Preparation and Properties of Wood Flour Reinforced Lignin-Epoxy Resin Composite

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A lignin-epoxy resin composite was prepared by blending lignin/wood flour with an epoxy resin and polyamine. The effects of the wood flour on the mechanical, thermal creep, and creep recovery properties, as well as the microstructure of the composite, were studied. Among the mechanical properties, the initial modulus increased with increasing content of wood flour. The glass transition temperature (T_g) decreased, and the thermal stability first decreased and then increased, as the wood flour content increased. As the wood flour's particle size was decreased, the initial modulus and other mechanical properties first increased and then decreased slightly. The T_g increased, and the thermal stability first decreased and then increased. The creep resistances of the composite were improved after the addition of the wood flour, and the 40 to 60 mesh wood flour exhibited better improvement than 60 to 120 mesh. The scanning electron microscopy (SEM) analysis revealed good interfacial bonding between the lignin, epoxy resin, and wood flour. Fiber breakage and fiber pullout were the main failure modes observed in this study.

Keywords: Lignin; Epoxy resin; Composite; Wood flour reinforcement

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INTRODUCTION

Lignin is a renewable and abundant biomass resource. It has been approximately 170 years since lignin was first discovered by Payen. Lignin has several advantages as a by-product of the paper and bioethanol industries, such as widely abundant sources, low cost, biodegradability, and renewability. The utilization of lignin in composite materials is possible because of its structure, which comprises a variety of functional groups, such as aromatic and aliphatic hydroxyls, methoxyl, and carbonyl groups, which impart high polarity and sufficient reactivity with various chemicals (Simionescu *et al*. 1993; Lora and Glasser 2002; Mansouri and Salvadó 2007). There are at least two methods currently available to utilize lignin: (i) the inclusion of lignin in polymer blends and composites as filler; and (ii) the obtaining of various products, such as polyphenolics, polyurethanes, and epoxy resins after chemical modification, as well as chemical raw materials after catalytic pyrolysis. The comprehensive utilization of lignin has drawn much attention for more than a century. However, only a small portion of lignin and its derivatives have been used for commercial applications (Feldman *et al*. 1986). There may be an effective utilization process allowing lignin to blend with thermoset phenolic resin (Cavdar *et al*. 2008), polyurethane (Cateto *et al*. 2009), and epoxy resin (Malutan *et al*. 2008), or lignin could be a partial replacement for these resins (Stewart 2008). Lignin has also been explored and used in many different formulation applications (Kadla *et al*. 2002; Thielemans *et al*. 2002; Huang *et al*. 2004; Wu *et al*. 2009; Sahoo *et al*. 2011).

Recently, enzymatic hydrolysis lignin (EHL) has received considerable attention because its purity and reactivity are higher than several common types of industrial lignins (Jin *et al*. 2010; He *et al*. 2011; Vishtal and Kraslawski 2011; Zhang *et al*. 2013). EHL is a novel form of lignin that is isolated from the enzymatic hydrolysis residues of biomass. It is obtained as a by-product of the biomass conversion industry and possesses greater chemical reactivity and applicability than lignosulfonate or kraft lignins (Hatakeyama *et al*. 2004; Mansouri and Salvadó 2007). Because the enzymatic hydrolysis process of the biomass is carried out under relatively mild conditions, functional groups such as phenolic hydroxyl and alcoholic hydroxyl groups are preserved. Therefore, EHL could potentially be used as an active filler or modifier to improve the properties of polymer materials by blending with the polymers.

Epoxy resin is a type of cross-linked polymer that possesses excellent chemical resistance, good electrical insulating properties, and good adhesion to glass, metals, *etc*. These properties help epoxy resin to meet the performance requirements of some demanding applications. These applications include areas as diverse as construction, electronics, adhesives, and coatings (Musto *et al*. 2007; Zheng *et al*. 2009; Saad *et al*. 2011). In epoxy cross-linked polymers, additive agents, such as the curing agent and the filler, play decisive roles in its properties. When using lignin as filler or modifying agent for blending with epoxy resin, the presence of the reactive functional groups of lignin and its phenolic ether structure can improve the mechanical and thermal properties of the epoxy resin. This has been confirmed in previous studies (Feldman *et al*. 1991; Kadla *et al*. 2002; Malutan *et al*. 2008; Abdul Khalil *et al*. 2011; Mansouri *et al*. 2011; Wood *et al*. 2011).

