

# Microstructure-Property Relationship in Self-Crosslinked Non-Derivative Acetic Acid Lignin-Containing Polyurethane Membranes

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## Abstract

With the assistance of different solvents, self-crosslinked acetic acid lignin-containing polyurethane (LPU) membranes were synthesized. Compared with tetrahydrofuran and dioxane, N, N-dimethylacetamide with stronger polarity together with higher boiling point was demonstrated to be beneficial for preparing LPU particles of smaller size and enhanced binding force. It was also found that lignin domain can interpenetrate into polyurethane domain well with 43.3% lignin addition, resulting in enhanced phase mixing and better performance. In addition, relative homogeneous and smooth LPU membrane can be obtained with 2% TMP addition, while stress crack took place when TMP content was greater than 3%.

## Keywords

Polyurethane, Phase Behavior, Acetic Acid Lignin, Membrane, Microstructure

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## 1. Introduction

The utilization of renewable biomass resources in polymer has received increased attention due to their potential for substitution of petrochemical derivatives [1] [2]. Lignin, as a nontoxic, low-cost and renewable biomass resource, has been considered to replace for some petrochemical products for a number of good causes, such as relying less on petroleum resources, decreasing environment pressure caused by non-biodegradable polymers [3] [4]. In the literature, there are many publications available in using ethanol [5]-[7], acetic acid [8] [9] and banana stem [10] [11] to dissolve the lignin in the lignocellulosic material. The lignin thus obtained has higher relative

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amount of functional groups, better plastic behavior and processing performance [12] [13].

The high reactivity associated with lignin-based polyols makes them ideal for the synthesis of polyurethane (PU) [14]-[18]. For segmented PU, lignin has been extensively adopted as the thermal plastic elastomers because of their excellent mechanical and chemical characteristics [19] [20]. However, PU films prepared from the ethanol lignin (also known as Alcell lignin) and 4, 4'-diphenyl methane diisocyanate (MDI) by solution casting were very brittle [21], similar results were obtained by others [22]. This can be attributed to the aromatic nature of the hard segments of lignin and MDI, and the crosslinked structure. As a result, soft segment such as polyethylene glycol (PEG) [23] [24] can be introduced into the network to improve their thermal and mechanical properties. A maximum of 18% Alcell lignin fraction was used to prepare PU [23]. A low loading level of lignin could enhance the strength and elongation. While a high lignin loading results in decreases in the toughness and other strength properties [25]. Therefore, the incorporation of high amount of lignin to synthesize lignin-containing polyurethane with good mechanical properties and water resistance is still a hot topic.

It is well known that the physicochemical properties of PU always depend on the morphology and phase behavior, while the morphology of PU relies on the state of compatibility and microphase segregation between the soft and hard segments [19]. Three important factors can influence the formation of the phase-separated microstructure of segmented PU block copolymers: block lengths, their chemical composition and thermodynamic miscibility between the hard and soft segments [26] [27]. The hard/soft segment miscibility can be attributed to hydrogen-bonds formed between the carbonyl groups of the soft segments and urethane amide groups in the hard segments [27]. Furthermore, the cross-link density, the relative rate of network formation of each component, the rate of phase separation and composition ratio can all influence the phase continuity and domain size [28]. In addition, the polar groups in lignin tend to produce aggregated domain, in which hydrogen bonding induces supramolecular characteristics [29] [30], which may change the microstructure of polyurethane.

The literature so far has focused on modification and properties of lignin-containing polyurethane, and most of them were carried out on ethanol-(Alcell) lignin, limited publications were available on the acetic acid lignin (AL) [31]-[34]. The acetic acid process has been reported to be an effective alternative method to delignify lignocellulosic materials to prepare pulp, and it is also demonstrated to be an environmentally friendly method [35] [36]. Organic acid lignin is an optimal feedstock for many value added products due to its lower molecular weight and high reactivity [37] [38]. As to the preparation for ethanol (Alcell) lignin-containing polyurethane, tetrahydrofuran (THF) was often employed as solvent [14] [39]. However, to our knowledge, there is no systematic study available. The motivation of this work is to provide fundamental insights of utilizing AL to prepare polyurethane membranes with good mechanical properties and water resistance for plastic or rubber application. Our previous study has suggested that the thermal stability can be enhanced with the addition of lignin and trimethylolpropane (TMP, as a crosslinking agent) [34]. In this study, we introduced AL as a renewable resource to prepare PU and determined the influence of solvent, AL and TMP content on the microstructure, phase behavior, mechanical properties and water resistance of the resulting lignin-containing polyurethane (LPU) membranes. Various complementary analytical techniques, such as Environmental Scanning electron microscope (ESEM), Dynamic mechanical analysis (DMA) and X-ray photoelectron spectroscopy (XPS) were used.

## 2. Experimental

### 2.1. Materials

The following reagents were used without further purification: methylene diphenyl diisocyanate (MDI), polyethylene glycol (PEG), trimethylolpropane (TMP), N, N-dimethylacetamide (DMAc); acetic acid, HCl, dioxane, diethyl ether, all of which were from Aldrich Chemicals; the acetic acid lignin (AL) was prepared in our laboratory.

