

## Mechanical and Thermal Properties of Polyurethane Films from Peroxy-acid Wheat Straw Lignin

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In the present work, a type of PU film was made from peroxy-acid-derived wheat straw lignin by reacting varying amounts of lignin ranging from 10 to 50 wt% (with respect to PEG), polyethylene glycol ( $M_n = 1000$ ), and tolylene 2,4-diisocyanate without catalyst. The effects of lignin content on the tensile property and thermostability of the lignin polyurethane films obtained were investigated. The thermal conductivity of lignin polyurethane films was also studied. Results showed that when the lignin content increased, the glass transition temperature ( $T_g$ ) and tensile strength of the lignin polyurethane film increased, but the onset decomposition temperature and elongation at break decreased. When the lignin content was 40 wt%, the lignin polyurethane film had the best overall properties. In addition, compared with PU films, lignin PU films showed better heat-insulating properties.

*Keywords:* CIMV wheat straw lignin; Polyurethane films; Tensile property; Thermostability; Thermal conductivity

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### INTRODUCTION

Lignin, as possibly the third most abundant biopolymer in nature after cellulose and chitin, has a complex, non-crystalline, and three-dimensional network structure polymer that has been considered a substitute for some petrochemical products to mitigate the effects of the petroleum resources crisis and the environmental pollution caused by non-biodegradable polymers. Traditionally, drastic measures such as strong bases or mineral acids have been used to exploit the lignocellulosic biomass. In these processes, the extracted fractions are severely and irreversibly altered, and environmental pollution is also of great concern. Moreover, conventional processes are not able to make full use of non-cellulose biopolymers, *i.e.*, lignin and hemicelluloses. To overcome these obstacles, organosolv methods have received much attention as replacements for chlorine- and sulfur-based chemical processes (Ligero *et al.* 2008).

Compared with traditional kraft lignin (Reimann *et al.* 1990; Yoshida *et al.* 1987, 1990) and alkali lignin (Liu *et al.* 2002), organosolv lignin possesses some valuable characteristics, such as a low molecular weight with a low poly-dispersity index and high free hydroxyl content (Cheng and Jin 2008). Many attempts have concentrated on the preparation of lignin-modified phenolic resin (Cetin and Ozmen 2002a,b; Cheng *et al.* 2013) and also on polyurethane (Evtuguin *et al.* 1998; Li and Ragauskas 2012; Pan and Saddler 2013).

Recently, several types of organosolv lignin substituting polyol to make polyurethane (PU) films have been reported, such as Alcell lignin (Thring *et al.* 1997; Vanderlaan and Thring 1998) and acetic acid lignin (Wang *et al.* 2004, 2011a-c). These can be directly added to make PU films without any modifications, and the PU films perform well. However, the extraction processes are inefficient and require severe conditions, which make them difficult for industrial applications.

A new separation technology has been proposed (Delmas *et al.* 2003, 2011; Kham *et al.* 2005; Lam *et al.* 2001, 2004), *i.e.*, a CIMV process, which offers a new alternative to the paper industry, as it allows for the separation of the main components of lignocellulosic biomass, such as cellulose, lignin, and hemicelluloses. In the CIMV process, lignocellulose is treated by peroxy acids, and the reaction condition is relatively mild. This process yields 50% pulp, 25% C5 sugar syrup, and 25% lignin.

The wheat straw lignin employed in the present work not only has low molecular weight ( $M_n = 1600$  g/mol) and a low poly dispersity index ( $M_w/M_n = 1.6$ ), but its purity (up to 97%) and free hydroxyl content are also very high, resulting in a potentially suitable material to synthesize value-added polymers. Herein, wheat straw lignin-based PU films were made, and their mechanical properties, thermal stability, and thermal conductivity were investigated.

