

Research Article

Development of Flexible Polyurethane Nanostructured Biocomposite Foams Derived from Palm Olein-Based Polyol

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This study examined the effect of organoclay montmorillonite (OMMT) on the mechanical properties and morphology of flexible polyurethane/OMMT nanocomposite (PU/OMMT) foams prepared from petroleum- and palm olein-based polyols. Palm-based PU foams exhibited inferior mechanical strength as compared to neat petroleum PU foams. However, addition of OMMT significantly improved the foams strength of flexible polyurethane/OMMT nanocomposite foams prepared from palm olein-based polyol (PU bionanocomposite foam). The morphology analysed by scanning electron microscopy (SEM) showed that the cell size of the foam decreased with increasing OMMT content. PU bionanocomposite foam with 5 wt% of OMMT had the most improved tensile (63%) and tear (48%) strengths compared to its neat counterpart. Transmission electron microscopy (TEM) revealed the exfoliated structure of the respective foam. It was concluded that OMMT improved mechanical properties and morphology of PU foams.

1. Introduction

Polyurethanes (PUs) are recognized as the most versatile polymers. They consist of soft and hard segments. Factors that influence the properties and application suitability of the polyurethane include segmental flexibility, chain entanglement, interchain forces, and cross-linking [1]. Generally, polyurethanes are widely used in coatings, adhesives, foams, elastomers, and composites [2]. In making PUs, polyol is one of the main raw materials. Almost all polyurethanes are derived from petroleum-based raw materials. However, issues surrounding petrochemical derived feedstock including unpredictable petroleum price, sustainability, stability of production, environment impact, and waste disposal have led to studies on renewable raw materials. Over the years, polyols have been successfully developed from natural resources. Vegetable oils such as soybean, castor, palm, and canola oils have been reported to be the potential sources for natural polyols [3–7]. Polyols synthesised from cashew nut shell

were also reported in the literature [8]. Nonetheless, the properties of vegetable oil derived PU are generally inferior in comparison to the petroleum derived counterparts due to the position of hydroxyl groups that are pendent in the aliphatic backbone of the triglycerides structure. In contrast, the petroleum-based polyols are telechelic polymers [9]. This contributes to lower physical properties of PU foam made from the former [9–12].

In general, to cope with the limitations such as low stiffness and low strength of polymers, particularly PUs derived from vegetable oils, inorganic fillers such as talc, glass, Al_2O_3 , $CaCO_3$, and SiO_2 were used to enhance the mechanical properties of polymer composites [13]. Three main attributes of the fillers as reinforcement agents that impact the development of mechanical properties are chemistry, size, and shape [14]. The mechanism of the reinforcement is based on the higher resistance of rigid filler materials against straining due to their higher module. When a rigid filler is added to the soft polymer matrix, it will carry major portion of applied load to

the polymer matrix under stress conditions, if the interfacial interactions between filler and matrix are adequate [15, 16].

It has been shown that dramatic improvements in mechanical properties can be achieved by incorporation of a few weight percentages (wt%) of inorganic clay minerals consisting of layered silicates in polymer matrices [17–21]. A commonly used layered silicate, montmorillonite (MMT), is dioctahedral clay of smectite group that have a thickness of ~1 nm and lateral dimensions of ~30 nm to several microns or larger. The large aspect ratios of layered silicates dominate the interaction with polymers, resulting in enhanced mechanical properties of particulate-polymer nanocomposites.

Nanocomposites can be defined as composites having more than one solid phase with a dimension in the range of 1–20 nm [1]. Intercalation of polymer chains between individual platelets of layered silicates introduced into the polymer is the key to the polymer nanocomposite technology. Therefore, it is crucial to completely disperse the silicate layers in the polymer matrix for the development of remarkable polymer nanocomposites. This is accomplished by the surface modification of montmorillonite (MMT) with organophilic groups. Since MMT is hydrophilic and lacks affinity with hydrophobic organic polymers, modification of MMT is needed in order to give partially hydrophobic character. OMMT is produced by exchange of metal cations in MMT with organic ammonium salts. The affinity of PU to the surface of the clay and the organic surfactant of the OMMT is essential to promote favourable interaction between these two materials [22].

There are three types of nanocomposites structures, which depend on the OMMT opening degree after integration with polymer matrix. The composites are classified as exfoliated or delaminated when silicate layers are fully dispersed in the matrix. This type of composite yields the greatest improvement in properties because maximum reinforcement is reached. Most of the composites reported in the literature are intercalated. Intercalated composites are categorised when the layers are partially open. Composites with closed layers (tactoid) are classified as immiscible [23].

Nanocomposites have been used commercially since the world largest car manufacturer, Toyota, introduced the first polymer/clay auto parts in the 1980s [24]. Since then, clay nanocomposites with several polymers such as polypropylene [25, 26], polyamide-6 [27], polystyrene [28], poly(methyl methacrylate) [29], poly(ethylene terephthalate) [30], elastomeric polyurethane [31], and polyurethane foam [32–34] were explored.

