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Preparation and Characterization of High Boiling Solvent Lignin-Based Polyurethane Film with Lignin as the Only Hydroxyl Group Provider

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A novel dissocyanate-modified lignin-based polyurethane (LPU) film was facilely prepared using renewable lignin as the only hydroxyl groups provider at ambient temperature and pressure for the first time. The lignin was extracted through modified high boiling solvent (HBS) method with 1, 4- dioxane as solvent, and then dried through freeze drying. The ash content of HBS lignin sample was about 0.25%, which was lower than the other lignin. The HBS lignin had a large number of hydroxyl groups, which indicated the potential values in substitution of polyols in the synthesis of polyurethane (PU). From the results, the LPU film prossessed high performance in hardness, solvent resistance and hydrophilicity with no need for further modification. The LPU film also had high tensile strength with a maximum value of 41.6 MPa. In order to investigate the thermal properties of the LPU film, thermal gravimetric analysis (TGA) and thermogravimetric infrared analysis (TGA-FTIR) were performed, and the LPU film could be stable under 114 °C in air and N_2 atmosphere. This study developed a novel LPU film and it would show promising future applications in coating and basement.

1. Introduction

Polyurethane (PU) is one of the most important and versatile classes of polymeric plastics. This importance is derived from the wide variety of physical properties and forms which can be produced by the ingenious combination of polyisocyanates and polyhydroxyl compounds.[1,2] What's more, it offers the potential of preparing a wide range of products depending on different applications, such as low temperature elastomers, high tensile adhesives, coating or basement. In general, the PU products provide various forms including films, foams, gels and so on. In recent years, the PU films have been prepared through different methods, and then applied into many fields. The raw materials of PU were almost all derived from fossil resources, and PU was always synthesized through a polymerization between polyols, including polyol polyether or polyol polyester, and polyisocyanate to form urethane linkages. However, the expensive and non-renewable raw materials from fossil resources and environmental protection have applied pressure on the polyurethane products industry currently. Consequently, more and more industrials and researchers were looking for bio-based alternatives of these fossil based chemical compounds, including the use of renewable polyols in the polyurethane synthesis.[3]

Recently, there is an increasing trend to study and utilize renewable natural materials as a result of environmental protection and the growing shortage of oil resources. Lignin, as the second abundant biopolymer on land after cellulose, is a heterogeneous and amorphous polymer of a phenolic nature[4]. Most of lignin used in the previous reports was industrial lignin. Generally, industrial lignin can be separated from the black liquor of kraft pulp as a by-product of chemical wood pulping[5,6] which was called kraft lignin, or extracted from biomass through chemical methods, such as extraction using an organic solvent aqueous solution at high temperature or pressure[7,8] or protic ionic liquids[9]. Unfortunately, most of lignin from industrial products had high ash content and wide distribution of molecular weight, which would hinder the wide application of lignin into most fields, especially in high value products. Here, lignin extracted with high boiling solvent (HBS) was a kind of organosolv lignin. Its low ash content and narrow distribution of molecular weight made HBS lignin easy following by coupling reaction or other treatments. To the best of our knowledge, HBS lignin was little used in the synthesis of LPU. Furthermore, the extraction process of the HBS lignin was eco-environmental due to the recycle of HBS.

The structural model of HBS lignin[10-14] had proved it had a large number of hydroxyl groups, which implied potential values in PUs industry as hydroxyl group (-OH) provider[15]. Therefore, many researchers have attempted to obtain highly valuable lignin based products on account of this property. Even though most of them [16-21] have investigated the lignin based PU film, the lignin just played a role of filler or partly substitution of polyols. During the previous preparation

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process, researchers always tried to search for another soft segment to improve the flexibility of the hard segment that the lignin and diisocyanate played the role of in the multicomponent system. However, both flexible and rigid material had wide applications, such as rigid films could be used as coating or basement. In this work, the hydrophilic lignin-derived film was successfully prepared by a simple and environmental method for the first time. It should be noted that the lignin without any pre-modification was the only source of hydroxyl group in the films. Moreover, this work also further decreased the dependence on fossil resource. To be specific, monolithic polyurethane film was achieved by condensation polymerization of lignin and 4, 4-diphenyl methane dissocyanate (MDI) in 1, 4-dioxane solution, and then ambient pressure curing at 85 °C was applied to the as-prepared film with solvent resulting in lignin-based polyurethane (LPU) film. The obtained LPU films possessed multifunctional characteristics including high tensile strength, high hardness and hydrophilicity. The LPU films were further quantified and characterized by comprehensive set of analytical methods.

