

Preparation and Characterization of Bamboo Fiber-Graft-Lauryl Methacrylate and Its Composites with Polypropylene

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ABSTRACT: In this study, lauryl methacrylate grafted onto bamboo fibers (BF-g-LM) was prepared to improve the interfacial compatibility between hydrophilic bamboo fibers (BFs) and hydrophobic plastic. The lauryl methacrylate (LM) was initiated by benzoyl peroxide (BPO) and grafted onto BFs via a free-radical chain-transfer reaction. LM was grafted onto BFs with ether bonds, and differential scanning calorimetry indicated that the ether pyrolysis of BF-g-LM occurred at 280°C. The optimum preparation conditions were obtained as follows: 0.30 g of pretreated bamboo flour was immersed in 0.225 mol/L LM. The reaction was then initiated by 0.025 mol/L BPO, and this reaction was sustained for 4 h at 80°C. BF-g-LM served as coupling agent between the BFs and the polypropylene (PP) matrix, as shown by scanning electron microscopy analysis. The elongation at break of the BF/PP composites with BF-g-LM increased to two times compared to that of the BF/PP composites without BF-g-LM. The impact strength and maximum deflection also increased to 75 and 580%, respectively. In conclusion, BF-g-LM is a promising coupling agent that can be used in BF-reinforced thermoplastic composites. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2377–2382, 2013

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INTRODUCTION

Pollution from plastic waste is seriously growing with the increasing use of plastics.^{1–3} This has led to the use of natural products that decrease the pollution and reduce the widespread dependence on fossil resources.^{4–6} Bamboo, a natural lignocellulose-based composite material, is abundant in Asia and South America.⁷ Large amounts of it, such as in the form of powder, is wasted every year in China. As consciousness of environmental protection increases, bamboo fibers are being extracted from bamboo's raw form with a steam explosion method^{8,9} for use as reinforcement fillers in plastics. However, because of the abundant hydroxyl groups present on the surface of bamboo fibers (BFs), it is difficult to make hydrophilic BF compatible with hydrophobic plastics.^{10–13} Urgent modifications of its fibers are therefore necessary to improve their ability to disperse into the plastic matrix and gain interfacial strength.

An extensive literature survey has revealed that considerable efforts, such as alkylation reactions, bamboo's use with coupling agents, and graft copolymerizations, have been made in this area.^{14–18} Among them, the graft copolymerization technique dominates because it reduces the surface energy of cellulose. It also improves the compatibility of the composite materials of bamboo and plastic.^{15,16} With an initiator system, Abu-Ilaiwi

et al.¹⁵ used H₂O₂ and Fe²⁺ to graft-copolymerize methyl methacrylate onto wood fiber. In our study, we used this technique to graft lauryl methacrylate (LM), a long alkyl chain, onto BFs initiated by benzoyl peroxide (BPO). BFs possess a better hydrophobicity when the longer alkyl chain is grafted onto them. Lauryl methacrylate grafted onto bamboo fibers (BF-g-LM) was expected to serve as a coupling agent and improve the interfacial compatibility between the hydrophilic BFs and hydrophobic plastic. The mechanical properties and microscopic structure were evaluated to ensure the improvement of the surface energy of BF-g-LM.

EXPERIMENTAL

Materials

Bamboo powder was kindly supplied by Yongan Forestry (China). LM (96%) and BPO (96%) were purchased from Aladdin Reagent Shanghai Co. Isotactic polypropylene (PP) homopolymer powder (PPH-XD-045, melt flow index = 2.1–6.0 g/10 min) was purchased from Shandong Kairi Chemical Industry, Ltd., Co. (China).

Pretreatment of the Bamboo Powder

An appropriate amount of bamboo powder was dispersed in absolute ethanol in a high-pressure reactor. The high-pressure

Table I. Formulas of the BF/BF-g-LM/PP Composites

	BF (portion)	PP (portion)	BF-g-LM (portion)	Olefin (portion)	Stearic acid (portion)
BF/BF-g-LM ₀ /PP	70	30	0	1	1
BF/BF-g-LM ₅ /PP	70	30	5	1	1
BF/BF-g-LM ₁₀ /PP	70	30	10	1	1
BF/BF-g-LM ₁₅ /PP	70	30	15	1	1

Olefin and stearic acid were used as lubricants.

