Characterization of Laccase-Treated Kenaf Fibre Reinforced Recycled Polypropylene Composites

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Raw and laccase-treated kenaf fibre (KF) were used individually to reinforce recycled polypropylene (RPP) using extrusion and injection moulding. Laccase was used to modify the surface of the fibre to improve the compatibility between fibre and matrix. Enzyme concentration and soaking time were considered as the treatment parameters. Maleic anhydride grafted polypropylene (MAPP) was used with a ratio of 1:10 as coupling agent to fibre. Fibres were characterized by density, energy dispersive X-ray (EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), whereas composites were characterized by density, melt flow index (MFI), mechanical tests (tensile, flexural, and impact), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), field emission electron microscopy (FE-SEM), and water uptake analysis. Density, O/C ratio, and crystallinity of the treated fibre were increased. An optimum fibre loading of 40% gave the highest tensile properties. Tensile strength improved due to coupling agent by 37%, whereas treatment of fibre did the same by 40%. Flexural, impact, and thermal properties of the composites and crystallinity of the matrix were improved due to treatment. Morphological images of the composites showed better adhesion, and moisture absorption was reduced by 37% due to treatment and use of coupling agent.

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INTRODUCTION

Fibre reinforcement in the polymer matrix is a well known technique to improve the properties of the resulted composites. Additionally, a significant amount of fibres while loaded can reduce the usage of the synthetic polymers in the composites. To serve this purpose, synthetic fibres such as glass, carbon, aramid, *etc.* have been used earlier (Rijsdijk *et al.* 1993; Rezaei *et al.* 2009; Larin *et al.* 2008). Previous reports on synthetic fibres have indicated certain drawbacks, such as non-renewability, non-environment friendly character, high cost, health hazards, and consumption of large amounts of energy while being prepared; on the other hand, composites incorporating synthetic fibers have been found to exhibit favorable thermal and mechanical properties (Wambua *et al.* 2003; Khan *et al.* 2010; Alam *et al.* 2011). Nowadays, natural fibres (NFs)-based polymer composites are drawing much attention among researchers because of their low price, annually renewability, bio-degradability, and availability. The motivations for using natural fibers are greater in cases where low density and high specific properties of the composites are desired. Examples of some widely used NFs for the preparation of

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composites are flax, sisal, jute, kenaf, silk, hemp, oil palm flour and fibre, abaca, *etc.* (Cantero *et al.* 2003; Paul *et al.* 1997; Khan *et al.* 2010; Islam *et al.* 2013a; Alam *et al.* 2011; Yan and Pickering 2008, Ramli *et al.* 2011, Suradi *et al.* 2010; Bledzki *et al.* 2010). Composites prepared with these NFs are being utilized as body parts of vehicles, packaging materials, domestic furniture, building materials, *etc.* The properties of those materials have been found to be comparable with the traditional materials and also involve a low-cost manufacturing process. Some challenges inherent in the use of NFs-based composites are: NFs absorb moisture due to their hydrophilic nature, and they have limited processing temperature, low dimensional stability, and poor compatibility with the completely hydrophobic polymers, resulting in poor properties (Nadzai *et al*. 2006; Gaceva *et al*. 2007).

Kenaf is a fast-growing long-length natural fibre having a composition as follows: cellulose (45 to 57%), lignin (8 to 13%), hemicelluloses (21.5%), and pectin (3 to 5%) (Bismarck *et al.* 2005). As a reinforcing agent, this fibre has already been utilized successfully with various types of thermoplastic and thermosetting polymers, as cited in previous work (Islam *et al.* 2013a,b; Akil *et al.* 2011). Like other natural fibres, kenaf absorbs moisture due to its hydrophilicity, and it exhibits poor compatibility with polymer matrices while compounded. Thus the prepared composites show poor strength and mechanical properties. To improve the compatibility between fibre and matrix, fibre surface modification and use of compatibilizers or coupling agents are found to be useful, as reported in previous studies. Fibre surface modification can be done successfully with chemical treatments such as alkylation, acylation, mercerization, and peroxide treatment (Lee and Rowell 1991; Zafeiropoulos *et al.* 2002; Sreekala and Thomas 2003; Islam *et al.* 2013a; Paul *et al.* 1997; John *et al.* 2008; Li *et al.* 2007). Moreover, coupling agents such as maleic anhydride grafted polypropylene, silane, *etc.* have been used to achieve better interfacial adhesion (Rijsdijk *et al.* 1993; Xie *et al.* 2010). A few researchers also have reported the modification of fibre by ultrasound and enzymatic treatments as alternative and environmentally-friendly techniques for the removal of lignin, as well as modification of cellulose in the fibre (Islam *et al.* 2013b; Bledzki *et al.* 2010).

Enzymatic treatment of fibres has been found to be very effective because the reactions catalyzed are specific for a focused purpose (Bledzki *et al.* 2010). Moreover, energy and water savings, cost reduction, improved product quality, and process integration are the other benefits related to this process (Aehle 2004). The technical benefit of enzymatic treatment includes the removal of lignin, wax, and non-crystalline parts from the fibre surface. There are enzymes namely laccase, protease, lipase, and cellulase, that are effective, particularly for lignin, protein, lipid, and cellulose, respectively. Among the enzymes, laccase is effective at breaking the aliphatic and aromatic rings of the substrate (Aehle 2004; Stuart *et al.* 2006). Laccase has already been used to treat NFs for the preparation of composites (Peng *et al.* 2010). The properties of the composites mostly depend on the fibre properties (surface chemistry, morphology, chemical composition, and crystalline content) and matrix properties (nature and functionality) (Bledzki *et al.* 2010). The wetting and adhesion properties increase significantly due to treatment, which improves the interfacial bonding between fibre and matrix. Lignin is a common type of natural polymeric compound present in all types of plant fibres at different percentages; it holds and binds the cellulose fibres as a cementious material. Additionally lignin is more reactive towards polymer matrix as well as coupling agent than cellulose due to the presence of phenolic groups. Enzymatic treatments degrade (or/and partly remove) the lignin by modifying the functional groups,

and this may result in a more reactive surface. Previous reports showed that enzymatic treatments can remove the lignin to a significant extent, leading to improvements in interfacial bonding with the polymer matrix. In some other works, due to treatment, water absorption was found to be reduced significantly. Yan and Pickering (2008), in their work with enzyme-treated hemp fibre, found that hemp fibre composites treated with a high concentration of chelator showed the highest tensile strength (42 MPa), representing an increase of 19% compared to composites with untreated hemp fibre. Enzyme-treated abaca fibres for polypropylene composites were studied by Bledzki *et al.* (2010). A significant reduction of moisture absorption and a significant increase of flexural strength of the composites were reported. The cited authors claimed that nearly 20 to 45% moisture absorption had been reduced due to treatment, with a 10 to 35% increase of flexural modulus.