## EXPERIMENTAL

### Materials

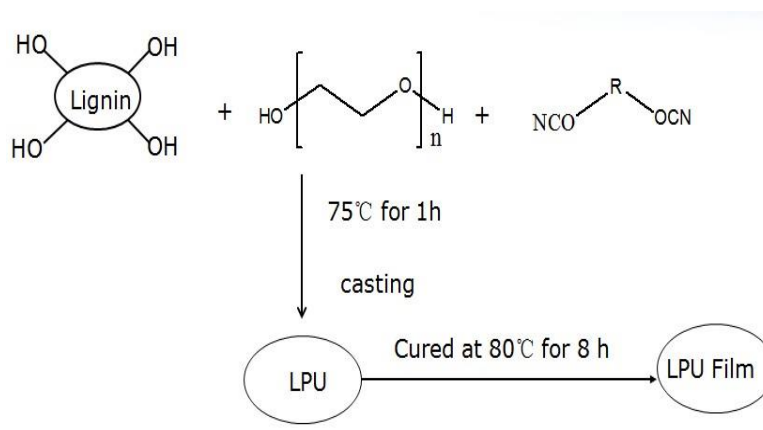
Wheat straw lignin was supplied by Compagnie Industrielle de la Matière Végétale (CIMV, Danton, Levallois Perret, France). Some typical but important characteristics of this lignin are the weight average molecular weight ( $M_w = 2152$  g/mol) and the number average molecular weight ( $M_n = 1634$  g/mol). The total hydroxyl of lignin is 4.92 mmol/g, including 3.92 mmol/g aliphatic hydroxyl. The lignin supplied was dehydrated at 50 °C in vacuum for 24 h before its use, and the moisture of lignin was 0.9% to 1.6% (Sartorius Infrared moisture meter -MA150).

Polyethylene glycol (PEG) of molecular weight ( $M_n$ ) 1000 was purchased from Sinopharm Chemical Reagent. Toluene 2,4-diisocyanatoluene (TDI), analytical grade, was obtained from Aladdin Chemistry (Shanghai, China). N,N-dimethylformamide (DMF) and acetone were obtained from Nanjing Chemical Reagent company. DMF and acetone were treated with 3A molecular sieves to dehydrate. PEG was dehydrated at 120 °C in vacuum for 2 h before use.

### Methods

#### *Preparation of lignin PU films*

A number of attempts were made to produce testable films by varying the weight ratios of the PEG and CIMV wheat straw lignin, which were both dissolved in mixed solvent with a DMF/acetone ratio of 3:2 (v/v). The mixture was constantly stirred in a water bath at 60 °C for 0.5 h. TDI was added, and the temperature was increased to 75 °C. Then, the reaction was continued for 1 h. The main steps of the synthetic route are indicated in Scheme 1, and the experimental conditions for preparing the lignin PU films are given in Table 1.



**Scheme 1.** Polymerisation process for lignin PU (LPU) film

**Table 1.** Experimental Conditions for Preparing Lignin PU Films

Sample	Molecular Weight of PEG	[NCO]/[OH] Ratio	Lignin (wt%) <sup>a</sup>
PU	1000	1.15	0
LPU1	1000	1.15	10
LPU2	1000	1.15	20
LPU3	1000	1.15	30
LPU4	1000	1.15	40
LPU5	1000	1.15	50

<sup>a</sup> with respect to PEG

After the polymerization, the solution was immediately poured onto a Teflon disk on a horizontal table, allowed to dry at room temperature for 12 h, and then cured for 6 h at 80 °C. After de-molding, the films were submitted to vacuum drying over phosphorous pentoxide for 2 days. PEG, with a large molecular weight of 1000, was employed in this research, as PEG plays the part of the soft segment in lignin PU films. The larger the molecular weight of the PEG contained in PU films, the softer the films can be.

#### *FT-IR analysis*

The samples were analyzed by recording FT-IR spectra using a Nicolet Magna IR 550 FT-IR spectrometer, from 4000 to 600  $\text{cm}^{-1}$  for each sample. A total of 256 scans were obtained at 4  $\text{cm}^{-1}$  resolution.

#### *Stress-strain testing*

Tensile strength and elongation at break of the samples were evaluated using a SANS7 CMT-4304 universal tester (Shenzhen Xinsansi Jiliang Instrument, China) employing a crosshead speed of 200 mm/min. Samples were dumbbell cut, as shown in Fig. 1. Tensile characteristics were calculated on the basis of initial dimensions (gage length 25 mm and width 5 mm). At least six specimens of each lignin PU film sample were tested, and five results were selected to calculate the mean values for these mechanical tests. All samples were stored in a controlled room kept at 22 °C and 55% relative humidity for 24 h prior to testing, and the tests were conducted with the same conditions.