### 2.2. Preparation of AL

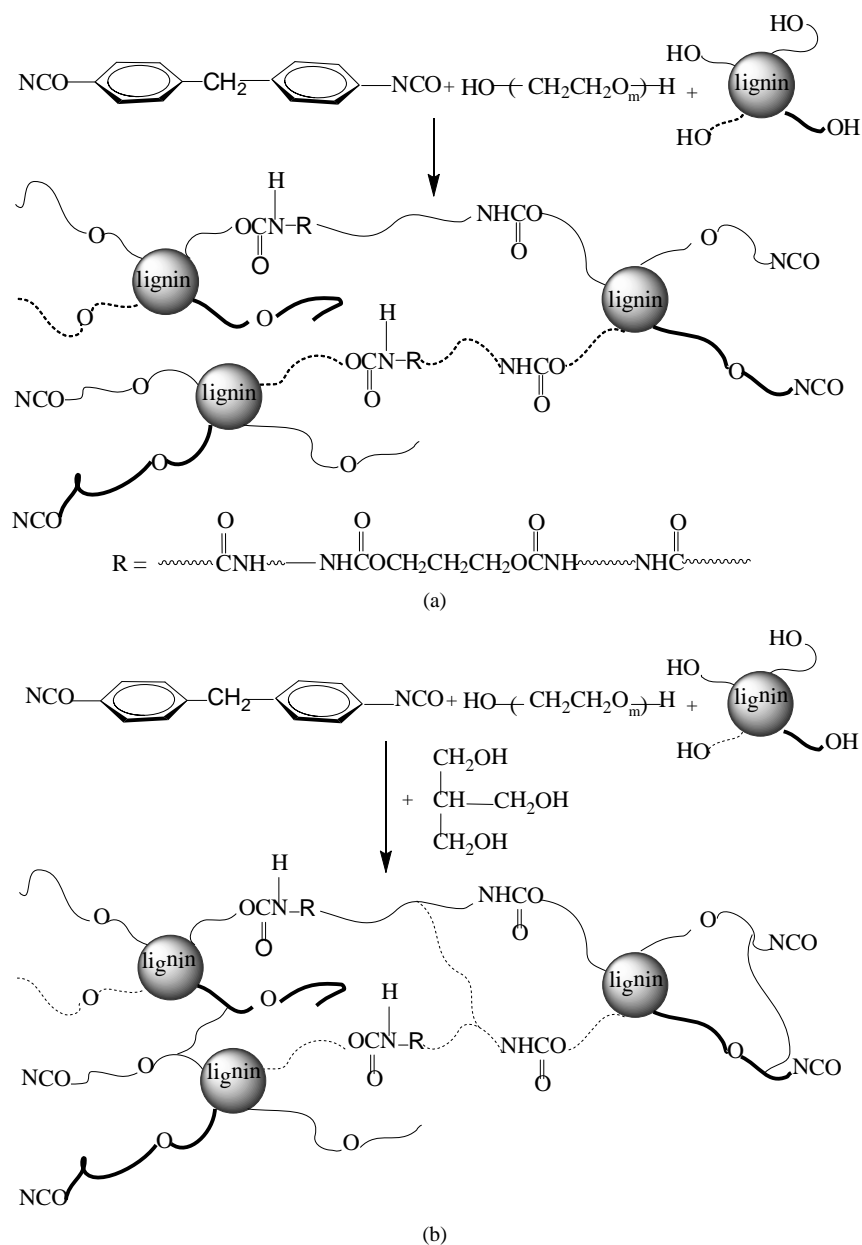
Spruce wood chips were submitted to a treatment with 90% acetic-acid solutions (500 ml) catalyzed by small amount (0.6%) of HCl (8.3 g). The mixture was refluxed using a liquor/wood ratio equal to 5 g/g for 3 h. Lignin was dissolved in the spent liquor, which was then separated by filtration, and subsequently concentrated in a rotary vacuum evaporator at 60°C. The AL was then obtained by diluting the above-obtained concentrated filtrate with deionized water (a dilution factor of 9) and filtrated. The procedure and the subsequent purification processes were given in an earlier paper [34].

### 2.3. Preparation of LPU

AL, TMP and PEG with different molecular weight were dissolved in solvent. MDI was added. The mixture was kept stirring in a water bath at 60°C for 2 h. Then the temperature was increased to 70°C, the reaction was continued for another 0.5 h. The experimental conditions for preparing LPU are given in **Table 1**, as well as their tensile strength and water absorption. The experiment schemes and model of LPU without and with TMP were illustrated in **Figure 1**.

### 2.4. Preparation of LPU Membranes

After the polymerization, the solution was immediately poured onto a PTFE plate, which was allowed to dry at room temperature for 2 days and then at 100°C for 6 h. After de-molding, the film was submitted to vacuum drying over phosphorous pentoxide for 5 days.



