

Characterization of Cross-linked Alkaline Lignin/Poly (Vinyl Alcohol) Film with a Formaldehyde Cross-linker

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On the basis of previous experiments, industrial alkaline lignin/poly (vinyl alcohol) (PVOH) cross-linked films, industrial alkaline lignin/poly (vinyl alcohol) blend films, and neat poly (vinyl alcohol) films were prepared by casting. The films were investigated by Fourier transform infra-red spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetry analysis (TGA), and dynamic mechanical analysis (DMA). The water contact angles for the three kinds of films were studied as well. The crosslinking reaction between alkaline lignin and PVOH was strong, which was attributed to the high hydrolysis degree of PVOH and the high reactivity of formaldehyde. Compared with the neat PVOH film, the crystallinity of the cross-linked film decreased slightly; the thermal stability of the cross-linked film was higher; DMA analysis showed that the T_g and the $\tan\delta$ magnitude of the alkaline lignin/PVOH reaction film both decreased slightly. Lignin and the cross-linking reaction both improved the water resistance of films. Therefore, this research has provided a detailed analysis of the characterization of the films while exploring the potential of direct usage of industrial alkaline lignin in polymer materials.

Keywords: Alkaline lignin; Poly (vinyl alcohol); Cross-linking reaction; Thermal properties; Contact angle

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INTRODUCTION

Recently, renewable and natural polymers have been extensively developed to address the growth of environmental concerns about non-biodegradable materials and the energy crisis (Huang *et al.* 2012). Lignin, cellulose, and hemicellulose are the main components that form the plant skeleton. Lignin, second only to cellulose in nature, is the second most abundant natural organic polymer. Alkaline lignin is generated as a co-product in the paper pulp industry. The direct emissions of alkaline lignin cause serious environmental pollution, and although alkaline lignin is an aromatic renewable resource, the large quantity of emissions represents a tremendous waste of resources. Alkaline lignin of low molecular weight and a high degree of dispersion is difficult for industrial use. Only a small amount of lignin is being used for value-added applications, while the rest is used as burning fuel in the same generating industries. Therefore, regardless of the use of resources or the environmental protection, the research, development, and utilization of lignin are very important (Monteil-Rivera *et al.* 2013). A large number of studies on lignin have focused on finding a higher-value application for lignin than fuel. Lignin is a promising compound for use in polymers (Sahoo *et al.* 2011a) because of its phenolic base structure, which could lead to improvement of the mechanical properties when incorporated in a plastic (Panesar *et al.* 2013). Lignin has interesting grafting and cross-linking abilities that make it an interesting material for use in polyvinyl alcohol (PVOH) and other polymeric systems. Lignin has been proven to be degradable by

certain wood-rotting fungi, such as white rot fungi, which makes it possible to break down lignin-based materials in some environments (Mousavioun *et al.* 2012; Thielemans *et al.* 2002; Yamamoto *et al.* 2000).

During the last decade, a great deal of research has been devoted to the development of polymers containing lignin because of its renewable, non-toxic, and biodegradable character (Kadla and Kubo 2004; Laurichesse and Averous 2013; Mishra *et al.* 2007; Sahoo *et al.* 2011b). Several researchers have reported the characterization of lignin-PVOH blend films. With reproducible sodium lignosulfonate (LS) and poly (vinyl alcohol) (PVOH) as primary materials, as well as borax and gelatin, blend films were prepared using the film casting method. With increasing content of sodium lignosulfonate, film tensile strength first increased and then decreased, and the breaking elongation first decreased, then increased (Li and Luo 2011). Hardwood kraft lignin/polyethylene oxide, hardwood kraft lignin/polyethylene terephthalate, hardwood kraft lignin/PVOH, and hardwood kraft lignin/polypropylene were also studied. Thermal analysis revealed miscible blend behavior in the lignin blends containing polyethylene oxide and polyethylene terephthalate, whereas the PVOH and polypropylene lignin blends appeared immiscible (Kadla and Kubo 2004). Incorporation of 65% lignin material into PBS was achieved with an improvement in the tensile and flexural properties of composites. Polyaniline/lignin blends had greater thermal stability than pure polymers (Rodrigues *et al.* 2001). A single T_g value was obtained for the blend of soda lignin/poly(butylene succinate). This suggested compatibility for the blends containing up to 40 wt% soda lignin (Mousavioun *et al.* 2010).