**Fig. 1.** The sample of PU films for stress and strain testing

#### *Differential scanning calorimetry (DSC)*

The glass transition temperature ( $T_g$ ) of each PU film was measured using a differential scanning calorimeter (PerkinElmer Diamond DSC model, America). The data were collected on the second scan of samples (2 to 5 mg) heated from  $-60\text{ }^{\circ}\text{C}$  to  $160\text{ }^{\circ}\text{C}$  at  $20\text{ }^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere. The  $T_g$  was defined as one-half the change in heat capacity over the transition.

#### *Thermogravimetric analysis (TGA)*

Thermogravimetric analysis (TGA) was tested in a thermogravimeter (NETZSCH TG209 F1 model, Germany). About 5 mg dried sample was heated from  $25\text{ }^{\circ}\text{C}$  to  $800\text{ }^{\circ}\text{C}$  at a rate of  $20\text{ }^{\circ}\text{C}/\text{min}$  in an  $\text{Al}_2\text{O}_3$  crucible under a nitrogen atmosphere, and the weight loss was recorded.

#### *Thermal Conductivity*

The conductivity coefficient of PU films was measured using a thermal conductivity analyzer (C-THERM T322 model, Canada). The smooth side of the films entirely covered the probe of the analyzer.

## RESULTS AND DISCUSSION

### FT-IR Analysis

FT-IR spectra of PU, LPU1, LPU3, LPU5, and CIMV lignin are presented in Fig. 2. The characteristic peaks in Fig. 2 show that the entire IR pattern of LPU shifted to that of the pure lignin by gradually increasing the lignin concentration in the blends.

The IR spectra show clear signs of interaction between the urethane groups and lignin functions. The decreases in the relative intensity of urethane carbonyl ( $1725\text{ cm}^{-1}$ ) coupled with increases in the associated urea carbonyl ( $1668\text{ cm}^{-1}$ ) indicate that the urethane groups decreased simultaneously with the urea groups' increase, most likely because of the low activity of the hydroxyl groups of lignin, which caused extra

isocyanate groups to react with amide to form urea linkages. Also, the  $\text{CH}_2$  symmetric band ( $2917\text{ cm}^{-1}$ ) increased in relative intensity because of the lignin contribution.

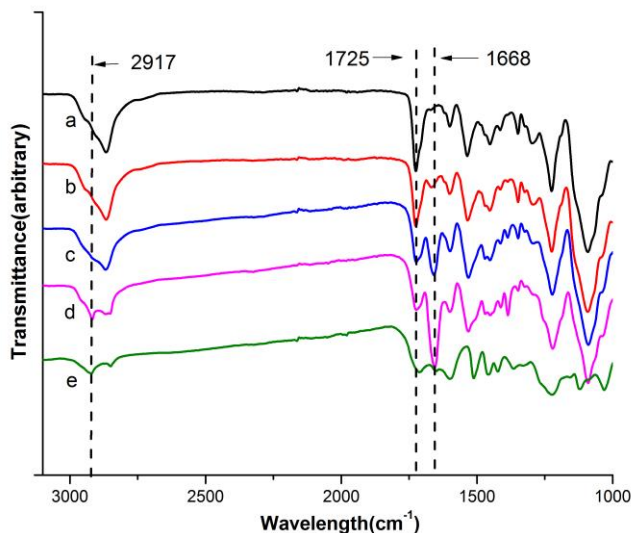


Fig. 2. IR spectrum of PU (a), LPU1 (b), LPU3 (c), and LPU5 (d) samples and CIMV lignin (e)

### Mechanical Properties

From the tensile strength ( $\sigma_B$ ) and the elongation at break ( $\varepsilon$ ) of the lignin PU films shown in Fig. 3 and Table 2, it can be seen that tensile strength increased at first and then decreased as the lignin content ratio increased. When the lignin content ratio was 40 wt%, the tensile strength reached a maximum. This may be due to the role of the lignin in PU.

