Preparation and Characterization of Oil Palm Leaf Fiber/Polypropylene/Epolene® E-43 Composite

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Oil palm leaf fiber was used as a reinforcement material for the preparation of polypropylene composite. First, the influence of fiber loading on the mechanical and thermal characteristics of the composite was investigated. Epolene® E-43 was used as a compatibilizing agent to enhance the mechanical and thermal properties as well as the morphology of the oil palm leaf fiber/polypropylene composite. The composites were prepared with 10, 20, 30, 40, 50, and 60% ratios of fiber by melt blending technique using internal mixer machines and compressing molding. The addition of fiber led to an increase in the tensile and flexural properties of the composite in comparison to virgin polypropylene. Similarly, Epolene® E-43 was found to improve all the studied properties. Water absorption increased with increasing fiber loading; however, the addition of Epolene® E-43 reduced this property. According to Fourier transform infrared spectroscopy results, interactions between the components of the composite were physically indicated for all fiber content ratios, except 20% due to more interaction between the components. Dynamic mechanical analysis (DMA) showed that the presence of the oil palm leaf fiber enhances mobility but reduces stiffness. The morphological analysis of the composites using a field-emission scanning electron microscope showed that Epolene® E-43 reduced the size and number of voids, which is consistent with the results from the mechanical analysis.

Keywords: Oil palm leaf fiber; Epolene® E-43; Dynamic mechanical properties; Mechanical properties

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INTRODUCTION

The dangers of global warming and pollution necessitate the use of certain materials for multiple purposes. The widespread utilization of non-natural plastics, especially in packaging for various food products, has caused many complications affecting public health, society, and the economy. Therefore, the replacement of this material is a top priority. Recently, the waste management industry has faced problems of rapidly reducing landfill fields and a dramatic increase in the cost of plastic waste disposal. The requirement of using safe and degradable materials is a prominent research subject with serious legislative aspects. The use of plant fibers for reinforcement in the industrial fabrication of composites could be a suitable solution. For instance, natural fiber filler from oil palm, flax, hemp, sisal, kenaf, and fruits can be used as an alternative and appropriate applicant to replace currently used synthetic fibers. Several studies on the properties of natural fiber reported that the benefit of these materials lies in their low weight, free formability, and low density, which leads to high specific strength (Jawaid and Abdul Khalil 2011). The use of natural fillers as reinforcement in composite could produce cheap and environmentally friendly products that also reduce environmental pollution because of their naturally degradable constituents (Yang *et al.* 2007).

Tropical countries such as Malaysia ordinarily dispose of large quantities of oil palm leaves (OPL) in the process of pruning palm oil trees. Lignocellulosic fiber from OPL has been considered as a prospective reinforcement fiber because it has numerous advantages, such as biodegradability, renewability, and being environmentally friendly (Arbelaiz *et al.* 2005). However, there is a lack of information about the use of OPLF as reinforcing fillers in composites.

The fast progress in the research of naturally based fiber composites has continued vigorously to find methods for using lignocellulosic material as reinforcing fillers in synthetic polymers such as polyethylene (PE) and polypropylene (PP). The differences between hydrophilic lignocellulosic fiber and hydrophobic polymer matrix lead to weak interfacial bonds between them, which reduces the mechanical properties of the resulting composite (Cantero *et al.* 2003). Coupling or compatibilizing agents have also had positive results in better adhesion between lignocellulosic fiber and PP matrix (Colom *et al.* 2003). Several effective coupling agents for lignocellulosic/PP composite have been established, such as graft copolymers of PP and maleic anhydride (MAH) (Felix and Gatenholm 2003; Li *et al.* 2001; Sathe *et al.* 2003). The compatibility between fibers and PP matrix has been improved with the use of these coupling agents (Van De Velde and Kiekens 2001), and the distribution of flax fiber in PP was also enhanced (Arbelaiz *et al.* 2005). Different compatibilizers, such as Epolene® E-43 (maleic anhydride modified-poly-propylene) (García-López *et al.* 2007; Rozman *et al.* 2001), polymethylene (polyphenyl isocyanate) (Pickering and Ji 2004), g-methacryloxypropyltrimethoxysilane (A-174), vinyltri (2-methoxy ethoxy) silane (A-172) (Yazdani *et al.* 2006), g-aminopropyltriethoxysilane (Liu and Wang 2007), poly(propylene-acrylic acid), and poly(propylene ± ethylene acrylic acid) have also been studied for lignocellulosic fiber/PP compatibilization.

Among the studied coupling chemicals, Epolene® E-43 (E-43) is the most efficient because of its three main advantages: (i) its large market availability, (ii) its content of alkoxysilane groups at one end, which are able to react with large amounts of hydroxyl groups on the surface, and (iii) its large number of functional groups that are capable of modification by the matrix function. It has been reported that E-43 enhanced the mechanical properties of composites because it has large numbers of MAH groups, which tend to form chemical bonds with hydrophilic lignocellulosic fibers. This could smooth the progress of wetting the hydrophobic polymer chain, which can enhance the compatibility between both components (Yang *et al.* 2007).

There is a scarcity of information regarding the impact of fiber loading and E-43 content on the mechanical and thermal properties of composites. Thus, this study focused on determining the optimum ratio of PP to oil palm leaf lignocellulose and identifying the influence of coupling agents on the mechanical and dynamic properties of the composites. Maleic anhydride from the coupling agent E-43 was used to evaluate the improvement in interfacial bonding between PP matrix and OPL lignocellulosic fiber; their mechanical and dynamic mechanical characteristics were assessed using several different methods of analysis.

EXPERIMENTAL

Materials

Homopolymer polypropylene was supplied by Polypropylene Malaysia Sdn. Bhd. (Malaysia), with a melt flow index and density of 12.0 g/10 min and 0.903 g/cm^3, respectively. Epolene® E-43 (Eastman Chemical Products; Malaysia) with a low molecular weight (M_w = 9100) and density (0.934 g/mL) was added to improve the properties of the composites. For lignocellulosic fiber extraction, several chemicals were used, including sodium hydroxide and hydrochloric acid. Oil palm leaves were collected and transported to the polymer laboratory. Hydrophilic lignocellulosic fiber extracted from OPL and hydrophobic PP matrix were used for composite preparation.

Methods

Preparation of fiber

Oil palm leaves (20 kg) were air-dried in an open area for 6 to 7 days. The leaves were cut to about 2 to 3 cm in length and then dried in an air oven at 40 °C for 24 h to remove any remaining moisture content. The dried material was then powdered and sieved to a consistent filler size through a 150 µm sieve.