The effect of MMT on the palm oil-based rigid PUFs was studied by Chuayjuljit et al. [35]. Rigid PUFs were prepared with incorporation of 1, 3, and 5 wt% MMT in the formulation. Foam with incorporation of 5 wt% MMT showed the highest compressive strength of 172 kPa as compared to the neat foam of 117 kPa. In another study, integration of modified diaminopropane montmorillonite (DAP-MMT) into palm olein-based polyol improved the compressive strength of the rigid PU nanocomposite foams. It was reported that DAP-MMT was capable of reducing the cell size of the rigid PU nanocomposite foams without altering the chemical structure. Rigid PU nanocomposite foams exhibited exfoliated

structure due to uniformly dispersed DAP-MMT within PU matrix. It was suggested that the formation of urea linkages between $-NH_2$ groups of DAP-MMT and $-NCO$ groups of diisocyanates could enhance the interfacial adhesion between filler and the matrix [36]. In a study carried out by Piszczyk et al. [37], modified MMT enhanced the compressive stress at 20% strain from 100 to 174 kPa of the rigid PUF. It was recommended that the presence of hydroxyl group of OMMT facilitates the dispersion of the nanofillers in the polyol mixture, hence resulting in improved compressive stress. In a similar way, comparative study of the properties of rigid PU/OMMT nanocomposite foams prepared using organoclay as blowing agent was conducted by Xu et al. [38]. The resultant foams demonstrated uniform and finer cell structures as compared to the rigid PUFs prepared from unmodified clay. Incorporation of up to 8 phr organoclay in the formulation revealed that rigid PUF with 2 phr organoclay resulted in the improvements of 110 and 152%, in the tensile and compressive strengths, respectively. The study also highlighted that the highest carbonyl hydrogen-bonding index (2.17) was achieved at 2 phr of organoclay. The index decreased (0.96) when incorporation of organoclay was more than 4 phr. The results from the study proved that finer cell structure of rigid PU/OMMT nanocomposite foams can be accomplished using organoclay as blowing agent. In addition, more hydrogen bonding between PU and organoclay contributes to the improvement of the strengths.

A great number of literatures addressed the improvement of mechanical and thermal performance of rigid polyurethane/organoclay nanocomposite foams [35–41]. These properties include heat and flame resistance, mechanical strength, gas barrier resistance, thermal stability, and ionic conductivity. However, studies on the effect of OMMT on palm oil-based flexible PUF are quite scarce.

The objectives of the study were to prepare flexible PU nanocomposite foams using palm olein-based polyol, Pioneer E-135 (US 7,932, 409) [42], and petroleum-based polyol with OMMT as nanoclay. The effects of the Pioneer E-135 as a drop in replacement for petroleum-based polyol in the formulation and the effects of OMMT on mechanical properties and morphology of flexible PU foams prepared from petroleum- and palm olein-based polyol and the respective PU/OMMT nanocomposite foams were investigated. The flexible PU foams produced could have a high potential to be used for mattresses or car seat.

2. Experimental

2.1. Materials. Nanoclay, Cloisite® 20A, a natural montmorillonite modified with a dimethyl, dihydrogenated tallow, quaternary ammonium with a concentration of 95 meq/100 g clay was purchased from Southern Clay Products (USA). Petroleum-based polyols, Poly-G® 85–29 (hydroxyl number 28 mg KOH/g, ethylene oxide capped polyether polyol, equivalent weight 2062) and Poly-G 92–27 (hydroxyl number 28 mg KOH/g, polyether polyol, equivalent weight 2004), were obtained from Arc Chemicals Inc. (China). Desmodur 3133 (polymeric diphenylmethane diisocyanate, pMDI) was

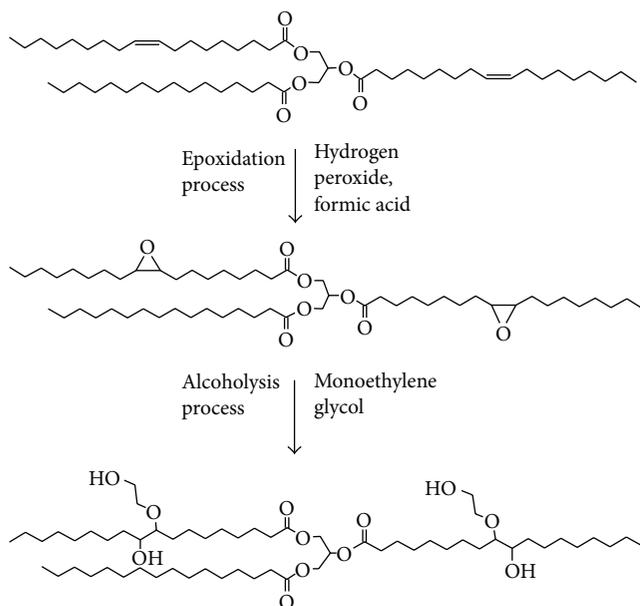


FIGURE 1: Schematic diagram for the synthesis of polyol from palm olein.

purchased from Bayer (Malaysia). Pioneer E-135 was prepared by Malaysian Palm Oil Board (MPOB). In all formulations studied, water was used as the blowing agent. Catalysts, Dabco 33LV and NiAx A-1, were purchased from Kimia Cergas (Malaysia) and dibutyltin dilaurate (DBTDL) was obtained from GoldShmidt (Malaysia). Surfactant, Tegostab B 4113, was purchased from Evonik (Malaysia). Lumulse POE 26 as a cell opener was obtained from Lambert Technologies (Malaysia). All materials were used as received.

