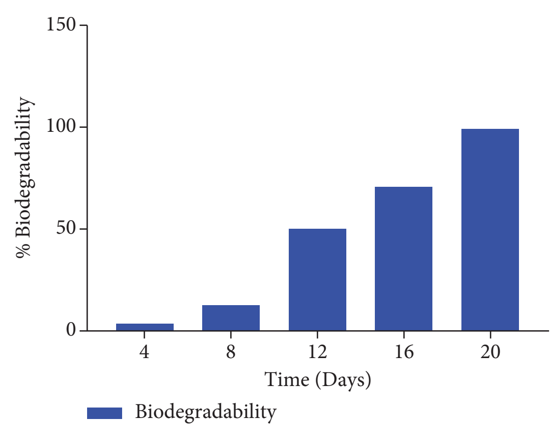

Figure 6: % Biodegradability of the biopolymer with respect to time.

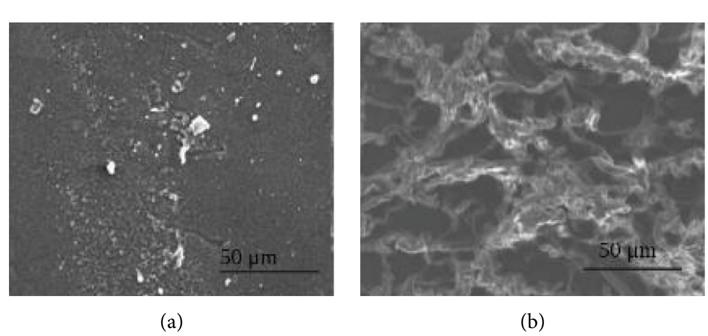

Figure 7: SEM images of (a) plastic film before and (b) after degradation.

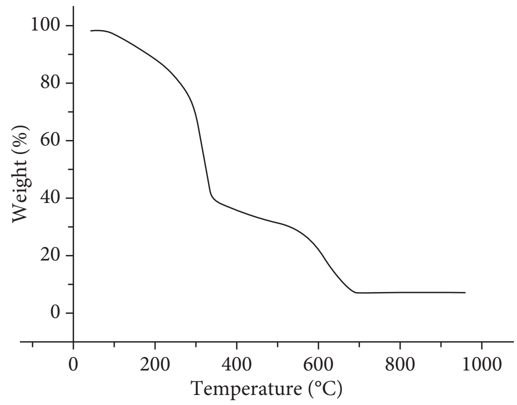

Figure 8: TGA curve of the plastic film.

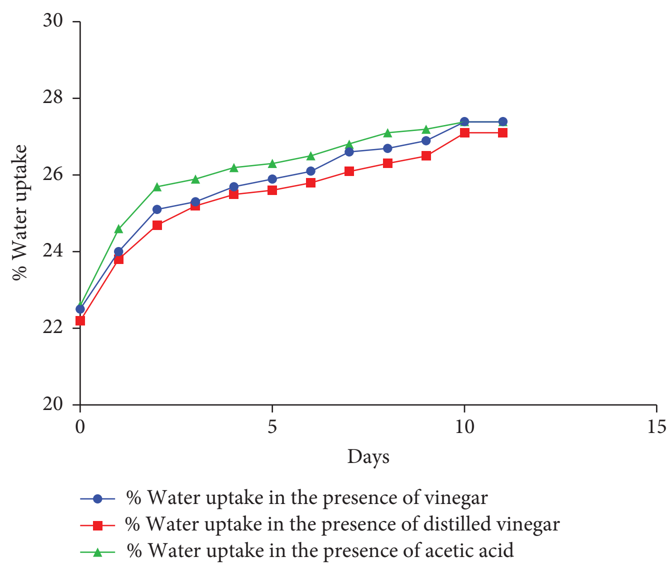

Figure 9: Water uptake for films in the presence of vinegar, distilled vinegar, and acetic acid.

260°C to 300°C, which is because of the decomposition of the polymer. Thermogravimetry analysis indicates that the synthesized polymer films can even be used for the applications which require elevated temperatures.

3.4. Water Uptake Test. Water uptake against the number of days for films in the presence of vinegar, distilled vinegar, and acetic acid has been shown in Figure 9. Equation (2) was used to calculate water uptake of the films in the presence of vinegar, distilled vinegar, and acetic acid, respectively. Water uptake of the film made in the presence of distilled vinegar (22.07%) exhibited high water upholding capacity as compared to vinegar (21.7%) and acetic acid (21.23%). This can be attributed to the fact that vinegar is distilled at high temperature, and hence, all impurities and water are removed leaving behind the pure plastic. As a result of this, the film made in the presence of distilled vinegar has more humidity holding capacity. Water uptake reported for starch-based blends with date palm and fibers showed a similar effect of humidity on films produced from this material [23].

4. Conclusion

Biodegradable plastic films were synthesized from cornmeal using the microwave polymerization technique. Structural characterization was performed by FTIR to confirm the formation of the desired functional groups in the product and in its composites. Rheological properties in terms of flow behaviour were studied which indicated the presence of the same shear thinning effect in the product and composites. The biodegradability test of films was performed by burying the films in a mixture of sand and soil to study the biodegradability of films. The water uptake test of the films was carried out, and results showed that films made from distilled vinegar had slightly greater water holding capacity as compared to vinegar-based films. Hence, it can be concluded that the films made from cornmeal in the presence of vinegar, distilled vinegar, and acetic acid have the same properties related to spectroscopy, rheology, biodegradation, and water uptake ability. In particular, films made from cornmeal in the presence of vinegar are a novel green approach in the plastic industry. In addition, films made from cornmeal in the presence of vinegar are biodegradable, economical, green, and an excellent alternative to conventional plastic.

Data Availability

The data that support the findings of this study are available in this article.

Conflicts of Interest

The authors declare no conflicts of interest.

Authors' Contributions

Muhammad Imran Din conducted supervision, review, and editing; Tayabba Ghaffar performed methodology, formal analysis, and synthesis; Zaib Hussain carried out review; Rida Khalid conducted optimization and writing of the original draft; Abdul Samad performed formal analysis and review; Muhammad Ahmad carried out review and editing; Mahmood Ahmed conducted investigation, methodology, formal analysis, review, and editing.

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