

Enhanced Thermal and Mechanical Properties of Lignin/Polypropylene Wood-Plastic Composite by Using Flexible Segment-Containing Reactive Compatibilizer

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Abstract: A reactive compatibilizer containing flexible segment (RCFS) was synthesized and characterized by Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). The RCFS was used as a compatibilizer for the preparation of lignin/polypropylene (PP) wood plastic composites, and the effect of the RCFS on the properties of composites (*e.g.*, mechanical properties, thermal properties, crystal structure, and morphology) were investigated in detail. Experimental results indicated that the lignin/PP composite displayed the best performance with the addition of 2 wt% RCFS. Its impact strength, flexural strength, and modulus were 56.8%, 37.3%, and 20.6%, respectively, which are higher than those of the untreated composites. Moreover, RCFS treatment could also increase the thermal stability, crystallization rate, and degree of crystallinity of lignin/PP composites.

Keywords: lignin, polypropylene, flexible segment, compatibilizer, wood-plastic composites.

Introduction

The use of natural fibers as reinforcement in polymeric matrix has attained great academic and commercial interest in the past decade due to low cost, large availability, and biodegradability of the fibers.¹⁻⁶ Lignin is a complex organic phenolic polymer skeleton available as industrial waste material from pulp and paper industry in large quantity. It has been used for many new products, such as resins⁷ and adhesives for polymer blending⁸ and for the preparation of low-molecular weight fuel additives.⁹ For example, Kharade¹⁰ reported that the mechanical properties of lignin/polypropylene (PP) blends, it was found that the tensile strength was reduced, whereas the impact properties remained unaffected, and the melt viscosity increased with the lignin content. Pucciariello *et al.*¹¹ reported that the elongation was drastically reduced, whereas the modulus values were improved. Atul V. Maldhure¹² studied on the mechanical properties of polypropylene blended with modified lignin. The advantages of using lignin in composites with polymers are low density, low abrasion to equipment, increase in modulus of elasticity (Young's modulus) and renew-

ability. This indicated that the development of lignin/polypropylene (PP) wood-plastic composites has good application prospects.

However, the main polymers of lignin materials (especially cellulose and hemicellulose) contain large amounts of hydroxyl groups, making them hydrophilic. The highly hydrophilic characterization of lignin materials also makes them incompatible with polypropylene, which is highly hydrophobic. This incompatibility produces poor interfacial adhesion between matrix and filler, which results in poor mechanical properties because stress cannot be transferred properly from the matrix to the fibers.^{13,14} One way to improve the interactions between lignin and PP is through the use of compatibilizers and various chemical reagents. These include maleic anhydride modified polypropylene (MAPP),^{15,16} γ -aminopropyltriethoxysilane,^{17,18} treatment with sodium hydroxide,¹⁹ *etc.* The function of these materials is to improve polymer-polymer interaction through covalent or hydrogen bonding between hydroxyl groups and the compatibilizer, composed of a long hydrocarbon chain in the case of silane coupling agents, or even the homopolymers MAPP.

In spite of the wealth of information about lignin-plastics composites,²⁰⁻²⁴ there is much less information concerning the use of reactive compatibilizer in commodity plastics such as polypropylene and polyethylene. In this study, a new kind of reactive compatibilizer containing flexible segment (RCFS)

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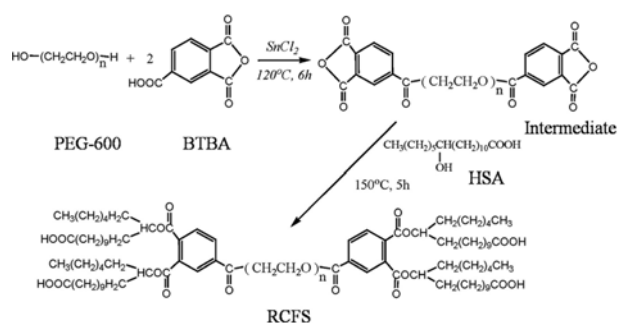
was synthesized through the esterification reaction of 1,2,4-benzenetricarboxylic anhydride, polyethylene glycol 600 and 1,2-hydroxystearic acid. The RCFS was used as a compatibilizer to modify the lignin/PP wood plastic composite, the mechanical properties, thermal properties, crystal structure and morphology resulted composites were investigated. The products were used to compare with the lignin/PP composites which were modified using Fusabond M613-05 as a compatibilizer.