2.2. Methods. The foam was prepared by mixing palm olein-based polyol (Pioneer E-135), commercial petroleum-based polyols, amine and tin catalyst, silicone surfactant, and water together in a plastic cup. The mixture was stirred under high shear rate with a mechanical stirrer at 2500 rpm for one minute. Then, an appropriate amount of pMDI which was calculated based on the isocyanate index was poured into the mixture. Stirring was continued and stopped just before the cream time. The mixture was then quickly poured into a plastic container (20 × 20 × 10 cm). The foam was allowed to rise and cured at 80°C in the oven for 10 minutes. The demoulded foams were hand crushed to open the cell windows. Mechanical and morphology analysis were conducted after aging the foams at 25°C for a minimum of 7 days.

Pioneer E-135 was synthesised from 100% RBD palm olein. Schematic diagram of the synthesis and flowchart of the production are given in Figures 1 and 2, respectively. The properties of Pioneer E-135 were provided by MPOB as shown in Table 1. In this study, four sets of PU foams were prepared. The first set of foams were prepared from 100% petroleum-based polyol and followed by PU foams made from 10%, 20%, and 30% palm olein-based polyol as a drop in replacement of the petroleum-based polyol. All foams prepared were incorporated with 3, 5 and 7 wt% OMMT.

TABLE 1: Properties of Pioneer E-135.

Properties	Pioneer E-135
Hydroxyl value, mg KOH/g	134
Equivalent weight, (Eq. Wt.)	419
Acid value, mg KOH/g	0.70
Moisture content, %	0.15
Oxirane oxygen content, %	0.03
Iodine value, g I ₂ /100 g	7.02
Viscosity at 25°C, cP	4400
Glass transition (T_g), °C	14.75
Molecular number (M_n), Daltons	2537
Molecular weight (M_w), Daltons	5798
Polydispersity index	2.28

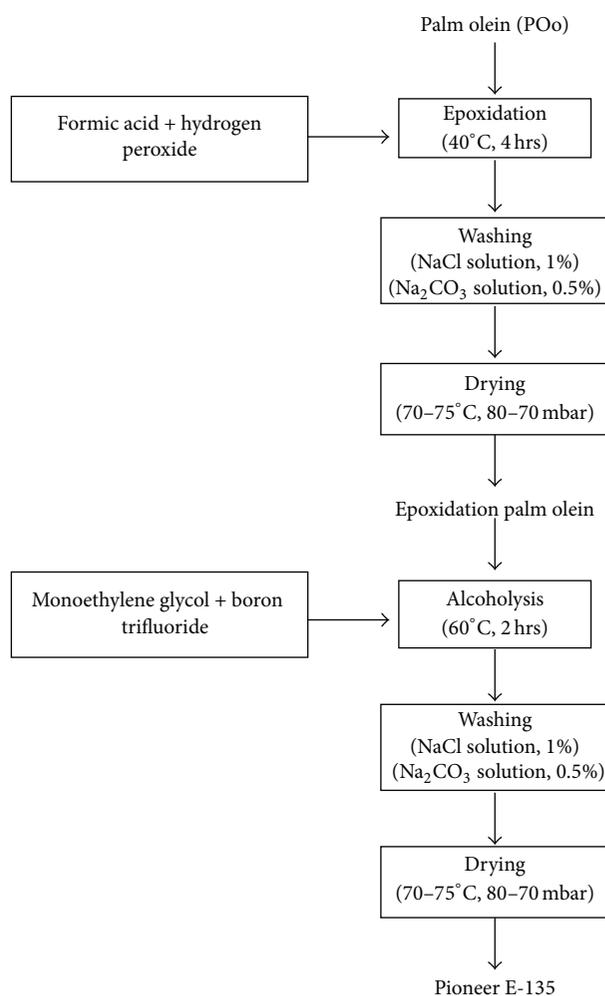


FIGURE 2: Flowchart of the production of Pioneer E-135.

Formulations of PU foams prepared are shown in Table 2. Foams densities were in the range of 45 to 48 kg/m³. The designations of the PU foams are tabulated in Table 3.

2.3. Fourier Transform Infrared (FTIR). Identification of functional groups of neat petroleum- and palm-based PU

TABLE 2: Formulation of petroleum- and palm-based PU foams.

Ingredients	Concentration, php ^a	
	Petroleum-based PUF	Palm-based PUF
Poly-G 85-29	93.5	83.5
Poly-G 92-27	5.0	5.0
Pioneer E-135	—	10
Lumulse POE 26 (cell opener)	1.5	1.5
Diethanolamine (chain extender)	0.5	0.5
Tegostab B 4113 (surfactant)	2.0	2.0
Dabco 33LV (catalyst)	0.1	0.1
Niax A-1 (catalyst)	0.1	0.1
DBTDL (catalyst)	0.15	0.15
Distilled water (blowing agent)	3.75	3.75
Isocyanates index ^b of Desmodur 3133	90	90

^aThe concentrations of all ingredients are expressed in parts per hundred parts of polyol.