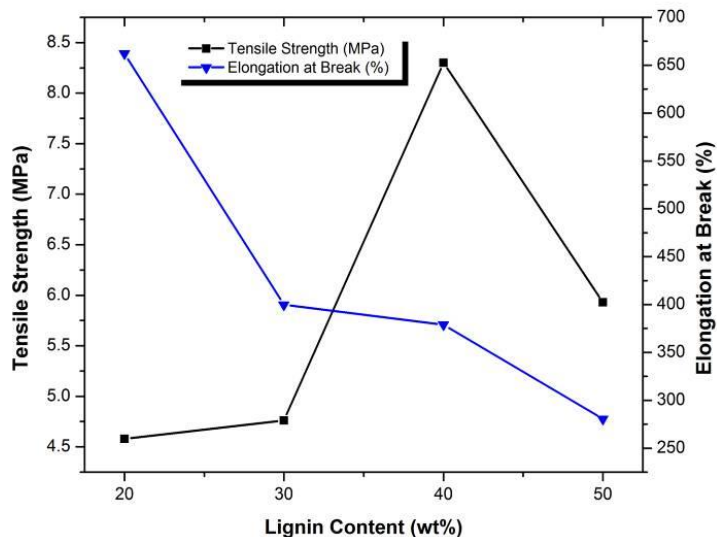


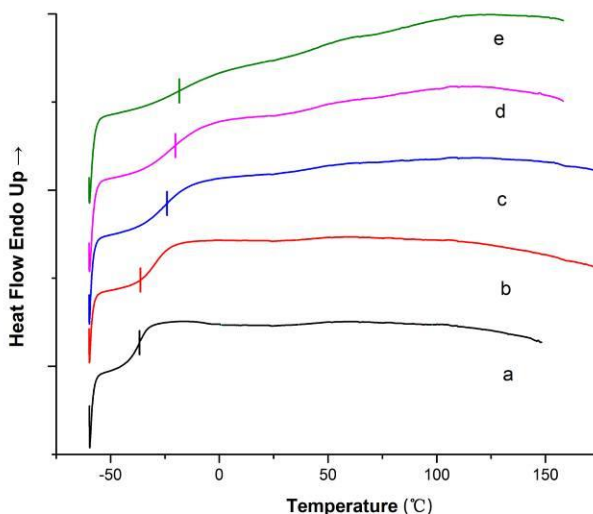
Fig. 3. Tensile strength and elongation at break of lignin PU films with varying lignin content

It has long been known that lignin contains hydroxyl groups on the propanoic sidechain units and various phenolic –OH units which may behave as polyols, so lignin can act as a crosslinking agent in the reaction, leading to the formation of three-dimensional net structure PU polymers, which apparently can increase tensile strength. The degree of crosslinking increased as the lignin content increased, with the ultimate degree of crosslinking occurring when the lignin content reached 40 wt%. In addition, increasing the lignin content also increased the hard segments of the lignin PU films, which can also improve the tensile strength of PU films. However, when the lignin content exceeded 40%, further addition of lignin did not strengthen the lignin PU films, but instead made them to be poorer blends. This is probably due to the lack of uniformity in lignin distribution, which likely makes the lignin tend to blend instead of interact with the polyurethane chains at higher concentrations (Ciobanu *et al.* 2004). Therefore, tensile strength decreased abruptly after the lignin content exceeded 40 wt%.

On the other hand, lignin increased the hard segments of PU films, making the films less elastic and more brittle, which led to the elongation at break decreasing. This explains why the elongation at break decreased as the lignin content ratio increased.

## DSC

The results of the glass transition temperature ( $T_g$ ) determinations are reflected in Fig. 4, showing that when the lignin content increased, the values of  $T_g$  varied from a sharp transition within a narrow temperature range to an indistinct transition within a broad temperature range. This can be attributed to the increase in crosslink density with increasing lignin content. The values of  $T_g$  and the heat capacity change ( $\Delta C_p$ ) are shown in Table 2.