Extraction of fiber

The extraction of lignocellulosic fiber from OPL was performed by soaking 100 g of the dried powder in 1000 mL of 4% NaOH, then leaving the mixture at room temperature for 4 h. The residual solvent was then completely removed by vacuum filtration after washing the fiber with distilled water to eliminate any debris. A 2% HCl solution was used to adjust the pH to 7.3 and hydrolyze the dark green waxy material obtained from the filtration process. The resulting material was again washed with distilled water and filtered. To remove residual moisture, the lignocellulosic fiber was dried in a hot air oven at 60 °C. Finally, the dried material was ground, sieved with a 150-µm strainer, and stored in a chiller (4 °C) for further experiments.

Preparation of composites

The composite preparation was performed by mixing the constituents (PP, OPLF, and 2% E-43) in a Haake Rheomix 600 (Thermo Fisher Scientific Inc.; MA, USA) with a twin-roll mixer. The compounder was set at 160 °C with a rotor speed of 50 rpm for 10 min. The percentages of the components used to prepare the composites are given in Table 1 and Table 2.

Table 1. Composition of PP/OPLF

Composites	PP (wt. %)	OPLF (wt. %)
0%	100	0
10%	90	10
20%	80	20
30%	70	30
40%	60	40
50%	50	50
60%	40	60

Table 2. Composition of PP/OPLF with 2% E-43

Composites	PP (wt. %)	OPLF (wt. %)
0%	100	0
10%	90	88
20%	80	78
30%	70	68
40%	60	58
50%	50	48
60%	40	58

The mixture was put in a mold with a length of 160 by 160 mm and a thickness of 1 and 3 mm. The mold was then placed in a hydraulic hot-press (Hsin-Chi Machinery Company Ltd.; Taiwan). Finally, the composites were pressed at 170 °C for 10 min, followed by 5 min of preheating and 5 min of cooling under pressure.

Mechanical properties

The mechanical properties of PP/OPLF composites, including tensile properties, flexural properties, and water absorption, were evaluated. All the mechanical properties were performed using the average values of at least five tested samples.

Tensile properties

For the tensile test, specimens were cut into a dog-bone shape. An Instron Universal Testing Machine (Model 4302, Series IX, Instron; PA, USA) with a loading cell of 1.0 kN and a crosshead speed of 5 mm/min was used to test the tensile properties of the composites according to ASTM D 638-01 (Haque *et al*. 2009). The Instron Series IX software was implemented to determine the tensile strength, tensile modulus, and elongation at break.

Flexural properties

The flexural strength and modulus of the composites were assessed using the three-point bending mode of the testing machine mentioned above at a crosshead speed of 3 mm/min, according to ASTM D 790- 10 (Haque *et al*. 2009). The samples used for this test were cut to a rectangular shape measuring 127 mm by 13 mm by 3 mm in length, width, and thickness, respectively. Flexural strength and flexural modulus were used to determine using Instron Series IX software.

Water absorption

The water absorption test was carried out using rectangular specimens with proportions of 39 mm by 10 mm by 3.1 mm. The drying of samples was performed in an oven at 150 °C for about 5 min; afterwards, the samples were cooled in silica gel desiccators and then weighed using an analytical balance to obtain the initial weight of the specimens. The water uptake was evaluated according to ASTM D 570-99 (Haque *et al*. 2009). Weighed specimens were placed in distilled water for 2 h and 24 h in 100 °C and 23 °C, respectively. After the inundation period, the water attached to the specimens' surface was removed using a cloth tissue, and the final weights of the specimens were determined. To measure the amount of absorbed water, the weight changes of the specimens were calculated using the following equation:

$$\text{Water absorption (\%): (final weight-initial weight)/(initial weight)} \times 100$$

Dynamic mechanical analysis (DMA)

DMA curves of the pure PP and PP/OPLF composites were tested in a temperature range of -150 to 150 °C on a Perkin Elmer Diamond DMA (PA, USA) with a 20-μm strain amplitude and a 98-mN initial force amplitude. Analyses were performed at frequencies of 1 Hz and at a heating rate of 7 $°C \cdot min^{-1}$ under nitrogen atmosphere. Rectangular specimens measuring 20 mm × 10 mm × 0.7 mm were used for the measurements. The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of each specimen were acquired as a function of temperature according to ASTM D4440 – 08 (Essabir *et al.* 2013).

Fourier transform infrared spectroscopy (FT-IR)

Changes in the characteristic functional groups of the samples caused by OPLF loading and the addition of E-43 were scanned using a 1650 Perkin Elmer Fourier transform infrared (FT-IR) spectrophotometer (Perkin-Elmer; Los Angeles, CA, USA). The data were scanned at 4000 cm^{-1} and 280 cm^{-1} scan ranges with 4 cm^{-1} spectral resolution. The program FT-IR Spectrum Software (Perkin Elmer) was implemented to analyze the data.

Field emission scanning electron microscopy (FE-SEM)

The surface structure and interfacial bonding between the filler and the PP matrix of PP/OPLF composites before and after compatibilization with E-43 were examined using a JEOL JSM-6701F field-emission scanning electron microscope (FE-SEM, Hitachi High-Technologies Europe GmbH.; Krefeld, Germany) under an accelerating of voltage of 20 kV. The images were taken from the fracture surface after the tensile test. Micrographs at a magnification of 250X were chosen to show the variation among samples.

RESULTS AND DISCUSSION

Tensile Properties

Figure 1 shows the tensile properties of untreated OPLF-reinforced PP composites at various fiber loadings. The incorporation of natural fibers into a polymer matrix can either increase or decrease the strength of the composite. The tensile strength markedly declined as the amount of fiber increased (Fig. 1a). According to Fernandes *et al.* (2013), for irregularly shaped fillers, the strength of the composites decreases because the filler is unable to support the stresses transferred from the polymer matrix. There is no compatibility between the fiber and matrix with incorporation of OPLF, which led to the decline in tensile strength. The most significant decline in tensile strength was observed for the 20% OPLF content, whereas there were no significant changes with the addition of fiber over 20%, which indicates that there was no significant interaction between PP and OPLF. The Young's modulus significantly declined as the amount of OPLF increased as supported by SEM results, which showed that with the increase of OPLF ratio, the micro-voids increased and resulted in stiffness decline. One possible reason for this is the decline of the destruction capability within the elastic zone caused by OPLF, as shown in Fig. 1b (Demir *et al.* 2006). In addition, the PP matrix could provide deformation ability under tensile stress, where the displayed fragility performance of the OPLF is associated with a subsequent loss of toughness in the PP matrix.