**Figure 1.** Experimental scheme and model of LPU (a) without TMP; (b) with TMP.

**Table 1.** Composition of lignin-containing polyurethanes.

Sample	Molecular weight of PEG	n(NCO)/n(OH)	Lignin/% <sup>a</sup>	TMP/% <sup>b</sup>	Tensile strength/MPa	Water absorption/%
PU	1000	1.7:1	0	0	13.4	73.83
LPU1	1000	1.7:1	43.3%	0	16.2	35.07
LPU2	1000	1.7:1	50.0%	0	--	--
LPU3	1000	1.5:1	43.3%	0	8.12	37.81
LPU4	1000	2.2:1	43.3%	0	--	--
LPUP1	200	1.7:1	43.3%	0	--	--
LPUP2	400	1.7:1	43.3%	0	--	--
LPUP3	600	1.7:1	43.3%	0	--	--
LPUP4	1000	1.7:1	43.3%	0	16.2	35.07
LPUP5	1500	1.7:1	43.3%	0	7.93	30.21
LPUT1	1000	1.7:1	43.3%	1%	18.8	23.63
LPUT2	1000	1.7:1	43.3%	2%	21.1	12.01
LPUT3	1000	1.7:1	43.3%	3%	14.1	14.10
LPUT4	1000	1.7:1	43.3%	5%	--	--

<sup>a</sup>With respect to PEG; <sup>b</sup>With respect to total monomer mass.

## 2.5. Swelling Test

Samples of approximately 3 mm × 3 mm were immersed in flasks containing dimethyl formamide (DMF) and allowed them to stand at ambient temperature. After 5 days equilibrium, samples were removed from DMF and patted with lint-free tissue paper to remove excess solvent, and the dimensions were measured again. The crosslink density (mol·cm<sup>-3</sup>) of the NCO-OH bonds for each specimen was estimated using Equation (1) which was proposed by Flory and Rehner [12] [40].

$$\frac{v_c}{V_0} (\text{mol/cm}^3) = \frac{-2[v + \chi v^2 + \ln \ln(1-v)]}{V_1(2v^{1/3} - v)} \quad (1)$$

where  $v_c$  is the effective number of moles of crosslinked chains,  $V_1$  is the molar volume of solvent,  $\chi$  is the polymer-solvent interaction parameter,  $v$  is the volume fraction of polymer in swollen gel ( $v = V_0/V$ ),  $V_0$  is the volume of dry polymer, and  $V$  is volume of swollen gel at equilibrium.

In order to determine  $\chi$  for our PU-DMF system, swelling tests were carried out 25°C, 30°C and 35°C. From the temperature dependency of the swelling volume,  $\chi$  value was obtained from Equation (2) [21]. In the present study, the polymer-solvent interaction parameter ( $\chi$ ) was determined to be 0.49.

$$\frac{\partial \ln v}{\partial \ln T} = \frac{-3\chi(1-v)}{5(1-\chi)} \quad (2)$$

## 2.6. Characterization

Environmental scanning electron microscope (ESEM) was carried out on a Hitachi SU-70 SEM. The sample surface was coated by carbon to remove the charge effect.

The temperature dependence of dynamic mechanical properties was conducted using an America TA Q800 dynamic viscoelastometer at an operating frequency of 1 Hz from -110°C to 200°C at a heating rate of 3°C·min<sup>-1</sup>.

The tensile strength of the films was measured on a multifunctional electronic strength tester TS 2000-S (Scientific and Technological et. Taiwan). Tensile test bars (5 × 70 mm<sup>2</sup>) were cut from hybrid films of 0.4 - 0.7 mm thickness. The standard tensile testing was performed by following ASTM 412-83.

Angular dependent X-ray photoelectronic spectroscopy (XPS) was performed on a Perkin-Elmer physical Electronic Model 5400 with a hemisphere analyzer and a position sensitive detector. The spectrometer was equipped with a Mg/K $\alpha$  (1253.6 eV) achromatic X-ray source operated at a power of 400 W and a 45° angle was used with the X-ray source. A pass energy of 89.45 eV was chosen for all angle-dependent acquisitions. The spectrometer was typically run at  $6.7 \times 10^{-7}$  Torr vacuum. A wide scan (0 - 1000 eV) was recorded for each sample, and the information of different sample depth was obtained by extending the ion sputtering time.

Contact angles were measured with a JJC- I contact angle goniometer.

The membranes were cut into circular disks by using a sharp-edged stainless steel die with inner diameter of 20 mm. The samples were dried in vacuum oven for 24 h to determine their dry weight ( $W$ ). Absorption of LPU membranes was determined by immersing the membranes in a baker of water for 24 h. After wiping off the surface water with a piece of filter paper, its weight ( $W_1$ ) was determined. The water absorption ( $WS$ ) of the membranes was calculated by