The aforementioned studies only address the other types of lignin as filler in polymer materials for preparing films. Little data on industrial wheat straw alkaline lignin/PVOH cross-linked membranes have been reported. The big difference compared with the previous study (glutaraldehyde) is that formaldehyde was chosen as the cross-linker because of its higher reactivity and lower cost (Su *et al.* 2013). In this study, the aim was to characterize the reaction films with good mechanical properties based on the previous experiment and to determine the differences among the films. The contact angle of the films was also studied.

EXPERIMENTAL

Materials and Methods

Poly (vinyl alcohol) 1799 (polymerization degree 1750 ± 50 , alcoholysis degree 98~100%, M_w 72,600 to 81,400) was obtained from the Shangdong Chemical Plant, China. Industrial alkaline lignin was purchased from the Shangdong Paper Mill. It is a wheat straw lignin precipitated from black liquor. First, industrial alkaline lignin was dissolved in sodium hydroxide aqueous solution (0.1 M), resulting in a solution of 5 wt% wheat straw alkaline lignin. The solution was then filtered to remove impurities. Finally, it was directly dried with an experimental spray drier (model No. Yc-015, Shanghai Pilotech Instrument and Equipment Co., Ltd) to obtain alkaline lignin (AL). It is well-known that raw materials and the preparation process both affect the chemical properties of lignin. In this study, the contents of the different substances in alkaline lignin were as follows: lignin 77.69, carbohydrate 8.45, ash 14.96, and hydroxyl group 2.95 mmol/g. Formaldehyde solution (37% to 40% w/w, analytical reagent grade) was obtained from

the Tianjin Hengxing Chemical Reagent Co., Ltd. Sodium hydroxide (analytical reagent grade).

Preparation of Films

Alkaline lignin and PVOH were simultaneously put in a three-neck flask with an alkaline lignin content of 20% of the dry matter. A certain amount of distilled water was added to the flask, resulting in a solution of 5 wt% dry matter. The alkaline lignin, PVOH, and water were then mixed for 50 min with constant stirring (300 rpm) in the flask connected to a water bath at 90 °C (Li *et al.* 2012). Then, 8.80% formaldehyde content was added to the flask. The blends were cross-linked for 40 min to increase the interaction between the components, and then the stirring was stopped. The film-forming solutions were kept under vacuum for 30 min for de-foaming, then poured and spread evenly over a PVC plastic surface (Belbekhouche *et al.* 2011). The industrial alkaline lignin/poly (vinyl alcohol) reaction films were dried at room temperature. Films with a thickness of 40 to 80 μm and with the best mechanical properties were prepared (Su *et al.* 2013). Neat poly (vinyl alcohol) films and industrial alkaline lignin/poly (vinyl alcohol) blend films were also prepared in accordance with the above method and analyzed in the same way. Unlike industrial alkaline lignin/poly (vinyl alcohol) reaction films, neat poly (vinyl alcohol) films were prepared without formaldehyde and industrial alkaline lignin and industrial alkaline lignin/poly (vinyl alcohol) blend films were prepared without formaldehyde.

Film Characterization

Atomic absorption spectrophotometer

The measurement of Na^+ was performed with a Purkinje General TAS-990 atomic absorption spectrometer (Beijing, China) equipped with a sodium hollow cathode lamp and a deuterium background corrector at the respective wavelengths using an acetylene flame. The instrument parameters were as follows: hollow cathode lamp at a wavelength of 590.0 nm with slit width of 0.4 nm, current 6.0 mA, acetylene flow rate of 1300 mL/min, and burner height of 5 mm. The measurements were performed in triplicate.

Attenuated total reflection Fourier-transformed infrared spectroscopy (ATR-FTIR)

Infrared spectra of dry films were recorded between 4000 and 600 cm^{-1} at a resolution of 16 cm^{-1} with a Spectrum One (Magna-IR560; Nicolet USA) spectrometer supplied with a universal attenuated total reflectance (ATR) accessory.

X-ray diffraction (XRD)

XRD measurements were performed with a D/max-r B X-ray diffractometer (Rigaku Corp., Tokyo, Japan) using Cu Ka radiation. The samples were scanned over a 2θ ($^\circ$) range varying from 10 $^\circ$ to 50 $^\circ$.