In a previous study (Yin *et al*. 2012), a lignin-epoxy resin composite was prepared by blending EHL (> 50 wt%) with an epoxy resin and polyamine. The obtained composite material showed good thermostability; however, its mechanical strength and other properties were still insufficient when compared with the high-performance native epoxy resins. A viable approach to enhance the resin’s performance with fiber reinforcement has been attempted. At present, the main fibers used in fiber reinforced composites are glass fibers (Ray 2006; Fan *et al*. 2008), carbon fibers (Bekyarova *et al*. 2007; Xu and Hoa 2008), aramid fibers (Wu and Cheng 2006; Ren *et al*. 2007), and basalt fibers (Chen *et al*. 2009; Lee *et al*. 2010). The properties of these fiber-reinforced epoxy resin composites can be greatly improved. However, a coupling agent must be used to improve the compatibility between the fiber and the resin. Also, the production processes are relatively complex and costly when using these fibers to reinforce epoxy resin properties.

In recent years, the utilization of plant fibers to reinforce polymers has drawn the attention of various researchers (Shibata *et al*. 2004; Lee and Wang 2006; Li *et al.* 2007; Ku *et al*. 2011; Faruk *et al*. 2014). Plant fibers, such as wood fibers, bamboo fibers, and jute, not only have great specific strength and a wide range of sources, but also are inexpensive, renewable, and biodegradable. Plant fibers have good compatibility with lignin, as they have similar structural units (Rozman *et al*. 2000; Felby *et al*. 2004). Plant fibers also have a good compatibility with epoxy resin because the hydroxyl groups on the fiber surface have the ability to react with the epoxy groups to form strong chemical bonds. Therefore, using plant fibers to reinforce epoxy resin and its composites can not only improve the materials’ properties, but also can reduce the cost, add a certain extent of bio-degradation to the materials, and slow down the oil crisis.

In this study, poplar wood flour was used as the reinforcement to improve the properties of a lignin-epoxy resin composite. The effects of the contents of wood flour and its particle size on the mechanical, thermal, creep, and creep recovery properties, as well as the microstructure of the composite, were studied.

EXPERIMENTAL

Materials

Highly purified enzymatic hydrolysis corn straw lignin with a bulk density of 0.6 g/cm^3 and an average particle size of 11 μm was provided by Songyuan Laihe Chemicals Co., Ltd. of China. It was dried at 50 °C for 24 h in a vacuum oven before use in blending. An epoxy resin of diglycidyl ether of bisphenol-A (DGEBA) with an epoxy content of 0.51 was provided by Nantong Xingchen Synthetic Material Co., Ltd. of China. The curing agent polyamine with an amine value (mg KOH/g) of 210, trademarked as TY-200, was provided by Tianjin YanHai Chemical Co., Ltd. of China. Poplar wood flour was purchased from a local timber market.

Preparation of the Composite

The lignin, epoxy resin, polyamine, and wood flour were blended using a two-roll mill (SK-160, Yangzhou Tianfa testing Machine Co., Ltd., China) at 20 rpm and a temperature of 20 to 30 °C for 15 to 25 min. The mixed materials were removed and put into a home-made mold for hot pressing at a temperature of 130 °C and pressure of 12 MPa (Yin *et al*. 2012). Cold pressing was carried out at room temperature after the hot pressing process was completed. Finally, the composites were demolded and removed for further testing. The choice of the content for the wood flour and lignin was based on our previous study (Yin *et al.* 2012). The total mass fraction of the mixtures of wood flour and lignin was 60%, and in the mixture of wood flour and lignin, the content of wood flour was changed to replace the content of the lignin.

Table 1. Blending Weight Ratio of Lignin, Wood Flour, Epoxy Resin, and Polyamine

Lignin (wt%)	Wood flour (wt%)	Epoxy resin (wt%)	Polyamine (wt%)
60	0	16	24
45	15	16	24
30	30	16	24
15	45	16	24
0	60	16	24

Tests and Analyses

Morphology

The microscopic structures of the composites were examined using a Quanta 200 scanning electron microscope (SEM) (FEI Co., USA). The samples for the SEM test were immersed in liquid nitrogen for approximately 5 min for quick freezing and were then immediately broken by an impact force. A fractured surface was selected for the SEM observation. All the samples were coated with approximately 10 to 20 nm of gold by a Cressington 108 auto ion sputter coater (UK) before being observed.

Thermal properties

The dynamic mechanical analysis (DMA) was performed using the temperature scanning mode in an Oscillation Rheometer (AR2000ex, TA Co., Ltd., USA) equipped with a torque sensor. The temperature scanning rate was 5 K/min, the temperature scanning range was from 30 to 180 °C, the shear stress was 1.5 MPa, the frequency was 2.5 Hz, and the span length was 45 mm. Samples measuring 55 mm × 12 mm × 4 mm (length × width × thickness) were prepared for DMA analysis. The glass transition temperature T_g was determined from the peak of the tan δ curve.