$$WS = (W_1 - W_2) / W \times 100\% \quad (3)$$

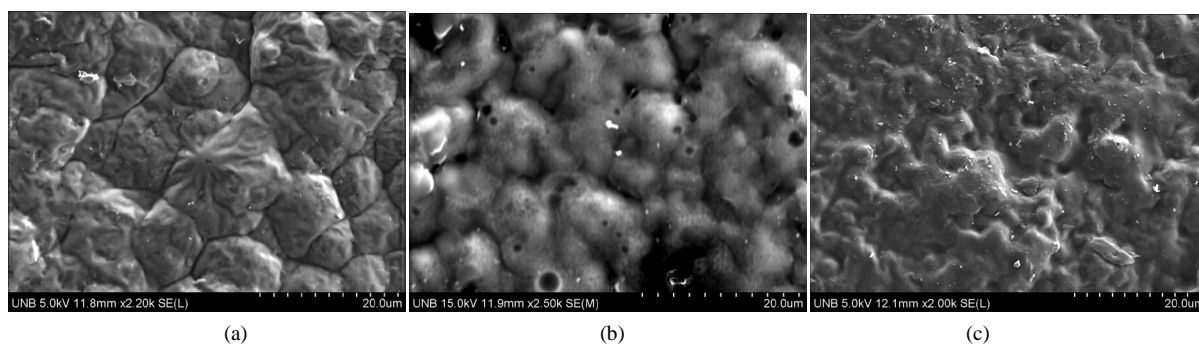
### 3. Results and Discussions

#### 3.1. Effects of Solvents on Morphology

THF, dioxane and DMAc were employed as the solvent for preparing LPU, the ESEM morphology of LPU membranes prepared was shown in **Figure 2**. The membranes prepared from THF and Dioxane were very brittle, and easy for rupture to take place in the membranes. As shown in **Figure 2**, membranes prepared from different solvents displayed totally different morphology. LPU1-THF particles had the biggest dimension with about 10  $\mu\text{m}$  in diameter; LPU1-dioxane had globular particles about 5  $\mu\text{m}$  in diameter, and the LPU1-DMAc had smallest diameter of about 2  $\mu\text{m}$  in grain shape. It was reported that PU from lignin and MDI in THF appeared as grain with dimension higher than 200  $\mu\text{m}$  [41]. In contrast, our research showed that LPU particles had much smaller particle size. This is because PEG was added into the system, so that the lignin hard segment was well dispersed into the soft segment and formed smaller domains.

Individual particles with relatively well defined boundary can be seen for the LPU1-THF membrane. In contrast, for the LPU1-DMAc membrane, no boundary is evident and the particles were dispersed in continuous phase instead. The particles of LPU1-dioxane were separated, but with less defined boundary in comparison with the LPU1-THF membrane. These morphological characteristics are consistent with the mechanical properties that the LPU1-DMAc membranes are the strongest, as shown in **Table 1**. Therefore, all of the samples in the following research were prepared by using DMAc as solvent.

The solvents used had different polarity and boiling point. The boiling point of THF, dioxane and DMAc is 65.4°C, 101°C, 166°C, and the dielectric constant is 7.5, 2.3 and 36.7, respectively, suggesting that DMAc had the highest polarity and dioxane the lowest. Our results indicate that higher polarity and higher boiling point were beneficial for the preparation of LPU particles with smaller size and stronger mechanical properties. However, as to dioxane which has higher boiling point and weaker polarity than THF, LPU showed smaller diameter, indicating boiling point acted as a predominant factor instead of polarity.



**Figure 2.** ESEM morphology of LPU1 membranes (a) prepared from THF (LPU1-THF); (b) prepared from dioxane (LPU1-dioxane); (c) prepared from DMAc (LPU1-DMAc).



### 3.2. Effects of Lignin on Morphology

The morphology of LPU membranes with different lignin content was investigated. **Figure 3(a)** showed the results at 50% AL content. In comparison with those in **Figure 2(c)**, which were obtained at 43.3% AL content, one can find that the particles of LPU1 adhere to each other while boundary among particles became clear with the increase of lignin concentration. It can be postulated that lignin can disperse into polyurethane molecular chain well with lower concentration, as well as the interpenetration of polyurethanes into lignin domains. It is well understood that interpenetration plays a significant role in enhancing the compatibility of polymer since physical interlocking prohibits the phase separation [28]. As the lignin concentration increased, self-aggregate of star-like lignin was facilitated and resulted in many supramolecular domains, which displayed as separated oblate particles and suggested enhanced phase separation. This was consistent with tensile strength results; the membrane became brittle and weak with the further increase in lignin concentration.

### 3.3. Effect of TMP Content on Morphology

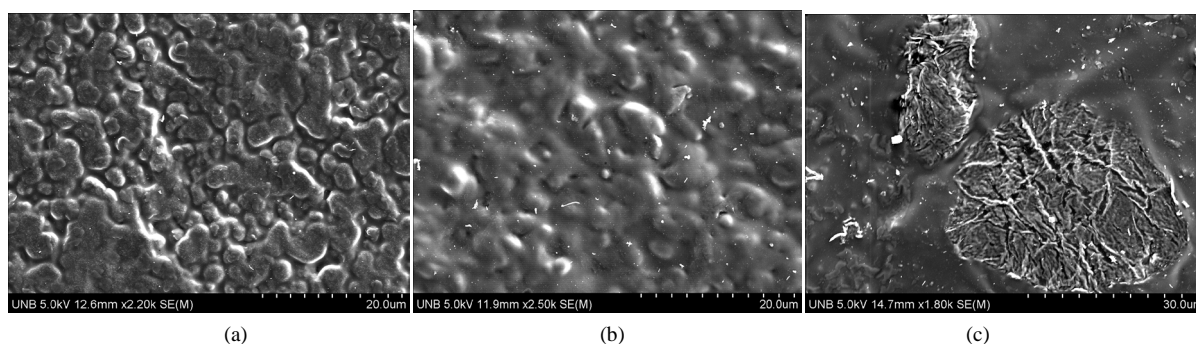
Different TMP content, namely 0%, 2% and 3% was investigated and the ESEM morphology of LPU membranes was illustrated in **Figure 2(c)**, **Figure 3(b)** and **Figure 3(c)**, respectively. Increasing the TMP content from 0% to 2%, the LPUT2 membrane became more homogeneous. The results can be explained by the hypothesis that the PU domains and lignin domains are interpenetrated into each other, due to the increased physical and chemical interlocks when two molecules are simultaneously crosslinked in the close vicinity of the other component [41]. This interlocks will minimize phase separation and improve the compatibility. As a result, the glass transition ( $T_g$ ) of polymers is increased, and the mobility of the chain is decreased, which is in agreement with DMA results.