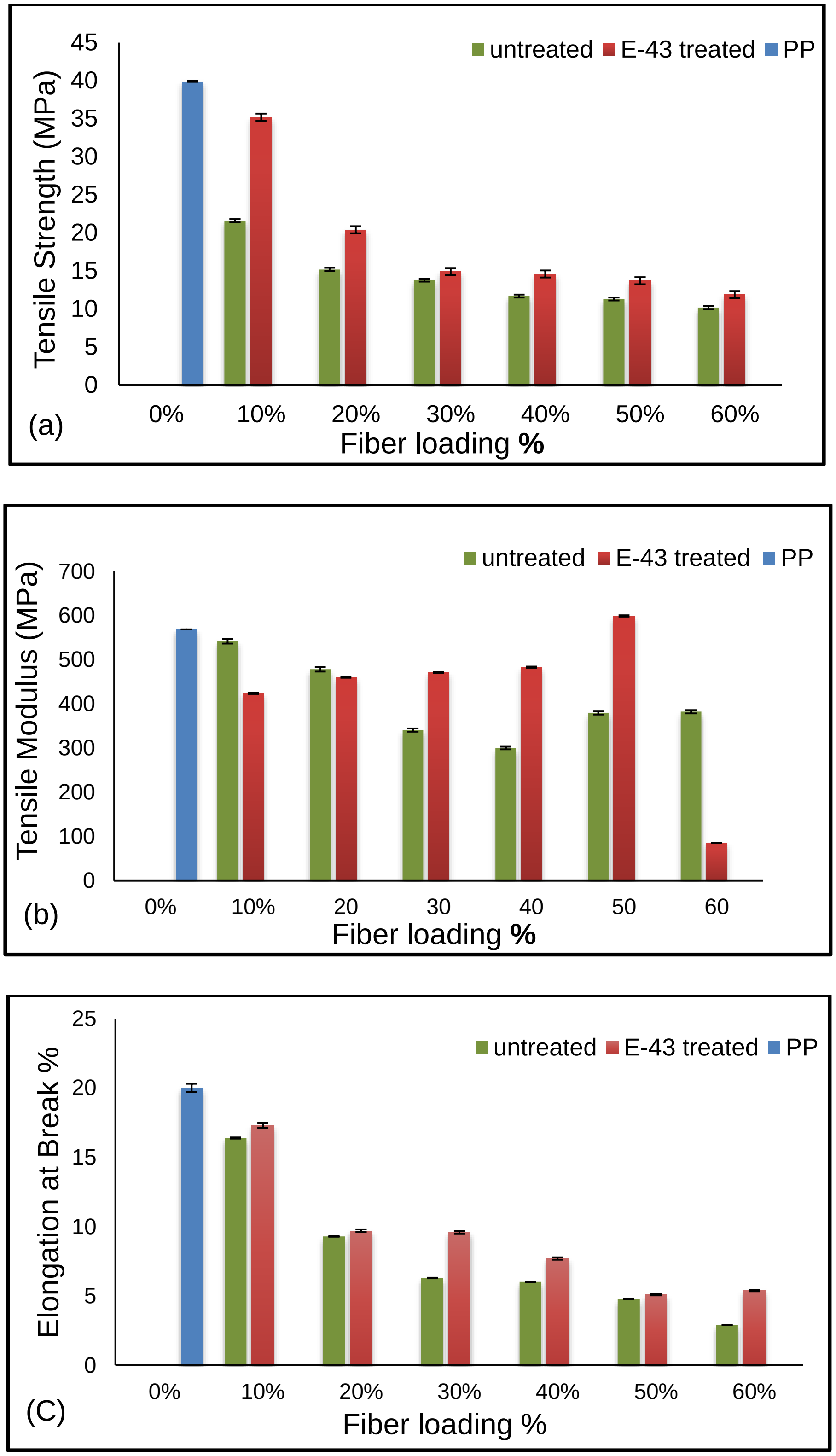


Fig. 1. (a) Effect of fiber loading and E-43 treatment of PP/OPLF composites on tensile strength.
(b) Effect of fiber loading and E-43 treatment of PP/OPLF composites on tensile modulus.
(c) Effect of fiber loading and E-43 treatment of PP/OPLF composites on elongation at break

For untreated composites, the Young's modulus slightly increased when 50% and 60% OPLF was incorporated. This may be because of OPLF dispersal in the PP matrix as made clear from SEM images (not supplied here). OPLF content has the most significant effect on the elongation at breaking point, as shown in Fig. 1c. This parameter showed a decrease from 20% to 11% when 20% of untreated PP/OPLF composites were incorporated compared with net PP. However, there was an insignificant difference in the elongation for untreated composites with OPLF content of more than 40%.

A comparison between both treated and untreated composites with a coupling agent can explain the significance and efficacy of a coupling agent. Figure 1a shows a decrease in tensile strength with increasing OPLF content in the E-43 modified composites. This decline was significantly lower in E-43-treated composites (by approximately 12.5%) compared with untreated composites (50%) for 10% wt OPLF. Thus, E-43 possibly improved adhesion capability at the interface section and might accordingly increase the tensile strength of the E-43-modified composites as compared with untreated ones. One possible explanation for these results is that stress was transmitted from the matrix to the fiber, demonstrating enhanced the mechanical properties, which is supported by the SEM results. This is probably a result of the effective reaction of the maleic anhydride component on Epolene® E-43 with hydroxyl groups of OPLF. It has been shown that maleic anhydride can readily react with lignocellulosic hydroxyl groups (Vilaseca *et al.* 2008). The tensile modulus results show that the stiffness of a composite increases as OPLF is increased in the presence of E-43 (Fig. 1b). Thus, OPLF and coupling agents are able to interact synergistically and enhance the stiffness of composites. This may be attributed to the ability of the coupling agents to improve the compatibility between both OPLF and PP matrix, resulting in increased stiffness. The results are in agreement with various studies on thermoplastic composites (Liu *et al.* 2009; Zhang *et al.* 2010; Rozman *et al.* 2011). The addition of E-43 slightly improved the strain at break compared with untreated composites (Fig. 1c). This trend can be explained by the enhancement of wettability and stress transfer between the fiber and the matrix. Another possible explanation to these results is that stress was transmitted from the matrix to the fiber, demonstrating an ultimate interfacial bonding, which enhances the mechanical properties. This is probably as a result of the affectivity of maleic anhydride component on Epolene E-43, to react with hydroxyl groups of OPLF. It has been shown that maleic anhydride can readily react with lignocellulosic hydroxyl groups (Vilaseca *et al.* 2008).

Flexural Properties

The influence of OPLF on the flexural properties of PP/OPLF composites is illustrated in Figs. 2 and 3. Generally, the flexural strength of untreated composites was lower than the PP alone. The addition of a low concentration of OPLF (10 to 30%) exhibited no significant variation in the flexural strength of the composites, but increased ratio of above 40% OPLF slightly improved the flexural strength. The same trend was reported by Rana *et al.* (2003), who studied the effect of palm and coir fiber on the flexural strength of PP bio-composites. This improvement in flexural strength with an increase in the percentage of reinforcement is caused by the degree of dispersion of reinforcement in the matrix, which is obvious in SEM results (Vilaseca *et al.* 2008). This is also might be caused by the availability of distributed fiber with high stiffness (Wang *et al.* 2014). Hence, the increment of the flexural strength was associated with an increase in fiber concentration, which leads to well-distributed fiber.