The thermogravimetric analysis (TGA) was performed using a TG 209-F3 thermogravimetric analyzer (Netzsch Scientific Instruments, Germany) at a heating rate of 10 K/min from 30 to 750 °C under argon flow.

Mechanical properties

The bending strength of the composites was tested according to ASTM D790-10 (2010) using a CMT-6104 electronic universal testing machine (Shenzhen Reger Instrument Co. Ltd., China). Sample bars measuring 80 mm × 12 mm × 4 mm (length × width × thickness) were prepared for testing. The test was performed at a speed of 2 mm/min with a span of 64 mm. The notched Izod impact properties of the composite were tested according to ASTM D256-10 (2010) using a XJC-25Z pendulum impact testing machine (Chengde Experiment Machine Co. Ltd., China). The dimensions of the samples used were 64 mm × 12 mm × 4 mm (length × width × thickness), and the test was performed at a speed of 3.5 ms^{-1} on the samples with a span of 60 mm. The impact energy was 1.0 J. All measurements were performed under ambient conditions with a relative humidity of approximately 50%. At least five samples were tested for each composite formulation.

Creep and creep recovery properties

The rapid (short-term) creep and creep recovery properties of the composites were performed according to ASTM D6112-13 (2013) using an oscillation rheometer (AR2000ex, TA Co., Ltd., USA) equipped with a torque sensor at 25 °C, a rotational frequency of 2.5 Hz, and a shear stress of 1.5 MPa. The dimensions of the samples used were 55 mm × 12 mm × 4 mm (length × width × thickness). Each stage for creep and creep recovery lasted 15 min.

RESULTS AND DISCUSSION

SEM Observation

The SEM observation was performed on the fracture surfaces of the samples with brittle failure in liquid nitrogen. The SEM images of the wood flour reinforced lignin-epoxy resin composites containing 0, 30, and 60 wt% of 40- to 60-mesh (0.25 to 0.40 mm) wood flour (Fig. 1) were recorded at various locations across the fracture surface.

Images (a) and (b) in Fig.1 show the fracture surfaces of neat lignin-epoxy resin composites. Lignin was well distributed in the epoxy resin matrix, and no obvious interphase was observed, which explained the good interface bonding between the lignin and the epoxy resin. Images (c), (d), (e), and (f) in Fig. 1 show the fracture surfaces of the lignin-epoxy resin composites with 30 wt% and 60 wt% wood flour, respectively. Fiber breakage and a small amount of fiber pullout were observed in the images c, d, e, and f, which illustrated that good interface bonding was formed between the wood flour and epoxy resin, and there were no agglomerations of lignin found in these wood flour reinforced composites.

More of the wood flour became gathered together (e and f of Fig. 1) as the wood flour content was increased. The fracture morphology (a, b of Fig.1) of the lignin-epoxy resin composite without wood flour was smooth and characterized by fracture surfaces with a certain degree of brittle fracture. The fracture morphology was rougher following the addition of the wood flour, and more resin fragments were found. This indicated an improvement of the composites' toughness.

As our previous study reported (Yin *et al.* 2012), epoxy group of the epoxy resin could react with the hydroxyl group of the lignin. However, the reaction needs a higher temperature. When the polyamine was used as curing agent, it can catalyze the reaction of the epoxy group with the hydroxyl group of the lignin as well, and decrease the reaction temperature. As it is well known, the content and activity of hydroxyl group within the wood flour is much higher than that of the lignin, and the reaction of epoxy group with hydroxyl group within the wood flour is able to be predicted.