Experimental

Materials. Lignin, in the powder form, was obtained from Hangzhou Xinhua Group (Hangzhou, China), and it contains about one hydroxyl group per phenylpropane unit with almost 25% aliphatic hydroxyl groups and 75% aromatic hydroxyl groups. The total hydroxyl group content was taken from the literature. The polypropylene (T30S, graininess) was purchased from Hunan Changsheng Petrochemical Co., Ltd. Fusabond M613-05 (Defined as M613) is a compatibilizer from Dupont (U.S.A). 1,2,4-Benzenetricarboxylic anhydride (BTBA), 12-hydroxystearic acid (HSA) and polyethylene glycol 600 (PEG-600) were supplied by Tianjin Damao Chemical Reagent Factory, China. All the other starting materials were purchased from commercial sources and used without further purification.

Synthesis of RCFS. The typical procedure is as follows. To a 250 mL three-neck flask, BTBA (0.2 mol), PEG-600 (0.1 mol), 100 mL acetone and 0.2 g SnCl₂ were mixed and heated at 120 °C under nitrogen atmosphere. The reaction mixture was stirred at this temperature for a further 6 h, Then 0.4 mol HSA was added and stirred at 150 °C for additional 5 h. The acetone was distilled under vacuum at 50 °C to get the white waxy solid objective product. The synthetic route of RCFS is shown in Scheme I.

Preparation of Lignin/PP Composites. The lignin/PP composite was prepared in a two-roll mill. The nip gap, mill roll, speed ratio and the number of passes were kept the same in all the mixes. In the melt mixing method, 30 wt% lignin, 40 wt% PP, and 30 wt% CaCO₃ with different amount of RCFS were mixed in a Haake rheocord mixer. When a homogeneous mixture of PP, lignin, calcium carbonate powder and compat-



Scheme I. The synthetic route of RCFS.

ibilizer was obtained, the mixture was put into the mould at 180 °C for about 10 min under mild pressure followed by 5-15 MPa for about 4 min and cooled to room temperature under the pressure to obtain the final composite plaques for testing.

Characterization. Fourier transform infrared spectroscopy (FTIR) was recorded between 4000 and 500 cm⁻¹ on a Perkin-Elmer 1710 spectrophotometer using KBr pellets at room temperature. The gel chromatography was measured in a Marvin 270 gel permeation chromatography (GPC).

Mechanical properties of lignin/PP composites were evaluated by impact and flexural measurements. Mechanical data presented in this study were the average of at least five parallels. Izod impact strength was performed on unnotched lignin/PP composites according to GB 1043-1993. Flexural tests were performed according to WDW-20 (Shenzhen Jun Red Instrument Equipment Co., Ltd., China) using a three-point bending mode of the universal testing machine with a cross-head speed of 10 mm/min. The conditions of the tests and the specimens conformed to GB1449-2005. Thermo-mechanical properties, modulus, and glass transition temperature were determined using a linear rheometer (Q 800 dynamic mechanical analyzer was made with a TA instruments) in a single cantilever bending mode, at a frequency of 1.0 Hz from 25 to 150 °C at a heating rate of 3 °C/min. The melt rheological studies were performed on an SRZ-400E MFR instrument (Changchun intelligent instrument equipment Co., Ltd.) according to GB3682-2000. The differential scanning calorimetry (DSC) test was carried out with a Netzsch differential scanning calorimeter (DSC-204) at heating and cooling rates of 10 °C/min under flowing nitrogen within the temperature range of 40-200 °C. Scanning electron micrographs (SEM, JSM-6380LV) were taken to analyze the morphologies of the composites.