A further increase in the TMP content from 2% to 3%, **Figure 3(c)** showed that fewer particles were evident in comparison with **Figure 3(b)** (at a 2% TMP content), further supporting the conclusion that the PU domains and lignin domains are interpenetrated into each other. However, **Figure 3(c)** showed that there are stress cracks at a 3% TMP, also the LPU obtained had much lower strength properties, which may be caused by localized crosslinking.

### 3.4. Crosslinking Density and Mechanical Properties

PEG of different molecular weight was used to prepare LPU. It was found that LPU films derived from PEG200, PEG400 and PEG600 were very brittle and unable for tensile testing. However, continuous flexible film can be obtained with PEG1000 and PEG1500. And PEG1000 was utilized for all the other experiments since the tensile strength of LPU films produced from PEG1000 was higher than that of PEG1500, as shown in **Table 2**.

It can be also observed from **Table 1** that the tensile strength increased to a maximum with the ratio of the NCO group to the OH of 1.7. It is well known that more crosslinking between -NCO and -OH and more effective hydrogen bond can be formed with a higher NCO/OH ratio, resulting in stronger polyurethane network [23] [42]. PU with lower hydroxyl functionality displayed less elastic and more brittle since crosslinking process is formed within the isocyanate groups [23]. However, it is worth noting that it was impossible to test LPU4 membrane when  $n(\text{NCO})/n(\text{OH})$  was 2.2, since it was found to be brittle, which was different from pure PU. In gen-



**Figure 3.** ESEM morphology of LPU membranes (a) LPU2; (b) LPUT2; (c) LPUT3.

**Table 2.** Effects of lignin and TMP on crosslinking density.

Sample	$V_0$	$V$	$\nu = V_0/V$	$\nu^2$	$\nu^{1/3}$	Crosslinking density $\times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$
PU	18.308	--	--	--	--	--
LPU1	21.949	73.359	0.29920	0.08952	0.66884	0.31024
LPUT1	26.162	72.816	0.35929	0.12909	0.71091	0.55047
LPUP2	17.444	29.047	0.60054	0.36065	0.84369	3.33768
LPUT3	30.421	55.011	0.55299	0.30580	0.82080	2.42933

eral, the inclusion of AL in the preparation of PU resulted in higher tensile strength can be obtained with the same  $n(\text{NCO})/n(\text{OH})$  [43]. This can be attributed to the introduction of AL.

The crosslinking density of LPU membranes with various AL and TMP contents was determined based on the swelling test in DMF, and the results are shown in **Table 2**. Without the addition of AL, the PU was totally dissolved in DMF, therefore no data can be obtained. For the addition of lignin, the LPU samples prepared swelled in DMF, however the original shape was retained. The swollen membranes still exhibit elastic and plastic behavior.

As shown in **Table 2**, the crosslinking density increased from  $0.31 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$  to  $3.34 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$  when increasing the TMP content from 0% to 2%, resulting in more crosslinking points, as illustrated in **Figure 1**. But it decreased to  $2.42 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$  when further increasing the TMP content to 3%. Evidently the optimum TMP content was 2%. The results in **Table 1** showed that the PU membranes obtained under this condition (LPUT2) had the highest tensile strength.

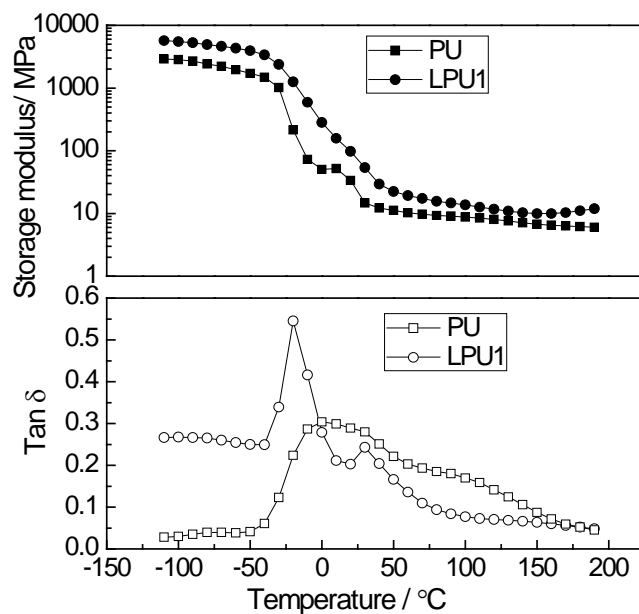
### 3.5. Dynamic Mechanical Properties of LPU Membranes