The numbers after "LM" represent the portions of BF-g-LM added into the composites in this table.

reactor was heated up to 150°C, and this temperature was maintained for 2 h to remove the lignin and hemicellulose of bamboo powder. Finally, the precipitate of BFs was filtered, rinsed with distilled water, and dried at 100°C.

Preparation of BF-g-LM

The graft reaction was carried out under nitrogen atmosphere in a 150-mL, three-necked flask. BF (0.45 g) and a pre-calculated amount of the monomer of LM were put into the flask and mixed at ambient temperature under ultrasonic activation. The mixture was stirred in a water bath at a selected temperature for a period of time. *N,N*-Dimethylformamide (25 mL) and a certain quantity of BPO were added to the flask to start the grafting reaction. After a chosen time interval, the grafted product and the homopolymer were filtered and rinsed several times with absolute ethanol. Finally, the grafted product was extracted with acetone to remove the homopolymer of LM and was then dried at 100°C. The grafting ratio (R_g) of BF-g-LM was expressed with the weight gain rate:

$$R_g = \frac{M - M_0}{M}$$

where M and M_0 are the masses of BF-g-LM and BF, respectively.

Preparation of the BF/PP composites

Pre-calculated amounts (listed in Table I) of BF, PP, and BF-g-LM were premixed in a high-speed disintegrating machine (JFW-A, China) at 2600 rpm under ambient conditions. The premixed mixtures were extruded by corotation in a twin-screw extruder (Haake PolyLab Rheomix PTW24/28, Germany) at a temperature of 170–190°C and at a screw rotation rate of 50 rpm; then, the extrusion materials were calendered into sheets 0.5 mm thick.

CHARACTERIZATION

Fourier Transform Infrared Spectroscopy (FTIR)

Measurements

The infrared spectra were analyzed by a Nicolet-5700 FTIR spectrometer with KBr pellets to determine whether the LM was grafted onto the BF.

Thermogravimetric Analysis (TGA)

TGA was carried out with a Mettler TGA/SDTA851 under a nitrogen atmosphere at a heating rate of 10°C/min. The temperature range was 30–500°C. The weights of all of the specimens were approximately 3–5 mg.

Differential Scanning Calorimetry (DSC) Measurements

DSC was done on a Mettler DSC822° differential scanning calorimeter under a nitrogen atmosphere at a heating rate of 10°C/min. The temperature range was 30–500°C. The weights of all of the specimens were approximately 3–5 mg.

Mechanical Properties Measurements

The BF/PP composite specimens were cut off in the form of rectangular strips from the calendered plate, and the dimensions of the specimens were 130 × 10 mm². The elongation at break was tested on a universal testing machine (Lloyd LR 5k, United Kingdom) at a crosshead speed of 5 cm/min. The maximum deflections were also determined with the same universal testing machine with the method of three-point bending at a press speed of 1 cm/min and at a span length of 50 mm. The impact strength was tested with an impact testing machine (JJ-20, China) with the method of cantilever beams. Each result reported represents the average values from five samples.

Scanning Electron Microscopy (SEM)

To evaluate the impregnation state of the BFs into PP, the tensile fracture surfaces were checked by a JEOL 7500 field emission scanning electron microscope at an accelerating voltage of 15 kV. The scanned surfaces were vacuum-sputtered with platinum.