**Fig. 4.** DSC curves for LPU1 (a), LPU2 (b), LPU3 (c), LPU4 (d), and LPU5 (e) samples

In PU, the urethane–hydrogen bonds, considered hard segments, form domains that are dispersed in the continuous soft phase. In the case of perfect phase separation between the soft and hard segments, the glass transition of the soft segment should occur at a low temperature and be relatively insensitive to variations in the soft/hard segment ratio (Reimann *et al.* 1990). The behavior of  $T_g$  shown in Fig. 4 implies that lignin, as a

cross-linking agent, prevents, or at least limits, the phase separation of the soft and hard segments.

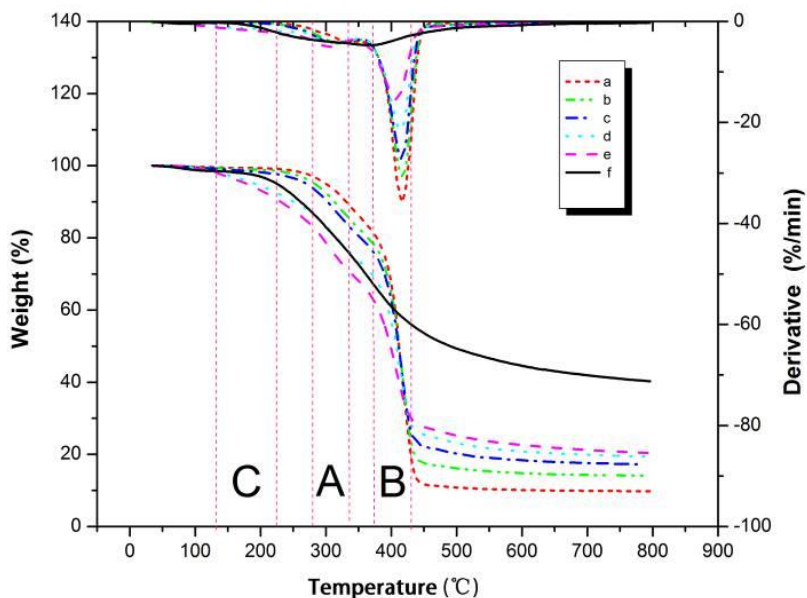
**Table 2.** Data for Lignin PU Films with Varying CIMV Lignin Contents

Sample	$T_g$ (°C)	$\Delta C_p$ (J/g·K)	$\sigma_B$ (mPa)	$\varepsilon$ (%)	$T_c$ (W/mK)
PU	—	—	—	—	0.263
LPU1	-36.41	0.482	—	—	0.270
LPU2	-35.77	0.468	4.58	662.21	0.279
LPU3	-23.20	0.472	4.76	399.72	0.244
LPU4	-20.08	0.306	8.30	379.10	0.172
LPU5	-18.04	0.249	5.93	280.48	0.061

$T_g$  Glass transition temperature;  $\Delta C_p$  Heat capacity change;  $\sigma_B$  Tensile strength;  $\varepsilon$  Elongation at break;  $T_c$  Thermal conductivity; — No test

### TGA Analysis

Thermogravimetry provides information about the thermal stability of a material, which is a very important property that defines the application range of the material. The TGA curves of lignin PU films are shown in Fig. 5. The lignin PU films displayed a weight loss at temperatures from 35 to 800 °C. The onset decomposition temperature (TOD) of the lignin PU films decreased with increased lignin content, which showed that the thermal stability of lignin PU films was suddenly decreased. Before the lignin content reached 40 wt%, the lignin PU films decomposed in two main stages: Stage A and Stage B. Stage A (280 to 340 °C, peak at 300 °C) is related to hard segment degradation, whereas the soft segment contributes to Stage B (370 to 430 °C, peak at 420 °C). After the lignin content exceeded 40 wt%, the polyurethane decomposed in one more main stage, Stage C, where the onset decomposition temperature (TOD) of the lignin PU films sharply decreased (140 to 230 °C).



**Fig. 5.** TG and DTG curves for LPU1 (a), LPU2 (b), LPU3 (c), LPU4 (d), and LPU5 (e) samples, and CIMV wheat straw lignin (f)



To determine why the TOD of lignin PU film decreased when lignin content increased, the thermal degradation of CIMV wheat straw lignin was also analyzed. The first stage (180 to 260 °C) involves the breaking of  $\alpha$ - and  $\beta$ -aryl-alkyl-ether linkages, dehydration, and decarboxylation reactions. The aliphatic side chains are furthermore split from the aromatic ring (260 to 290 °C), and carbon-carbon linkages between lignin structural units break (290 to 400 °C, plateau at 310 to 350 °C) (Ellis *et al.* 1987).