Thermogravimetric analysis (TGA)

The thermal decomposition studies were carried out in a Netzsch TG-209F3. Samples (6 mg) were placed into platinum pans. Heating took place at a rate of 10 $^\circ\text{C}/\text{min}$ and was performed from room temperature to approximately 800 $^\circ\text{C}$. The test was performed in an atmosphere of nitrogen, which was injected at a flow rate of 20 mL/min.

Dynamic mechanical analysis (DMA)

The viscoelastic behavior of the cross-linked polymers was tested on a Polymer Laboratories Netzsch dynamic mechanical thermal analyzer working in tensile mode at a constant stress. The storage modulus and loss tangent values were determined at a frequency of 1 Hz over a temperature range of 35 °C to about 320 °C. The experiments were carried out in a nitrogen atmosphere at a heating rate of 1.58 °C/min.

Water contact angle (WCA)

The contact angle (CA) with water droplets (5 μL) was evaluated at room temperature with a Dataphysics OCA20 contact angle analyzer (Bad Vilbel; Germany).

RESULTS AND DISCUSSION

ATR-FTIR Analysis

The ATR-FTIR spectra of AL (alkaline lignin), PVOH films, AL/PVOH blend films, and AL/PVOH reaction films are shown in Fig. 1. Figure 2 shows the cross-linking reaction scheme of PVOH and alkaline lignin (Funaoka 1998; Nemoto *et al.* 2011). The following bands were observed for lignin: (a) the absorbance of OH bands at 3352 and 1033 cm^{-1} ; (b) β -O-4 ether bond band at 1117 cm^{-1} ; (c) methoxy group band at 2939, 2881, 1460, and 1425 cm^{-1} ; (d) the C=C vibration of aromatic rings at 1514 cm^{-1} ; (e) the band at 1603 cm^{-1} , which is characteristic for quinoid structure; and (f) the carbonyl group at 1664 and 1720 cm^{-1} (Rodrigues *et al.* 2002; Yang *et al.* 2011). In the spectra of the PVOH film, the 3282- cm^{-1} and 2930- cm^{-1} peaks are the -OH and -CH₂- stretching vibrations (Krumova *et al.* 2000), respectively. The bending vibration of -OH is at 1410~1260 cm^{-1} . The 1140- cm^{-1} peak is the C-O stretching vibrations (-CH(OH)-). It is well-known that the ether bond band (C-O-C) at 1060 to 1300 cm^{-1} has a strong and broad absorption peak (Fan *et al.* 2008; Hu *et al.* 2013).