^bThe amount of isocyanates used relative to the theoretical equivalent amount. Isocyanate index is defined as the ratio of the equivalent amount of isocyanate used relative to the theoretical equivalent amount times 100.

TABLE 3: Designations of the prepared PU foams.

Designations	Descriptions
Neat petroleum PU foam	PU foam prepared from 100% petroleum-based polyol.
PU nanocomposite foams	PU foams prepared from 100% petroleum-based polyol with incorporation of 3, 5, and 7 wt% OMMT.
Palm-based PU foam	PU foam prepared from petroleum-based polyol and Pioneer E-135 (90 : 10, 80 : 20, and 70 : 30).
PU bionanocomposite foams	PU foam prepared from petroleum-based polyol and Pioneer E-135 (90 : 10) with incorporation of 3, 5, and 7 wt% OMMT.

foams and the nanocomposite foams was conducted using Perkin Elmer, Spectrum 100 FT-IR Spectrometer (Llantrisant, UK). The samples were scanned between 4000 and 650 cm^{-1} wavenumbers.

2.4. Tensile Properties. The test was conducted according to the ASTM D3574 (Test E). Foams were cut into flat sheets of 12.5 ± 1.5 mm thickness and stamped to dumb-bell shape as described in ASTM D 412. The test was carried out using Hounsfield S-Series Machine (Surrey, UK). The specimens were placed in the grips of the testing machine and pulled at a speed of 500 ± 50 mm/min. The tensile strength of the foam was obtained using the average value from three samples.

2.5. Tear Resistance. Tear resistance of the foams was determined using Hounsfield S-Series Machine (Surrey, UK) according to the ASTM D3574 (Test F). The specimens were clamped at the jaws of the testing machine and pulled across at the speed of 500 ± 50 mm/min.

2.6. Resilience. Foam resilience was measured according to ASTM D3574 (Test H). This test is principally a ball rebound test in which a steel ball is dropped from a prescribed height onto the sample and the percentage of recovered height is recorded. The specimen size was 100 mm \times 100 mm \times 50 mm.

Average value of three specimens from different locations of a sample was recorded.

2.7. Scanning Electron Microscopy (SEM). Morphology of the foam such as cell size was observed using Zeiss, Leo 1450 VP Scanning Electron Microscopy (Oberkochen, Germany). A thin piece of foam was carefully sliced with a sharp blade and stuck to aluminium stubs. The samples were then sputter-coated with a total of 15 nm of Au/Pd and observed under the microscope employing an accelerating voltage of 10 kV and a probe current of 6×10^{-11} amps.

2.8. Transmission Electron Microscopy (TEM). Morphology of the PU/OMMT foam with 5 wt% OMMT was also studied using CM 12 Philips Transmission Electron Microscopy (Eindhoven, Netherlands). The 70 nm sectioned ribbons were placed on 400-mesh copper grids for imaging using TEM. The samples were imaged at high magnification of 28 000X with accelerating voltage of 100 kV.

3. Results and Discussion

3.1. Preparation of Polyurethane Bionanocomposite Foams. PU bionanocomposite foams were prepared by replacing petroleum-based polyol with 10 (PUF10), 20 (PUF20), and 30% (PUF30) Pioneer E-135 with incorporation of 3, 5,

