

Preparations and Properties of Polyurethane Adhesives Modified by Corn Straw Lignin

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The conversion of lignin into valuable products has attracted the interest of researchers. A series of modified polyurethane adhesives were prepared by blending corn straw enzymatic hydrolyzed lignin with polyester polyol and tolylene-2,4-diisocyanate. Mechanical properties, chemical structures, and thermal stability of the adhesives were characterized by mechanical properties tests, Fourier transform infrared spectrometry (FTIR), and thermogravimetric analysis (TGA). The results of shear strength test under room temperature and high temperature showed that the shear strength for modified polyurethane adhesives was improved by introduction of lignin. The introduction of lignin also improved the heat resistance of polyurethane adhesive. The TGA analysis results showed there were two stages in the thermal decomposition of the lignin blend modified polyurethane adhesive, and the maximum decomposition temperature of the first stage increased with the increase of lignin content, while the maximum decomposition temperature of the second stage decreased with the increase of lignin content. The TGA-FTIR combination analysis studied the main gas generated in the two decomposition stage's peak times, of which CO₂ was produced in the first stage, and CH₄ was created in the second stage, indicating that the molecular chain fracture process of the two kinds of adhesives was similar in the whole decomposition process.

Keywords: Polyurethane adhesive; Blending modification; Corn straw enzymatic hydrolyzed lignin; Bonding properties; Heat resistance

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INTRODUCTION

As one of the most abundant organic biopolymers on earth, lignin is the only non-petroleum resource in nature that can provide renewable aryl compounds. However, at present, the use of lignin is not complete. Because of its complex chemical structure and difficult separation and extraction, lignin is often burned as a cheap solid fuel to recover part of the heat energy, and only a small part of it is used in high value-added products (Markarian 2005). Therefore, improving the use value of lignin and expanding the scope of use not only can improve the utilization rate of resources, but also it can contribute to the protection of the environment, helping to meet the requirements of today's green and environmental protection era. Lignin, with a three-dimensional amorphous structure, is a polyphenol natural macromolecular organic matter formed by the connection of a C-C bond and -O- bond with phenylpropane structural unit (Collins *et al.* 2019). The main chemical functional groups in the lignin molecule's structure include the aromatic,

hydroxyl, methoxyl, carbonyl, and carboxyl groups, *etc.* (Yang *et al.* 2007; Ralph *et al.* 2019). Its microstructures make it an interesting raw material for a wide variety of applications. Due to its phenolic ether structure, lignin can be used in blends with other polymers to improve the heat-resistance of the polymers (Zakzeski *et al.* 2010).

Polyurethane adhesive is a type of reactive adhesive with excellent properties. The isocyanate group and urethane group contained in the polyurethane molecular chain segment are strong in polarity, good chemical activity, and excellent chemical adhesion toward materials containing active hydrogen components (Desai *et al.* 2003; Tavares *et al.* 2016; Tenorio-Alfonso *et al.* 2019). In addition, polyurethane adhesive also has a high degree of flexibility in formulation design, reaction activity, excellent impact resistance, and chemical resistance, which introduces a wide variety of applications of the polyurethane (Osman *et al.* 2003). However, at present, the polyurethane raw materials produced are all derived from petrochemical derivatives. This kind polyurethane is not easy to degrade, and this can lead to problems, such as soil deterioration and air pollution, in the treatment of its waste. Hence, renewable resources are more advantageous used as precursors to produce polyurethane and provide a more sustainable route for the production of polyurethane. The methoxy, hydroxyl and ether bonds in the lignin structure make it a potential substitute for polyols in several polyurethane materials, such as resins.

In the past, researchers studied lignin-based polyurethane products, such as thermoplastics, elastomers, coatings, film adhesives, *etc.* (Saito *et al.* 2013; Chauhan *et al.* 2014; Jia *et al.* 2015; Lee and Deng 2015; Oluwasina *et al.* 2015; Zhang *et al.* 2015; Sanjiv Kasbe *et al.* 2017; Gadhav *et al.* 2018). However, the chemical modification of lignin before preparation polyurethane increased the cost of preparation, while at the same time, the complex chemical and macromolecular structure of lignin made the elasticity and brittleness control of products difficult. These may be some of the reasons that limited its application in lignin-based polyurethane adhesives. The lignin used in this study has not been treated by complex chemical treatment and the lignin-based polyurethane adhesive was prepared by simple blending, which reduced the complexity of the experimental operation and reduces the experimental cost. In this work, a series of bi-component blended polyurethane adhesives were obtained by the unchemically modified corn straw enzymatic hydrolyzed lignin mixed with polyester polyol and tolylene-2,4-diisocyanate (TDI). The effect of different lignin additions on the bonding strength under room temperature and high temperature were studied. At the same time, it lays a foundation for the application of lignin in other adhesives.