Results and Discussion

FTIR and GPC Analysis. The FTIR spectra of (a) PEG-600, (b) RCFS, and (c) HSA are shown in Figure 1. In (a), a

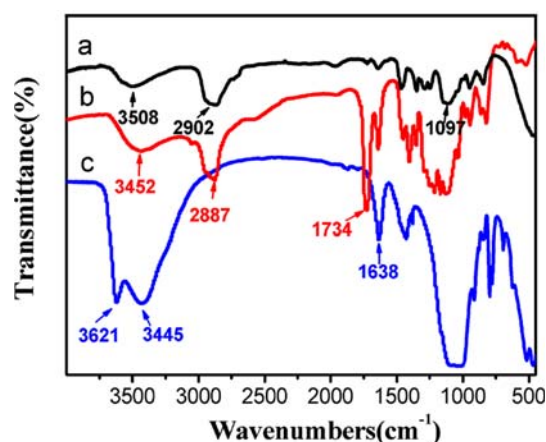


Figure 1. The FTIR spectra of the (a) PEG-600, (b) RCFS, and (c) HSA.

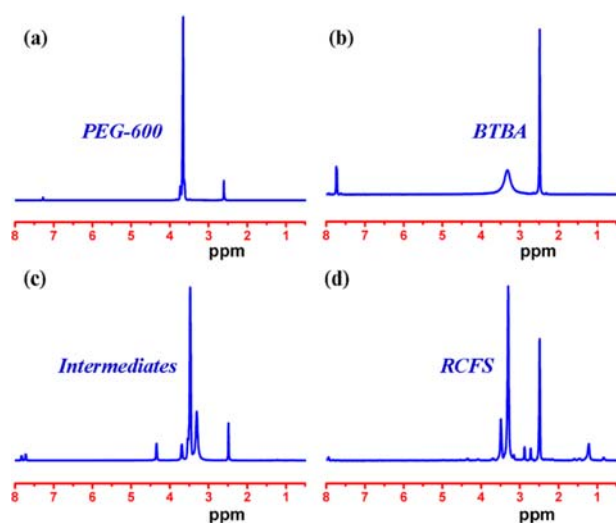


Figure 2. ^1H NMR spectra of (a) PEG-600, (b) BTBA, (c) intermediates, and (d) RCFS.

distinct absorption peak at 1097 cm^{-1} is in the region of $-\text{C}-\text{O}-\text{C}$ stretching for ether groups and the peak at 3508 cm^{-1} belongs to $-\text{OH}$ group. In (b) the absorption peak located at 1630 cm^{-1} owe to the stretching vibrations of benzene ring. The stretching vibrations of methylene are observed at about 2880 cm^{-1} . The strong peak at 1730 cm^{-1} can be attributed to vibrations of ester group, while vibration band of anhydride of the 1,2,4-benzenetricarboxylic anhydride (at about 1800 cm^{-1}) is disappeared. In (c) the peak at 3621 and 3445 cm^{-1} belong to $-\text{OH}$ group, and the absorption bands at 1638 cm^{-1} was mainly due to $-\text{C}=\text{O}$ asymmetric stretching. Compared to the curves (a), (b), and (c), it indicated that RCFS has been successfully synthesized.

The ^1H nuclear magnetic resonance (NMR) spectra was obtained for PEG-600, BTBA, intermediates and RCFS, as shown in Figure 2. Figure 2(a) and (b) show the ^1H NMR spectra of PEG-600 and BTBA, which is in agreement with the previous report. The ^1H NMR spectra of intermediates and RCFS, as shown in Figure 2(c) and 2(d), are similar, but some differences can still be detected. As can be seen from Figure 2(d), the characteristic peaks from the HSA molecular are clearly detected in the ^1H NMR spectra of the RCFS. ^1H NMR spectra provide more detailed evidence to prove that RCFS are successfully synthesized. As shown in Figure 3, the GPC curve of the RCFS displays single peak, indicating that the RCFS is synthesized with high purity. The number-average and weight-average molecular weight of the RCFS are 1736 and 2803, respectively.

Mechanical Properties of Lignin/PP Composites.