2. Materials and Methods

2.1 Materials

The raw material was wood meal (300 meshes) purchased from Spruce (from wooden Jiang Weihua perfumery plant). The wood meal was dried in a vacuum oven at 90 °C for 24 h before being used. 1, 4-butanediol used as high boiling solvent was purchased from Tianjin Fuchen Chemical Reagent Factory. 4, 4-diphenyl methane diisocyanate (MDI) was purchased from Tokyo Chemical Industry (TCI) Shanghai, China. 1, 4-dioxane, dimethyl sulfoxide (DMSO) and triethylamine (TEA) were achieved from Shanghai Civi Chemicla Technology Co, China. All the chemicals were reagent grade without further purification.

2.2 Extraction of HBS lignin

The HBS lignin was extracted through the modified HBS method [22]. Briefly, 300 g wood meal of spruce was dispersed in 5 L aqueous solution with 3 ml HCl, and then stirred at 95 °C for 2 h. After cooling at room temperature, it was filtered with vacuum filter. Then the filter cake was put into a 5 L stainless autoclave with 2400 ml 1, 4-butanediol aqueous (80wt %). It was heated to 220 °C, and kept for 1 h. After being filtered, the filter liquor containing HBS lignin was separated from the reaction mixture. Then 3 times volume of HBS lignin filtered liquor water was added into it at the room temperature with stirring for 15 min. Finally, the precipitated lignin was collected through vacuum filter and then dried in freeze direr for 24 h.

2.3 Preparation of the LPU films

Various LPU films were prepared based on different monomer ratios and concentrations shown in Table 1. In a typical experiment, 1g lignin and 1.134 g MDI were dissolved in 8 ml 1, 4- dioxane, and then 40 μl TEA was added, the polymerization was activated and stayed for 1h at room temperature. Finally, the as-prepared pre-gel was curing at 85 °C for 3h, and then obtained the lignin-based film.

Table 1 Parameters of the LPU films

Sample No.	NCO: OH (mol/mol)	Lignin (g)	MDI (g)	1,4-dioxane (ml)	TEA (μl)
1	1	1	0.667	8	40
2	1.2	1	0.801	8	40
3	1.7	1	1.134	8	40
4	2	1	1.335	8	40
5	2.2	1	1.468	8	40

2.4 Characterization

Element analysis was carried out in an elemental analyzer (vario EL, elementar analysensysteme GmbH, Germany). During the characterization, the carbon, hydrogen, nitrogen in the lignin sample was determined. The weight percentage of oxygen was calculated by the difference. The ash contents of HBS lignin were determined according to Chinese national standard (GB/T 2677.3-93). The weight-average (M_w) and number-average (M_n) molecular weights of the lignin were determined by gel permeation chromatograph (GPC, SXIS RLTRA DLD, Kratos, UK). Tetrahydrofuran (THF) was used as the mobile phase with a run time of 15 minutes and the injecting volume was 50 μL. Polystyrene standards were used for making the calibration curve at different molecular weights. The chemical compositions and surface binding state of HBS lignin was examined by X-ray photoelectron spectroscopy (XPS, AXIS ULTRA DLD, Kratos, UK).

The micro morphology of the surface and cross section of LPU films was observed using scanning electron microscopy (SEM, JSM-7001F, Japanese electron). X-ray diffraction (XRD) was carried out on an X-ray diffractometer (D8 ADVANCE, Germany). Fourier transform infrared (FTIR) spectra of HBS lignin and LPU film was recorded with a Magna-IR 750 Fourier transform infrared spectrophotometer (Nicolet Company, USA). The spectra were recorded in the range from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution. The thermal property of the HBS lignin sample was tested with thermogravimetric analyzer (TGA, Q600, TA Instrument) in nitrogen atmosphere. The samples were heated from room temperature (25 °C) to 800 °C at a heating rate of 10 °C /min. Thermogravimetric infrared analysis (TGA-IR) was conducted on an high temperature thermal analyzer (SETSYS EVOLUTION TGA 16/18, SETARAM, France). The sample was heated from room temperature (25 °C) to 800 °C at a heating rate of 5 °C/min. Static water contact angle was conducted on a contact angle meter (POWEREACH, JC2000D2G). The hardness of LPU film was measured through nano-indentation test on a nanoindentor (nanoindenter-G150, USA).The LPU films measured through FTIR, XRD, TGA, TGA-FTIR, contact angle and nano-indentation test were prepared with the NCO: OH molar ratio as 1.7.