RESULTS AND DISCUSSION

Pretreatment with the Bamboo Powder

Bamboo powder is mainly composed of cellulose, hemicellulose, and lignin. Cellulose is a semicrystalline polymer with the molecular formula (C₆H₁₀O₅)_n. This polysaccharide consists of a linear chain of several hundred to over 10,000 β-(1→4)-linked D-glucose units.¹⁹ The hydroxyl groups on celluloses form hydrogen bonds with oxygen molecules on the same chain or on a neighboring chain. The hydrogen bonds hold the chains firmly together side by side to form fibers. Hemicellulose, a branched polymer, is crosslinked together with celluloses. Lignin further strengthens the attachment.²⁰ The accessible degree of chemical reagents acting on celluloses decreases because of its crystal crosslinking with hemicellulose and lignified lignin. Hence, bamboo powder was used in this study as a pretreatment to remove hemicellulose and lignin, and this reduced the degree of crystallization to a certain extent. These properties could therefore improve the accessible degree of chemical reagents acting on cellulose.

FTIR Spectroscopy

The FTIR spectra of bamboo powder, BFs, and BF-g-LM are shown in Figure 1. A broad, strong absorption band in the

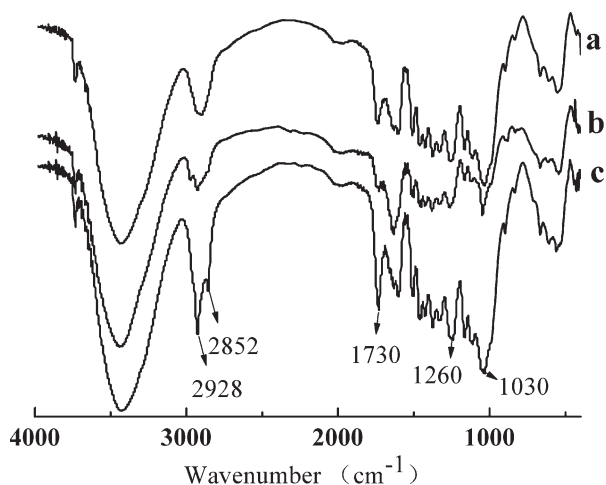


Figure 1. FTIR spectra of the (a) bamboo powder, (b) BFs, and (c) BF-g-LM.

region 3600–3200 cm^{-1} corresponded to the hydroxyl ($-\text{OH}$) stretching vibrations of cellulose.²¹ For bamboo powder (spectrum a), the presence of the peak near 1730 cm^{-1} was associated with the carbonyl ($\text{C}=\text{O}$) stretching vibrations of hemicellulose.²² However, a significant reduction in the absorbance intensity ratio at 1730 cm^{-1} was observed for BF (spectrum b). Meanwhile, the bands at 1260 and 1030 cm^{-1} , targeted as the asymmetric stretching vibrations of the ether bonds ($\text{C}-\text{O}-\text{C}$) of hemicellulose and lignin, were sharper and smaller than those of bamboo powder. These changes were considered to be results of the removal of hemicellulose and lignin. Compared with the BF spectrum, there was a sharper and stronger peak observed at 1730 cm^{-1} in the BF-g-LM spectrum (spectrum c); this was attributed to the carbonyl ($\text{C}=\text{O}$) group of LM. The stronger vibrations near 2928–2852 cm^{-1} were attributed to the stretching vibrations of aliphatic methylene and methoxy groups in BF-g-LM. Moreover, the intensities of the ether bonds at 1260 and 1030 cm^{-1} were strengthened once again because of the grafting reaction of LM onto the BFs. The results of the FTIR measurements confirmed the reaction of BF-g-LM, and a possible reaction mechanism is shown in Scheme 1.

Effect of the Monomer and Initiator Concentration on the Grafting Ratio of BF-g-LM

The effect of the monomer and initiator concentration on the grafting ratio (the mass ratio of BF-g-LM to BF) was investigated (Figures 2 and 3) to quantify the grafting degree of BF-g-LM.