Effect of the Amount of RCFS on Mechanical Properties of Composites: Figure 4 shows the mechanical properties of lignin/PP composites with different amount of RCFS. With increasing the RCFS content, the mechanical properties of lignin/PP composites increase first and then decrease. The opti-

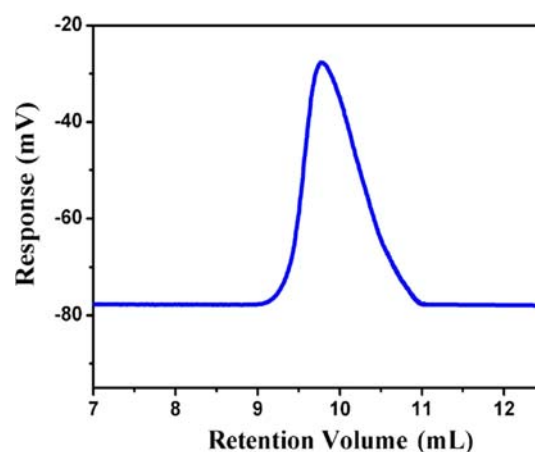


Figure 3. The GPC curve of the RCFS.

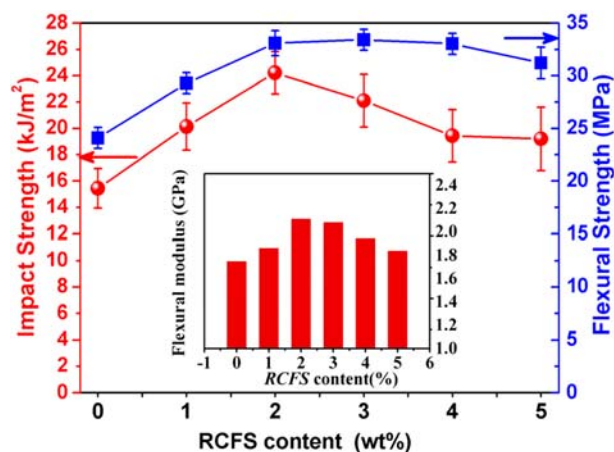


Figure 4. Effects of RCFS content on mechanical properties of composites.

mal amount of RCFS is found at about 2 wt%. As shown in Figure 4, the impact strength, flexural strength and flexural modulus of the lignin/PP composites with 2 wt% RCFS are 24.22 kJ/m^2 , 33.1 MPa , and 2.11 GPa , respectively. It can be concluded that proper amount of RCFS can improve the interfacial compatibility among CaCO_3 , lignin and PP. However, excess RCFS may prohibit the formation of interface monomolecular and weaken the mechanical properties of the composites.

Effect of Compatibilizer Kinds on Mechanical Properties of Composites: For comparison, mechanical properties of pure lignin/PP composite and composites with 2 wt% of RCFS and commercial M613 compatibilizer were investigated as presented Table I. It is observed that by treating with RCFS, the impact strength, bending strength and modulus of the lignin/PP composite can reach up to $24.22\text{ kJ}\cdot\text{m}^{-2}$, 33.10 MPa , and 2.11 GPa , respectively, which are 56.8%, 37.3%, and 20.6% higher than that those of the untreated composite. The reason for this may be due to the hydrogen bonding between compatibilizer and lignin/PP that gives rise to an intermolecular

Table I. The Effects of Compatibilizer on Mechanical Properties of Composites^a

Samples	Impact Strength (kJ·m ⁻²)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Toughness (MJ/m ³)	MFR (g/10 min)
Lignin/PP	15.45 (±0.26)	24.10 (±0.43)	1.75 (±0.14)	0.56	1.34 (±0.05)
Lignin/PP/M613	23.10 (±0.25)	34.80 (±0.42)	1.95 (±0.13)	0.67	1.78 (±0.04)
Lignin/PP/RCFS	24.22 (±0.24)	33.10 (±0.44)	2.11 (±0.15)	0.71	2.04 (±0.04)

^aValues in bracket are the standard deviation of the results.