The structural porosity caused by high fiber content could also influence the flexural properties of the composites. The interfacial adhesion strength in a composite directly affected its flexural strength, whereas it only slightly affected its flexural modulus. Since OPLF is a high-modulus material, the elevation of its content above 40% could increase the stress fiber/fiber deformation. This resulted in high flexural modulus values at high fiber loadings, as also reported by Lou *et al.* (2007) and Rana *et al.* (2003). Thus, the stiffness of the OPLF filler positively affected the overall stiffness of the composite.

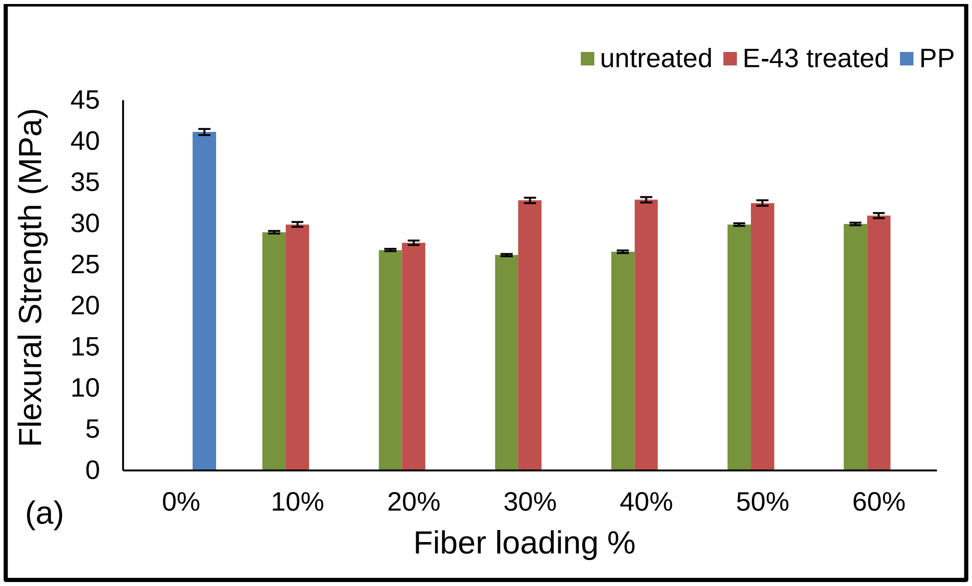


Fig. 2. Effect of fiber loading and E-43 treatment of PP/OPLF composites on flexural strength

The flexural properties of the PP/OPLF composites modified with E-43 are shown in Figs. 2 and 3. Generally, the flexural strength of E-43-modified composites was higher than that of untreated PP/OPLF composites as a function of filler loading.

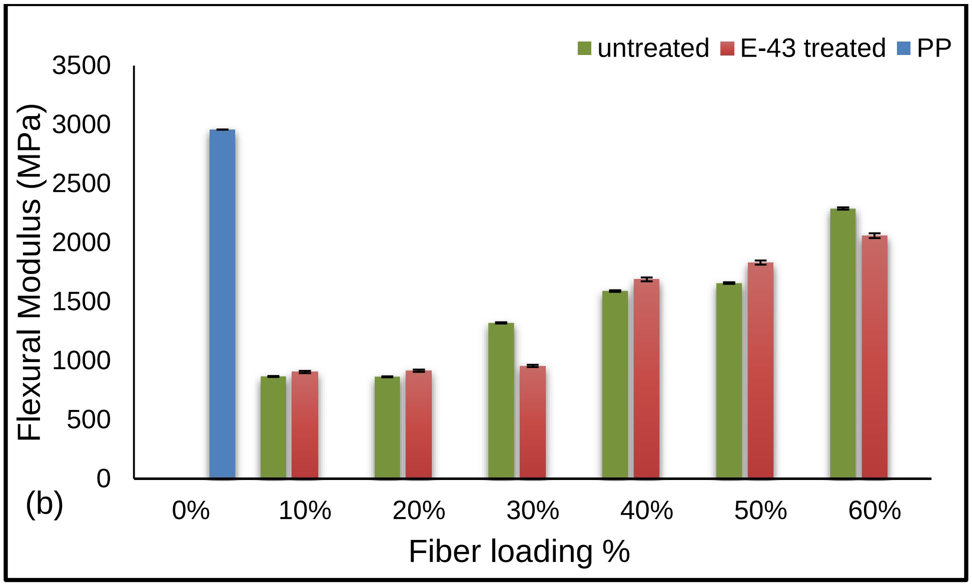


Fig. 3. Effect of fiber loading and E-43 treatment of PP/OPLF composites on flexural modulus

The flexural strength augmented with fiber content above 30%. This improvement was probably due to enhance the stress transferred from the matrix to the OPLF. This may lead to an improvement in the interfacial links between these two components as a result of interactions between the (MAH) of E-43 and OPLF. With increased fiber loading (30% and above), the flexural strength was stagnant due to E-43 equalize the dispersion degree of OPL fibers in the PP matrix above this percentage, as shown from SEM images.

E-43-treated composites showed no significant change in flexural modulus with increasing OPLF loading (Fig. 3). A possible explanation for this could be the similarity between PP and E-43 compositions. Moreover, flexural properties most likely depend on fiber properties.

Water Absorption Characteristics

The overall water absorption of PP/OPLF composites increased as a function of fiber content as shown in Fig. 4. A similar observation was reported by Yang *et al.* (2007). Water uptake of the composites is caused by hydroxyl groups in OPLF and the micro-voids in the composite surface. The increase in fiber loading leads to high concentrations of hydroxyl groups and voids in the composites, which results in an increase in water absorption (Abdul Khalil *et al.* 2001). The effects of E-43-based composites showed reduction in the water content of the composites compared with unmodified samples. When the composites were modified with E-43, the number of hydroxyl groups dropped because of the formation of ester bonds between the lignocellulosic fiber and the PP matrix. In addition, the modification of the composites enhanced the compatibility between the components, which might decrease micro-spaces in the composite surface.