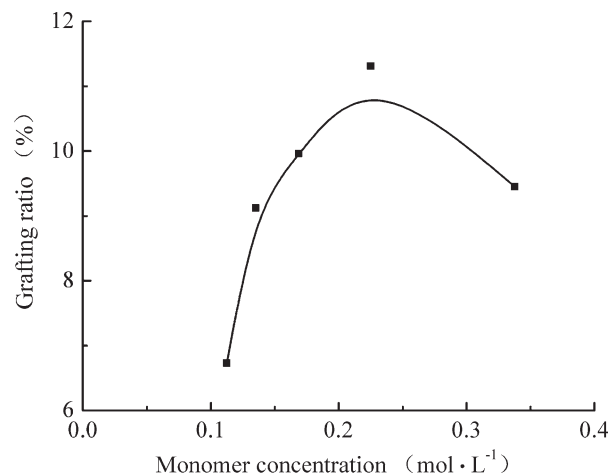


Figure 2. Effect of the monomer concentration on the grafting ratio with 0.30 g of BF and 0.025 mol/L BPO at a temperature of 80°C and a reaction time of 24 h.

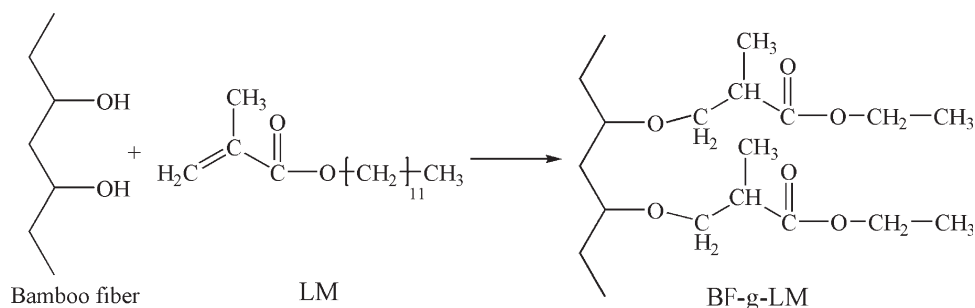
Figure 2 shows that it increased to a value of 11.3% and then decreased when the concentration of LM exceeded 0.225 mol/L in the presence of 0.025 mol/L BPO. Superfluous monomer is not beneficial to a grafting reaction because the gel effect increases the probability of homopolymerization. The effect of the initiator concentration of BPO on BF (Figure 3) was the same as that of LM in this reaction. The ratio of LM grafted to BF increased with increasing initiator concentration up to 0.020 mol/L but decreased beyond this concentration because the homopolymer of LM increased the viscosity of the reaction system at a high concentration of initiator.

Effect of the Reaction Temperature and Reaction Time on the Grafting Ratio of BF-g-LM

Theoretically, it is better to use a higher reaction temperature because it is beneficial to the improvement of the fluidity of the reaction system and to the decomposition of BPO to produce peroxy radicals. The grafting ratio therefore increased with increasing reaction temperature from 50 to 75°C and then arrived at a plateau because of an increase in the radical termination (Figure 4). The grafting ratio increased with the prolonging of the reaction time first (Figure 5). Then, it reached 14.3% at the end of the grafting reaction at 4 h and maintained an invariable value; this was ascribed to the decrease in monomer beyond 4 h.

Thermal Decomposition Process of BF and BF-g-LM

TGA and DSC were used in the investigation of the thermal decomposition of BF and BF-g-LM. The typical thermal weight



Scheme 1. Possible reaction mechanism of BF-g-LM.

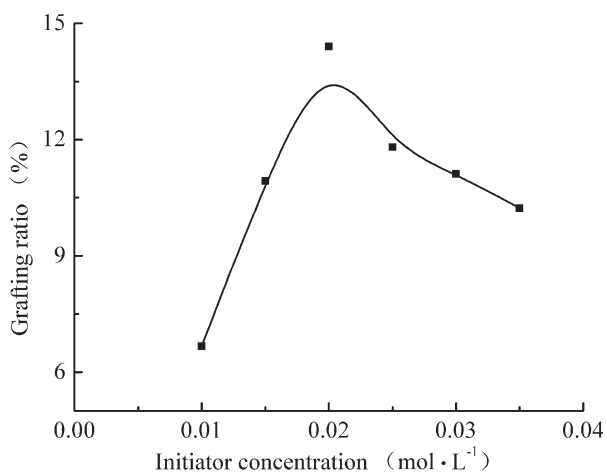


Figure 3. Effect of the BPO concentration on the grafting ratio with 0.30 g of BF and 0.225 mol/L LM at a temperature of 80°C and a reaction time of 24 h.