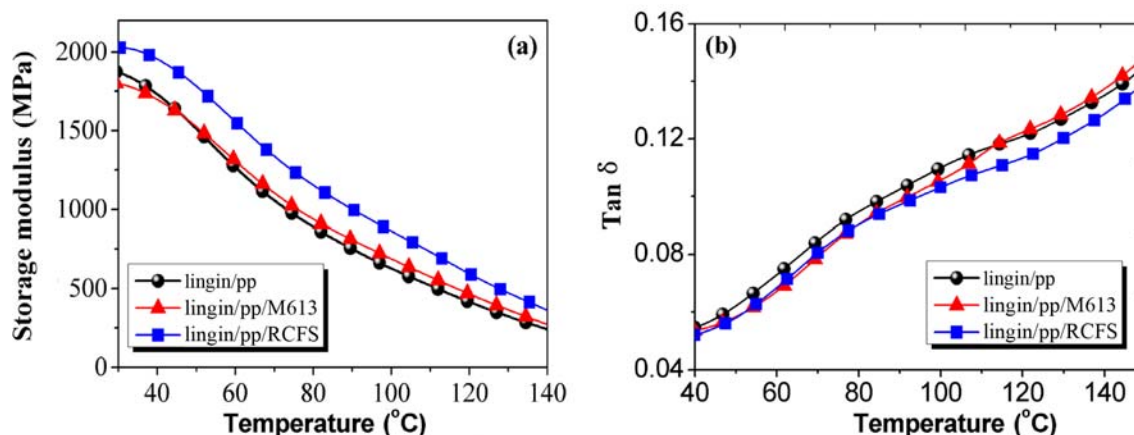


Figure 5. DMA curves of lignin/PP composites, (a) storage modulus and (b) loss factor.

network and/or chemical cross-links. Table I also indicates further improvement in the flexural modulus by adding RCFS compatibilizer, which confirms DMA results at low temperature (see Figure 5). Meanwhile, the toughness (area under stress-strain curve) of pure lignin/PP composite and composites with 2 wt% of RCFS and commercial M613 compatibilizer are 0.56, 0.67, and 0.71 MJ/m³, respectively. This indicates that an applied mechanical load might effectively be transferred through the interfacial interactions.

In addition, treating with RCFS can also help to improve the melt flow rate (MFR). The melt viscosity decrease due to the interfacial compatibility of lignin/PP composites was enhanced after adding compatibilizer, which can form hydrogen bonding or chemical cross-links between compatibilizer and lignin. This will reduce the hydroxyl number of the lignin surface and improve the interfacial compatibility of lignin and PP matrix.

Dynamic Mechanical Analysis: Dynamic mechanical properties such as the storage modulus (E') and $\tan \delta$ of the pure lignin/PP, lignin/PP/M613 and lignin/PP/RCFS composites (RCFS or M613 content is 2 wt%) are investigated and given in Figure 5. Figure 5(a) shows that the storage modulus of the composites decreased with increasing temperature. As compared to composite without RCFS or M613 compatibilizer treatment, the composites with the compatibilizer systems obtain slightly higher storage modulus. This indicates that the compatibilizer can increase the adhesive force between the resin and packing, and make them connect tightly with strong

chemical bonds, which can strongly restrict the motion of PP matrix chains, thereby increasing the stiffness of the matrix. The $\tan \delta$ of the lignin/PP composites is shown in Figure 5(b). In the $\tan \delta$ curves, the $\tan \delta$ peaks temperature (often referred as glass transition temperature T_g) of the composites, which added compatibilizer, are slightly lower than that of composite without RCFS or M613 compatibilizer treatment. This may be attributed to compatibilizer containing flexible spacers, which led to the glass transition temperature peak decreased.

Crystalline Structure of Lignin/PP Composites. Figure 6 shows the wide-angle X-ray diffraction (WAXD) patterns of the neat lignin/PP, lignin/PP/M613, and lignin/PP/RCFS com-

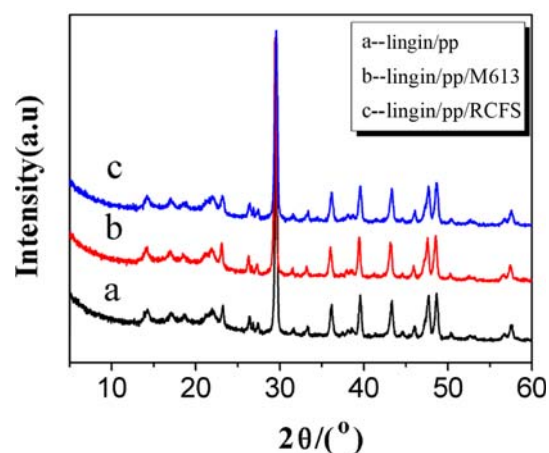


Figure 6. WAXD of lignin/PP composites.