The tensile tests (GB/T 1040.3-2006) were conducted at room temperature on an electronics universal tensile testing machine (TRAPEZIUM, Japan). The tensile tests were used to investigate the influence of the NCO: OH molar ratio on the tensile strength and strain-to-failure values. Swelling tests in dimethyl sulfoxide (DMSO) and distilled water (H_2O) were conducted at constant 30 °C for 24 h to arrive equilibrium. After swelling, the excess solvent on the surface of each sample was removed by filter paper. And then the samples were weighted quickly on account of accuracy. The swelling rate was calculated as follows.

$$\Delta g = \frac{\Delta g_1 - \Delta g_0}{\Delta g_0} \times 100\%$$

Where the Δg was the swelling ratio, Δg_0 and Δg_1 were the weight of the LPU film samples before and after swelling test, respectively.

3. Results and Discussion

3.1 General properties of HBS lignin

The lignin fraction obtained from extraction process was 12.57% based on the dry starting material. In this paper, lignin meant the lignin fraction extracted from wood powder directly. The number of hydroxyl groups of HBS lignin was 5.33mmol/g, which was obtained through chemical titration[23]. During this process, the HBS lignin was acetylated with acetic anhydride (Ac_2O), and then the solution was titrated with 1 M sodium hydroxide (NaOH) solution.

Some general properties of the HBS lignin sample were presented in Table 2. Generally, one of the disadvantage of the biomass as chemical raw material was the high ash content, and it has a significantly negative influence on the property of the material and chemicals from biomass. The ash content of HBS lignin sample was about 0.25%, which was lower than the former HBS lignin with 0.6% ash content[24] and Kraft lignin with 3.12% ash content[23]. This reflected that most of the water-soluble and alcohol-insoluble ash was removed during the extraction process. The lower ash content indicated that the HBS lignin was easy to be purified or modified. The content of C element was 64.31%, higher than that of lignin from Kraft lignin (61.8%)[23].

Table 2 Element composition and content of lignin

	Ash	Element analysis (%, w/w)						
Sample	(%, w/w)	C	H	O	N	M_w	M_n	M_w/M_n
HBS Lignin	0.25	64.31	6.36	28.33	1.00	3778	2483	1.52

According to the results of GPC, weight-average (M_w) and number-average (M_n) molecular weight, and the polydispersity (M_w/M_n) of lignin sample were presented in Table 2. The weight-average molecular weight was 3778 g/mol, which might be caused by the cleavages of α-O-4 and phenolic β-O-4 linkages in lignin. The polydispersity of the HBS lignin sample was 1.52, which was advantageous to modifying the lignin.

3.2 Chemical properties of HBS lignin

To determine the chemical composition of lignin, the sample was evaluated by XPS. The hypothesis was that the lignin sample was uniform intermixing of the components. As shown in Figure 1, the peak of the spectra had a better fit than the condition that every peak had the same G-L ratio if the Gauss-Lorentz-ratio was unfixed. C, O and traced N elements were detected by XPS wide scan spectra (Figure 1(a)). C, H and O as the main elements were presented in lignin, which was corresponding with the results of element analysis. N element existed in the lignin was from the wood meal, and it could not be removed completely during the extraction process.

Vasile et al. analyzed lignin by XPS and fitted the C 1s curves with four peaks at around 285 eV (C-C, C-H), 286.5 eV (C-OR, C-OH), 288 eV (C=O, HO-C-OR) and 289 eV (O-C=O), respectively[25]. But different lignin has different structure. The curve-fitted XPS C1s spectra showed four peaks at around 284.57 eV (C-C), 285.86 eV, 286.50 eV (C-O), 288.81 eV (C=O), and the percentage of every carbon type was 47.18%, 24.13%, 10.58% and 8.12%, respectively. It was indicated that the content of carbonyl group was low in lignin molecular. These carbonyl groups might assign to the CHO in coniferyl aldehyde and vanillin substructures which derived from native lignin due to the low activity under HBS pulping conditions. The peak at 285.86 eV was not detected in other lignin samples reported previously. The C-N bonding peak at 286 eV was detected in aminated lignin[26]. However, due to the trace content of N element and absence of C-N bond in original lignin, the peak at 285.86 eV should not be assigned to C-N. Therefore, the peak at 285.86 eV can be assigned to C-O, which was associated with the large content of O element. The results suggested that content of the hydroxyl groups in HBS lignin was high, and this HBS lignin can be used as the substitution of polyols in the synthesis of PU.