Recycled polypropylene was selected as the polymer matrix for the present research. Reinforcement of polypropylene with natural fibre has shown improved mechanical and thermal properties (Islam *et al*. 2013a,b). Recycled-based materials were found to show comparable properties and in some cases were better than the pure polymer-based composites due to fibre incorporation. Recycling sometimes is unwanted due to processing cost and quality concern. Thus to add value to recycling materials, to mitigate disposal problems, and to reduce the high demand for synthetic polymer, recycled-based polymer was used in this research. Moreover, enzymatic treatment of kenaf fibre (KF) for the case of recycled-based polypropylene composites has not been reported yet in research databases. Therefore, the aim of this research was to find the effect of enzymatic treatment of KF to improve the interfacial bonding with recycled-based polypropylene for better mechanical, thermal, and structural properties. Additionally, water uptake characteristics are also examined as an important consequence of enzymatic treatment.

EXPERIMENTAL

Materials

KFs were collected from Kampung Merchong, Pahang, Malaysia. They were washed with water and then dried under sunlight for one day followed by oven-drying at 80 °C. Recycled polypropylene (RPP) of commercial name PP black copo, having density 0.91 g/cm^{-1} and melting point 163 °C, was kindly supplied by Efficient Growth Sdn Bhd, Selangor, Malaysia. Maleic anhydride grafted polypropylene (MAPP) (Polybond 3200, density 0.91 g/cm^{-1} and MA level 1.0 weight %) was used as coupling agent; it was purchased from MTBE Sdn Bhd, Gebeng, Kuantan, Malaysia. Laccase (Novozyme-51003) was purchased from Novozymes, Denmark. Acetic acid (purity >98.8%) was obtained from Sigma, Aldrich, USA. Except for the fibre, all the materials were used as received without further modification.

Methods

Fibre treatment

Enzyme concentrations of 1, 1.5, and 2 wt% were used separately to treat 100 g of fibres for 2 h of soaking time duration. Acetic acid was used to control the pH of the solution at 5.5. Soaking was done at 25 °C with air flow for better treatment. Then, fibres were washed for 2 h with tap water until the pH reached 7 to avoid acidic effects. Then,

fibres were air dried. Enzyme concentration was optimized based on the highest tensile strength (TS) of the prepared composites with the above mentioned treated fibres. After that, the same treatment process was applied to treat the fibres at optimized enzyme concentration to optimize the soaking time as 2, 4, and 6 h based on the same.

Preparation of composites

Air-dried KFs were shredded into a small size (2 to 5 mm) by a crusher. After that, fibres were dried at 80 ^{o}C in an oven until the moisture content reached below 5%. Untreated fibres were compounded into RPP with and without coupling agent, whereas treated fibres were mixed with RPP with coupling agent by means of a Prism Eurolab 16 twin-screw compounder at a barrel temperature of 190 ^{o}C. The fibre to coupling agent ratio was 10:1. The incorporated fibre contents in composites were 10, 20, 30, 40, and 50% (by weight) for the case of raw fibre, but optimum loading only considered based on the tensile strength (TS) for the case of treated fibre. The compounded samples were prepared into test specimens with an injection moulder using NESSEI injection molding machine model- PNX60.

X-ray diffraction measurements

X-ray diffraction (XRD) measurements were conducted using a Rigaku Mini Flex II, Japan. The operating voltage and the tube current of the X-ray generator were 30 kV, 15 mA, respectively. The experimental details have been published elsewhere (Mina *et al.* 2013).

Fourier-transform infrared spectroscopy

Chemical textures of untreated and treated fibres were detected by a Nicolet 6700 FT-IR spectrometer, Thermo Scientific, Germany. Fourier transformation infrared (FTIR) spectroscopy was performed using the standard KBr pellet technique in the wavenumber range of 500 to 4000 cm^{-1}.

Melt flow index (MFI) and density

The melt flow index of each sample was determined according to ASTM D1238 and the experimental details of MFI and density has been published elsewhere (Islam *et al.* 2013b).

Mechanical test

The tensile tests for composites were carried out according to the method as described in ASTM D 638 - Type I: Test method for tensile properties of plastic. The flexural test was conducted according to ASTM D790-97 standard. Impact strength (IS) was measured by the Charpy impact test, according to ASTM D256. The experimental details for the above mentioned tests have been published elsewhere (Islam *et al.* 2013b).

Thermogravimetric analysis

For thermogravimetric analysis, a TA instrument (TGA Q500) was used in a nitrogen atmosphere. The maximum temperature was 600 ^{o}C with heating rate 20 ^{o}C/min. Kinetic parameters for the thermal degradation was determined using the following equation, given by Broido (1969),

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{RT} + \ln\left(\frac{RZ}{E_a\beta}T_{max}^2\right) \tag{1}$$

where y is the fraction of non-volatilized material not yet decomposed, T_{max} is the temperature of maximum reaction rate (^{o}C), β is the heating rate (^{o}C/min), Z is the frequency factor, E_a is the activation energy (J/mol), and R is the gas constant (8.314 J/mol.K). From the TGA data, lnln(1/y) versus 1/T plots was drawn, and from the slope of each line, the activation energy of the samples were calculated.