loss curves of BF and BF-g-LM are shown in Figure 6. The decomposition of BF had two stages. The first stage was the dehydration and decomposition of volatile components at low temperatures (ca. 90°C), and the second stage was the rapid weight loss from the thermal decomposition of celluloses in an inert atmosphere²³ (from 325 to 375°C). The corresponding peaks of DSC curves and the two stages of the thermal weight loss curves were observed for BF decomposition and BF-g-LM pyrolysis (Figure 7). There was an endothermic peak at 280°C because of the pyrolysis of the ether bond between BF and LM. The decomposition stage of cellulose masked the corresponding thermal weight loss of BF-g-LM at 280°C.

Mechanical Properties of the BF/BF-g-LM/PP Composites

Microvoid coalescence is a high-energy microscopic fracture mechanism observed in the majority of composite materials. Nucleation, growth, and the coalescence of microvoids are its three stages.²⁴ In the absence of the coupling agent of BF-g-LM, the nucleation of microvoids were caused by interfacial failure

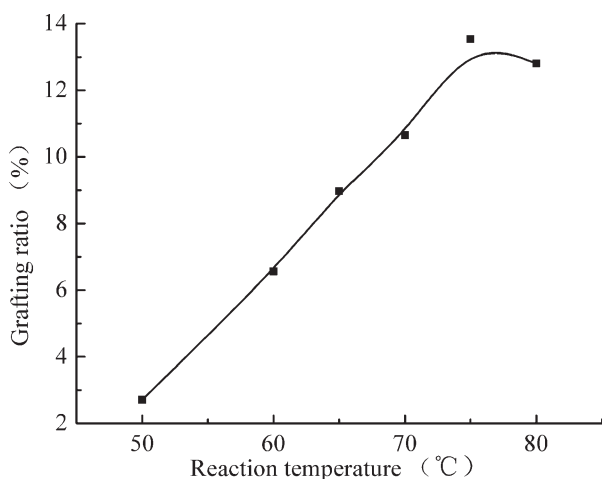


Figure 4. Effect of the reaction temperature on the grafting ratio with 0.30 g of BF, 0.225 mol/L LM, and 0.025 mol/L BPO at a reaction time of 24 h.

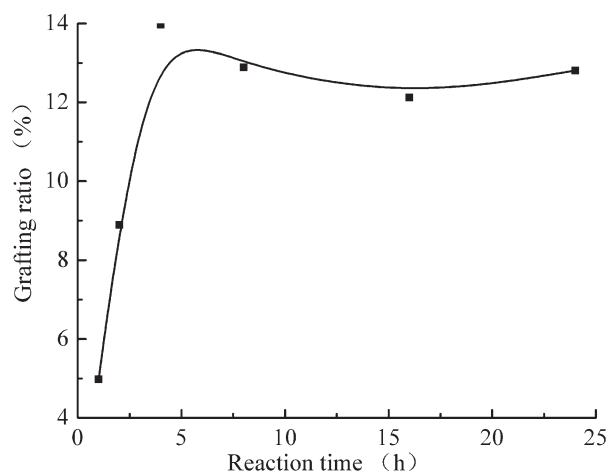


Figure 5. Effect of the reaction time on the grafting ratio with 0.30 g of BF, 0.225 mol/L LM, and 0.025 mol/L BPO at a temperature of 80°C.

between the BFs and the PP matrix. The microvoids grew during tensile testing, and they coalesced when adjacent neighbors linked with each other or the material between them experienced necking. Their coalescence led to fracture. However, BF-g-LM improved the interfacial adhesion between the BFs and PP matrix but restrained their coalescence for the BF/BF-g-LM/PP composites.

