Original article

Wen-Jau Lee, Ming-Shan Hu, Chao-Yun Yu and Yi-Chun Chen*

Influences of liquefied lignin content on the properties of waterborne polyurethane prepared with different chain extenders

Abstract: Waterborne polyurethane resins (WPUs) were prepared from polytetramethylene ether glycol (PTMG) and PTMG/polyhydric alcohol liquefied lignin (LL) with isophorone diisocyanate (IPDI), and ethylenediamine (EDA) and 1,4-butanediol (1,4-BD) were used as chain extenders. The effects of LL and the kind of chain extender on the properties of the WPU suspensions and dried films were studied. WPU suspensions prepared with PTMG/LL as the polyol had higher viscosity and larger average particle dimension than those with PTMG alone. WPU films prepared with EDA as the chain extender had higher tensile strength with less tensile deformation. LL can enhance the stiffness of WPU films, but the breaking deformation decreases. Dynamic mechanical analyzer (DMA) results showed that the main effect of LL was reduced thermal activity of the soft segment. Thermogravimetric analyzer (TGA) results showed WPU films prepared with EDA as the chain extender had better heat-resistance than those with 1,4-BD.

Keywords: chain extender; isophorone diisocyanate; liquefied lignin; polytetramethylene ether glycol; waterborne polyurethane resin.

1 Introduction

Thermal plastic polyurethane (TPU) is a linear polymer prepared by reacting a diol with a diisocyanate, generally in two steps. The diol is first reacted with an excess of diisocyanate to form NCO-terminated pre-polymers, followed by reaction with a low molecular weight chain extender, such as diamine and diol, to undergo a chain-extending reaction to form polymers. TPU is a block copolymer composed of alternating soft segments and hard segments. Isocyanate and the chain extenders mainly form the hard segments. These hard segments may aggregate and form a hard domain due to the intermolecular hydrogen bond, giving stiffness and mechanical strength to PU resins. The soft segments are composed of long-chain polyols, giving polyurethane (PU) resin low-temperature flexibility and room-temperature elastomeric properties (Šebenik and Krajnc 2007).

Using water instead of organic solvents as a dispersion phase can help TPU meet the demands of environmental protection, economic benefit, and human healthy. However, PU resins are intrinsically hydrophobic, so emulsion polymerization must be used to obtain a waterborne polyurethane (WPU) resin (Noble 1997). Dimethylolpropionic acid (DMPA) is a commonly used internal emulsifier and carboxylic acid groups are introduced into the molecular structure of WPUs to give hydrophilic capability (Jang et al. 2002).

The main components used for preparing WPUs include polyol, isocyanate, internal emulsifier, neutralizer, and chain extender, all of which affect the properties of WPUs. Rahman et al. (2011) prepared WPUs by reacting aliphatic/aromatic diisocyanate with poly(tetramethyleneoxideglycol) and showed that the storage modulus and Young's modulus of WPU films increased with increases in the ratio of aromatic diisocyanate. Lin and Lee (2017) demonstrated that increasing the NCO/OH ratio of WPUs yields low viscosity and small average particle size. Films prepared with a higher NCO/OH ratio had better solvent resistance and mechanical strength because of the additional urea and amide structure. Delpech and Coutinho (2000) found that using ethylenediamine (EDA) or ethylene glycol as a chain extender would yield WPUs with poly(urethane-urea)s and only a PUs structure, respectively. Kwak et al. (2003) showed that the kind of neutralizer and chain extender used influences the properties of WPUs. They pointed out using trimethylamine as the neutralizer and 1,4-butane diamine as the chain extender gave the PU films higher thermal stability, glass transition temperature, tensile strength and storage modulus.

*Corresponding author: Yi-Chun Chen, Department of Forestry, National Chung-Hsing University, Taichung, 402, Taiwan, E-mail: chenyc@nchu.edu.tw
Wen-Jau Lee, Ming-Shan Hu and Chao-Yun Yu, Department of Forestry, National Chung-Hsing University, Taichung, 402, Taiwan

Using natural renewable resources to replace petroleum-based resources is an important environmental issue. Zavastin et al. (2010) prepared a blend membrane by mixing cellulose acetate with PU and indicated its suitability for wastewater treatment in the textile industry. Santamaria-Echart et al. (2015) indicated poly (capro-lactone) could be used as the raw materials for WPUs by reacting with isophorone diisocyanate (IPDI). Solvent liquefaction is a unique thermochemical process for converting biomasses from a solid into a liquid and the liquefied biomass can be used as a raw material for preparing synthetic resins (Pan 2011). Polyethylene glycol (PEG) is one of the most commonly used chemicals for liquefying biomass. PEG-liquefied biomass is composed of PEG and PEG-biomass derivatives contains an abundance of OH groups (Kurimoto et al. 1999; Yamada et al. 2007) and can be used as a polyol raw material for preparing PU resins after blending with isocyanate (Ge et al. 2000; Kurimoto et al. 2000).