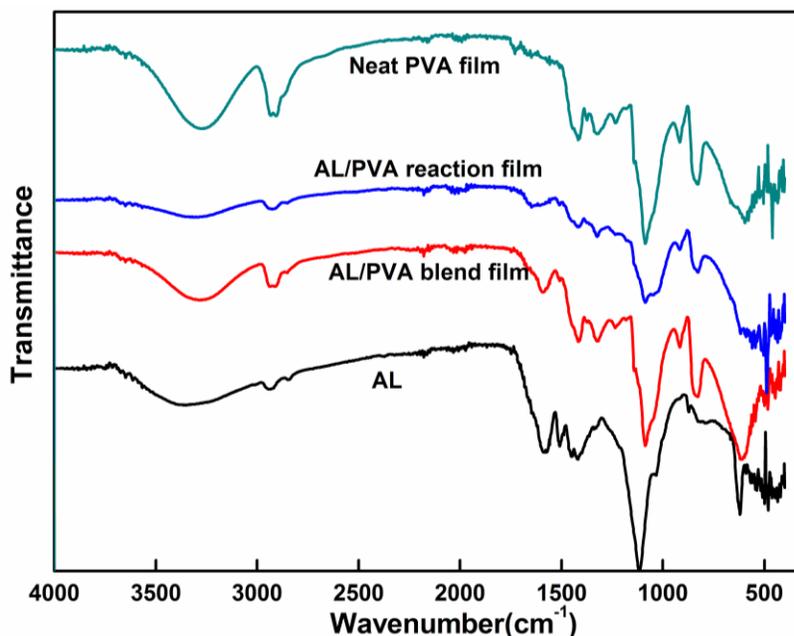


Fig. 1. ATR-FTIR spectra of AL(alkaline lignin) and the three films

Compared with the AL/PVOH blend films, there were three obvious changes in the spectra of AL/PVOH reaction films that differed from the previous reports (Su *et al.* 2013). First, at the range of 3500 to 3000 cm^{-1} , the O-H stretching vibration peak became smaller. Also, at the range of 1410 to 1260 cm^{-1} , the O-H bending vibration peak almost disappeared. Moreover, at 1060 to 1300 cm^{-1} , which represented the ether bond band absorption, the peak was broader. These changes indicate that the -OH bands were reduced and an ether bond (C-O-C) was formed between AL and PVOH (1799). The higher hydrolysis degree increased the amount of hydroxyl groups present in the PVOH molecule, allowing for the formation of hydrogen interactions between the -OH groups of the PVOH and -OH groups of the AL, reinforcing the film structure.

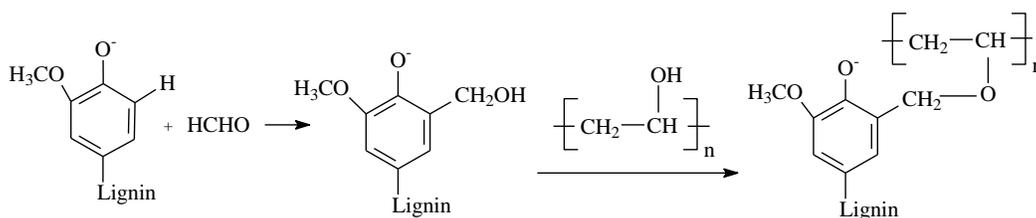


Fig. 2. Cross-linking reaction scheme of PVOH and alkaline lignin

XRD Analysis

Figure 3 shows the X-ray diffraction patterns of PVOH, AL/PVOH blend films, and AL/PVOH reaction films. The diffractogram of PVOH reveals a strong diffraction peak at $2\theta = 19.8^\circ$ and inconspicuous broad peaks at $2\theta = 11^\circ$ and 40° (Kumar *et al.* 2010), and that of AL shows a significant dispersion peak. These results show that PVOH was semi-crystalline and AL was amorphous. The peaks of the diffractogram of AL at $2\theta = 31^\circ$ depict the presence of Na.

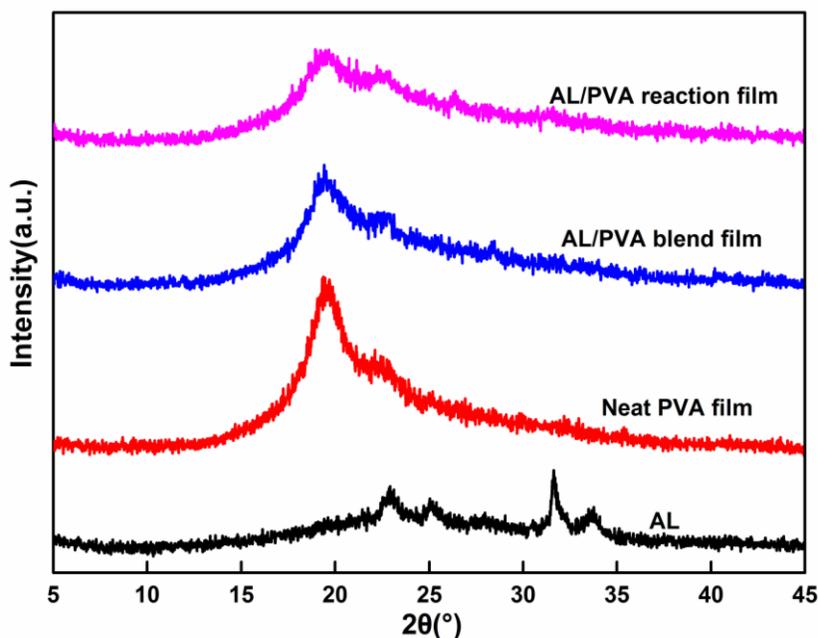


Fig. 3. X-ray diffraction patterns of AL (alkaline lignin) and the three films

Compared with the neat PVOH diffractogram, the peak for the blend and cross-linked films at $2\theta = 19.8^\circ$ became shorter and broader because of the added lignin, which indicated that the crystallinity decreased. Between them, the crystallinity of the cross-linked films was the smallest. This result may have been caused by the acetal reaction between the amorphous AL and PVOH.