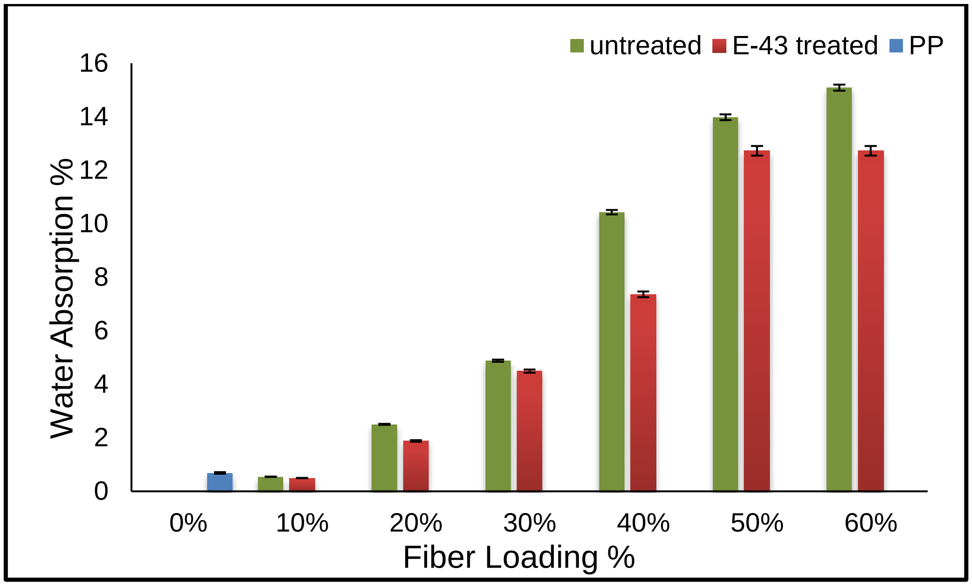


Fig. 4. Effect of fiber loading and E-43 treatment of PP/OPLF composites on water absorption

Infrared Spectroscopy Analysis

Fourier transform infrared (FT-IR) spectroscopy is one of the techniques used to study the composites' molecular structure and determine the known functional group interactions of PP with OPLF (Yang *et al.* 2004).

A summary of pertinent IR band assignments for PP and lignocellulose as found in literature (Amash and Zugenmaier 2000; Kaczmarek *et al*. 2005; Mhd Ramle *et al.* 2012) is provided in Table 3.

Table 3. Prominent IR band assignment

	Wavenumbers	Assignment
PP	2953, 2915, 2839	Asymmetric and symmetric C-H stretching vibration
	1455	CH_3 asymmetric deformation
	1375	CH_3 symmetric deformation
	973, 841, 808	C-H deformation out-of-plane
Lignocellulose	3333	OH stretching vibration
	2919	CH stretching
	1641	Adsorbed OH, conjugated C=O
	1427, 1363	CH deformation, asymmetric
	1316	OH in-plane deformation
	1164	C-O-C asymmetric
	1107, 903	Glucose ring stretch, asymmetric
	1054, 1033	C-O stretch
	1595	Carbonyl stretching C=O
	1704	C=O ester

Changes in the molecular structure of untreated PP/OPLF composites in different fiber loadings are shown in Fig. 5. The IR spectra of untreated composites in different fiber contents demonstrated change at a peak of 1595 cm^{-1}, which is related to the C=O group. This peak disappeared only in the 20% fiber loading composite. This may be because of increased interaction between the OPLF and PP matrix, forming hydrogen bonds between carbonyl groups of OPLF and hydrogen atoms of PP during the production of the composites. This reaction occurred probably due to incorporation of 20% OPLF as the best ratio, allowing the functional groups of both components to react most efficiently.

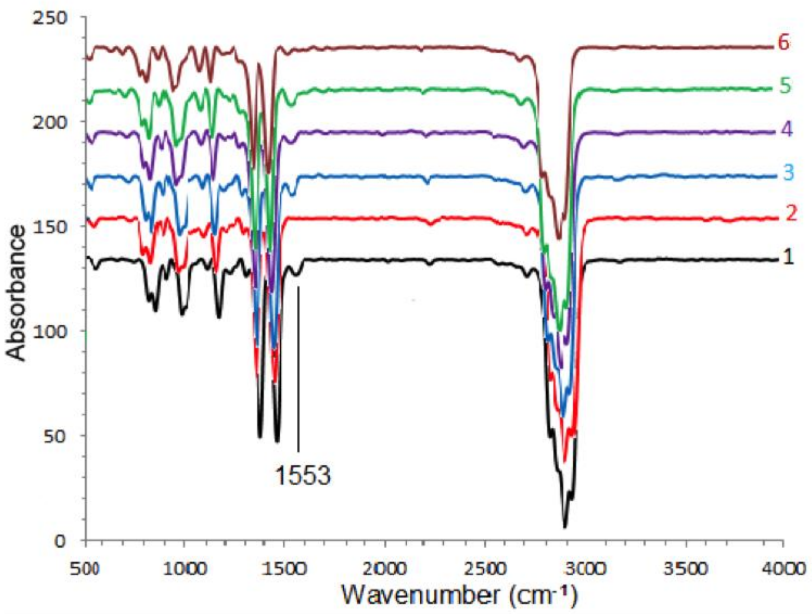


Fig. 5. FTIR spectra of untreated PP/OPLF composites

The characteristic spectra of E-43-modified composites containing 10 to 60% OPLF are shown in Fig. 6. New bonds formed because of the interaction between the lignocellulosic fiber from OPL and the PP matrix as a result of the addition of E-43, as indicated in the spectra. Differences in the shape and intensity of the bands were used to compare the structural changes in the composites. Epolene® has a high MAH content and low molecular weight; therefore, it can interact well with the lignocellulosic fiber of OPLF, but it could be difficult to compatibilize with the PP matrix, which leads to the minimization of its molecular weight.

The most important area of the spectra is the interaction between the anhydride groups of MAH and the hydroxyl groups of OPLF to form new ester bonds at 1164 cm^{-1} (Rozman *et al.* 2003). The intensity of this peak increased with increasing fiber content because it is depends on the number of reaction site available between the amount of OPLF and MAH. Thus, the high concentration of OH groups from the lignocellulosic fiber of OPL with the presence of E-43 treatment, more esterification reactions may take place.

It is clear from Fig. 6 that the peak intensity increased at high concentrations of OPLF at approximately 3344 cm^{-1}, which may correspond to the excessive hydroxyl groups that did not react with MAH (Rozman *et al.* 2003). With increasing OPLF level, the content of hydroxyl groups also increased. The increased absorption at about 1728 cm^{-1} of the E-43-treated samples indicated the presence of carbonyl (C=O) for the formation of ester bonding when MAH reacts with hydroxyl groups from OPLF (Rozman *et al.* 2001).