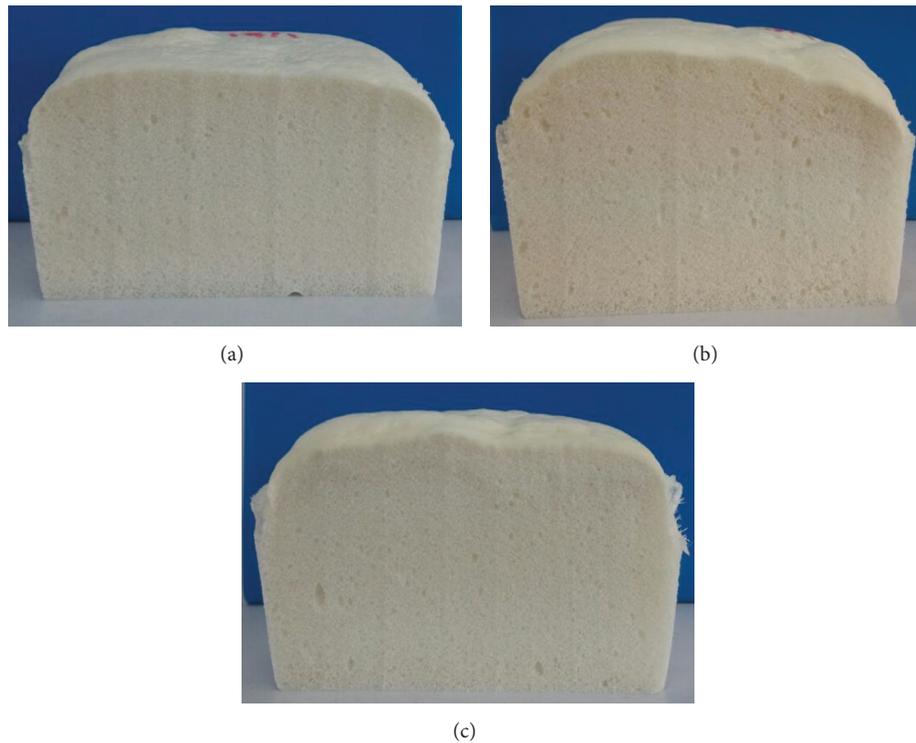


FIGURE 3: PU bionanocomposite foams prepared from 10% Pioneer E-135 with incorporation of (a) 3 wt% OMMT, (b) 5 wt% OMMT, and (c) 7 wt% OMMT.

and 7 wt% OMMT in the formulation. Figures 3 and 4 show the PUF10 and PUF20 with incorporation of 3, 5, and 7 wt% OMMT, respectively. PUF10 exhibited uniform cell structures. In the case of PUF20 and PUF30, coarse cell structures were clearly evident. Therefore, the respective foams were not evaluated further due to the defects of the foams. Another defect, shrinkage phenomenon, was reported by Pawlik and Prociak [12] when more than 15% palm olein-based polyol was incorporated in the formulation. It was found that significant changes in the foam formulation are required in order to eliminate undesirable effects such as shrinkage, coarse cell structures, and collapse. The optimisation of the foam formulation, including quantities of catalysts and surfactant to be added, has to be studied.

3.2. Fourier Transform Infrared (FTIR). In the synthesis of polyurethane (PU), there are a number of reactions that happen concurrently due to reactive isocyanate group, which reacts with molecules that have “active hydrogen” such as polyol (hydroxyl group), water, and amine [43], as illustrated in Figure 5. The most important reaction is between isocyanate and hydroxyl group of polyol (Reaction 1). This reaction leads to production of urethane group, which forms the majority of functional groups found in PU products. Water is used as a source of blowing agent in the production of PU foams, where it reacts with isocyanates to form unstable carbamic acid (Reaction 2). The unstable carbamic acid decomposes further to form amine compound and gaseous carbon dioxide. This reaction is a very convenient source

of a gas, which is necessary to generate the cellular structure of polyurethane foams. The amine, which comes from diethanolamine (chain extender) or decomposed unstable carbamic acid, reacts with an isocyanate group and generates symmetrical disubstituted urea (Reaction 3). In this study, the reaction (Reaction 1) was catalysed by an organotin compound known as dibutyltin dilaurate (DBTDL). At high temperature, the reaction between isocyanate and urethane group leads to formation of an allophanate (Reaction 4) while the reaction between urea group and isocyanates leads to formation of biuret linkage (Reaction 5) [44]. Some of the reactions discussed above can be monitored via FTIR through their functionalities.

FTIR spectra of neat petroleum- and palm-based PU foams prepared with 3, 5, and 7 wt% OMMT are illustrated in Figures 6 and 7, respectively. The characteristic of FTIR spectra for PU nanocomposite and PU bionanocomposite foams was almost unchanged when compared to the neat petroleum- and palm-based PU foams. This could indicate that chemical structures of the neat petroleum- and palm-based PU foams were not affected by incorporation of OMMT [35, 45]. Broad stretching of hydrogen-bonded urethane, N–H, was observed at 3405 cm^{-1} . The band at $2995\text{--}2860\text{ cm}^{-1}$ was attributed to the C–H stretching vibration. There was no stretching vibration band at 2270 cm^{-1} which is a characteristic peak of isocyanate (--N=C=O) group, indicating that all of the isocyanate groups reacted during polymerization. Wavenumbers at $1731\text{--}1718\text{ cm}^{-1}$ and at $1685\text{--}1706\text{ cm}^{-1}$ are assignable to the stretching of