EXPERIMENTAL

Materials

Corn straw enzymatic hydrolyzed lignin was obtained from Songyuan Laihe Chemicals (Jilin, China), with a bulk density of 0.6 g/cm³, an average particle size of 11 μm and the purity of 90%. The lignin was used after drying at 50 °C for 24 h in a vacuum oven. The phenolic hydroxyl content of the lignin was 3.64%, and the alcohol hydroxyl content of lignin was 7.62% (hydroxyl content data is provided by the manufacturer). Polyester polyol ($M_n = 2000$, acid value = 12.9 mgKOH/g, hydroxyl value = 160.4 mgKOH/g), which was prepared from sebacic acid, ethylene glycol, and glycerol, was provided by Petroleum Chemistry Research Institute of Heilongjiang Academy of Sciences (Harbin, China). Tolylene-2,4-diisocyanate (TDI) (chemically pure, Wanhua Chemical

Group Co., Ltd., Yantai, China), dibutyltin dilaurate (DBTDL) (chemically pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), triethylenediamine (TEDA) (analytically pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), acetone, butanone (analytically pure, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used as received. The substrate material used in the adhesive joints was aluminum alloy.

Preparation of Adhesive and Adhesion of Substrate Material

The lignin was added to a polyester polyol, heated to a molten state at 100 °C, and mixed for 30 min. The catalyst, DBTDL and TEDA, were added into the above mixture and stirred for another 30 min to prepare the A component of the polyurethane adhesive. The TDI was used as the B component. The polyurethane adhesive blended with lignin was prepared by dissolving A component with acetone, then adding B component, and after that it was stirred at room temperature every 20 min to 30 min until a paste was formed. A series of lignin blended polyurethane adhesives were prepared with different designed polyester polyol/lignin mass ratios, and the corresponding numbers are listed in Table 1. The surface of aluminum substrate was mechanically polished and then wiped with acetone before being adhered.

Table 1. Formula of the Two-component Polyurethane Adhesives

	Polyester Polyol (g)	Lignin (g)	DBTDL (g)	TEDA (g)	Acetone (g)	TDI (g)
BLN-0	100	0	4	2	100	100
BLN-5	100	5	4	2	100	100
BLN-10	100	10	4	2	100	100
BLN-15	100	15	4	2	100	100
BLN-20	100	20	4	2	100	100

Methods

Single lap shear joints of aluminum substrates with the size of 100 mm × 25 mm × 2 mm were used for evaluating the adhesive shear strength by tension loading with an overlap length of 12.5 mm. The adhesives were applied across both sides of the overlap area and cured at 110 °C for 3 h. During the curing, the specimens were under a constant pressure of 0.1 MPa.

After curing, the tests of the mechanical properties for the polyurethane adhesives were performed on an Instron 4467 machine (Instron (Shanghai) Test Equipment Trading Co., Ltd., Shanghai, China) at the speed of 10 mm/min at the room temperature and high temperature, respectively, according to ASTM D-1002 (2010).

Absorbance peaks of the characteristic groups of reaction mixture were obtained with a Fourier transform infrared (FT-IR) instrument (NICOLET-6700; Thermo Electron Corporation, New York, NY, USA).

Thermal properties of the adhesives were performed on the thermal gravimetric analyzer (TGA, NETZSCH TG-209F3; NETZSCH Scientific Instruments Trading (Shanghai) Ltd., Shanghai, China) at a heating rate of 10 K/min from 303.15 to 873.15 K under N₂ atmosphere (30 mL/min).

The TG-FTIR analysis was obtained using the combination of the TGA Q5000 (TA Instruments, New Castle, DE, USA) and Nicolet 6700 at heating rate of 10 K/min, and 20 mL/min of nitrogen.

RESULTS AND DISCUSSIONS

Bonding Properties

Shear strength under room temperature

Shear strength test was used to evaluate the bonding properties of the adhesive for the same material, and a single lap structure was used for shear specimens. The effect of lignin content on shear strength of polyurethane adhesives is shown in Fig. 1. In theory, active hydrogen in lignin will react with isocyanate, which affects the strength of polyurethane adhesives. Therefore, the addition of lignin will also affect the shear strength of polyurethane adhesives.

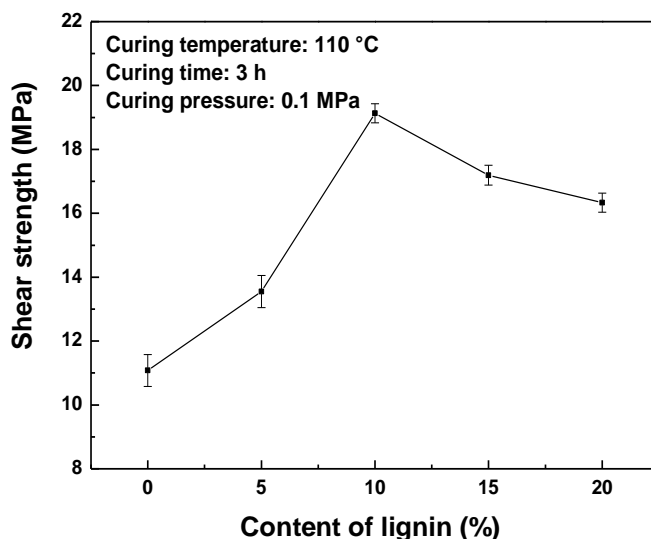


Fig. 1. Room temperature shear strength of the polyurethane adhesives modified by lignin