Differential scanning calorimetry

A TA instrument, Q-1000, was used to perform differential scanning calorimetry (DSC) of the samples using an aluminium pan with a heating rate of 20 ^{o}C/min. A heat/cool/heat method was applied using a temperature range of 25 to 250 ^{o}C. The percentage of crystallinity and the melting point of the samples were calculated.

Scanning electron microscopy

The surface morphologies of raw KF and enzyme-treated fibre were monitored by a scanning electron microscope (SEM) (model-ZEISS, EVO 50), and that of composites were examined by field emission scanning electron microscopy (FE-SEM) (model-JEOL, JSM-7800F). For this purpose, samples were placed onto a metal based holder with the help of double sided sticky carbon tape. Prior to observations, samples were coated with gold for fibres and platinum for composites by means of a vacuum sputter-coater for ease of conduction.

Water uptake measurement

Tensile specimens of the composites were immersed in distilled water at room temperature to study the moisture absorption. Samples were taken out from water periodically and weighed. This process was continued for 150 days. The water uptake (%) at time t was calculated from the following equation,

$$\text{Moisture content (\%)} = \frac{W_f - W_i}{W_i} \times 100 \tag{2}$$

where W_i is the initial weight of the sample before soaking and W_f is the final (after taking out the sample from the water).

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows the FTIR spectra of untreated and treated fibres. Changes in the intensities of the treated fibres were observed. The peaks in the ranges from 3200 to 3600 cm^{-1} are attributable to the –OH functional group. The intensities within this region were reduced for the case of treated fibres. This is may be due to the enzymatic action by reducing the hydrogen bonding in cellulosic hydroxyl groups, thereby decreasing –OH concentration. This intensity decrease is also attributed to hemicelluloses removal, and as a result, the OH groups of the cellulose are exposed. The better degree of exposure may permit the reinforcing fibre to mechanically entangle with the polymer matrix more

strongly. The band at 1728 cm^{-1} in the untreated fibre was significantly reduced in the treated fibre, indicating the removal of pectin and wax (Yan and Pickering 2008). The absorbance band at 1247 cm^{-1} is due to COO stretching in lignin; the band disappeared following treatment of the fibres, indicating the degradation or modification of lignin (Yan and Pickering 2008).
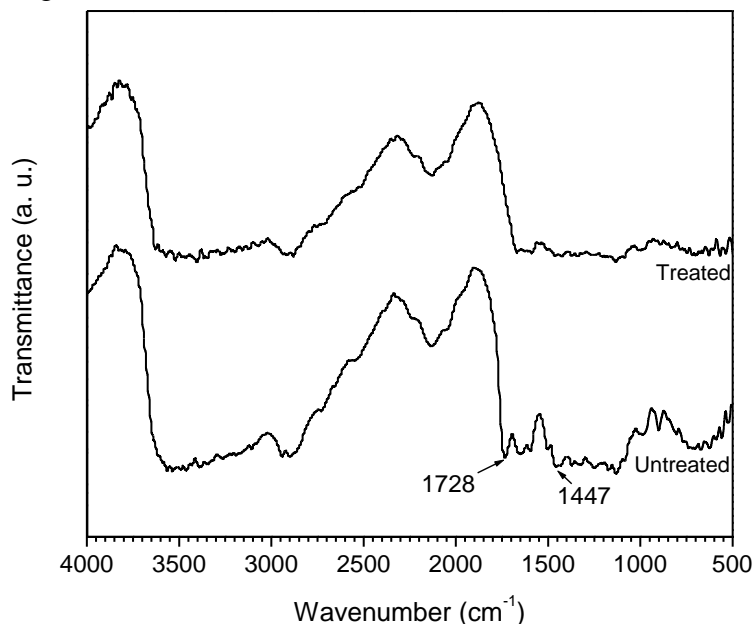

Fig.1. FTIR spectra of untreated and treated kenaf fibre

Density and EDX Analysis

The density of the untreated fibres was found to be 1.50 g/cm^{-1}, whereas the treated fibres showed a value of 1.52 g/cm^{-1} (Table 1). Elemental analysis of untreated and treated fibre is tabulated in Table 1. It was found that the weight percentage of C was decreased while that of O was increased. Laccase treatment was found to increase the O/C ratio (weight ratio) (from 1.02 to 1.15) due to removal of soluble extractives, leading to the increase of the oxygen exposure on fiber surface. This helps to improve interfacial bonding between fibres and matrix in the presence of coupling agent.

Table 1. Density and Elemental Analysis of Untreated and Treated Kenaf Fibre

Fibre types	Density g/cm^{-1}	Elements					
		C		O		Others	
		Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
Untreated	1.50	49.18	56.38	50.40	43.38	0.42	0.24
Treated	1.52	46.24	53.45	53.39	46.33	0.37	0.22

XRD analysis

The X-ray diffraction patterns of untreated and treated kenaf fibre are presented in Fig. 2. The important peaks found for both the fibres were at 2θ diffraction angles of 16.2^{o} and 22.6^{o}, representing the presence of type I cellulose (Yan and Pickering 2008). The crystallinity index values calculated by the Segal empirical method for the untreated and treated fibres were found to be 51 and 55%, respectively (Reddy and Yang 2005). The higher crystallinity of treated fibres indicates the removal of amorphous non-

cellulosic or cellulosic compounds, resulting in better packing of the cellulose chains (Yan and Pickering 2008).
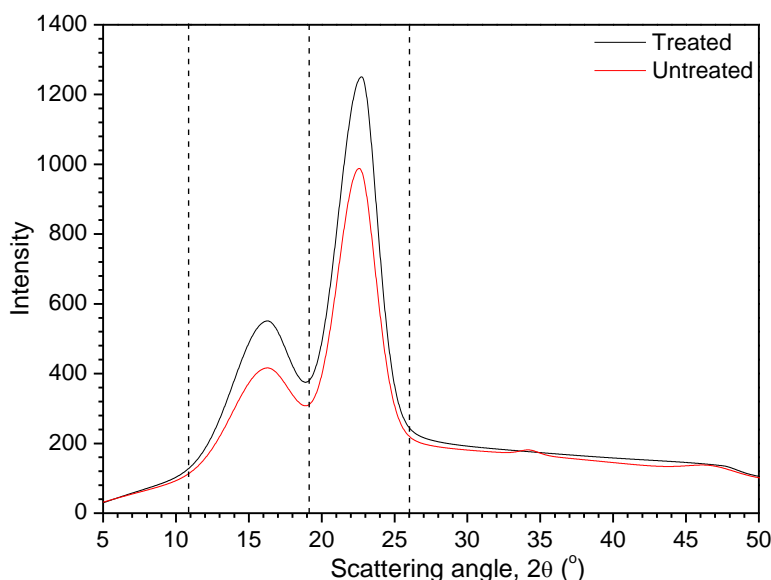