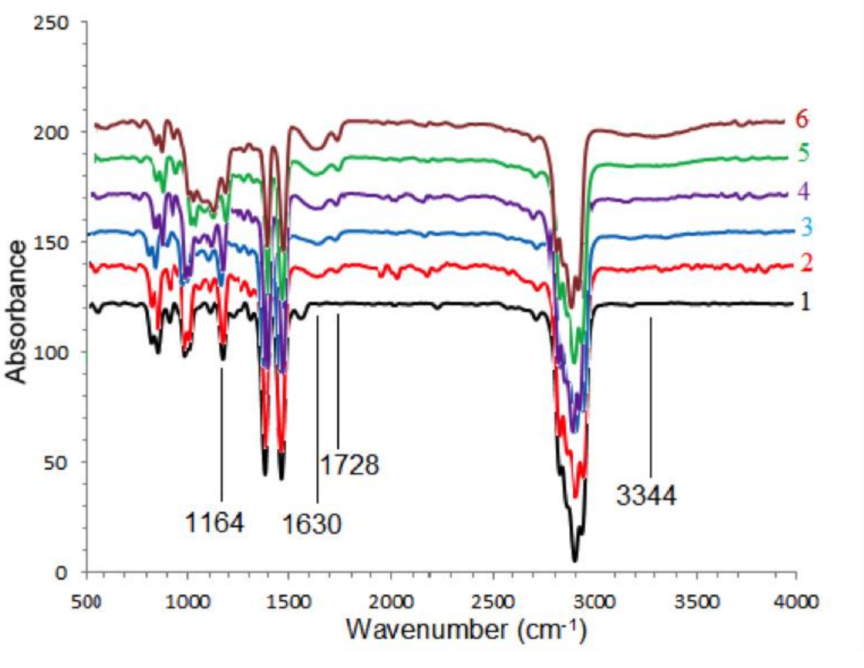
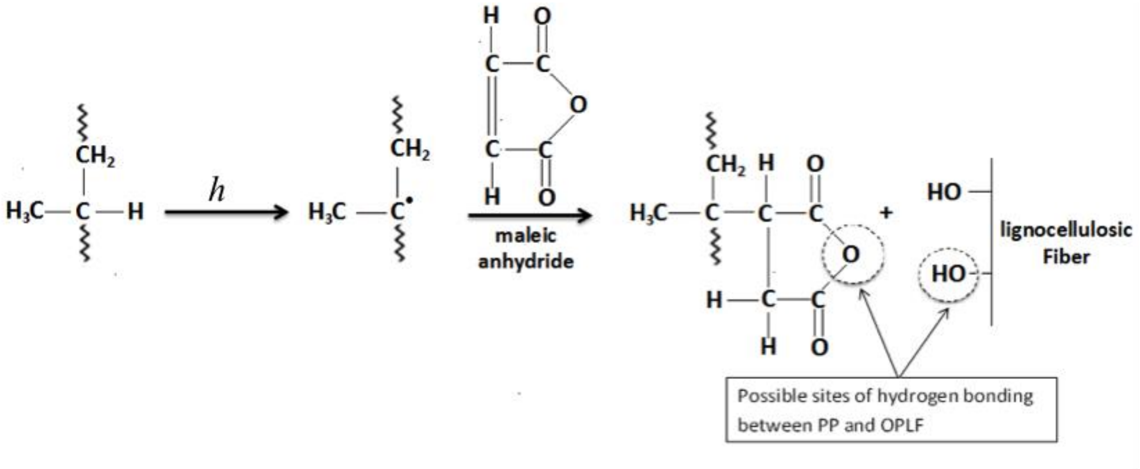


Fig. 6. FTIR spectra of E-43-treated PP/OPLF composites

Another increased absorption at 1630 cm^{-1} with increasing fiber ratio was observed in E-43-treated samples, which related to the presence of C=C bonds. Consequently, this suggests the expansion of interactions between the MAH and OPLF surfaces. Carboxylic groups of MAH tend to react with hydroxyl groups of OPL fiber, leaving long-chain PP back bones facing outward, which is may revealed covalent linkages. As a result, the adhesion between the PP matrix and OPLF surface improved with the addition of E-43.

This resulted in enhanced morphological property, which is confirmed by SEM results.

Generally, one of the most important issues for producing composites with acceptable mechanical properties is the compatibility between the matrix and reinforcing agents (Cantero *et al.* 2003). Therefore, the improvement in the component adhesion of the composite caused by the reaction between C=C groups and the PP matrix was clearly reflected in the mechanical characteristic (Scheme 1).



Scheme 1. The possible reaction of PP/E-43 and OPLF

Dynamic Mechanical Analysis (DMA)

DMA has been broadly used to study the structures and viscoelastic behavior of composite materials. Storage modulus E' is a characteristic of relevant stiffness, loss modulus E'' represents the viscous portion, and damping measurements (tan δ) give practical information on T_g. To assess the structural variation of pure PP and both untreated and E-43-treated PP/OPLF composites, a comparison was performed using DMA.

Figure 7 presents the storage modulus of pure PP and the composites made from 20% OPLF of untreated and E-43 as a function of temperature. The curves exhibited three zones: (i) from −50 to 10 °C, corresponding to the glassy domain, (ii) from 10 to 100 °C, related to the glass transition zone, and (iii) above 100 °C, referring to a rubbery state. This partition was also shown by Kim *et al.* (2005). In general, all the samples showed a decrease in storage modulus as the temperature increased (Gańán and Mondragon 2003; Kim *et al.* 2005).

For the composite with PP alone, the decline of storage modulus with increasing temperature can be explained by an increase in the segmental mobility of the polymer. With the incorporation of 20% OPLF, the storage modulus of this composite showed a slight increase compared with the PP-only composite. This is because the reinforcement of 20% OPL fiber may lead to great stress transfer across the interface from PP to the fiber, which improves the stiffness of PP (Thwe and Liao 2002; Huda *et al.* 2008). Reduction in the modulus values above 50 °C was associated with the softening of the blend at higher temperatures. The softening caused by increases the temperature, which led to the characteristic enhancement of polymer flow (greater) due to poor interfaces between matrix and filler.

The same trend was also observed for the variation of storage modulus of E-43-modified composite against the temperature (Fig. 7). As compared with PP, modified composite with E-43 showed higher storage modulus than untreated composites. These findings are in accordance with tensile results and some previous studies (Arrakhiz *et al.* 2012). The enhancement in the polymer chain displacement and the change in molecular dynamics explained the increase in storage modulus of 20% OPLF treated with E-43. As discussed earlier, the enhancement of the interface adhesion between fibers and matrix could be the main reason for this improvement (Albano *et al.* 1999). The chemical bonding mechanism could also explain this result. The migration of the compatibilizer to the fiber surface could form an ester linkage with the fiber that leads to improvement of the interface (Arrakhiz *et al.* 2012). These formed ester bonds by OH groups on the fibers' surface with the maleic anhydride of E-43 grafted to the PP chains (Scheme 1) could decrease the stress transfer from the matrix to the fiber. Consequently, the storage modulus was high. It was also found that the complex modulus (*E′*) was much more sensitive to the changes related to the fiber addition than the loss factor (Ray *et al.* 2002). The loss modulus shows the loss of energy to friction and internal motion. Thus, this can be clarified as a measurement of viscous components that are associated with unrecoverable oscillation energy dissipated per cycle.