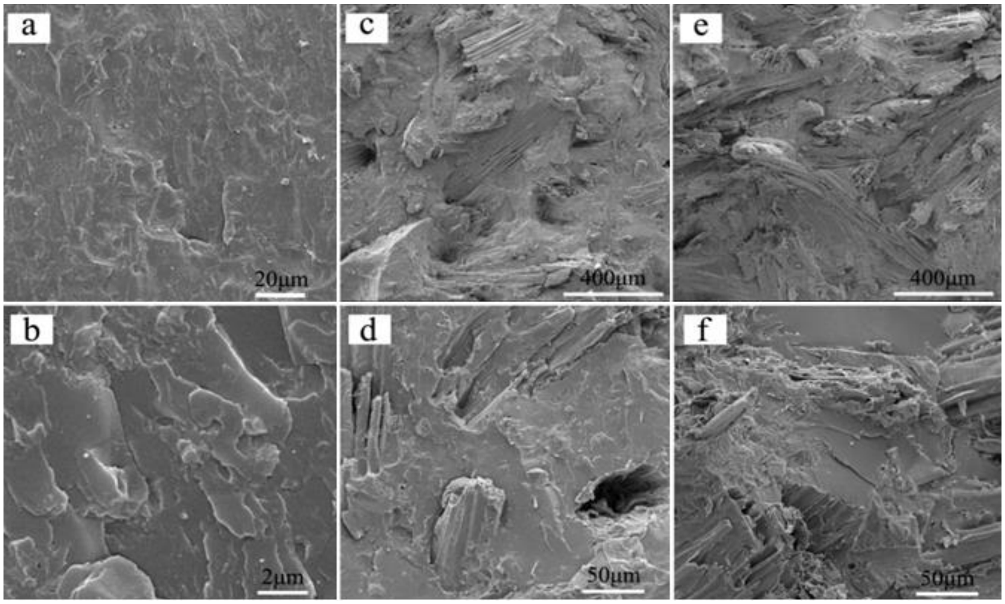

Fig. 1. SEM images of lignin-epoxy resin composites with various contents of wood flour at various magnifications: (a) 0%, 1000×; (b) 0%, 10000×; (c) 30%, 100×; (d) 30%, 500×; (e) 60%, 100×; (f) 60%, 500×

Figure 2 shows the SEM images of the lignin-epoxy composites reinforced with various wood flour particle sizes (with wood fiber content of 30 wt%) at various magnifications. The fiber breakage and fiber pullout can be observed clearly in images (g) and (c). The wood flour (60 to 120 mesh, *i.e.*, 0.12 to 0.25 mm) was also observed in (h) at low magnification, which was not apparent in the composites with the wood flour of 16 to 40 mesh (0.4 to 1.0 mm) and 40 to 60 mesh.

More fiber fracture or breakage was found in the composites with the wood flour of 16 to 40 mesh, but more fiber pullout was observed in the composites with the wood flour of 40 to 60 mesh. Both the fiber fracture and fiber pullout were reduced in the composites with the wood flour of 60 to 120 mesh size.

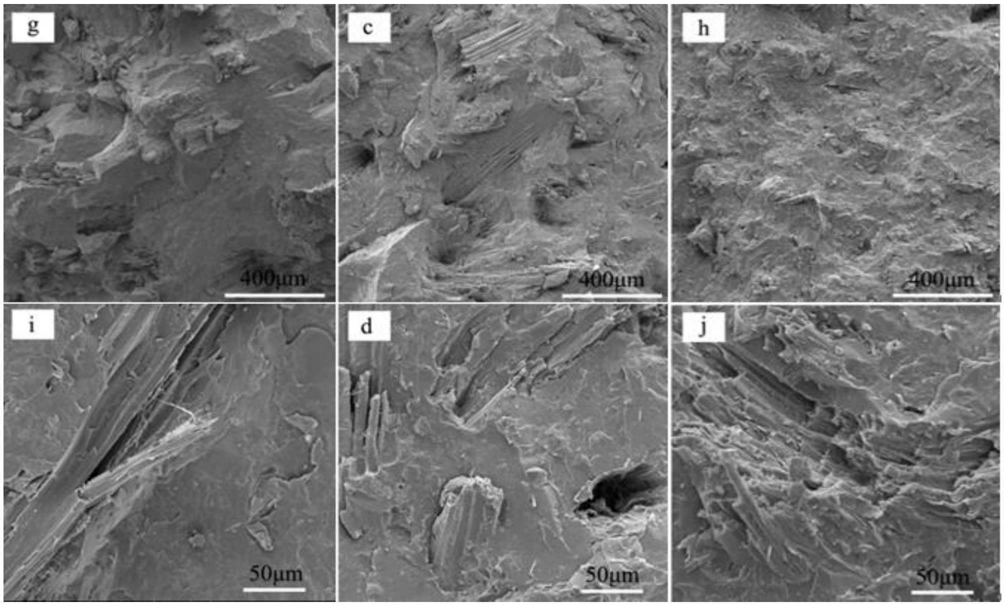

Fig. 2. SEM images of lignin-epoxy composites reinforced with various particle sizes of wood flour at various magnifications: (g) 16 to 40 mesh, 100×; (i) 16 to 40 mesh, 500×; (c) 40 to 60 mesh, 100×; (d) 40 to 60 mesh, 500×; (h) 60 to 120 mesh, 100×; (j) 60 to 120 mesh, 500×

DMA Analysis

Various properties of the composites, such as the storage modulus and tan *δ*, which are dependent on temperature, were obtained by performing a dynamic mechanical analysis (Hossain *et al.* 2014). Figures 3 and 4 show the temperature dependence of the storage modulus (*E*'), and the loss tangent (tan δ) in the temperature range of 30 to 180 °C.