It can be seen from Fig. 1 that the shear strength of polyurethane adhesive increased at first and then decreased with the addition of lignin. The highest shear strength of polyurethane adhesive was 19.1 MPa, which was observed for 10% lignin addition. When lignin content reached 20%, the shear strength of polyurethane adhesive was still 16.3 MPa. When the lignin content was increased from 10% to 20%, polyurethane adhesives had a high shear strength, even if the lignin content was 5%, the shear strength of polyurethane adhesives was 13.6 MPa, which showed that even if the lignin performance had a large fluctuation, the lignin blend modified polyurethane adhesives still had a satisfactory shear strength. When the proportion of lignin was small, the active hydrogen in lignin reacted with isocyanate increases the cross-linking degree and the hydrogen bonding interaction was enhanced with the introduction of lignin, so the shear strength increased. When a certain amount was reached, the three-dimensional structure of lignin destroyed the regularity of molecular chains in the polymer structure of polyurethane adhesives inversely, which reduced the shear strength. The obvious "fault-tolerant" ability of lignin blend modified polyurethane adhesive, which resulted from the corn straw enzymatic hydrolyzed lignin that was insoluble and had good compatibility with polyurethane adhesives, was an important basis for the practical application of lignin in polyurethane adhesive.

Shear strength under high temperature

To study the heat resistance of polyurethane adhesive blended with lignin, the shear strength of the bonding joint under various temperatures was also tested. The shear strengths for five polyurethane adhesives BLN-0, BLN-5, BLN-10, BLN-15, and BLN-20 under various temperatures are shown in Fig. 2. When the shear strength tests were performed at high temperatures of 60 °C and 80 °C, BLN-10 polyurethane adhesive showed the best bonding property, and BLN-5 showed a bonding property slightly worse than BLN-10. In contrast, when the temperature was 100 °C and 120 °C, the BLN-5 with lignin content of 5% showed the maximum shear strength while BLN-10 was weaker but still reached for the bonding strength of 7.37 MPa and 6.84 MPa, corresponding to 100 °C and 120 °C, respectively. With the increase of temperature, the amount of active hydrogen reaction between isocyanate and lignin was not increased; however, due to the large three-dimensional structure of lignin, the molecular chain in the polymer structure was damaged, and the degree of damage increased, which led to the decrease of the bonding properties of BLN-10 adhesive. Figure 2 also indicates that a higher temperature of the shear strength test resulted in a weaker bonding property of polyurethane adhesive with the same lignin content. This was because the introduction of lignin improved the heat resistance of polyurethane adhesives, and at the same time, the three-dimensional structure of lignin also destroyed the regularity of molecular chains in the polymer structure of polyurethane adhesives. This destruction increased the toughness of polyurethane adhesives, also reduced the crosslinking degree of polyurethane adhesive, resulting in the reduction of high temperature shear strength of polyurethane adhesives.