The temperature dependences of storage modulus ( $G'$ ) and loss tangent ( $\tan\delta$ ) of PU and AL-containing PU (LPU1) were presented in **Figure 4**. The  $\tan\delta$  peak is associated with the partial loosening of the polymer structure [43]. In general, the  $\alpha$  relaxation is defined as the onset of long-range, coordinated molecular motion; while the  $\beta$  transition is associated with the rotation of small side group such as methyl groups. The  $\tan\delta$  curve of PU displayed two  $\alpha$  relaxation at  $-20.03^\circ\text{C}$  and  $28.85^\circ\text{C}$ , which may be attributed to the glass transition temperature of the soft and hard segment, respectively. With the addition of AL, the two  $\tan\delta$  peaks merged together, resulting in a broadened peak at  $0.28^\circ\text{C}$ , indicating that enhanced phase mixing process occurred when AL was added.

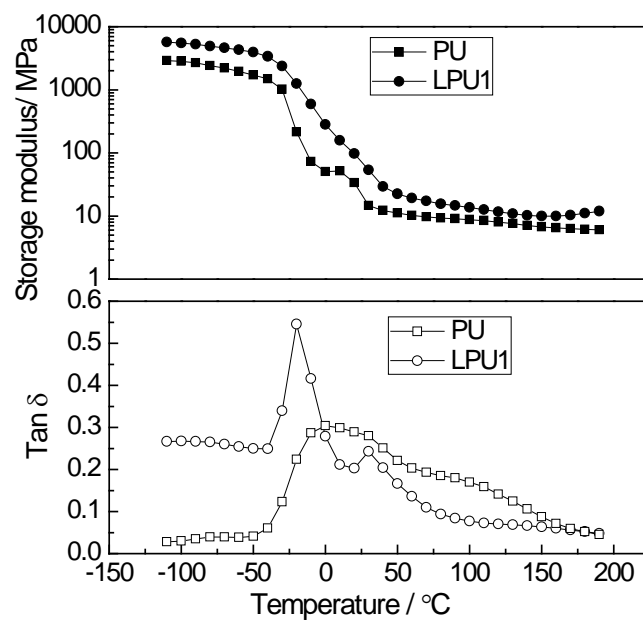
Shown in **Figure 4** was also the higher storage modulus for LPU1 than for PU, which may be attributed to enhanced intermolecular interactions from the lignin. Furthermore, a new  $\beta$  transition at  $-77.61^\circ\text{C}$  was seen for LPU1, which may be due to the rotation of side groups in lignin, as a result, the LPU1 sample can dissipate mechanical energy more effectively, thus, higher strength properties.

The temperature dependences of storage modulus ( $G'$ ) and loss tangent ( $\tan\delta$ ) of LPU1, LPUT1, LPUT2 and LPUT3 based at different TMP contents were illustrated in **Figure 5**. The glass transition temperature ( $T_g$ ,  $\alpha$  transition temperature) shifted from  $0.28^\circ\text{C}$  to  $12.45^\circ\text{C}$  when TMP content increased from 0% to 2%, while the intensity of  $\tan\delta$  peak also increased, suggesting that the thermal stability of LPU membranes increased with the increase in the TMP content. The increase in  $T_g$  also indicated that the mobility of chain for the phase separation was reduced. However, when the TMP content further increased to 3%, the  $T_g$  decreased to  $8.47^\circ\text{C}$ , suggesting the occurrence of enhanced phase separation, these results are consistent with the ESEM results, shown in **Figure 3(c)**.

The storage modulus of the glassy state for LPU, LPUT1, LPUT2 and LPUT3 displayed similar values, indicating similar structure of the soft segments for all of the samples. On the other hand, an increase in the rubbery state modulus was evident when increasing the TMP content, which may be due to the increased crosslinking density. There is a reduction in the storage modulus for LPUT3 after the  $\alpha$  transition. For copolymers with the same soft segment composition, the storage modulus is strongly dependent on the hard segment [44]. This above results further supported the conclusion that over-crosslinking occurred for LPUT3 due to the fact that TMP content is too high, resulting in the decrease in strength properties.