TG/DTG Analysis

The TGA results are summarized in Table 1 and Fig. 4 (Nemoto *et al.* 2010). In Table 1, T_{d5} and T_{d10} of the films were irregular, which may be attributed to the different water content or volatile matter. From T_{d20} ($^\circ\text{C}$), T_{d50} ($^\circ\text{C}$) and T_{d75} ($^\circ\text{C}$) and Fig. 4, it is apparent that the thermal degradation rate of the alkaline lignin was the slowest, and the residual mass was the largest, over the whole temperature range. Alkaline lignin represented the best thermal stability. The high thermal stability of lignin is due to the presence of complex phenylpropanoid units, which consist of aromatic phenyl groups. These aromatic structures are very stable, mostly because of the overlapping of p-orbitals, which allow complete delocalization of the π electrons (Morandim-Giannetti *et al.* 2012). Meanwhile, compared with the PVOH films, the residual mass of AL/PVOH blend films and AL/PVOH reaction films was higher, which indicated that the thermal stability of films increased with the addition of alkaline lignin. Similar results were obtained by Mousavioun *et al.* (2010). Moreover, the residual mass of AL/PVOH reaction films was higher than that of blend films due to the aldol reaction between the lignin and PVOH (1799).

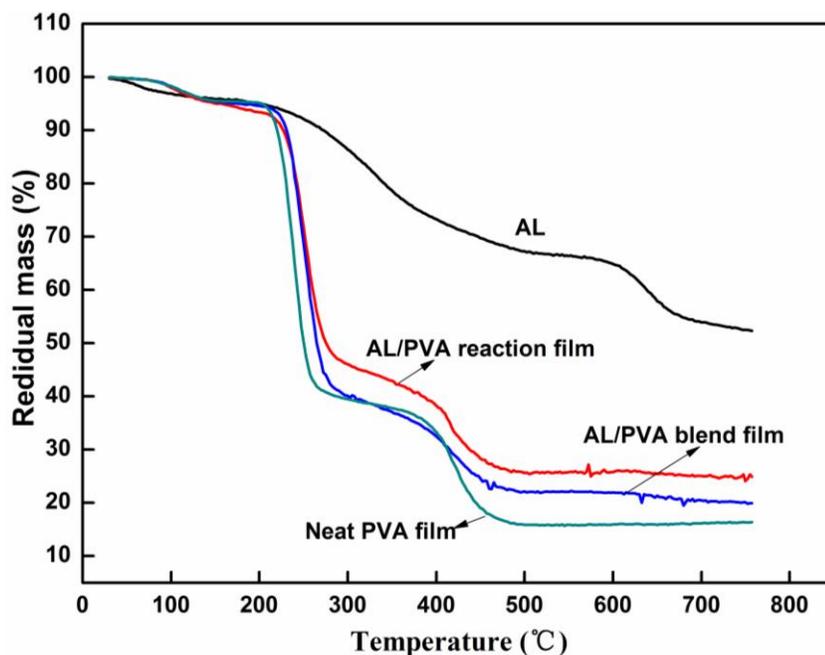


Fig. 4. TG curves for AL(alkaline lignin) and the three films

In Fig. 5, for alkaline lignin, a first mass loss between 30 and 150 $^\circ\text{C}$ was observed, which was attributed to the water contained in this polymer. The AL degradation was observed between 150 and 550 $^\circ\text{C}$ in the N_2 environment. The peak in alkaline lignin at about 650 $^\circ\text{C}$ was caused by the presence of sodium hydroxide (Su *et al.* 2013). By atomic absorption spectrophotometer analysis, the amounts of NaOH in

alkaline lignin and in the composite film were 22.09% and 3.68%, respectively. Because of the small content (3.68%) of NaOH, the peak at about 650 °C disappeared in the composite film (Fig. 5). The maximum degradation temperature (T_{max}) of both PVOH/AL blend films and reaction films was almost 250 °C, whereas that of the PVOH film was 240 °C. In addition, the T_{max} peak of PVOH films, AL/PVOH blend films, and AL/PVOH reaction films gradually became shorter and shorter. The peak of the reaction film was shortest. The shorter T_{max} peak showed the slower degradation speed. The results, consistent with the analysis in Fig. 4, may indicate that the thermal stability of films increased with added alkaline lignin, and the cross-linking reaction between AL and PVOH also increased the thermal stability of the film.