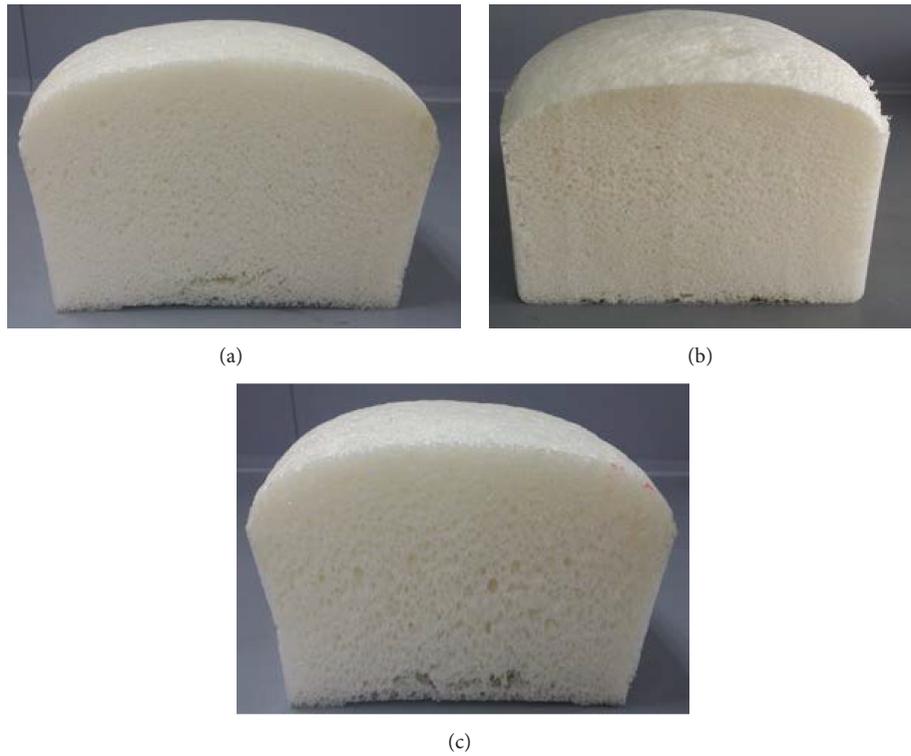


FIGURE 4: PU bionanocomposite foams prepared from 20% Pioneer E-135 with incorporation of (a) 3 wt% OMMT, (b) 5 wt% OMMT, and (c) 7 wt% OMMT.

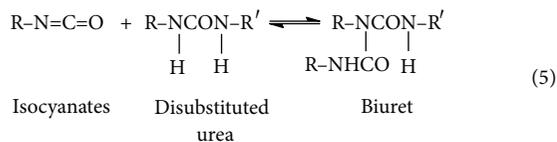
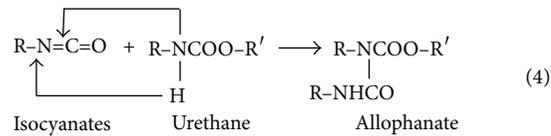
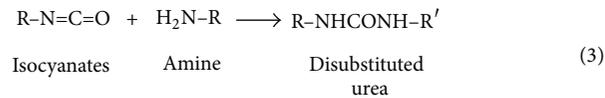
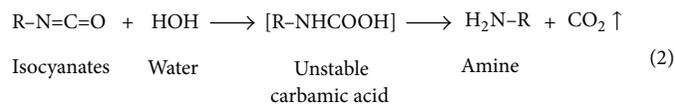
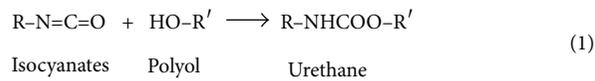


FIGURE 5: Schematic diagram for the reactions of isocyanates with (1) polyol, (2) water, (3) amine, (4) urethane, and (5) disubstituted urea in the synthesis of polyurethane. Source: Ionescu [44].

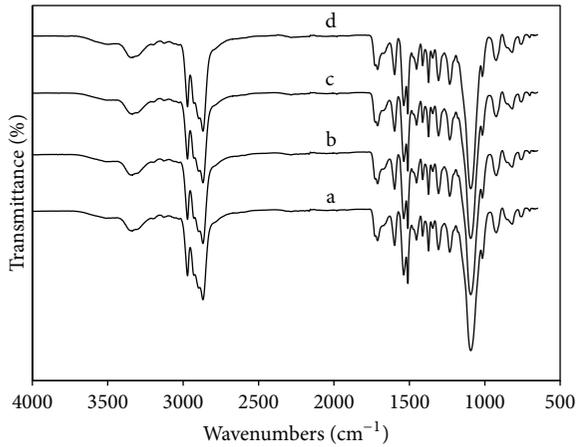


FIGURE 6: FTIR spectra of (a) neat petroleum PU foam and PU nanocomposite foams with (b) 3 wt% OMMT, (c) 5 wt% OMMT, and (d) 7 wt% OMMT.

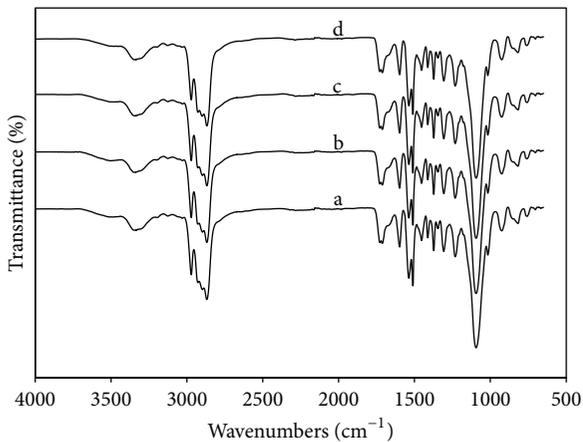


FIGURE 7: FTIR spectra of (a) palm-based PU foam and PU bionanocomposite foams with (b) 3 wt% OMMT, (c) 5 wt% OMMT, and (d) 7 wt% OMMT.

hydrogen-bonded carbonyl groups which leads to ordered and disordered conformation, respectively. These hydrogen-bonded carbonyl groups can be observed at lower wavenumbers compared to non-H-bonded (free) carbonyls group which appears at $1731\text{--}1733\text{ cm}^{-1}$ [45]. Combined motion of H–N–C=O in amide II was observed at 1510 cm^{-1} [46].