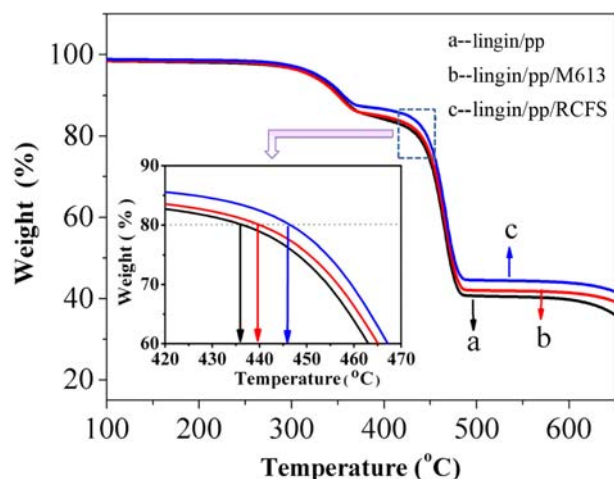


Figure 7. TGA curves of the PP composites.

posites, respectively. The PP phase in all samples is α -type crystal form. The strong peak located at 29.4° is corresponding to CaCO_3 phase. It can be seen that the WAXD patterns of all composites are almost same, which indicates the addition of compatibilizer shows negligible effect on the crystalline structure.

Thermal Properties of Lignin/PP Composites. Figure 7 shows the TGA curves of the pure lignin/PP, lignin/PP/M613, and lignin/PP/RCFS composites, respectively. It is observed that composite with RCFS displays the highest thermal decomposition temperature, and the initial thermal decomposition temperature of composites shifted towards high temperature

direction. For instance, the temperature at 20 wt% weight loss for the lignin/PP, lignin/PP/M613 and lignin/PP/RCFS composites are 435.9, 439.6, and 445.9 $^\circ\text{C}$, respectively. This is mainly because the RCFS compatibilizer can efficiently enhance adhesive force between lignin and PP, and formed interpenetrating polymer network. When the lignin/PP composites were damaged, it required more energy, so the thermal decomposition temperature was improved.

The DSC curves of heating and cooling process at 10 K/min of the composites are given in Figure 8. The relative parameters, such as melting temperature (T_m), crystallization temperature (T_p), melting peak temperature (T_{mp}), degree of supercooling (ΔT) ($\Delta T = T_{mp} - T_p$) and melting enthalpy (ΔH_m), the samples are listed in Table II. It is observed that, by adding 2 wt% of compatibilizer, the T_m and T_p of the composite increase, the ΔH_m enhances, while the ΔT decreases, which indicates that the compatibilizer can increase the crystallization rate and crystallinity of PP. Since the crystallinity affects the physical properties of composites such as strength and modulus. Therefore, the proportion of PP crystalline phase was increased by adding compatibilizing agent, and the mechanical properties of composites were improved.

Morphology of the Lignin/PP Composites. Figure 9 shows the SEM micrographs of impact fracture structures of the lignin/PP composites. As shown in Figure 9(a), without compatibilizer, the fracture surface is uneven and has many large holes, which illustrates a badly dispersion of the resin and packing. After addition of compatibilizer, the fracture surface of composites also shows many voids and agglomeration of lignin particles appeared. However, as the compatibilizer is added