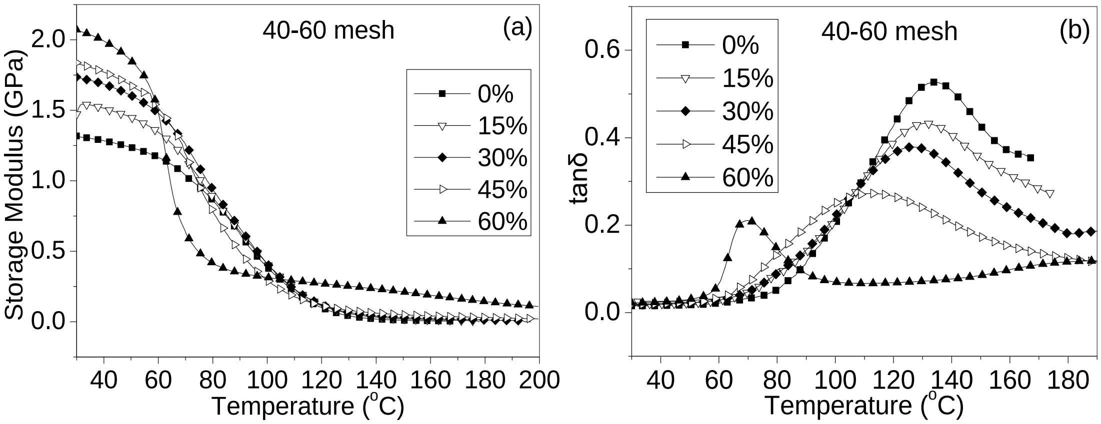

Fig. 3. Effects of the content of wood flour on (a) the *E*' and (b) the loss tangent (tan δ) for the lignin-epoxy resin composites

The effects of the content of the wood fiber (40 to 60 mesh) on the *E*' and tan *δ* are shown in Fig. 3. It can be seen that the addition of wood fiber resulted in a remarkable improvement in the storage modulus. The storage modulus improved by 12% with the addition of 15 wt% wood flour at 30 °C. The increase in the storage modulus for the composites at room temperature was mostly due to the reinforcement of the wood flour (Shah *et al.* 2008). The physical entanglement and chemical cross-linking between the polymeric molecular chain and the wood flour increased as the content of the wood flour increased. However, the glass transition temperature of the composites decreased. This is because the physical entanglement was the main interaction, and this has little effect on the rigidity of the matrix. Moreover, the rigidity of lignin was more than that of wood flour, together with the reaction of lignin with epoxy resin because of the activity of lignin, which contains several active functional groups and resulted in the rigidity of the composites being increased. Therefore, with increasing the content of wood flour, the molecular rigidity originated from chemical cross-linking between the polymeric molecular chain and the wood flour decreased due to the cellulose and hemicellulose within the wood flour, which resulted in the decrease of glass transition temperature for the polymer matrix. However, the modulus for the composites increased because of the physical entanglement of the wood fiber, which resulted in the reducing of the peak height of tan *δ*.

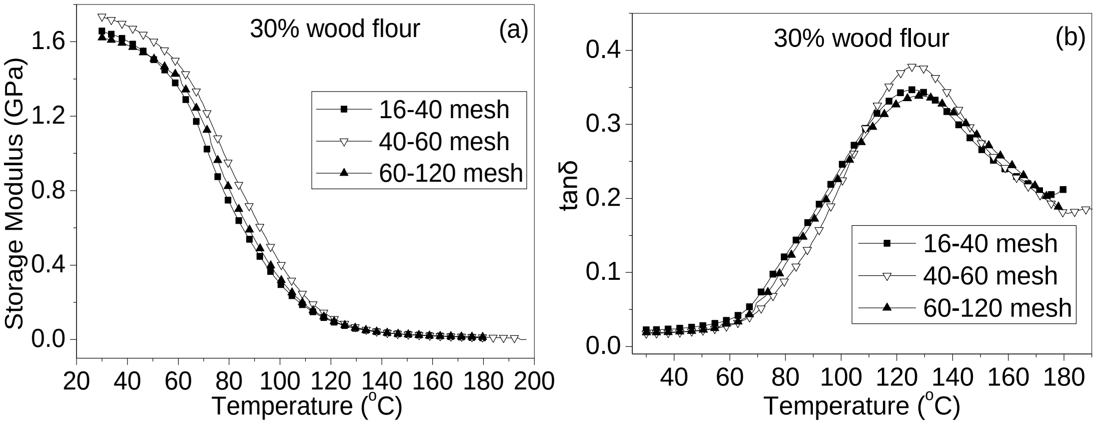

Fig. 4. Effects of the particle size of wood flour on (a) the *E*' and (b) the loss tangent (tan *δ*) for the lignin-epoxy resin composites