**Figure 4.** Temperature dependence of storage modulus and  $\tan\delta$  for PU and LPU1.



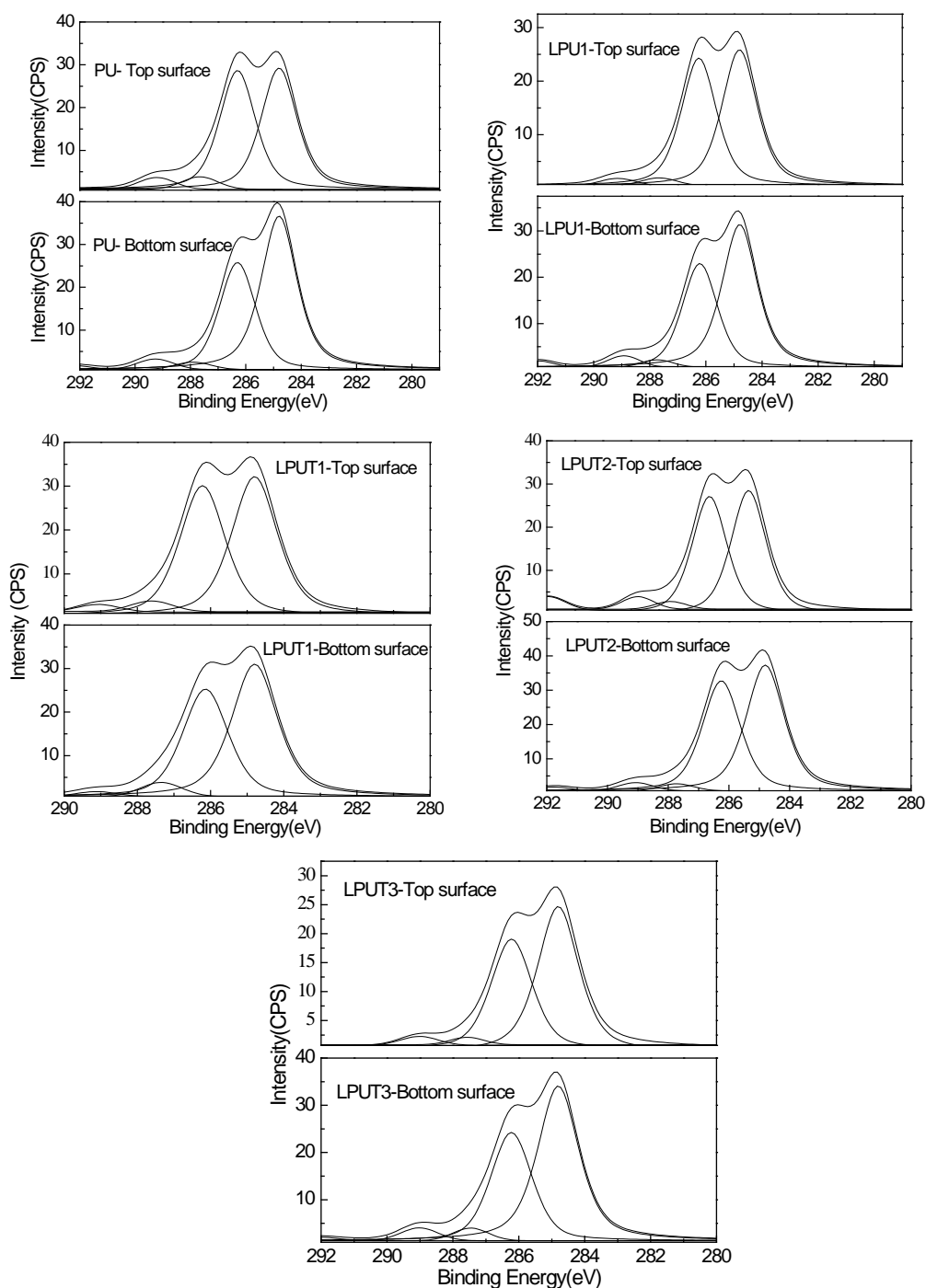
**Figure 5.** Temperature dependence of storage modulus and  $\tan\delta$  for LPU1, LPUT1, LPUT2 and LPUT3.

### 3.6. XPS Analysis

The high C1s XPS spectra of the top and bottom surfaces of LPU membranes were shown in **Figure 6**. The peak area of carbons associated with different environment and peak area ratio from the deconvoluted spectra were shown in **Table 3**. Polyurethane is well known about its surface segregation characteristics [45] [46], it is reported that low surface energy soft segment resides towards the top surface and high surface energy urethane/urea component resides inside the bulk of the polymer [45] [46].

As shown in **Table 3**, higher C-O/(C-C/C-H) peak area ratios were found on the top surface than the bottom surface of PU membrane. Similar trend was also observed for other samples, supporting the conclusion that the





**Figure 6.** The XPS spectra for surface and bottom of LPU membranes.

soft segment preferentially aggregated on the top surface. It was also found that C-O (surface)/C-O (bottom) decreased from 1.243 to 1.225 with the addition of lignin. This can be due to phase mixing process due to the introduction of lignin. And with the introduction of TMP, the C-O (surface)/C-O (bottom) kept decreasing from 1.225 to 1.000. In this research, the variation in the concentration of hard segment was achieved by changing lignin and TMP. It is apparent that the increase of lignin and TMP concentration results in the increase in the concentration of hard segment. So the results above suggested enhanced phase mixing and reduction in segregation behavior of high surface component with increased concentration of hard segment.

However, larger C-O (surface)/C-O (bottom) of 1.091 with lower C-O/(C-C/C-H) for both surface and bottom was found for LPUT3. This can be explained by the heterogeneous morphology formed with increased TMP concentration, but to some extent, this data is not representative due to the heterogeneity.