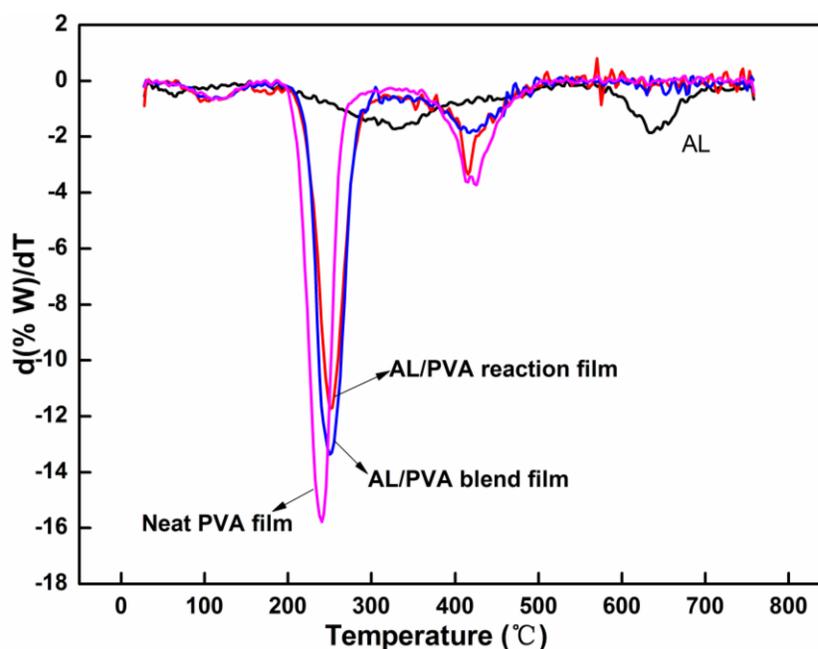


Fig. 5. DTG curves for AL(alkaline lignin) and the three films

Table 1. Thermal Properties of AL (alkaline lignin) and the Three Films Corresponding to Different Weight Loss Stages

Specimens	$T_{d5} (^{\circ}\text{C})^a$	$T_{d10} (^{\circ}\text{C})^b$	$T_{d20} (^{\circ}\text{C})^c$	$T_{d50} (^{\circ}\text{C})^d$	$T_{d75} (^{\circ}\text{C})^e$
AL	200.0	270.0	340.0	757.5	-
AL/PVOH reaction film	157.5	225.0	242.5	275.0	700
AL/PVOH blend film	175.0	230.0	240.0	265.0	447.5
Neat PVOH film	202.5	220.0	230.0	250.0	425.0

a,b,c,d and e show that temperature at 5%, 10%, 20%, 50%, 80% loss in weight, respectively.

DMA Analysis

The dynamic mechanical properties, *i.e.*, the storage component of the modulus and the loss factor, were evaluated for neat PVOH films, blends, and the reaction. The storage modulus (E') reflects the elastic component of the viscoelastic materials. In Fig. 6, the (E') value of AL/PVOH blend films, the PVOH films, and the reaction films gradually decreased in the range of 30 to 70 °C. That may be because the cross-linking reaction decreased the chain flexibility of molecular PVOH. Figure 7 shows $\tan\delta$ values *versus* temperature for the PVOH films, AL/PVOH blend films, and AL/PVOH reaction

films. The main peak observed (between 60 and 110 °C) was attributed to the vitreous transition. There was a decrease in the T_g value, as well as in the $\tan\delta$ magnitude, with increasing lignin concentration.