Fig. 2. XRD traces for untreated and treated fibres

Melt Flow Index of Composites

The melt flow index represents the flow behavior of the materials under heat and pressure. It is also an indirect indication of viscosity and molecular weight of the materials. The higher the molecular weight, the lower the MFI value. It also depends on the relative behavior as well as adhesion property of the counterparts of the composites. The MFI of supplied RPP was found to be 5 g/10 min but decreased with fibre loading for RPP/kenaf composites even with coupling agent (Table 2.). The MFI of RPP/kenaf at 40% fibre loading was found to be 0.4 and 0.3 g/10 min with and without coupling agent, respectively.

Enzyme-treated KF reinforced RPP composites showed a MFI of 0.22 g/10 min. Therefore, these results indicate that the more fibre in the composites, the more viscous the melt. Thus, it can be summarized that laccase treatment made the composite-melt more viscous while it was undergoing MFI testing, indicating difficult process ability as well as reduced molecular mobility.

Table 2. MFI, Density of RPP and Composites

Formulation	Density g/cc	MFI (g/10 min)	IS (J/m^2)
RPP	0.91	5.58	33.97
10%RKF+RPP	1.00	2.54	20.37
20%RKF+RPP	1.02	1.78	20.47
30%RKF+RPP	1.04	0.46	20.61
40%RKF+RPP	1.07	0.40	21.79
50%RKF+RPP	1.16	0.22	10.45
40%RKF+RPP+MAPP	1.12	0.33	22.51
40%RKF(Treated)+RPP+MAPP	1.13	0.22	24.13

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Density

The density of RPP was found to be 0.91 g/cm^{-1}. Fibre loading increased the density of the composites (Table 2). At 40% fibre loading, the density of the composites without and with coupling agent were found to be 1.07 g/cm^{-1} and 1.12 g/cm^{-1}, respectively. At 50% fibre loading without coupling agent, the value reached the maximum, 1.16 g/cm^{-1}, while laccase-treated composites at 40% fibre loading showed the density of 1.13 g/cm^{-1}. Removal of surface impurities probably helped to increase the density of the fibre as well as composites. The increased density indicates the compactness of the blends as well as improved interfacial adhesion between fibre and matrix for the case of treated fibre-based composites with coupling agent.

Tensile Properties

Figure 3 shows the TS and tensile modulus (TM) of RPP and composites based on untreated fibres at various percentages of fibre loading without and with coupling agent. Incorporation of fibre improved TS of the composites. TS increased with fibre loading (up to 40%), and after that it decreased. The maximum TS obtained at 40% fibre loading was 18.29 MPa, which is 18% higher than RPP (15.46 MPa). At higher percentage, such as 50%, it decreased because of agglomeration of fibres and uneven distribution throughout the matrix (Suradi *et al.* 2010). At 40% fibre loading, composites based on untreated fibres with coupling agent showed a TS value of 25.17 MPa, which is 37% higher than that of composites without coupling agent. Firstly, at fixed soaking time (2 h), the concentration of enzyme was varied as 1.0, 1.5 and 2.0 wt%. The best TS results were obtained at 1.5 wt% concentration (Fig. 4.). After that, at fixed concentration (1.5 wt%), soaking time results were optimized regarding TS value. The best value (25.77 MPa) was almost 40% higher than that of untreated fibre-based composites without coupling agent (Fig. 5.). It is assumed that in addition to the soaking time and enzyme concentration, the result also depends on the amount of fibres taken for the treatment. The improved result for the case of treated fibres-based composites may be due to the removal of lignin and modification of cellulose fibres.
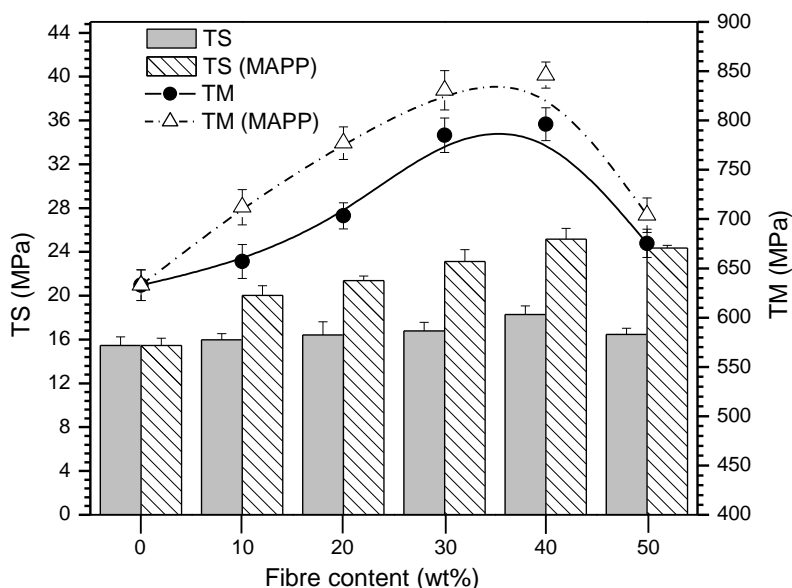