3.3. Mechanical Properties

3.3.1. Tensile and Tear Resistance. Mechanical properties of nanoclay-based polymer composites can be directly affected by intercalation/exfoliation levels in nanocomposites morphology. Figures 8 and 9 illustrate tensile and tear strength of neat petroleum- and palm-based PU foams prepared with 3, 5, and 7 wt% OMMT, respectively. Addition of OMMT had an effect on the strength of the nanocomposite foams. The tensile and tear strengths of the nanocomposites improved with the addition of up to 5 wt% of OMMT. It shows a 33% (petroleum) and 63% (palm-based) increase of the tensile strength from

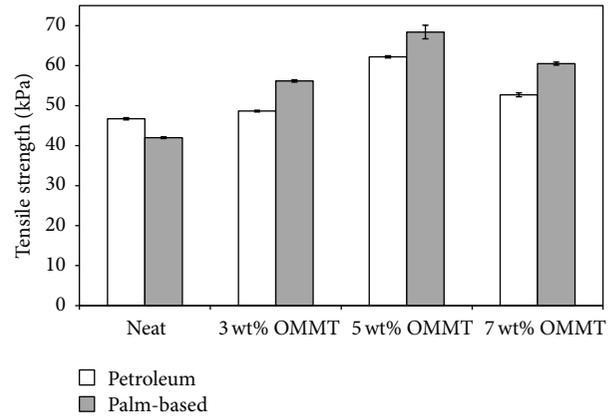


FIGURE 8: Tensile strength of PU nanocomposite foams and PU bionanocomposite foams with different amounts of OMMT.

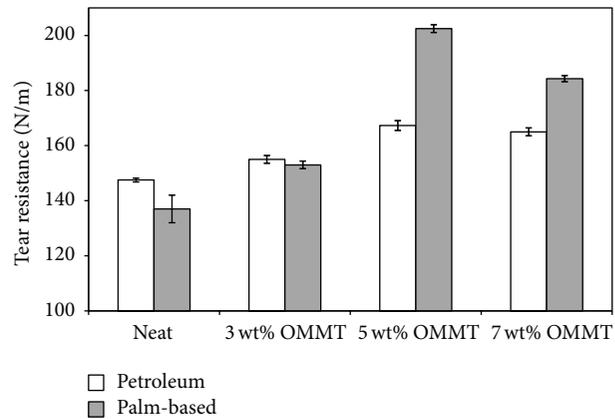


FIGURE 9: Tear resistance of PU nanocomposite foams and PU bionanocomposite foams with different amounts of OMMT.

46.7 kPa and 42.0 kPa to 62.2 kPa and 68.4 kPa, respectively (Figure 8). The tear strength increased 13% (petroleum) and 48% (palm-based) from 147.5 N/m and 137.0 N/m to 167.3 N/m and 202.5 N/m, respectively (Figure 9). However, further incorporation of OMMT (7 wt%) reduced its strength due to the agglomeration of the OMMT within the PU matrix. According to Chan et al. [47] a large amount of nanoclay added in the system may agglomerate or cluster of nanoclay will be formed. It was observed that OMMT had a more significant effect on mechanical properties of PU bionanocomposite foams compared to PU nanocomposite foams. The strength of the PU bionanocomposite foams was higher than the PU nanocomposite foams, regardless of the amount of OMMT added, although the palm-based PU foams had a lower strength as compared to the neat petroleum PU foam. This phenomenon was supported with smaller cell size of PU bionanocomposite foams compared to the cell size of PU nanocomposite foams as shown by SEM images. It is well known that improved strength of the nanocomposite foams can be achieved by smaller and uniform cell sizes. According to Wilkinson et al. [48] strong H-bond formation between the edge hydroxyl groups of