Figure 4 illustrates the effects of the particle size of the wood flour on the *E*' and tan *δ* for the lignin-epoxy resin composites. The lignin-epoxy resin composite reinforced by the wood flour with the particle size of 40 to 60 mesh had the highest storage modulus at 30 °C. Also, the composite reinforced by 40 to 60 mesh wood flour consistently had a higher modulus than the two others before the material was completely softened. These results can be explained by the good blending uniformity between the wood flour and the matrix, and the reinforcement of the wood flour to the matrix. The wood flour with the particle size of 40 to 60 mesh had a better uniformity in the composites as shown in Fig. 2 and a sufficient reinforcement because of its suitable length to diameter ratio. The glass transition temperature for the composites increased slightly as the particle size of the wood flour decreased. The composite reinforced by 60 to 120 mesh wood flour had the highest glass transition temperature (129 °C for 60 to 120 mesh, 127 °C for 40 to 60 mesh, 125 °C for 16 to 40 mesh). The explanations for these results are that the wood flour with the particle size of 60 to 120 mesh had a smaller particle size and a larger rigidity, and the composite reinforced by the 60 to 120 mesh wood flour had less energy dissipation than the composites reinforced by the 16 to 40 or the 40 to 60 mesh wood flour in thermal motion.

TG Analysis

The thermal stability of the composites was measured using TGA. The TGA curves of the composites with different particle sizes and contents of wood flour are shown in Fig.

5. The TGA values of the composites (degradation temperatures at 10%, 20%, and 50% weight loss; residual carbon content) are shown in Table 2.

As can be seen from Table 2, after the addition of wood flour into the composites, the degradation temperatures at 10%, 20%, and 50% weight loss for the composites decreased firstly, and then it increased with the increase of the content of wood flour. The control samples, neat lignin-epoxy resin composite, or neat wood flour-epoxy resin composite, both had higher thermal stability than the wood flour reinforced lignin-epoxy resin composite. This may be explained by the occurrence of a catalytic pyrolysis process between the wood flour and the lignin units (Fang *et al.* 2012). The residual carbon content decreased as the wood flour content increased. However, when the lignin was completely replaced by the wood flour, the residual carbon content increased slightly. This is due to the wood flour containing more oxygenic groups than the lignin. Therefore, the composites containing more wood flour had lower content of carbon in the elemental composition of the composites. When the lignin was completely replaced by the wood flour, the residual carbon content of the composite was increased in the absence of the catalytic pyrolysis of the lignin.

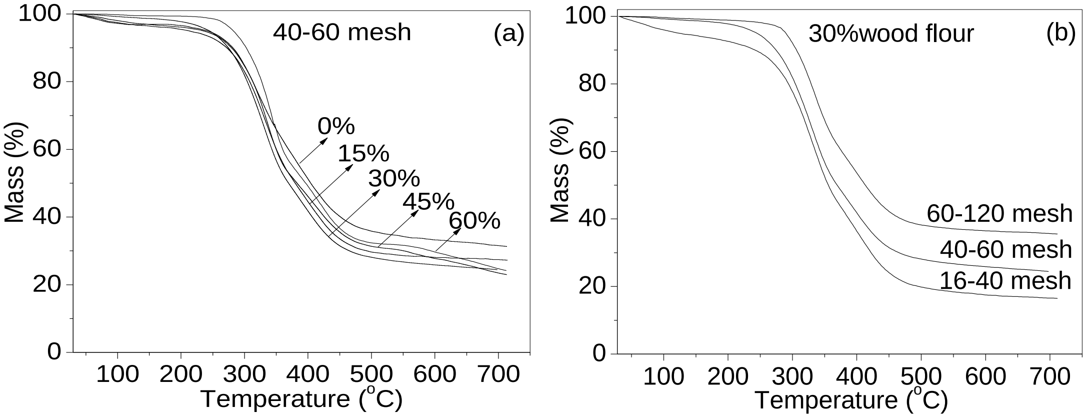

Fig. 5. TGA curves of the lignin-epoxy composites: (a) contents of wood flour (40 to 60 mesh); (b) particle size (30 wt%)

Table 2. TGA Values of the Composites

Samples	10% loss (°C)	20% loss (°C)	50% loss (°C)	Residual carbon (%)
40-60 mesh 0%	281.7	313.2	404.4	31.27
40-60 mesh 15%	272.2	308.3	380.0	27.26
40-60 mesh 30%	274.6	304.5	369.5	24.42
40-60 mesh 45%	279.6	313.1	382.8	22.97
40-60 mesh 60%	309.2	330.7	396.5	24.17
16-40 mesh 30%	242.1	293.8	355.7	16.43
40-60 mesh 30%	274.6	304.5	369.5	24.42
60-120 mesh 30%	306.4	329.1	413.0	35.49

The degradation temperatures at 10%, 20%, and 50% weight loss for the composites, along with the residual carbon content (Table 2), all showed an increasing trend as the wood flour particle size decreased. This suggested that the thermal stability of the composites increased as the wood flour particle size was decreased. This can be explained by the fact that the composites were influenced by a physical blend, and that the wood flour with larger particle size induced defects in the form of the concentration, and also the heterogeneities in the polymer matrix (Marcovich and Villar 2003).