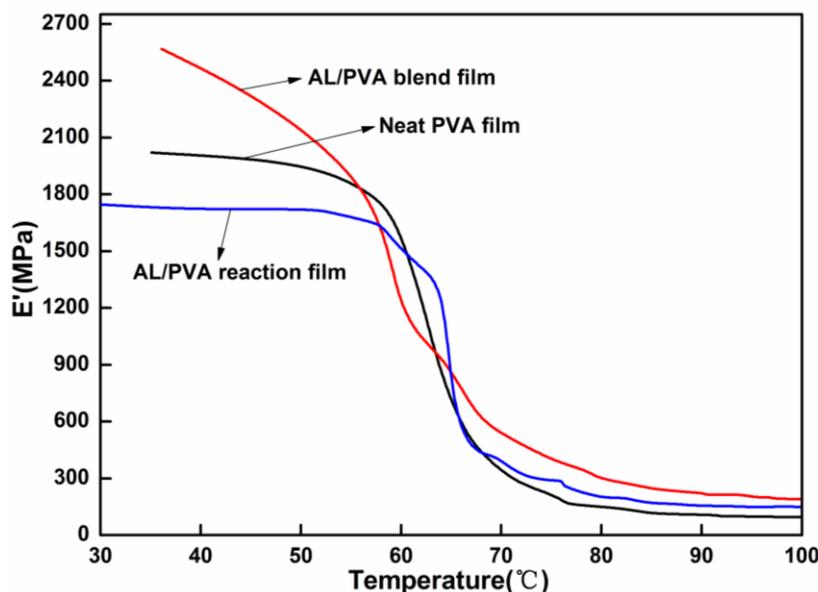


Fig. 6. Storage modulus (E' , a) as a function of temperature for the films evaluated by DMA

The $\tan\delta$ magnitude of the PVOH film was the highest, followed by that of the reaction film, and finally that of the blend film. The decrease in the $\tan\delta$ value indicates that the addition of filler increased the molecular mobility of the composite materials. There may be various explanations for the decrease in the $\tan\delta$ value of the composites. For the blend films, a hydrogen bond formation could be possible between the hydroxyl group of PVOH and the hydroxyl group of AL. For the reaction films, PVOH grafted a small amount of AL, which increased the distance between PVOH molecules as a branched chain. Then, the PVOH intermolecular force was weakened not only in the blend films, but also in the reaction films, and the relaxation of the polymer chains could be easily changed. Also, the cross-linked reaction was stronger than the interaction of the hydrogen bond, leading to the lowest peak of the blend films. Meanwhile, the $\tan\delta$ magnitude of the blend films was broader, which indicated that relaxation of the polymer occurred (Chen *et al.* 2009; Famá *et al.* 2012; Wang and Huang 2004).

The most accepted parameter for assessing polymer miscibility is T_g . A single T_g of a blend, whose value is an average of the individual component's T_g , implies complete miscibility between the polymer pairs in their amorphous fractions. Two or more T_g s suggest that the degree of miscibility is restricted (Mousavioun *et al.* 2010). For each film, a single T_g was observed. The T_g values of PVOH films, AL/PVOH blend films, and AL/PVOH reaction films obtained from Fig. 7 were 72.63, 70.65, and 68.25 °C, respectively. With alkaline lignin added, all the films showed a similar T_g . The T_g of the AL/PVOH reaction films was slightly decreased (Turi 1997), which corresponded to the decrease of the material crystallinity in Fig. 3. That result can be attributed to the lignin molecules, which may produce an internal plasticization effect and may have resulted in increased distance and weakened interaction between PVOH molecules (Feldman *et al.* 2007).

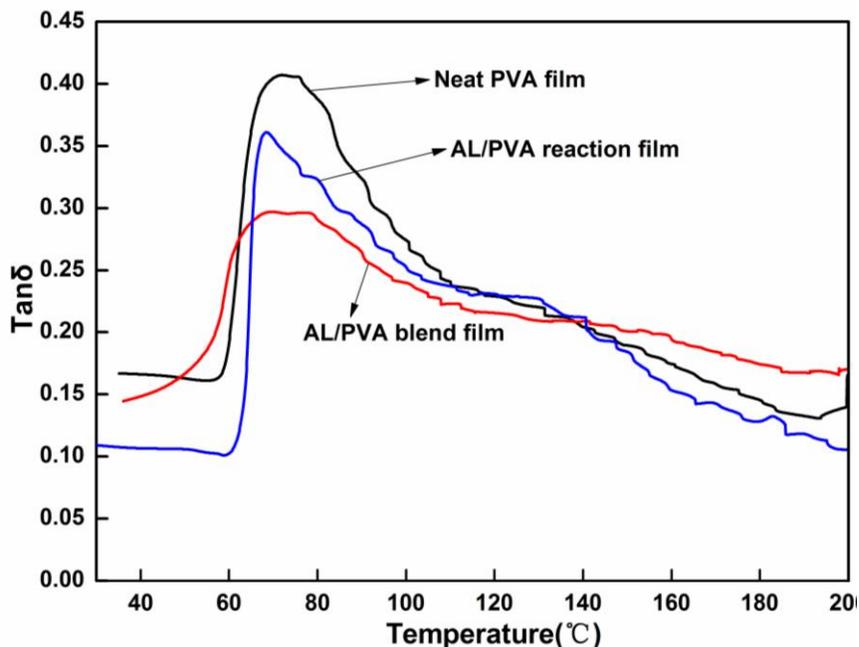


Fig. 7. Loss tangent values ($\tan\delta$) as a function of temperature for the films evaluated by DMA