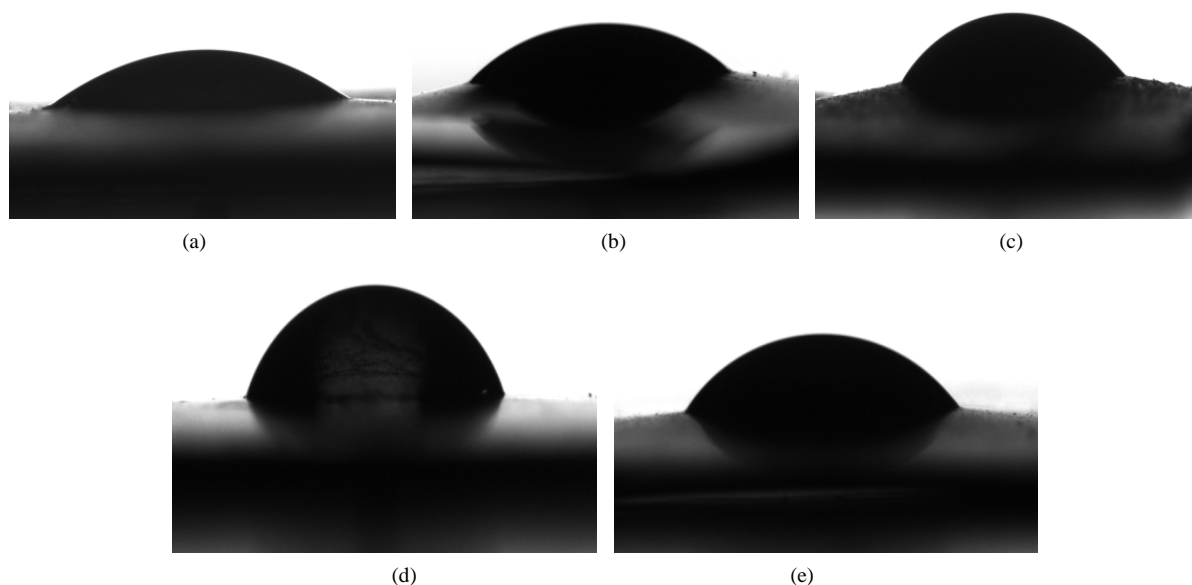
### 3.7. Water Resistance

As shown in **Table 1**, the water resistance can be improved when AL and TMP were used, that is, an increase in the crosslinking density was beneficial for the enhancement of water resistance. However, the water resistance decreased for LPUP5 when the PEG molecular weight increased.

The results of contact angle of LPU membranes were shown in **Figure 7**. It can be seen that the contact angle increased with the increase of the lignin and TMP contents, which are in agreement with the water resistance results in **Table 1**.

**Table 3.** The de-convoluted C1s peak area associated with carbons of LPU membranes.

Sample	C-C/C-H area%	C-O area%	C-N area%	C=O area%	C-O/(C-C/C-H) (A) (area ratio)	A surface/ A bottom	C-O(surface)/ C-O(bottom)
PU-surface	46.7	45.4	4.0	3.8	0.972	1.516	1.243
PU-bottom	56.9	36.5	2.2	3.1	0.641		
LPU1-surface	49.7	45.7	2.4	2.2	0.919	1.375	1.225
LPU1-bottom	55.8	37.3	2.1	3.2	0.668		
LPUT1-surface	49.8	45.4	2.8	2.0	0.911	1.186	1.107
LPUT1-bottom	53.4	41.0	4.2	1.5	0.768		
LPUT2-surface	46.7	43.2	2.2	3.5	0.925	1.094	1.000
LPUT2-bottom	51.1	43.2	2.1	2.4	0.845		
LPUT3-surface	56.3	39.4	1.8	2.5	0.700	1.092	1.091
LPUT3-bottom	56.3	36.1	3.2	3.4	0.641		



**Figure 7.** The contact angle photographs for PU and LPU membranes (a) PU (31.8°); (b) LPU1 (38.1°); (c) LPUT1 (47.3°); (d) LPUT2 (69.7°); (e) LPUT3 (51.6°).

## 4. Conclusion

Upon the addition of 2% TMP crosslinking agent as a crosslinking agent, the acetic acid lignin (AL)-containing polyurethane membranes with good mechanical properties and water resistance can be obtained by copolymerization of MDI, PEG1000 and 43.3% AL in DMAc as a solvent. The solvent with a strong polarity and higher boiling point was demonstrated to be beneficial for preparing AL-containing polyurethane. It was also found that the lignin domain can interpenetrate into polyurethane domain at the AL addition of 43.3%, resulting in enhanced phase mixing, thus, higher mechanical properties, crosslinking density and water resistance in comparison with pure polyurethane. However, lignin self-aggregation was evident, when the lignin addition was 50.0%. The addition of 2% TMP resulted in an increase in the crosslinking density (from  $0.31 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$  to  $3.33 \times 10^{-3} \text{ mol}\cdot\text{cm}^{-3}$ ). Furthermore, the increase in the glass transition temperature, together with XPS results demonstrated enhanced phase mixing with increasing crosslinking density due to the addition of lignin and TMP, which is beneficial for improving mechanical properties and water resistance. While stress crack took place and lower mechanical property was detected when TMP concentration was greater than 3%.

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