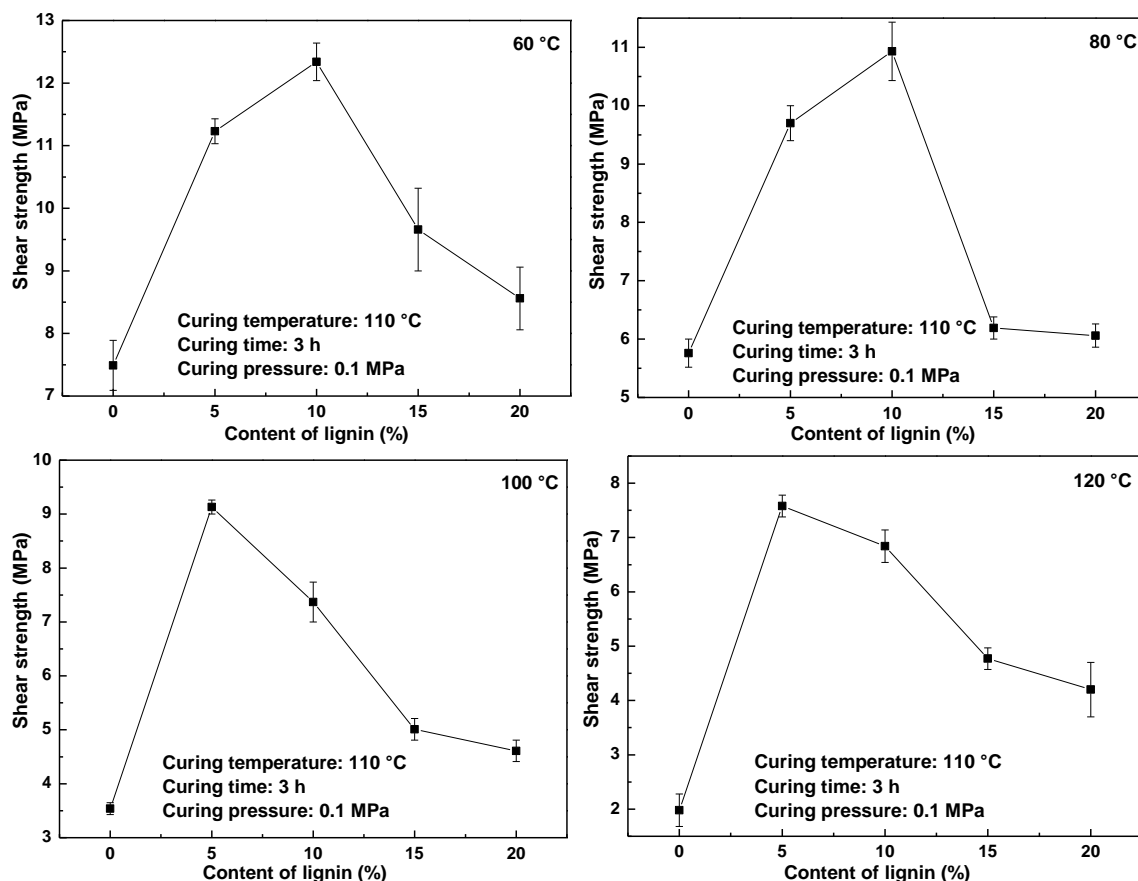


Fig. 2. Effect of lignin content on high temperature shear strength of the polyurethane adhesive

Figure 3 shows the shear strength of the polyurethane adhesives blended with lignin at different testing temperatures. Table 2 lists the decline rate of high temperature shear strength of lignin blend modified polyurethane adhesives compared with the room temperature shear strength. Although the introduction of lignin increased the strength at room and high temperature, the decrease rate of high temperature shear strength was reinforced with the increase of lignin content under the same temperature, which was due to the decrease of the regularity of polymer chain arrangement in polyurethane adhesive that was caused by the increase of lignin content.

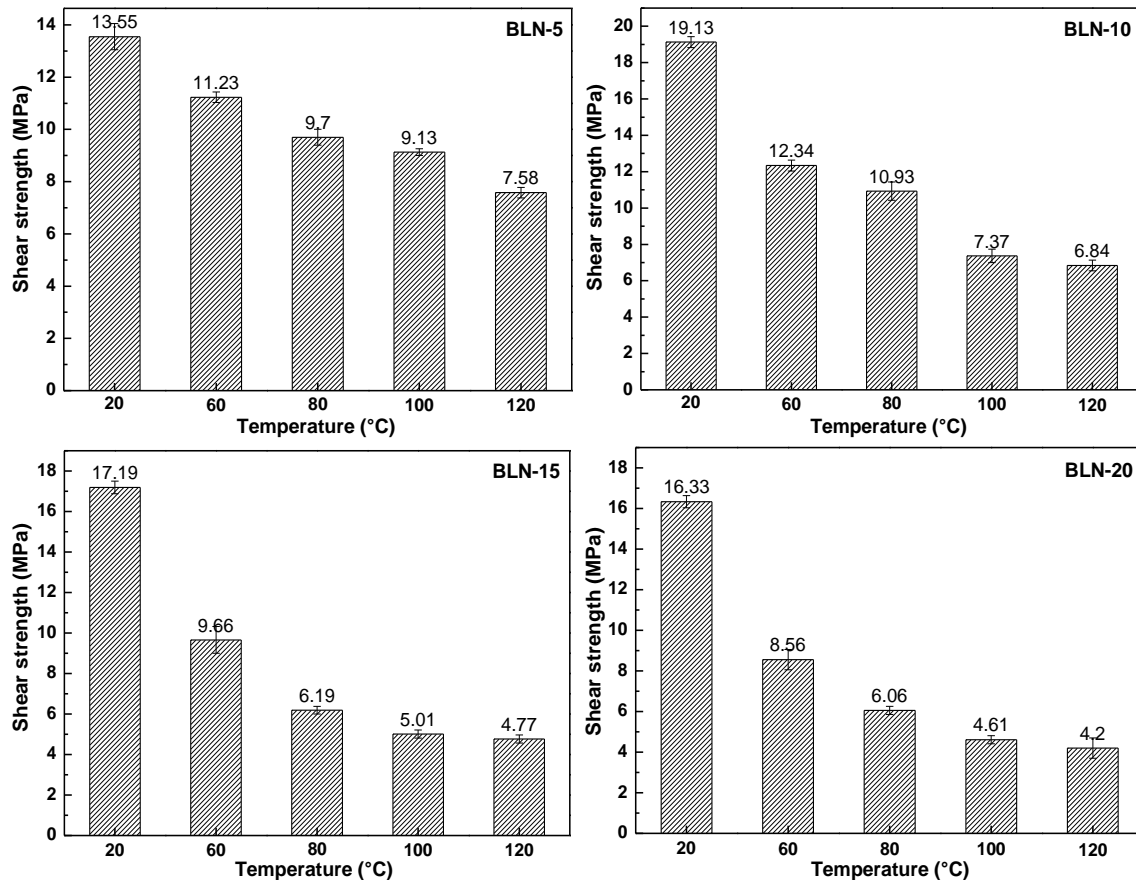


Fig. 3. Shear strength of the polyurethane adhesives blended with lignin at different testing temperature