Before the lignin content reached 40 wt%, the breaking of  $\alpha$ - and  $\beta$ -aryl-alkyl-ether linkages and the increase of the phenolic hydroxyl groups (which are not as stable as the aliphatic hydroxyl groups) reacting with the isocyanate groups caused the TOD to decrease. After the lignin content reached 40 wt%, as the FT-IR spectra shows, more and more lignin failed to react with isocyanate, and the extra isocyanate groups reacted with amide hydroxyl to form urea linkages, making the PU films more unstable; thus, the TOD sharply decreased.

### Thermal Conductivity

Because of increasing worldwide energy problems, thermal insulation is a major concern. In recent years, the thermal insulation of PU foams has received a lot of attention (Han *et al.* 2009; Kim *et al.* 2012; Yan *et al.* 2011). However, little research has focused on PU elastomers.

The thermal conductivity of lignin PU films from 0 to 20 wt% lignin was almost the same, but it decreased significantly from 20 to 50 wt% lignin (Fig. 6). As can be seen in Fig. 4, the  $T_g$  varies from a narrow temperature range to a broad temperature range. When the lignin content is low, it can be dissolved well and the reaction between lignin and TDI is sufficient. As lignin content increases, the lignin that cannot react with TDI increases too, and the residual lignin blends with PU. So the disorder of the lignin PU films increases as the lignin content is increased; the disorder makes the thermal conductivity of lignin PU films less viable, which means that the heat insulation of the lignin PU films increases. This makes it possible for lignin PU films to be used as composite thermal insulation material.

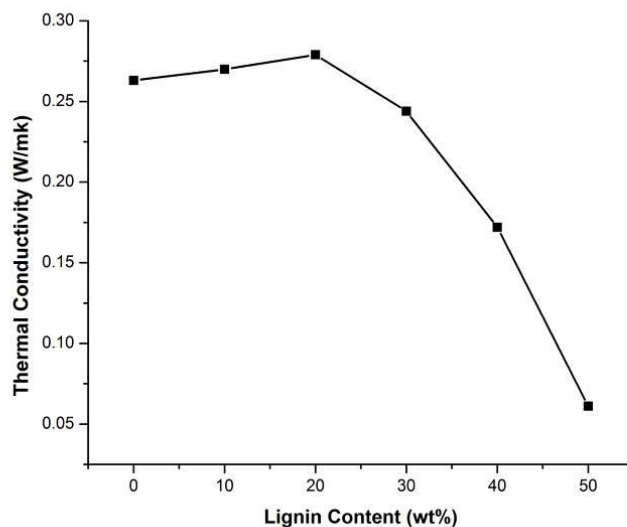


Fig. 6. Thermal conductivity of lignin PU films with varying lignin contents



## CONCLUSIONS

1. In this study, a type of lignin polyurethane (LPU) film from peroxy-acid-derived wheat straw lignin was formed without using a catalyst. Without any modifications or purifications, dry wheat straw lignin was used to make LPU, which can reduce raw material costs in PU products and would not cause unnecessary pollution.
2. Considering the mechanical properties and thermostability, the lignin PU film performed the best when the lignin content was 40 wt%. When the lignin content increased, the tensile strength and glass transition temperature ( $T_g$ ) of the lignin PU films increased, but the elongation at break and TOD decreased gradually until the lignin content reached 40 wt%, at which point it sharply decreased.
3. The thermal conductivity of lignin PU films decreased as well, which indicates that lignin PU films can be used as composite thermal insulation material.

## ACKNOWLEDGMENTS

The authors are grateful for the support of the National Natural Science Foundation of China (Grant No. 31200449).

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Article submitted: April 16, 2013; Peer review completed: May 14, 2013; Revised version received: May 23, 2013; Accepted: May 30, 2013; Published: June 3, 2013.