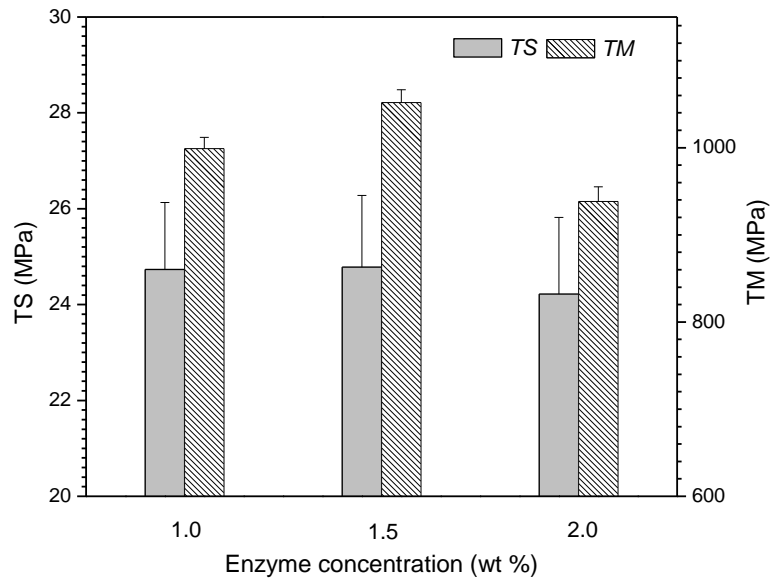**Fig. 3.** TS and TM of RPP and composites at various percentages of raw fibre loading (without coupling agent)

Fig. 4. TS and TM of composites at 40% fibre loading at various enzyme activity with coupling agent (at 2 h of soaking time duration)
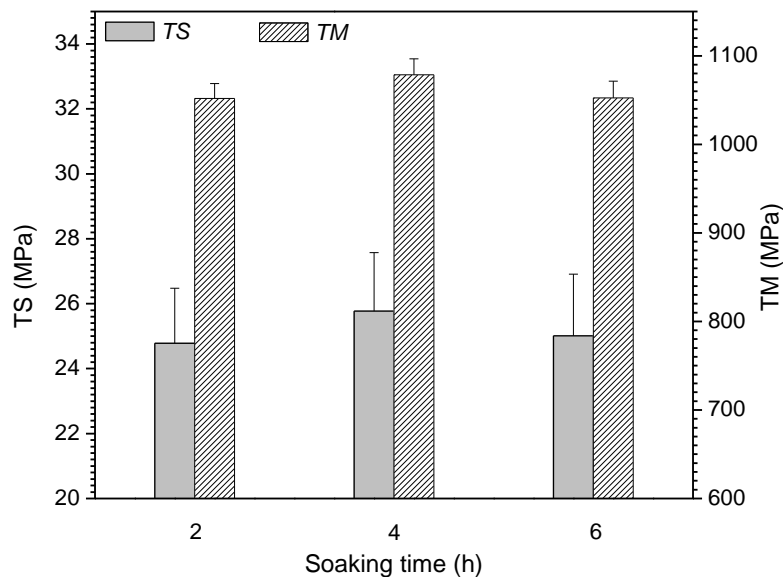

Fig. 5. TS and TM of composites at 40% fibre loading with MAPP at 1.5 wt% of enzyme concentration with various soaking time

Regarding tensile modulus (TM) (Figs. 3, 4, and 5), the same trend of results was observed for composites based on raw fibre with and without coupling agent and treated fibre-based composites with coupling agent. Tensile modulus at 40% fibre loading, for the case of raw fibre-based composites without coupling agent showed a value of 896 MPa, whereas with coupling agent it was 1051 MPa (1.5 wt% of enzyme concentration and 2 h of soaking time) and 1078 MPa (1.5 wt% of enzyme concentration and 4 h of soaking time).

Flexural Properties

Flexural strength (FS) and flexural modulus (FM) of the composites are presented in Fig. 6. Untreated fibre-based composite with coupling agent showed FS and FM values of 32.09 and 759 MPa, respectively, whereas FS and FM values of the treated fibre with coupling agent showed 33.31 and 806 MPa, respectively. The improved result for the case of treated fibre-based composites with coupling agent may be due to the increased stiffness as a consequence of fibre treatment.
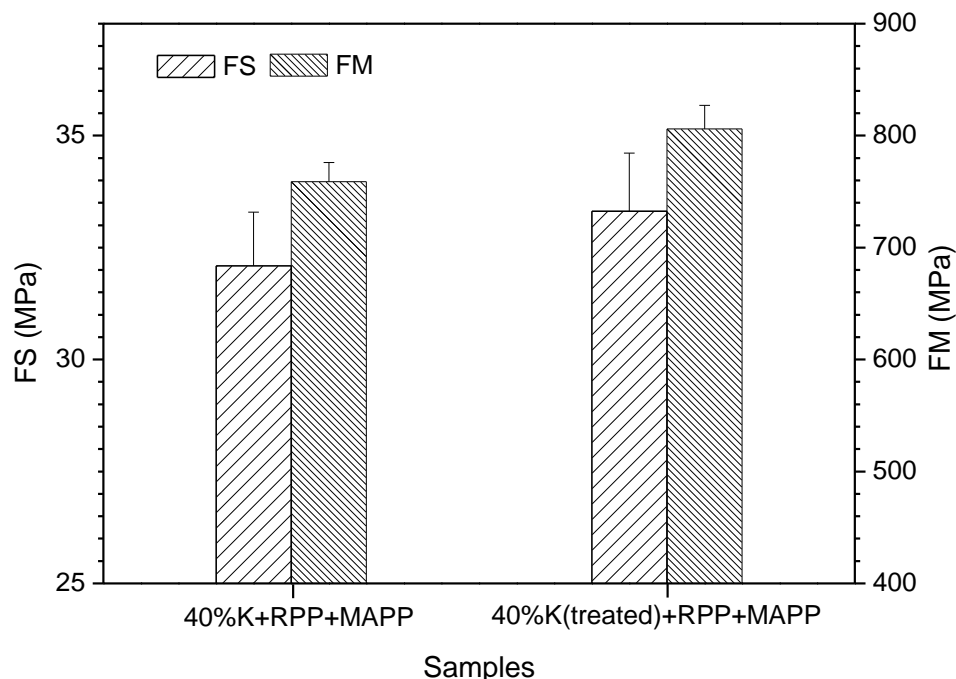
Fig. 6. FS and FM of composites

Impact Properties

Results for impact strength (IS) of the composites are presented in Table 2. Fibre incorporation decreased the impact strength gradually from 33.97 to 10.45 J/m^2. Untreated fibre-based composites without and with coupling agent showed the IS value of 21.79 and 22.51 J/m^2, respectively, whereas treatment of fibres enhanced the impact strength (24.13 J/m^2) by 2 J/m^2 compared to that of untreated fibre-based composite with coupling agent. This may be due to the removal of lignin and other impurities from the fibre surface, which improves the interfacial bonding between fibre and matrix.