Table 2. Decline Rate of High-temperature Strength of the Polyurethane Adhesives Blended with Lignin

Polyurethane Adhesive	60 °C Decline Rate (%)	80 °C Decline Rate (%)	100 °C Decline Rate (%)	120 °C Decline Rate (%)
BLN-5	17.1	28.4	32.6	44.1
BLN-10	35.4	42.9	61.5	64.2
BLN-15	43.8	64.0	70.9	72.3
BLN-20	47.6	62.9	71.8	74.3

Ordinary polyurethane adhesives are generally not used as temperature-resistant adhesives, which are determined by the molecular structure of polyurethane materials. In

polyurethanes synthesized from alcohols and isocyanates, the urethane bonds and maximum decomposition temperature in polyurethane molecular structure are different due to the reaction of different alcohols and isocyanates (Chattopadhyay and Webster 2009; Del Saz-Orozco *et al.* 2015). The heat resistance of adhesives depends not only on the heat resistance of the molecular structure, but also on the toughness, wettability, and the regularity between molecular chains. Lignin is a natural polyphenolic hydroxyl polymer, and the existence of a large number of polar groups in lignin improves the hydrogen bond interaction and thus improves the heat resistance of polyurethane.

FTIR Analysis

The FTIR spectra for the polyurethane adhesives with different lignin content cured at 110 °C for 3 h are shown in Fig. 4. The FTIR spectrum analysis was employed to characterize the raw materials and analyze the changes in the lignin-polyurethane adhesives structure during its curing reaction, mainly to observe the changes of functional groups introduced by the addition of different amounts of lignin within the adhesive.

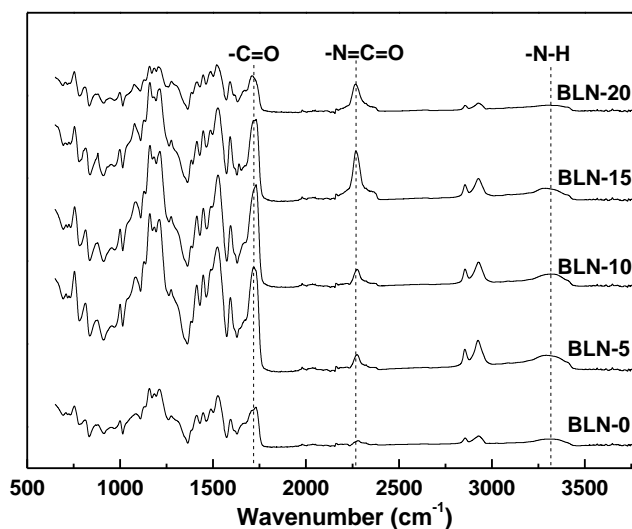


Fig. 4. FTIR spectra of cured polyurethane adhesives blended with lignin

It can be seen from Fig. 4 that the absorbance peak at 2270 cm⁻¹ that was attributed to the stretching vibration of isocyanate group (N=C=O) for polyurethane adhesives showed a strengthened peak with the increase of lignin until the lignin additions reached 15%. There were still isocyanate groups after curing of polyurethane adhesives modified by lignin, and the hydrogen bond between lignin and molecular chain increased, and the molecular chain in polyurethane was arranged more closely, which improved the water resistance of polyurethane adhesives and made it an idea of formulation design. The polyurethane adhesives without lignin had almost no stretching vibration peak of isocyanate groups, which indicated that isocyanate and polyester polyol reacted completely. When the lignin content was 5% and 10%, there was a stretching vibration peak of isocyanate with low peak intensity, indicating that the introduction of lignin influenced the reaction between isocyanate and polyester polyol to some extent. On the one hand, lignin partially hindered the reaction between isocyanate and polyester polyol. On the other hand, lignin can still react with isocyanate, which led to the increase of shear strength. When the lignin content continued to increase, the stretching vibration peak of

isocyanate intensified, and the three-dimensional network structure of lignin seriously hindered the reaction between isocyanate and hydroxyl group, which resulted in the decrease of shear strength. The result further indicated that the lignin could participate in the crosslinking curing reaction of polyurethane adhesives due to the increase of the multifunctional reactive groups, accompanied by the hydrogen bond between lignin and molecular chain, which resulted in a better performance of the adhesive. However, the addition of lignin interfered with the reaction between isocyanate and hydroxyl because of its three-dimensional network structure. The residual isocyanate groups reacted with water and further crosslinked, which was beneficial to the water resistance of the adhesives.