Water Contact Angle of the Films

The water contact angle of a solid partly reflects its water resistance ability (Hu *et al.* 2009) (Fig. 8).

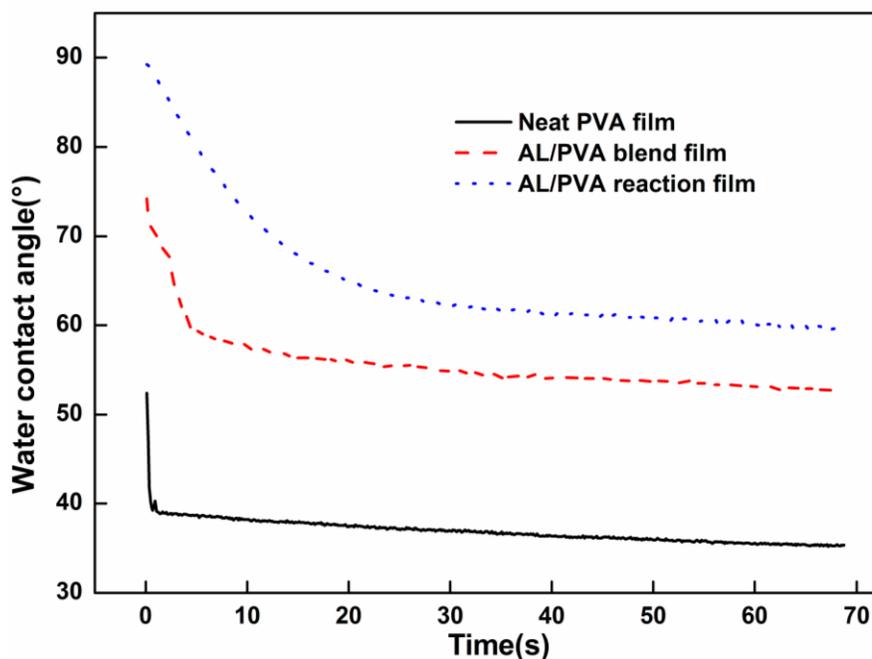


Fig. 8. Contact angle of the different kinds of films

PVOH contains a large number of hydroxyl groups. According to the principle of surface chemistry, neat PVOH film can be considered a hydrophilic film (Jayasekara *et*

al. 2004). In Fig. 8, the contact angle of neat PVOH film was the smallest, and the water contact angle ranged from 52.4° to 35.4° in 70 s. The alkaline lignin dissolved in aqueous solution because of the alkaline substance in it. The lignin is more hydrophobic, which leads to an increase in the contact angle of AL/PVOH films. The contact angle of AL/PVOH blend film was from 74.2° to 52.6°, while that of the AL/PVOH reaction film changed from 89.2° to 59.6°. The contact angle of the reaction film was larger than that of the blend film, which was attributed to the cross-linking between PVOH and alkaline lignin. This result offers basic data for the preparation of appropriate water-soluble films in future research.

CONCLUSIONS

1. The ATR-FTIR analysis showed a significant cross-linking reaction between alkaline lignin and PVOH (1799), which was attributed to the high hydrolysis degree of PVOH and the high reactivity of formaldehyde.
2. Compared with the neat PVOH film, the crystallinity of the reaction film decreased slightly, which was consistent with the previous report.
3. With the addition of alkaline lignin, the thermal stability of films was increased and there was a decrease in T_g value as well as in $\tan\delta$ magnitude. These results were attributed to the weakening of the PVOH intermolecular force with the addition of alkaline lignin.
4. Lignin and the crosslinking reaction could both improve the water resistance of films. This result offers basic data for the preparation of appropriate water-soluble films in future research.

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