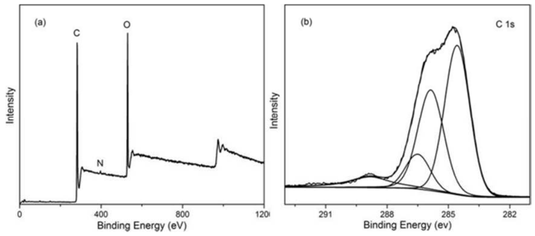

Figure 1 XPS spectra of lignin: (a) overview spectrum; (b) C 1s.

3.3 Morphology of the LPU film

The SEM pictures (Figure 2 (a-c)) revealed that the surface and cross section of the LPU film was composed of spherical nanoparticles, and the individual nanopaticle was not isolated but bonded together, which was similar with that of the HBS lignin. However, the particle size of the LPU film was smaller than that of the HBS lignin. This might be caused by the reaction between -NCO and –OH and the phase separation process. These two reasons caused the smaller nanoparticels in the LPU film. Further, the cross section and surface morphology of the LPU film was compact from the SEM images. This phenomenon was due to the solvent volatilization during the fabrication process of the LPU film, especially during the curing process. Additionally, the condensed structure resulted in the LPU film with high hardness of 0.186 GPa.

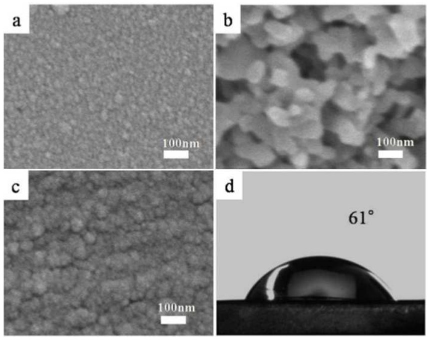

Figure 2 (a) SEM picture of surface of LPU film; (b) SEM picture of HBS lignin; (c) SEM picture of cross section of LPU film; (d) water contact angle on LPU film.

The reaction between the HBS lignin and isocyanate was confirmed by FTIR. From the FTIR results, the broad peak around 3340 cm^{-1} assigned to –NH bond appeared on spectrum of the LPU film merged with lignin –OH (3420 cm^{-1}), which indicated that the lignin was reacted with MDI. Compared to the HBS lignin, the peak around 1650 cm^{-1} of the LPU film was increased, which was assigned to urethane carbonyl. This could also confirm the reaction between the lignin and MDI. The peak at 2358 cm^{-1} which was attributed to isocyanate groups (-NCO) in MDI[27] indicated that the –NCO was excessive relative to hydroxyl groups in lignin or the reaction between hydroxyl groups and –NCO was not completely sufficient so that there were both –OH and –NCO absorption peak in the LPU film. The LPU film exhibited hydrophilicity with a static water contact angle of 61° (Figure 2 (d)), which was attributed to the hydroxyl group in the LPU film[28]. From the XRD results of the LPU films (Figure 3), the diffraction peak appeared at 2θ = 19.9°, demonstrating that there was crystal structure formed in the LPU film[29]. The results of nano-indentation test showed that the LPU film had a relative high modulus of 3.267 GPa. This might be relevant to the crystal structure of the LPU film. And this also demonstrated the reaction between lignin and MDI.

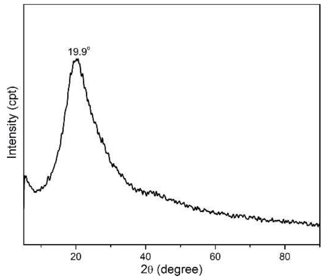

Figure 3 XRD curve of the LPU film

3.4 Thermal stability of the LPU film

3.4.1 TGA of the LPU film in N_2 atmosphere

From the TGA and DTG curves (Figure 4 (c)), the thermal degradation temperature was 253.5 °C, which was lower than that of the pure polyurethane (around 300 °C)[30] , and this was attributed to the decomposition of lignin segment at lower temperature. The degradation mechanism of lignin at around 200 °C was a dehydration reaction of hydroxyl groups in alkyl groups and heterolysis and homolysis dissociate of β-aryl ether bonds[31]. On the other hand, the onset decomposition (TOD) temperature of the LPU film (114 °C) was higher than that of HBS lignin. This was attributed to the crosslinking of isocyanate groups (-NCO), which could protect the hydroxyl groups in lignin segment from dehydration and increase the thermal stability. There were two decomposition stages of the LPU film, stage A (150~300 °C) and stage B (300~500 °C), where the sample weight decreased from 98% to 81% and 81% to 37.7%. The stage A of weight loss was dominated by the degradation of lignin, while the stage B was mainly attributed to the degradation of urethane structure of the LPU film. The weight of char residents were 30% on the base of the weight of the LPU film. This high char residue was ascribed to the high thermal resistance of lignin due to the large number of ether linkages and aromatic groups in its chemical structure.[32]