Mechanical Properties

The variations of the bending strength and impact strength for the composites with the content of the wood flour (40 to 60 mesh) are shown in Fig. 6(a). Both the bending strength and impact strength showed an increase with increasing the content of the wood flour. The composite reinforced with 15 wt% of the wood fiber showed approximately a 33% increase in the bending strength, and a 57% increase in the impact strength. When the lignin were totally replaced by the wood flour (60 wt% wood fiber), the strength increase reached approximately 144% in the bending strength, and 468% in the impact strength. The mechanical properties of the lignin-epoxy resin composite were significantly improved by the addition of the wood flour. The mechanical properties of the fiber-reinforced composites were strongly dependent on the extent of the load transfer between the matrix and the fiber. This indicated that the chemical bonding between the epoxy resin and the wood fibers caused an improved stress transfer between the lignin-epoxy matrix and the wood fiber (Marcovich and Villar 2003). Also, the continuity of reinforcement for the wood flour in the matrix had a positive effect on the bending strength. Compared with the wood flour, the lignin has greater rigidity, and a non-wood flour reinforced lignin-epoxy resin composite has greater brittleness. The improvement in the impact strength of the composites could be explained based on the length to diameter ratio of the wood flour and a good interfacial bonding between wood flour with the epoxy resin matrix.

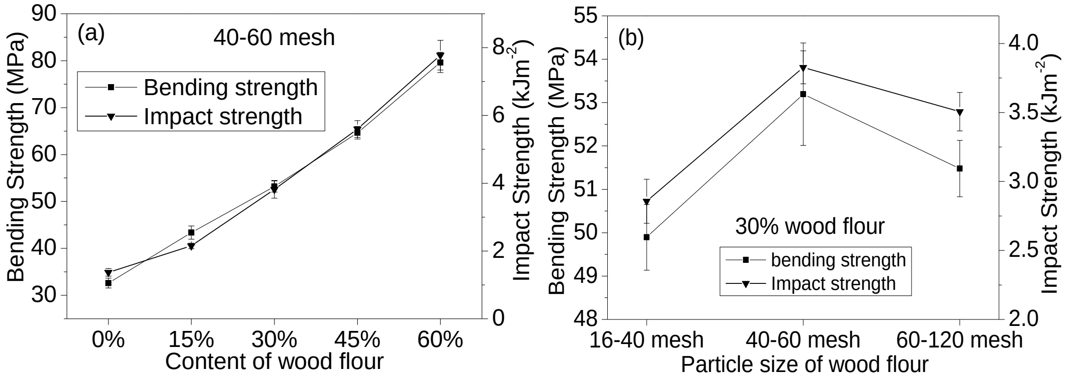

Fig. 6. Effects of wood flour on the bending strength and impact strength of lignin-epoxy resin composites: (a) contents of wood flour (40 to 60 mesh); (b) particle size (30 wt%)

The particle size of the wood fiber also had an influence on the mechanical properties for the composites. The variations of the bending strength and impact strength with the particle size of the wood fiber (30 wt%) are shown in Fig. 6(b). The bending strength and impact strength of the composites increased firstly, and then both decreased slightly with the decrease of the particle size for the wood flour. The 40 to 60 mesh wood flour reinforced composite had the maximum bending strength of 53.19 ± 1.18 MPa, and the impact strength of 3.82 ± 0.26 kJ/m^2. The possible reasons for these results are that the wood flour with larger particle size may easily form holes in the matrix, and those holes then become stress concentration points (Nuñez *et al.* 2002) under an applied load. Meanwhile, the continuity of the wood flour in the composites decreased as its particle size was reduced greatly.

Creep and Creep Recovery

The short-term creep and creep recovery tests of the composites were also carried out. The effects of the wood fiber content and its particle size on the short-term creep response, as well as the creep recovery for the samples tested at 25 °C are shown in Fig. 7. From Fig. 7(a), it can be seen that the neat lignin-epoxy resin composite showed the highest creep in the range of the time analyzed. When the wood flour was added, the creep obviously decreased, and it continued to decrease with the increase of the wood flour content up to a 60 wt%. This was the result of the increasing in the Young's modulus (Fig. 3) of the composite by the reinforcement of the wood flour (Park and Balatinecz 1998; Marcovich and Villar 2003). After the removal of the load, the final deformations of the composites decreased firstly, and then they increased within the range of the time analyzed. A possible reason for this may be that the lignin can react with the epoxy resin to act as a part of the resin chain segments, which increased the rigidity of the composites (Nuñez *et al.* 2003). Although the addition of the wood flour can potentially increase the composites' Young's modulus, it had little influence on the rigidity of the molecular chain segments. The rigidity of the molecular chain segments was reduced as the wood flour content was increased. The molecular chain segment was more prone to slippage due to the enlarged deformation under a continuing load increase. The composite reinforced with less content of the wood flour may result in large irreversible deformations under a load due to its low strength, weak modulus, and weak or lower fiber conduction.