There were a large number of functional groups that can form a hydrogen bond in polyurethane, such as carbonyl, ether oxygen, and amine. The formation of hydrogen bond changes the bond force constant of the functional group, which is reflected that the stretching vibration band shifts to low frequency, and the intensity and peak shape of the absorbance band also changed in the infrared spectrum (Chattopadhyay and Raju 2007). Among them, the amino group region (3100 cm^{-1} to 3500 cm^{-1}) and carbonyl group region (1600 cm^{-1} to 1800 cm^{-1}) are the most interesting spectral regions in the study of hydrogen bonding. The absorbance peak near 1730 cm^{-1} of the carbamate had the same change trend along the additions of lignin (Cateto *et al.* 2008; Ignat *et al.* 2011). With BLN-0 as a reference, the peak intensity greatly increased with 5% and 10% lignin addition in the polyurethane adhesives, and then the peak value decreased gradually, even lower than that of BLN-0. The polyurethane adhesives modified with lignin had an absorbance peak near 3310 cm^{-1} , which was due to the stretching vibration of hydroxyl group and N-H bonded with ammonia ester (NHCOO). The addition of lignin hindered the reaction of hydroxyl with isocyanate and the existence of hydroxyl in lignin itself, which resulted in the content of hydroxyl increased with the increase of lignin content. The peak values of N-H of BLN-5 and BLN-10 were higher, a large number of hydrogen bonds existed, and the strength of the adhesives was stronger. This result was consistent with the analysis on the bonding properties of the adhesives performed at room temperature mentioned above.

TGA Analysis

Figure 5 shows the TGA and derivative thermogravimetric (DTG) curves of lignin blend-modified polyurethane adhesives. It can be seen that the weight loss of lignin blending modified polyurethane adhesive can be divided into two stages.

The two stage's maximum decomposition temperatures of polyurethane adhesives modified by lignin are shown in Table 3. The maximum decomposition temperature of first stage increased with the increase of lignin content, and the maximum decomposition temperature of BLN-5/BLN-10/BLN-15 lignin modified polyurethane adhesives decreased after the introduction of lignin in the second stage. In the first stage, the intermolecular interaction force was destroyed under high temperature. However, higher lignin content resulted in a stronger intermolecular interaction force, such as hydrogen bonds, and compared with BLN-0, more energy was needed for destruction, which resulted in the increase of thermal decomposition temperature. The second stage was the chemical bond breaking in the molecular chain. The three-dimensional network structure of lignin destroyed the reaction between isocyanate and polyester polyol. Higher lignin content caused weaker chemical bond formation in the molecular chain, which resulted in a thermal decomposition of polyurethane adhesives under lower temperature.

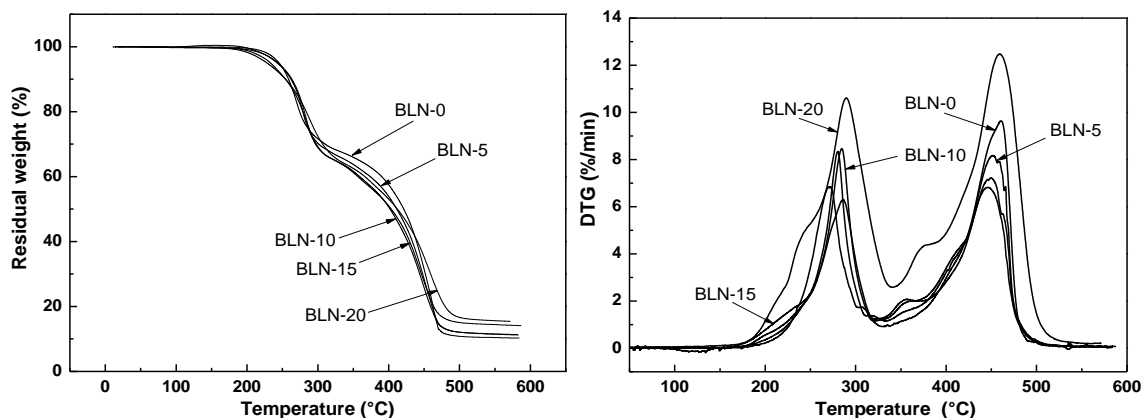


Fig. 5. The TGA and DTG curves of polyurethane adhesives modified by lignin

When lignin was introduced into polyurethane adhesives, the thermogravimetric loss of polyurethane adhesives increased generally before 500 °C. When the temperature reached 500 °C, the weight loss of polyurethane adhesive was lower than that of the pure polyurethane adhesive. This indicated that weak chemical forces, such as hydrogen bond between lignin and molecules, caused weight loss at a low temperature, but the phenol group of lignin at high temperature hindered the degradation of polyurethane adhesives (Ciobanu *et al.* 2004).