Representational histograms of the mechanical properties of the BF/BF-g-LM/PP composites are shown in Figure 8. The results show that the BF/BF-g-LM/PP composites were superior to the BF/PP composite in elongation at break. When 15 portions of BF-g-LM were added to the BF/PP composite, the elongation at break was approximately two times that of the composite without BF-g-LM. The improvement in the elongation at break indicated that the BF-g-LM restrained microvoid coalescence and transferred interfacial stress from the BFs to the PP matrix. Moreover, it clearly showed that the impact strength of the BF/PP composites intensified with increasing BF-g-LM. A high-velocity collision (an impact) did not provide sufficient time for

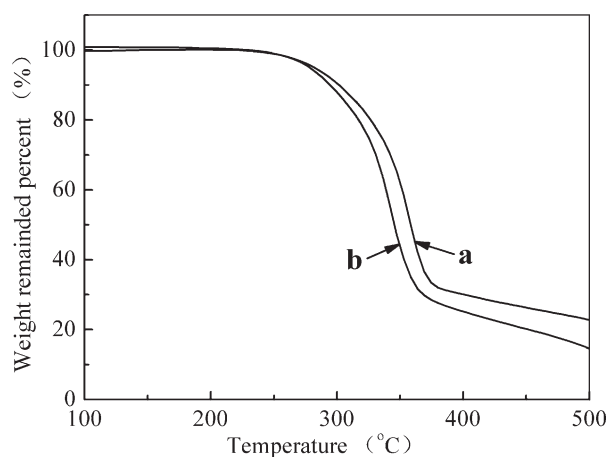


Figure 6. TG curves of (a) BF and (b) BF-g-LM.

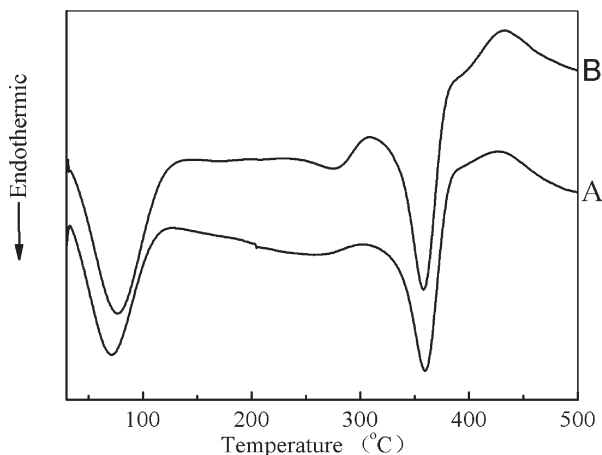


Figure 7. DSC curves of (a) BF and (b) BF-g-LM.

deformations and vibrations. Thus, the struck material behaved in a more brittle manner than in actuality, and the majority of the force was applied to fracture the material. The flexibility increased with increasing BF-g-LM when the Young's modulus decreased apparently (from 1074.2 ± 69.5 to 749.2 ± 46.5 MPa). Hence, the significant improvement in the impact strength of the hybrid composites was attributed to the enhancement of interfacial adhesion between the BFs and PP matrix; this was maintained by intermolecular forces, chain entanglements, or both. Third, the maximum deflection quickly increased with increasing BF-g-LM. This suggested a synergistic behavior between the PP matrix and BFs in the presence of BF-g-LM. The behavior diverted the path of crack growth and induced the formation of microcracking.

SEM Analysis

The improved properties of the BF/BF-g-LM/PP composites resulted from the improvements in the interfacial adhesion between the BFs and the PP matrix, which were attributed to BF-g-LM. This was also reflected in the fractured surfaces of the composites examined by SEM, as shown in the micrographs in Figure 9. Visible voids and unbroken BFs were observed on the fractured surface of the BF/PP composites [Figure 9(a)]; this