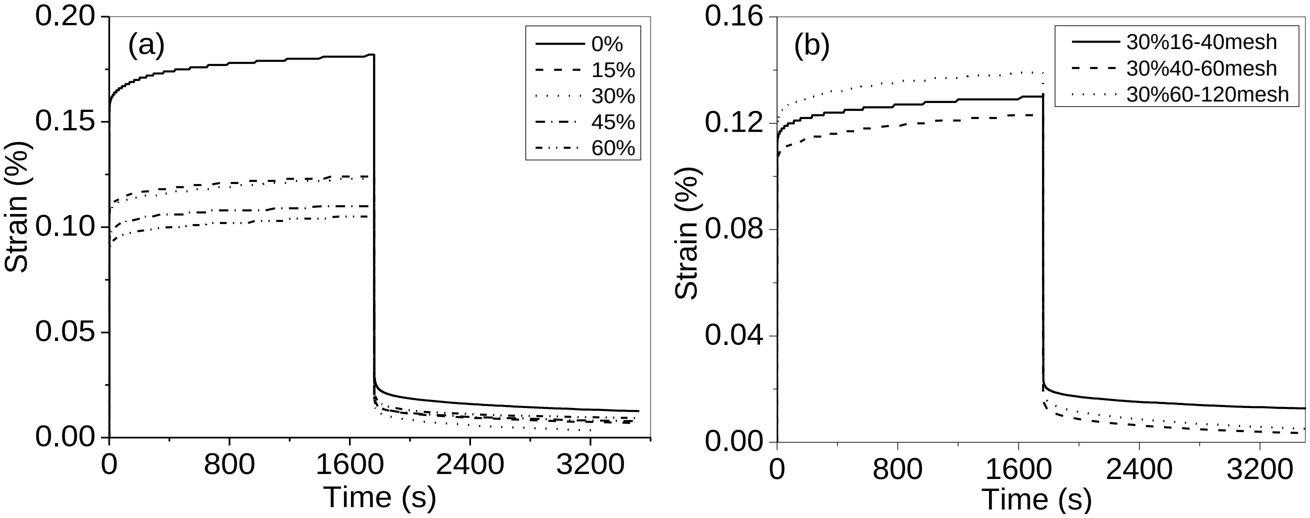

Fig. 7. Effects of wood flour on the creep and creep recovery of lignin-epoxy resin composites: (a) contents of wood flour (40 to 60 mesh); (b) particle size (30 wt%)

The composite reinforced by the wood flour with 60 to 120 mesh size had the largest initial deformation, followed by the wood flour with 16 to 40 mesh, and then the wood flour with 40 to 60 mesh. However, the composite reinforced by the wood flour with 40 to 60 mesh had the minimum deformation, and maximum for the wood flour with 16 to 40 mesh after the creep recovery. These results may be explained by the different interfacial bonding properties between the different particle sizes of wood flour with the polymer matrix. A moderate particle size (40 to 60 mesh) wood flour reinforced composite had a better creep resistance, as illustrated in Fig. 7(b).

CONCLUSIONS

1. The presence of wood flour was beneficial for the improvement of the mechanical properties of a composite formed with lignin and epoxy resin. This was due to the increasing extent of the load transfer among the matrix.
2. The glass transition temperature decreased, indicating that the wood flour had a plasticizing action on the composite material. The thermal stability also decreased, which suggested that some kind of mutual catalysis may have existed between the lignin and the wood flour *via* the process of pyrolysis. The addition of the wood flour improved the creep resistance of the materials.
3. The particle size of the wood flour had a great effect on the properties of the composite materials. The composites reinforced by the 40 to 60 mesh wood flour had optimum mechanical properties and creep resistance. The composites reinforced by the 60 to 120 mesh wood flour had a higher glass transition temperature and a better thermal stability.
4. The SEM analysis showed a good interfacial bonding between the lignin, epoxy resin, and wood flour. The fiber breakage and pullout were the main failure modes observed in this study.
5. Wood flour can be successfully used as a reinforcing material in lignin/epoxy composites. Therefore, a better performance of lignin/epoxy composite can be obtained after the addition of wood flour with an appropriate size and content.

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