The ratio of weight loss was shown in Figure 4(b). The maximum ratio of weight loss of the HBS lignin was at 337 °C, while that of lignin segment in the LPU film was 228 °C. This might be caused by the effect of MDI and urethane groups, and this could also indicate that the degradation of monomers was usually different from that of when they in the polymers, which was caused by the chemical structure change of the end-groups when they were reacted with the other monomers for synthesis polymer.

3.4.2 TGA-FTIR of the LPU film in air

TGA-FTIR measurement was carried out in air. The TGA curve of the LPU was shown in Figure 4(d) and the TGA curves measured in N_2 atmosphere were for comparison. The TGA curve of the LPU film in air suggested that the degradation process was divided into two stages; stage A was attributed to the degradation of lignin and stage B was attributed to the decomposition of urethane structure of the LPU film. In addition, the decomposition in the stage B was divided into two steps, while in N_2 the degradation proceeded in one step. The difference was caused by the reaction between oxygen and the LPU film. The main peaks on stacked FTIR curves of the LPU film sample decomposed in air were as follows: 678 cm^{-1} (δCO2), 1160 cm^{-1}(νC-O-), 1260 cm^{-1} (-C(C=O)-O-C-), 1515 cm^{-1} (νC=C), 1705 cm^{-1} (νC=O), 2347 cm^{-1} (νCO_2, νNO_2), 3254 cm^{-1} (C-H) and 3700 cm^{-1} (νH_2O)[33]. The peak intensity of 2347 cm^{-1} was strongest, and this brought out that the element of C and N were mainly evolved in the form of CO_2 and NO_2. From the TG curve in air, the TOD temperature of the LPU film was 114 °C, which was lower than the LPU film with PEG as soft segment[31]. This indicated that the existence of a large amount of lignin segment decreased the thermal stability because of the lower thermal stability of lignin than PEG. Even though the LPU film had lower thermal stability (114 °C) in air, it was enough as coating or basement for many conditions.

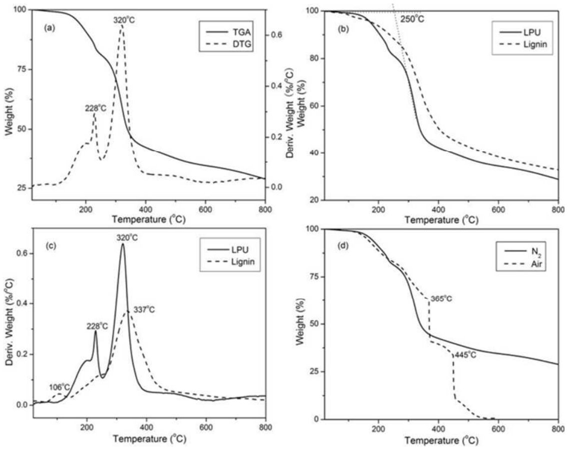

Figure 4 (a-d) Thermal properties of lignin and the LPU film

3.5 Solvent resistances of the LPU films

According to the results of swelling tests (Figure 5), the solvent resistance of the LPU films was increased with the increase of the NCO: OH molar ratio. It was clear that with the NCO: OH molar ratio increasing, the lignin without reacting with isocyanate decreased, and the crosslinking density was increased. The increasing of NCO: OH molar ratio until 1.7 resulted in the weight gain decreased quickly, and after increasing above 1.7, the decreasing ratio was slow. This might be attributed to that with the increasing of NCO: OH molar ratio, the crosslinking density was enhanced, and the effect of crosslinking density decreased. This indicated that until the NCO: OH molar ratio increased to 1.7, the crosslinking density was enough to ensure the solvent resistance to some extent. What's more, the colour of DMSO solution after swelling test (Figure 6) gradually became shallower as the increase of the NCO: OH molar ratio. Because only the lignin has a strong color when in solution, this indicated that a little lignin was not incorporated in the reaction with isocyanate or the crosslink density was low at low NCO: OH molar ratio. The insolubility of the LPU film in DMSO (swelling test solvent) and the complete solubility of lignin in DMSO confirmed the successful synthesis of a polyurethane network. The swelling test conducted in distilled water indicated that the LPU film was stable in water at 30 °C, and had low water adsorption. This trace water adsorption was corresponded with the result of static contact angle.