Surface Morphology

Surface morphologies of raw KF and enzyme-treated fibres are presented in Fig. 7. These results suggest that cellulose in raw KF is held together by means of binding components such as lignin, pectin, *etc*. (Fig.7a), which are removed after treatments (Fig. 7b).

On the other hand, treated fibre showed a comparatively smoother surface with narrow fibre-thickness (Fig. 7b). Surface morphologies of treated KFs were attributed to the removal of lignin, pectin, and hemicelluloses and agree with our observed surface structures.
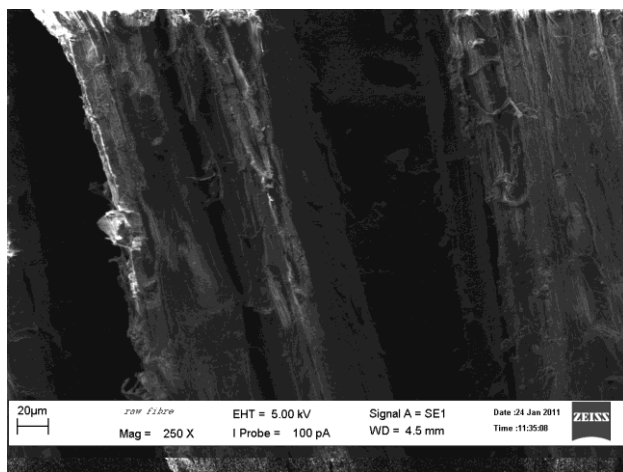
(a)
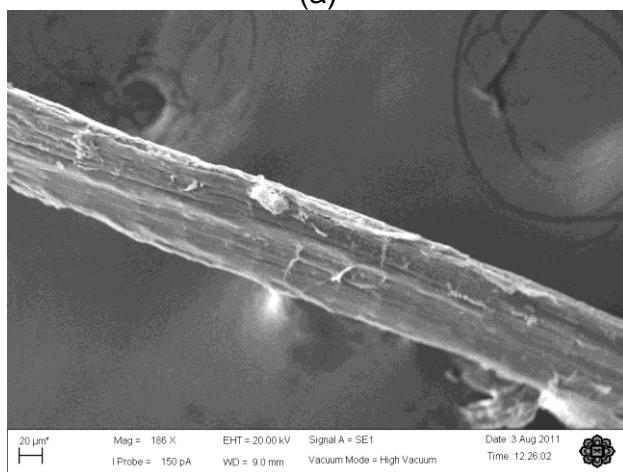
(b)

**Fig. 7.** SEM of (a) raw and (b) treated fibre

The FE-SEM examinations of fractured surfaces of untreated fibre-based composites without and with coupling agent are presented in Fig. 8a and 8b. Composites without coupling agent revealed poor interfacial bonding (Fig. 7a). Micrographs indicated fibre pull-out, debonding, delamination, and fibre breakage. On the other hand, untreated fibre-based composite with coupling agent showed relatively less fibre pull-out (Fig. 8.b), whereas treated fibre-based composites showed much less fibre pull out (Fig. 8.c) indicating the better interfacial adhesion between fibre and matrix due to treatment.

Thermogravimetric Analysis

Table 3 shows the thermal properties of the RPP, as well as composites with raw and treated fibre with coupling agent. Incorporation of MAPP did not show any significant improvement regarding thermal stability. The trends of the curve were almost the same except that the residue increased with fibre loading (Figs. 9 and 10.). It was found that composites degraded in two stages, whereas RPP degraded in only one stage. The first stage is assigned to the degradation of fibers while the second stage in the curve of the composites belongs to the degradation of matrix. The curve of lnln $(1/y)$ versus $1/T$ was used for the calculation of activation energies for RPP.
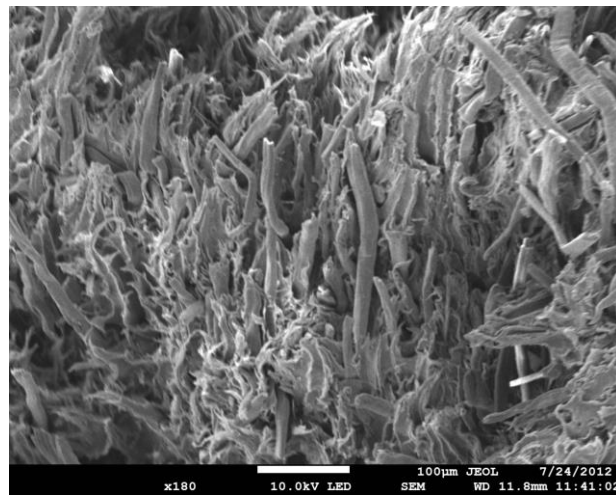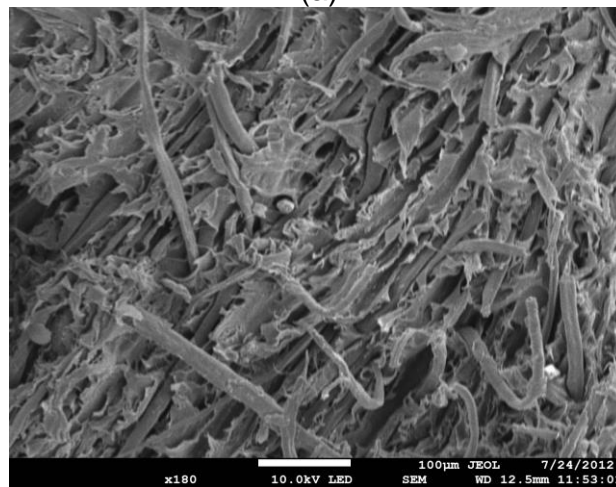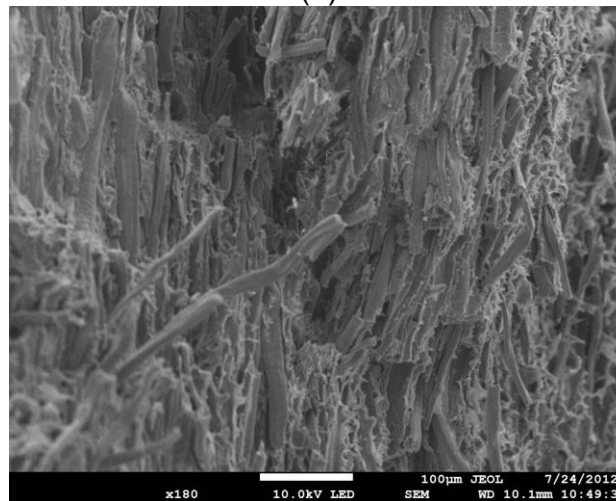
Fig. 8. FE-SEM of fractured surface of composites (a) without MAPP, (b) with MAPP, and (c) laccase-treated fibre with MAPP