Table 3. Maximum Decomposition Temperature of Polyurethane Adhesives Modified by Lignin

PU Adhesives	BLN-0 (°C)	BLN-5 (°C)	BLN-10 (°C)	BLN-15 (°C)	BLN-20 (°C)
First stage	271.68	279.30	283.91	287.10	291.58
Second stage	460.90	452.26	447.54	448.59	461.63

Crosslinking Degree Analysis

The crosslinking degree has a considerable effect on the elongation, strength, and medium resistance of polyurethane adhesive. The swelling equilibrium method was used to explore the effect of the introduction of lignin on the crosslinking degree of polyurethane adhesive. Figure 6 shows the crosslinking degree of BLN-0, BLN-1, BLN-2, BLN-3, BLN-4, and BLN-5 adhesives.

It can be seen from Fig. 6 that the introduction of lignin can increase the crosslinking degree of polyurethane adhesive. Among them, the cross-linking degree of BLN-5 was the highest, and it was 30.2% higher than that of BLN-0. The cross-linking degree of BLN-10 was the lowest, but it was also 13.7% higher than that of BLN-0. It follows that the introduction of lignin will increase the cross-linking degree of the adhesive to a certain extent. And too much lignin will decrease the cross-linking degree of the material. This is because lignin is a three-dimensional reticular macromolecular structure, which is not conducive to the regular arrangement and distribution of polymer chains in polyurethane adhesives, and also has an adverse effect on the heat and water resistance of polyurethane adhesives. However, this three-dimensional reticular macromolecular structure of lignin can hinder the further damage of heat and water to the polymer chain in the process of heating and water treatment of polyurethane adhesive, thus reducing the fracture number of polymer chain.

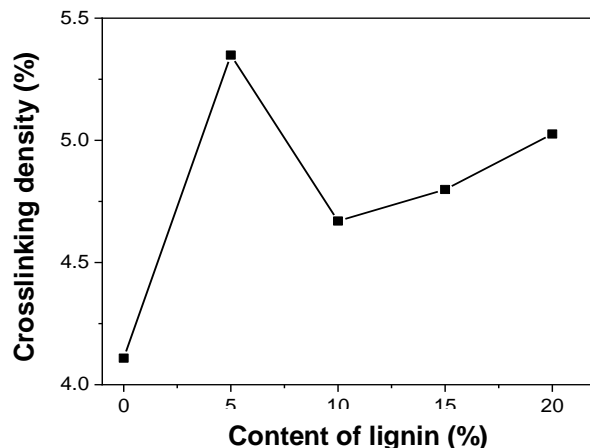


Fig. 6. The effect of lignin content on crosslinking degree of polyurethane adhesives

FTIR-TGA analysis

To better study the decomposition and functional changes of polyurethane adhesives during thermal degradation, polyurethane adhesives were analyzed by a combination of TGA-FTIR. Figure 7 shows the TGA-DTG curves of BLN-0 and BLN-20 adhesives during TGA-FTIR combination usage stage. The FTIR spectra of the vapor phase for thermal degradation of the two polyurethane adhesives at the peaks of two stages in the decomposition process can be seen from Fig. 8.