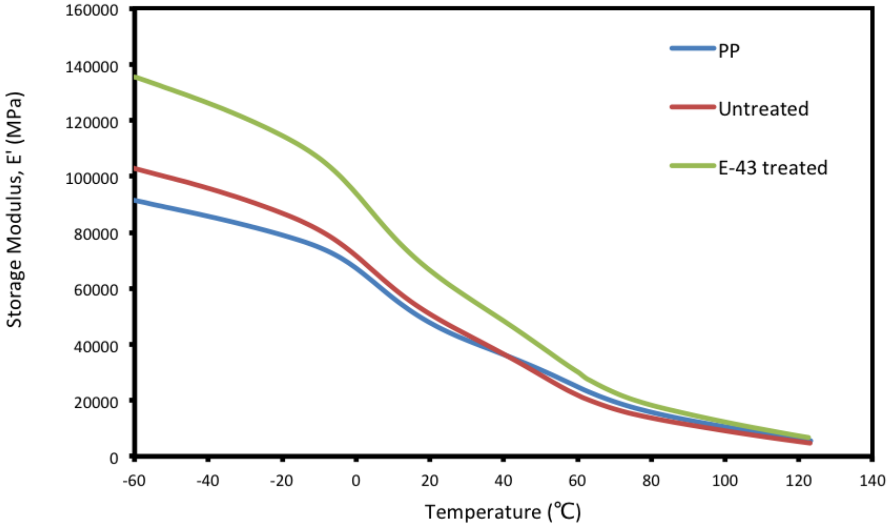


Fig. 7. Storage modulus of pure PP, 20% OPLF of untreated and E-43-treated composites

The melt viscosity of a polymer is characterized by the peak intensity of loss modulus (flow of matter). The loss modulus values (*E″*) of virgin PP and 20% OPLF of untreated and E-43 composites are shown in Fig. 8. The polymer matrix presented two transition peaks at different temperatures within the investigated range. The loss modulus peaked at its highest value at the glass transition temperature (Fig. 8). Then, it was drastically reduced, in accordance with a rise of the chain movement's flow above the transition temperature, which corresponds to the findings of Kiziltas *et al*. (2011). For both composites, with and without compatibilizer, the loss modulus was higher compared with PP alone through the temperature range.

From the loss modulus peak, the glass transition of PP is 8 °C. Generally, viscosity can be associated with the spread of the molecular weight of the polymer. Thus, the rise in viscosity is possibly related to the presence of fibers. Also, the influence of OPLF supplement on peak loss modulus temperature was not as pronounced as the peak was at about 8 °C in comparison with the glass transition temperature of PP/OPLF composite (Fig.

8). This indicated no interaction with the molecular motion of crystalline region of PP and that relaxation behavior was not affected by the OPLF. It was reported that T_g values obtained from the loss modulus were more accurate compared with those from the damping factor (Kiziltas *et al.* 2011). The T_g obtained from the loss modulus was indicated to be lower than that of the tan δ curves.

The loss modulus of the E-43-treated composites showed the highest values compared with the untreated composite and PP alone, as shown in Fig. 8. This is possibly because of the segmental motion at the polypropylene chains in the fiber–matrix surface. Improving the interface adhesion between OPLF and PP with an E-43 supplement leads to a highly viscous composite. The polymer molecule is also proposed to be more restricted in motion because of the increase in fiber–matrix linkage associated with the addition of E-43 (Feng *et al.* 2001). Moreover, the glass transition temperature showed a significant shifting to a lower value (4 °C) as compared with all composites. The composite with good interface bonding was reported to disperse less energy and vice versa (Pothan *et al.* 2003). Because E-43 reduced the non-uniform distribution of fiber in the matrix, the movement of chains increased. Thus, a decrease in the glass transition temperature was observed. This could explain the reduction of glass transition temperature of the E-43-treated composites (Essabir *et al.* 2013).

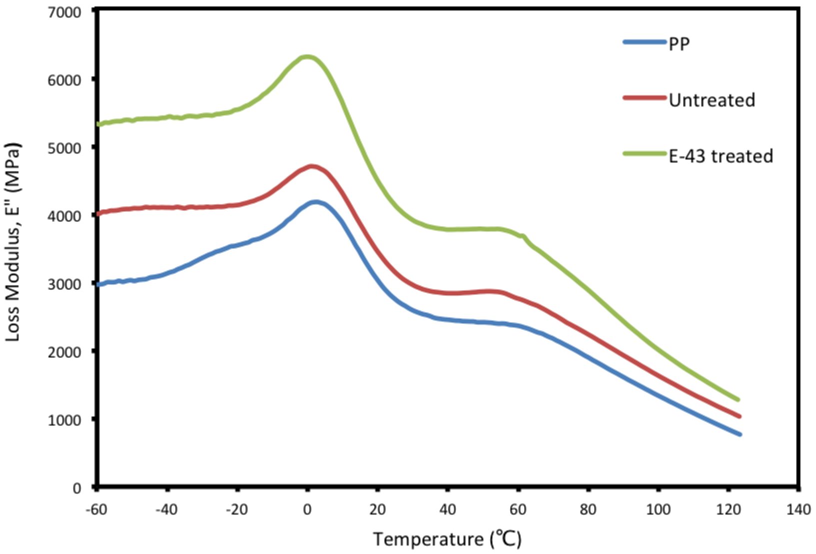


Fig. 8. Loss modulus of pure PP and 20% OPLF of untreated and E-43-treated composites

Figure 9 represents the development of damping (δ) of pure PP and 20% OPLF of treated and untreated composites. The highest tan peak is related to the ability of a material to dissipate energy through segmental motion of the amorphous region in the polymer composite. The variation in the tan curve specifies the relaxation manner and accompanies the movement of the small groups and the molecule chains within the polymer. The tan δ of PP displayed relaxation peaks at about 10 °C. The broad peak at 10 °C is mostly assigned to the glass transition temperature (T_g). A slight increase of tan values was exhibited between the composites with the addition of OPLF compared with PP alone (Fig. 9) (Santos *et al.* 2002).