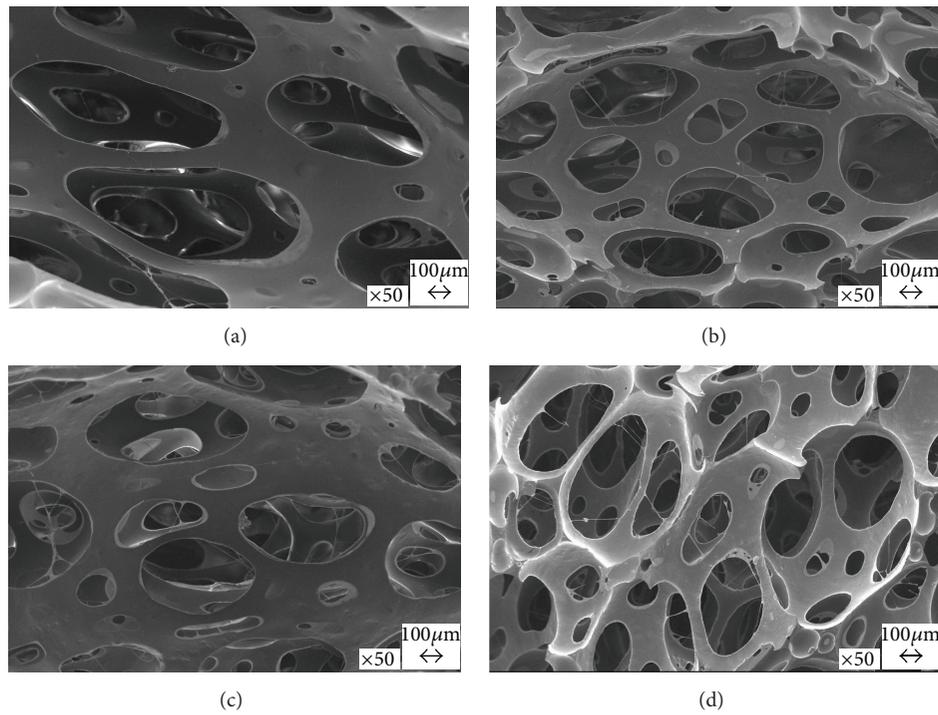


FIGURE 12: SEM micrographs of (a) neat petroleum PU foam and PU nanocomposite foams with (b) 3 wt% OMMT, (c) 5 wt% OMMT and (d) 7 wt% OMMT.

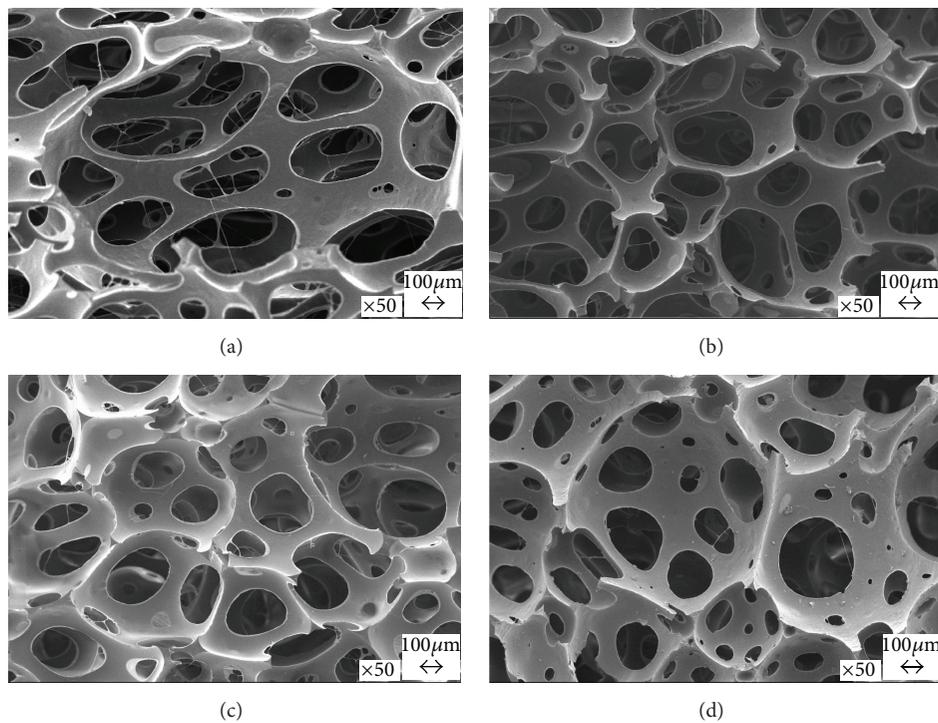


FIGURE 13: SEM micrographs of (a) palm-based PU foam and PU bionanocomposite foams with (b) 3 wt% OMMT (c) 5 wt% OMMT and (d) 7 wt% OMMT.

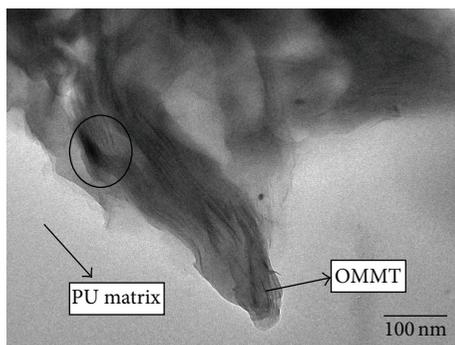


FIGURE 14: TEM image of PU nanocomposite foams with 5 wt% OMMT.

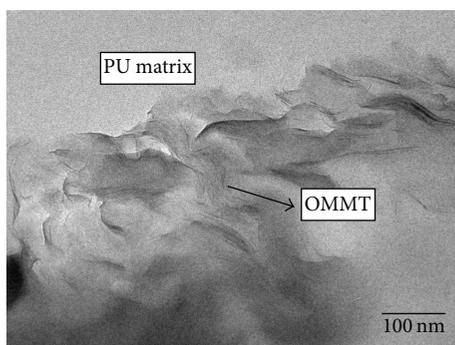


FIGURE 15: TEM image of PU bionanocomposite foams with 5 wt% OMMT.

Smaller cell sizes were observed for PU bionanocomposites foam with incorporation of 5 wt% OMMT and this in return improved 63%, 48%, and 21% of tensile and tear strength and resilience, respectively. Incorporation of more than 5 wt% OMMT however reduced the average performance of the PU nanocomposite foams.

Conflict of Interests

The authors have declared no conflict of interests.

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