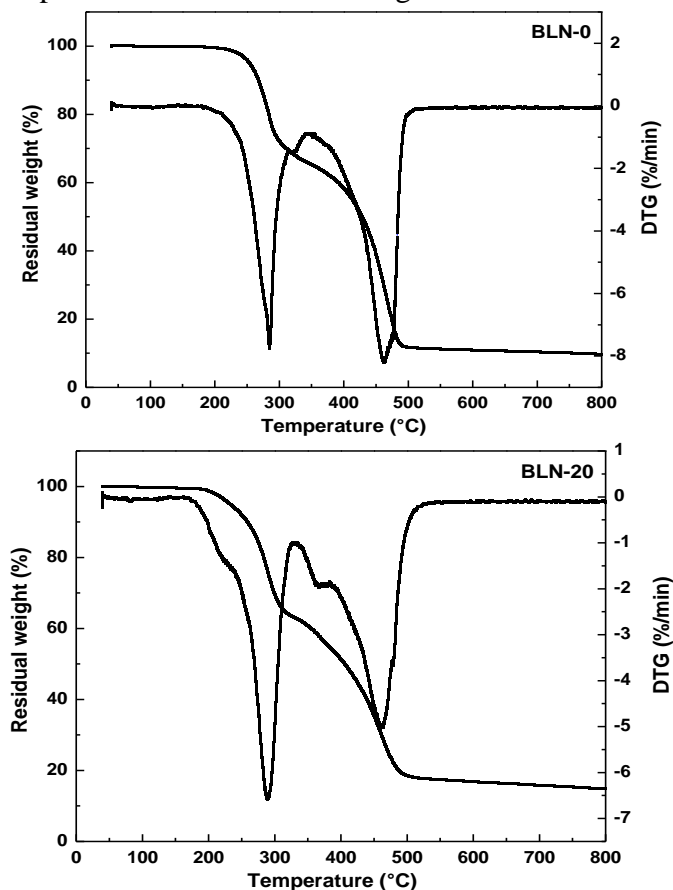


Fig. 7. The TGA-DTG curves of BLN-0 and BLN-20 adhesives

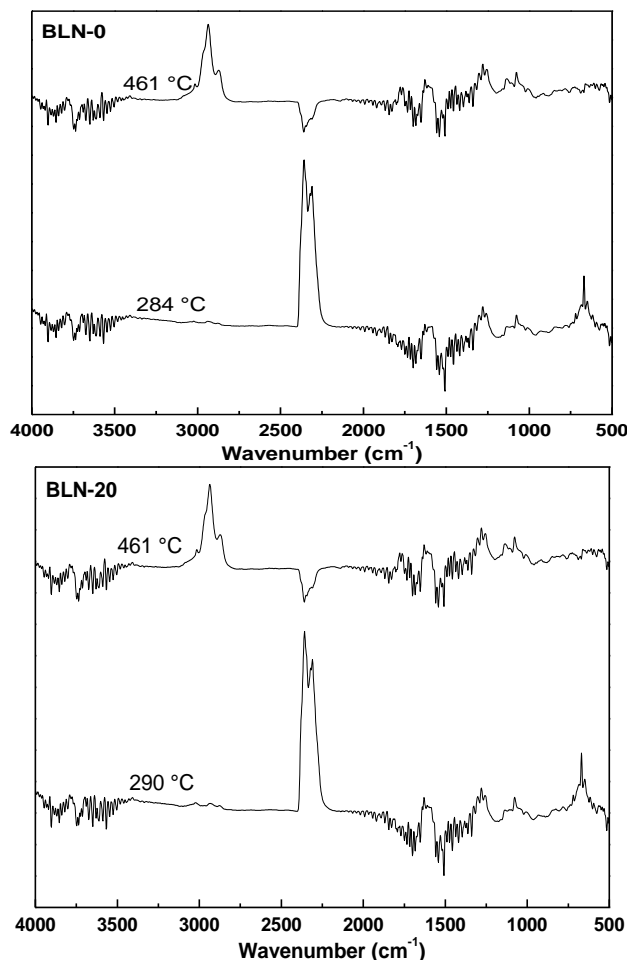


Fig. 8. FTIR spectra of the vapor phases for thermal degradation of polyurethane adhesives BLN-0 and BLN-20

Two distinct peaks, C-H (2940 cm^{-1}) and CO_2 (2360 cm^{-1}), can be found from Fig. 8. The peaks of H_2O (4000 to 3500 cm^{-1}), CO (2120 to 2180 cm^{-1}), and some phenols and phenolic peaks still were present, but were not obvious. According to Lambert-Beer's law, the gas product concentration is proportional to the absorbance intensity of the corresponding infrared spectrum. A larger infrared spectrum absorbance intensity value results in a higher gas concentration generated by pyrolysis. Therefore, the main gas generated at the first stage peak was CO_2 , and the gas produced at the peak of the second stage peak was mainly CH_4 . Figure 8 also shows that there was no obvious difference between the peak values of the two phases, which indicated that the molecular chain fracture process of the two kinds of adhesives was similar in the whole decomposition process. This may be due to the fact that in the first stage, the carbamate group on the polymer backbone breaks down at the C-O bond to form isocyanates and polyols, which are then further decomposed into CO_2 . In the second stage, when the temperature increases, the broken molecular segment is further decomposed to CH_4 (Shufen *et al.* 2006).

CONCLUSIONS

1. A series of modified polyurethane adhesives were prepared by blending corn straw enzymatic hydrolyzed lignin into polyester polyol, and this was reacted with tolylene-2,4-diisocyanate (TDI) under catalyst. The strength of modified polyurethane adhesives can be improved by introduction of lignin in the series of modified polyurethane adhesives. The highest shear strength at room temperature for polyurethane adhesives was found in adhesive BLN-10, which could reach 19.1 MPa. The high temperature strength measurement of polyurethane series adhesives modified by lignin blend showed lower values than that at room temperature, and BLN-5 adhesive had the lowest decrease.
2. The isocyanate group peak for polyurethane adhesives displayed stronger peak intensity with the increase of lignin content until the lignin additions reached 15%. Addition of lignin not only increased the number of reactive functional groups, but it also hindered the reaction between isocyanate and hydroxyl because of its three-dimensional network structure. The thermal decomposition process of lignin blend modified polyurethane adhesives was divided into two stages. The maximum decomposition temperature of the first stage increased with the increase of lignin content, while the decomposition temperature decreased in the second stage.
3. The results of TGA-FTIR analysis of two polyurethane adhesives, BLN-0 and BLN-20, showed that the main gas generated at the first stage peak time was CO₂, and the gas produced at the peak of the second stage peak was mainly CH₄. The trends of molecular chain fracture process of the two kinds of adhesives were similar in the whole decomposition process.

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