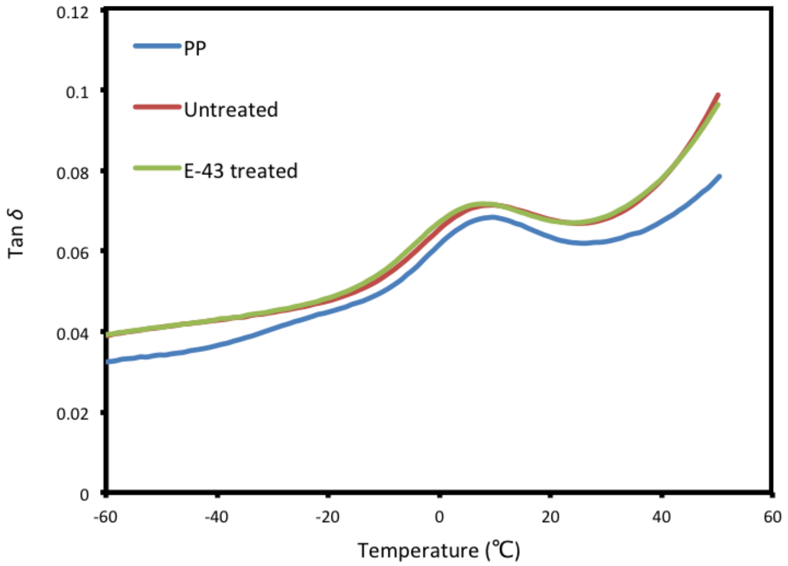


Fig. 9. Loss factor of pure PP and 20% OPLF of untreated and E-43-treated composites

With the addition of OPLF, the tan *δ* showed a higher value than for PP. This result could be due to OPLF causing more uniform heat distribution, leading to higher thermal conductivity, which causes an increase in chain mobility and viscosity of the blends (Zeng *et al.* 2004). For E-43-treated composite, the tan *δ* showed a slight change in the peak of glass transition compared with the untreated composite. A possible explanation of this result is that the improved in the viscosity of E-43-treated composites as a result segmental motion of PP chains at the surface, which was shown earlier. The justification of the peak shift mostly is indicated by the restricted molecular movement due to better linkage between fiber and matrix. This indicated that composite with E-43 had a good structure damping property.

SEM Characterization of Interfacial Adhesion

Scanning electron microscopy was used to assess the OPL fiber dispersion in the polymer matrix and to illustrate their fibrillar morphology. The micrographs were taken from the tensile fracture surface of composites to evaluate the microstructure. Figures 10a and 10c exhibited untreated PP/OPLF composites surfaces, which showed a gap between the fiber and the matrix and that the fibers were free of any matrix material sticking to them. At high concentration of OPLF (40%), fiber pull-out can be clearly observed as shown in Fig. 10c. This is an indication of poor linkage between the OPLF and PP matrix. This is a proof of the reduction in the mechanical properties as discussed early. The presence of E-43 changed the morphological structure, which can be seen in Figs. 10b and 10d. These also showed good compatibility between surfaces and that the fiber was completely covered with the matrix. Moreover, no fiber pull-out appeared, and most of the fibers were associated with the PP matrix. This is good evidence of E-43 enhancing the interfacial adhesion between the OPLF and the PP matrix. Several other studies reported the same findings (Joseph *et al.* 2003; García-López *et al.* 2007). In addition, SEM analysis of the composite fracture surface showed that E-43 enhanced the compatibility between the OPLF and PP matrix, thus improving the mechanical characteristics.

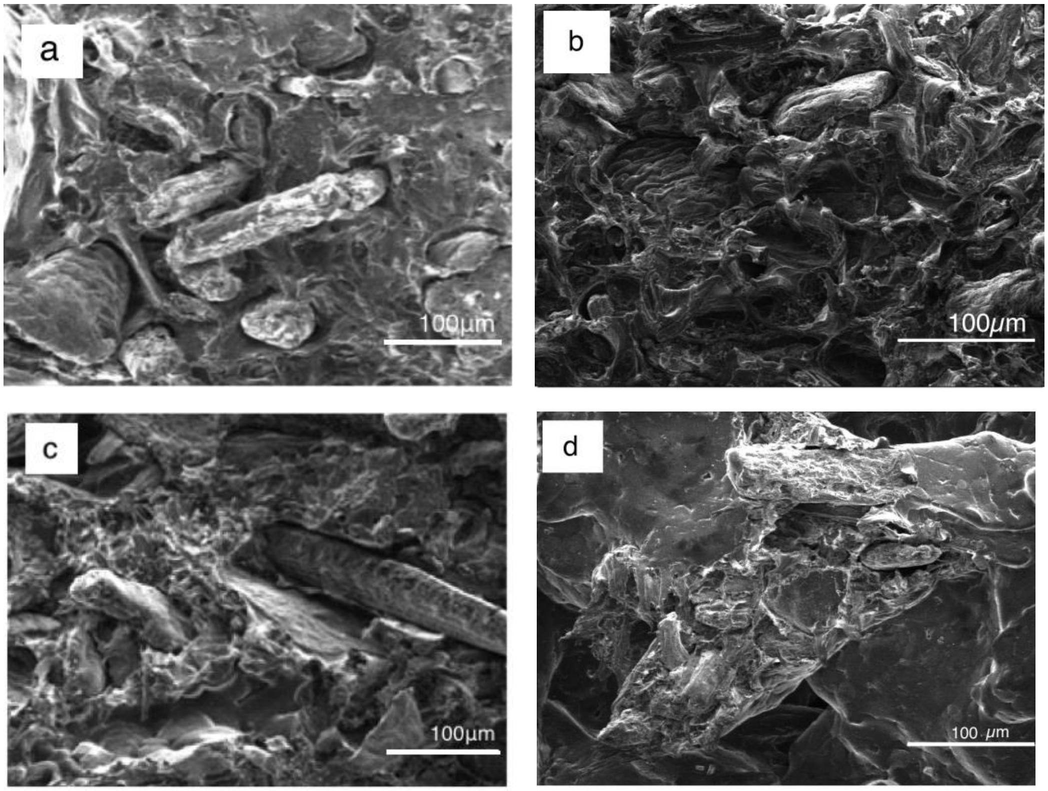


Fig. 10. SEM image of (a) 20% untreated PP/OPLF composite; (b) 20% E-43-treated PP/OPLF composite; (c) 40% untreated PP/OPLF composite; (d) 40% E-43-treated PP/OPLF composite

CONCLUSIONS

1. Using an appropriate quantity (20%) of OPLF as a filler of PP to produce composites will result in a new material with good properties that is low-cost and environmentally friendly and that can be used in multiple applications.
2. Epolene® E-43 enhanced the interaction between fiber and matrix, which resulted in an improvement of the composites' properties.
3. The mechanical and dynamic mechanical properties (Young's modulus, stress at yield, and storage modulus) declined as a consequence of OPLF reinforcement. Epolene® E-43 enhanced tensile strength by approximately 30% for 20%wt OPLF.
4. The effect of E-43 was chemically observed in the resulting composites in the formation of new ester bonds, which is good evidence of E-43 treatment enhancing the interfacial interactions (as shown from FTIR results). Field emission SEM confirmed the interfacial enhancement, with noticeable reduces of pull out fibers and totally sticking the fibers to the PP matrix, that indication of adhesion between the OPLF and PP matrix.

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