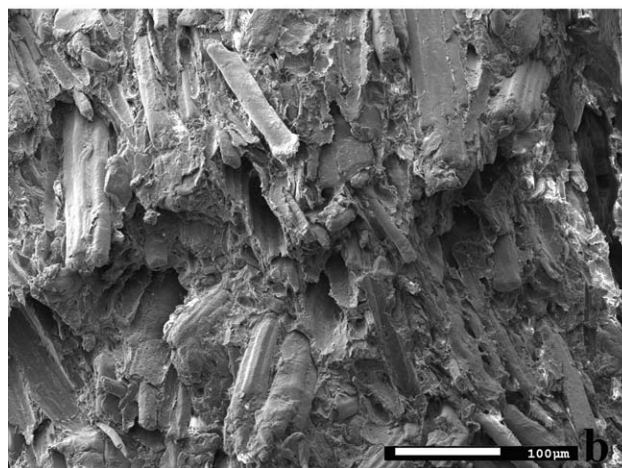
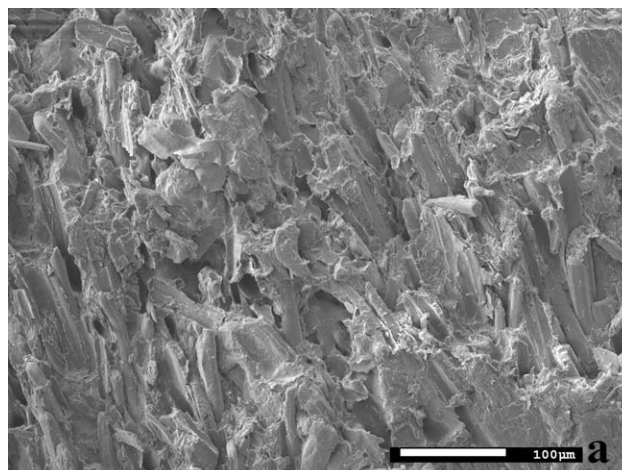


Figure 9. SEM micrographs of the tensile fracture surface of (a) BF/PP in the absence of BF-g-LM and (b) BF/PP in the presence of 10 portions of BF-g-LM.

was ascribed to the poor adhesion between the BFs and the PP matrix. BF-g-LM improved the interfacial adhesion between the BFs and the PP matrix, and so the dispersion of the BFs and interfacial bonding between the BFs and PP were evidently improved as BF-g-LM increased. The fracture surface showed a more brittle texture with extensive fracture and fewer pullouts of the fibers.

CONCLUSIONS

1. We concluded that LM was successfully grafted onto BFs; this reaction was initiated by BPO via a free-radical chain-transfer reaction, which was evident in the FTIR analysis. They were grafted together with ether bonds, which was shown in the DSC measurement of BF-g-LM's ether pyrolysis at 280°C.
2. The optimum preparation conditions were obtained as follows: 0.30 g of pretreated bamboo flour was immersed into 0.225 mol/L LM. This mixture was then initiated by 0.025 mol/L BPO, and the reaction was continued for 4 h at 80°C.
3. BF-g-LM served as a coupling agent between the BFs and the PP matrix, as shown by its mechanical properties, which were observed by SEM analysis. The elongation at break of

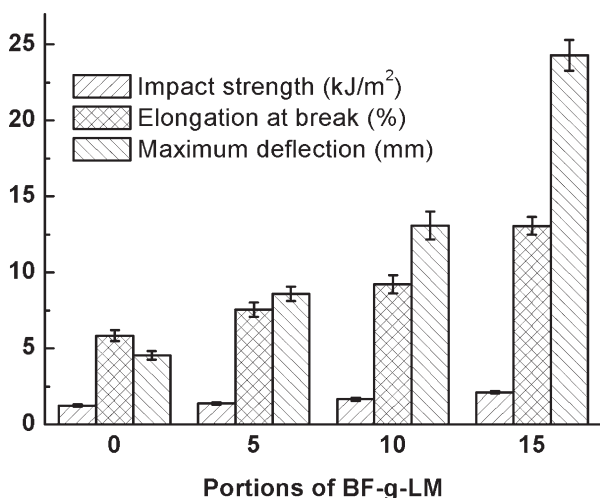


Figure 8. Mechanical properties of the BF/BF-g-LM/PP composites.

the BF/PP composite contained 15 portions of BF-g-LM increased to two times compared with that of the BF/PP composite without BF-g-LM. The impact strength and maximum deflection also increased to 75 and 580%, respectively.

In conclusion, BF-g-LM is a promising coupling agent that can be used in BF-reinforced thermoplastic composites.

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