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In the first stage of degradation of the composites, the activation energies were almost 42 KJ/mol, but in the second stage, it decreased with the fibre loading. This may be due to the diffusion of fibres at higher loading of fibres percentage in the composites. The coupling agent increased the activation energies by around 5 KJ/mol. Treated fibre with coupling agent at the first stage showed an activation energy of 46.28 KJ/mol, whereas at the second stage the value was 78.71 KJ/mol.
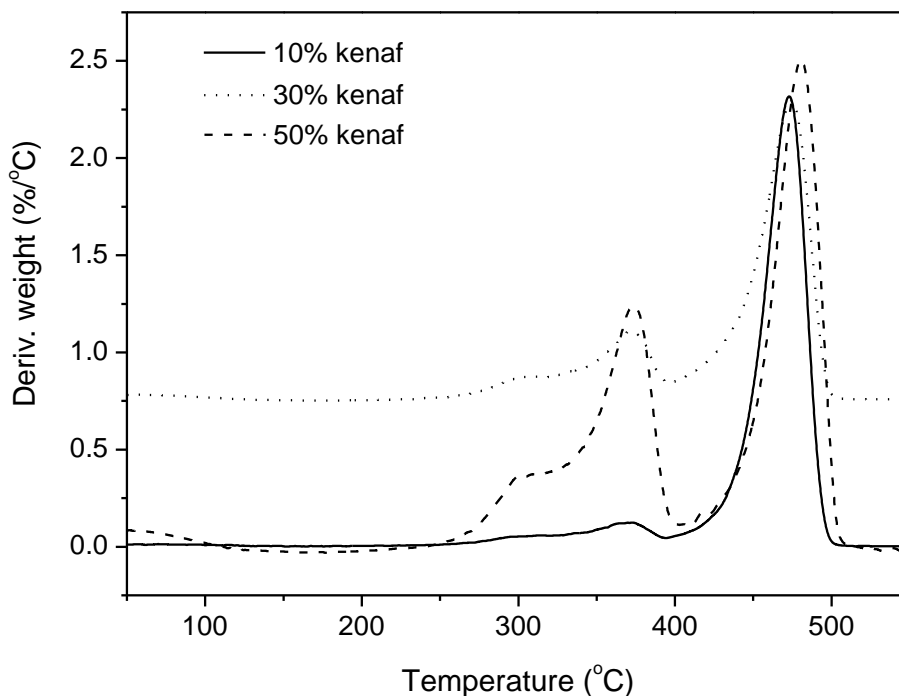

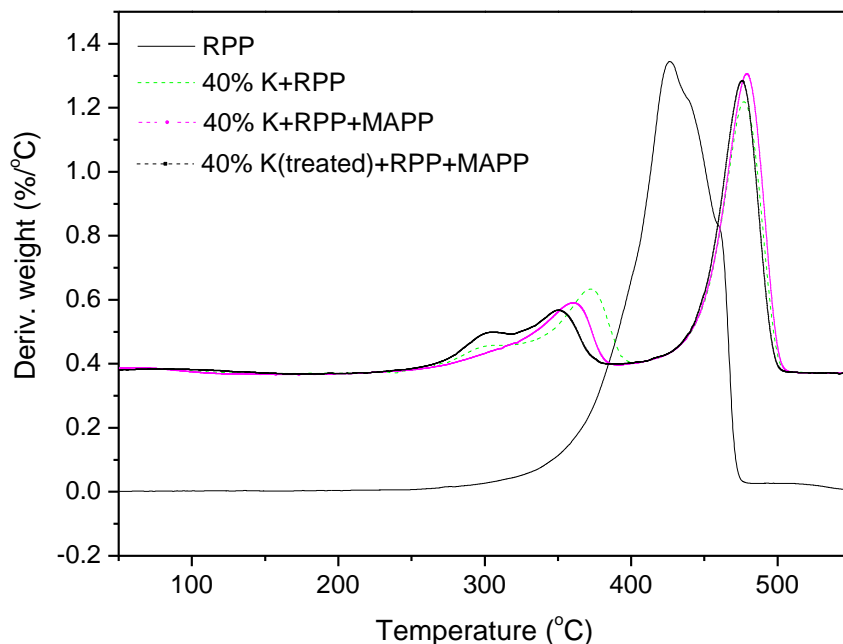**Fig. 9.** TGA analysis of composites with raw fibre