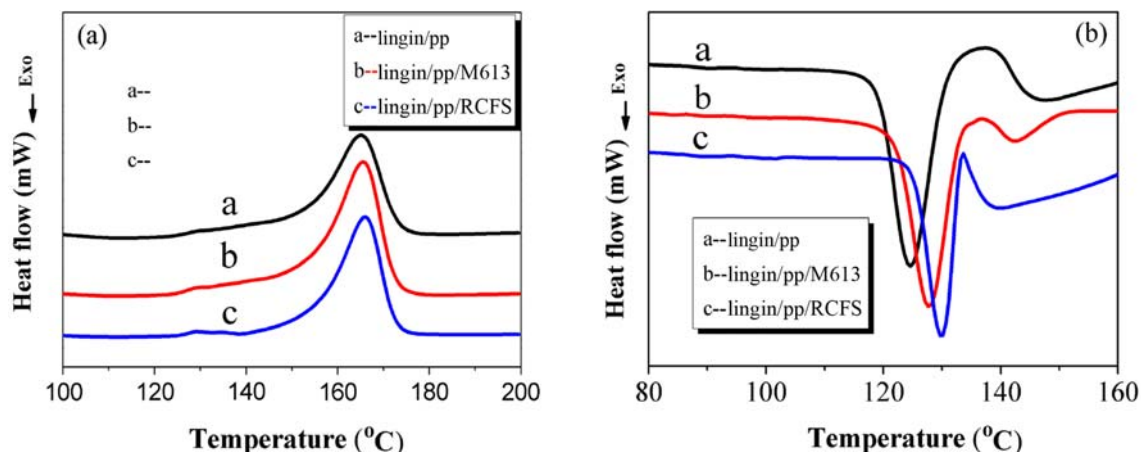


Figure 8. DSC curves of composites, (a) the heating curve and (b) the cooling curve.

Table II. Melting and Crystallization Properties of Composites

Sample	T_m ($^\circ\text{C}$)	T_{mp} ($^\circ\text{C}$)	T_p ($^\circ\text{C}$)	ΔT ($^\circ\text{C}$)	ΔH_m ($\text{J}\cdot\text{g}^{-1}$)
Lignin/PP	152.31	165.04	124.86	40.25	29.24
Lignin/PP/M613	153.64	165.43	127.84	37.62	32.23
Lignin/PP/RCFS	154.45	165.92	130.03	35.93	31.36

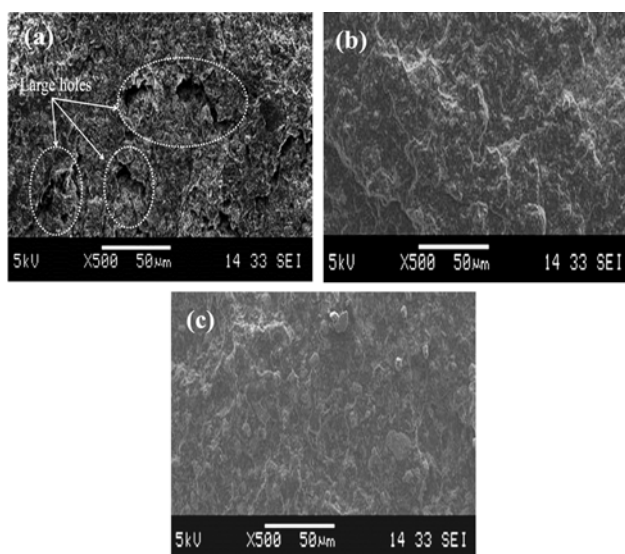


Figure 9. SEM images of the impact fracture surface of the composites, (a) Lignin/PP, (b) Lignin/PP/M613, and (c) Lignin/PP/RCFS.

to the PP and lignin blend systems, as shown in Figure 9(b) and Figure 9(c), the morphology of the blend trends to interpenetrating polymer network. It is clearly visible that the interface is rough and has smaller holes, indicating that the lubricating effect of the compatibilizer can improve the adhesive force and interfacial compatibility between the lignin and PP matrix. Therefore, the fracture of the composite needs additional force to tear the molecules after treating with compatibilizer. It is proved that compatibilizer can improve the compatibility between matrix resin and packing, enhance interface adhesive force, which can improve the impact strength of the composites.

Conclusions

A reactive compatibilizer containing flexible segment was synthesized and characterized. The RCFS was used as the compatibilizer for the synthesis of the lignin/PP wood plastic composites. The result shows that by adding 2 wt% of RCFS, the impact strength, bending strength and modulus of the lignin/pp composite increased by 56.8%, 37.3% and 20.6%, respectively, as compared with the untreated composites. In addition, the thermal stability, crystallization rate, degree of crystallinity and storage modulus of the composites with addition of RCFS are increased. SEM analysis shows that the RCFS can enhance the adhesive force and interfacial compatibility between resin and packing, as well as change the fracture mechanism of the composites.

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