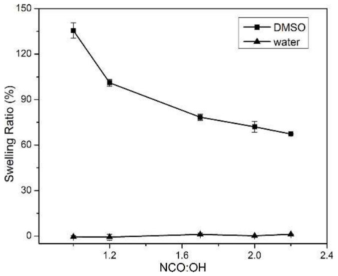

Figure 5 Effect of the NCO: OH molar ratio on the swelling behaviour in DMSO and water

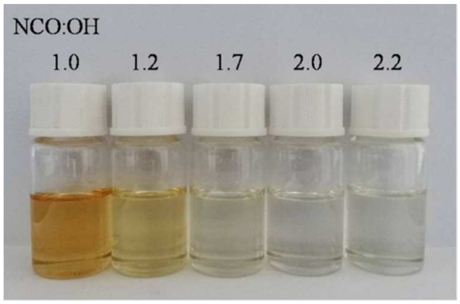

Figure 6 The colour of DMSO after swelling test

3.6 Tensile properties of the LPU films

The curves in Figure 7 revealed that the tensile strength and strain-to-failure values increased to a maximum value of 41.6 MPa and 2.2%, respectively, and then decreased with the increase of the NCO: OH molar ratio. This was attributed to that with the NCO: OH molar ratio increasing, there were more isocyanate groups to crosslink with hydroxyl groups and then increased the crosslinking density. The tensile strength of this HBS LPU was higher than that of other lignin- isocyanate polymer[34]. However, after the NCO: OH molar ratio increasing to above 1.7, the isocyanate groups became excessive, and a large number of isocyanate groups reacted with hydroxyl groups in lignin molecule, which might lead to more little molecular rather than the three-dimensional network intermolecular, and that might fabricate stiffer film with lower tensile strength and strain-to-failure values.

After swelling test in DMSO solution, the tensile strength of the HBS LPU film decreased seriously to 3.6 MPa with the NCO: OH molar ratio as 1.7. While the tensile strength of the LPU film after swelling in water was higher than that before swelling test, and this might be caused by the trace water existed in the LPU film acting as the lubricant. However, during the treatment in DMSO solution, the LPU film adsorbed a large number of solutions and was swelling, which resulted in the higher strain-to-failure value than the LPU film before being treated in DMSO. The trend of the change of the tensile strength of the LPU films either before or after swelling was same, which indicated that the influence of the NCO: OH molar ratio was greater than the swelling.

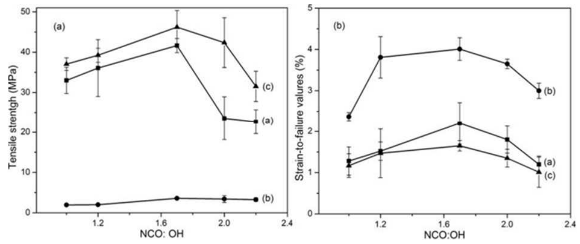

Figure 7 Effect of the NCO: OH molar ratio on the tensile strength (a) and strain-to-failure values (b) of LPU films: ((a) the LPU films without further treatment; (b) the LPU films swelling in DMSO; the LPU films swelling in distilled water.)

4. Conclusions

In conclusion, we have developed a facile and low-cost method to fabricate polyurethane film with HBS lignin as the only hydroxyl group resource using lignin modified by dissocyanate. The high C content and low ash content of HBS lignin was beneficial to prepare high values products. The large content of hydroxyl groups in HBS lignin indicated the potential values in the synthesis of PU. When the NCO: OH ratio was 1.7, the tensile strength and strain-to-failure value arrived to the maximum values of 41.6 MPa and 2.2%, respectively. After swelling test conducted in DMSO, the tensile strength decreased seriously while that had a slight increase after swelling in distilled water. From the results of TGA in N_2 and TGA-FTIR in air, the HBS LPU film can be stable under 114 °C. This method may open a new rote to utilizing natural renewable resources to design and synthesize polyurethane film for a wide range of application.

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