Fig. 10. TGA analysis of RPP and composites

Table 3. Thermal Properties of RPP and Composites

Formulation	Stage	Temp. range(^{0}C)	T_{max}	E_a
RPP	1st	267-472	420	99.41
10%RKF+RPP	1st	254-374	351	42.89
	2nd	380-497	469	120.73
20%RKF+RPP	1st	237-382	352	42.00
	2nd	390-497	470	107.36
30%RKF+RPP	1st	237-389	362	43.78
	2nd	389-497	470	83.86
40%RKF+RPP	1st	221-391	365	44.37
	2nd	392-501	473	67.44
50%RKF+RPP	1st	221-394	367	42.12
	2nd	402-504	477	61.75
40%RKF+RPP+MAPP	1st	247-381	351	50.90
	2nd	406-502	477	72.05
40%RKF(treated)+RPP+MAPP	1st	229-371	341	46.28
	2nd	389-495	470	87.71

DSC Analysis

DSC analysis was carried out to observe the behaviour of the composite materials when subjected to a heat/cool/heat process within a temperature range of 25 to 250 ^{o}C. Melt peak temperature and enthalpy are presented in Table 4. The crystallinity of the matrix in the treated fibre-based composite was found to be 20.32%, whereas it was 18.74% for the untreated fibre-based composite. Treatment of fibre and presence of coupling agent are responsible for strong chemical bonds between fibre and matrix, which provides the transcrystallinity, resulting in higher crystallinity of the polymer matrix in the composites.

Table 4. DSC analysis of Composites

Formulation	Melt peak temperature (^{o}C)	Enthalpy (J/g)	Crystallinity (%)
40%k(raw)+RPP+MAPP	163.80	39.16	18.74
40%k(treated)+RPP+MAPP	163.11	42.47	20.32

Water Uptake Analysis

Water uptake analyses are presented in Fig. 11. From the curves, it was found that absorbed water contents increased with increasing immersion time. The moisture content for all the samples except the RPP reached the equilibrium condition after 68 days of soaking. RPP can be expected to behave like pure PP and other completely hydrophobic polymers, whereas the other samples showed absorption of different amounts. Untreated fibre-based composite absorbed 8.37% moisture during the above-mentioned period. The treated fibre-based composite absorbed 5.19% moisture, whereas the composite with untreated fibre showed 6.67% in the presence of coupling agent. Thus, moisture absorption was found to be reduced for the case of 37% treated (with coupling agent) fibre-based composite as compared with the untreated (without coupling agent) based composite. The removal of wax, lignin, and other surface extractives may be the reason for better adhesion between cellulose and polymer matrix in the presence of coupling

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agent. Due to this improved compatibility, capillary action may be reduced, resulting in reduced moisture absorption.
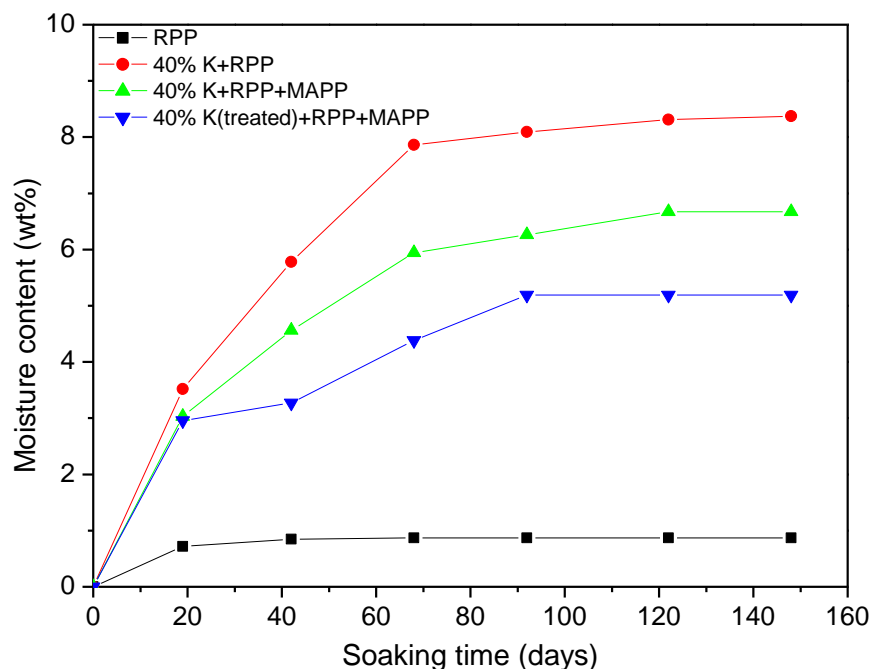

Fig. 11. Moisture content of composites against various soaking time duration

CONCLUSIONS

1. Significant improvements were found regarding tensile strength (TS) and tensile modulus (TM) of composites based on treated fibre with coupling agent. The best condition for fibre treatment occurred at 1.5 wt% of enzyme concentration with 4 h of soaking time.

2. In this investigation, it was found that TS and TM increased with fibre loading up to 40%.

3. Better adhesion between filler and matrix, as evidenced by field emission scanning electron microscopy, was found in the case of composites with treated fibre and coupling agent, while the rest of the composite materials without coupling agent showed debonding and agglomeration of fibre, thereby decreasing their interfacial adhesion. Removal of non-cellulosic compounds is also suspected to increase the amount of OH groups exposed on the fibre surface, which could assist in mechanical entanglement with the matrix in the presence of maleic anhydride-grafted polypropylene (MAPP), as evidenced by the increase in composites' tensile strength.

4. Melt flow index showed a negative trend with the incorporation of fibre and adding of MAPP. Fibre treatment in that case further reduced the value. Thus, very low processability at higher loading as well as for enzyme treatment can be expected.

5. Usage of fibres enhanced the thermal stability and crystallinity of the matrix, and during thermal decomposition it became decomposed in two stages, while recycled polypropylene decomposed in one stage.

6. The moisture absorption by the composites was found to be reduced by 37% due to treatment and the presence of coupling agent.

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