Lignin is one of the significant components for the cell walls of plants and is the primary waste product of paper pulp manufacture from wood. An enormous amount of it is used as fuel, and only a small amount is separated and used for value-added products. However, after liquefaction, lignin can be used for manufacturing synthetic resins. Jin et al. (2011) liquefied enzymatic lignin with PEG and indicated the product had a hydroxyl number of 80–120 mg-KOH/g. Jasiukaitytė et al. (2012) investigated the structural changes of lignin during liquefaction. Concurrent degradation and condensation reactions between the degraded lignin and ethylene glycol were found during liquefaction. Xue et al. (2015) indicated the liquefaction solvent reacted with the phenolic OH groups of lignin in the product, and rigid PU foams could form after mixing with methylene diphenylene diisocyanate (MDI). The mentioned studies related to the preparation of PU resins from liquefied biomass and their derivation by blending with isocyanate compounds, but liquefied lignin (LL)-containing WPUs have not been previously found.

Based on the anthors' knowledge of liquefied biomass-based polymers, this was the first use of LL as polyol to synthesize WPUs. EDA and 1,4-BD were chain extenders that reacted with the NCO groups to form the urethane and urea structure. Polytetramethylene ether glycol (PTMG) and PTMG/LL were used as polyols to prepare WPU suspensions and films. The concept and the structure of chain extenders were shown in Scheme 1. The pinky and white background jagged line of LL and PTMG indicated the polyfunctional aromatic and bifunctional linear structures (Yamada et al. 2007; Yamada and Ono 2001). The kinds of polyols and chain extenders may influence the chemical structure,
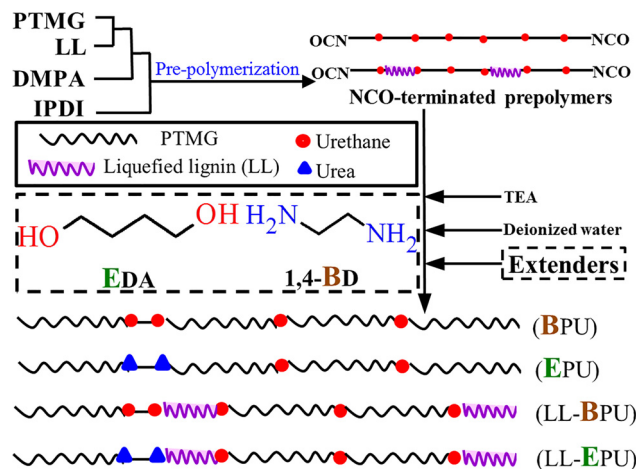
Scheme 1: Flowchart for the preparation of WPUs. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with 1,4-BD.

swelling ratio, water/solvent-resistance, mechanical and thermal characteristics.

2 Materials and methods

2.1 Materials

De-alkaline lignin (DAL), a reagent grade lignin with pH 4.1, was provided by Tokyo Chemical Industry Co., and used as the biomass component. PEG (Mn 400, Katayama Chemical Co., Ltd.), glycerol (*Choneye Pure Chemicals*), hydrochloric acid (36% HCl, Union Chemical Work Ltd.), sodium hydroxide (NaOH, Shimakyu's Pure Chemicals) and 1,4-dioxane (Avantor Performance Materials, Inc.) were used for liquefying lignin. PTMG (Mn 2000, Formosa Asahi Spandex Co., Ltd.), DMPA (Echo Chemical Co., Ltd.), IPDI (Tycoon Enterprises Ltd.), dimethyl acetamide (DMAc, *Choneye Pure Chemicals*), trimethylamine (37.8% TEA, Tedia company), EDA (*Choneye Pure Chemicals*), 1,4-butanediol (1,4-BD, Nihon Shiyaku Industries Ltd.), ethyl acetate (EA, Union Chemical Work Ltd.) and deionized water were used for preparing WPUs resins. The theoretical hydroxyl values of PEG, glycerol and PTMG were 280.5, 1827.6 and 56.1 mg KOH/g. The NCO content of IPDI determined by ASTM-D2572 was 37.8%.

2.2 Liquefaction of lignin

The liquefaction method followed Lee et al. (2018). Dealkaline-lignin was liquefied in the mixture of PEG/glycerol (9/1; wt/wt) with 10% HCl as a catalyst. The weight ratio of solvent to lignin was 2/1. The liquefaction time and temperature were 110 °C and 60 min. After the reaction, LL was diluted with 1,4-dioxane and neutralized with NaOH solution. Subsequently, the mixture was filtered remove un-LL residues, followed by evaporation in a vacuum to remove the diluter. The non-volatile content was the percentage of nonvolatile residue. Approximately 2 g LL was weighed in an aluminum cup and heated at 135 °C overnight. Then, non-volatile content was calculated using the

following equation where $(W_b - W_a)/W_b$; W_a and W_b are the weights of films before and after heating, respectively. The LL had a viscosity of 2426 cps, non-volatile content of 78.5% and a hydroxyl value of 260.9 mg-KOH/g.

2.3 Synthesis of WPU suspensions

PTMG and PTMG/LL mixture with an OH/OH molar ratio of 1/1 was used as the polyol. DMPA, IPDI, and TEA were used as internal emulsifier, isocyanate, and neutralizer, respectively. The chain extenders were EDA and 1,4-BD. The molar ratio of −OH/−NCO for polyols to isocyanate was set at 1.0/1.6. The OH/OH mole ratio of DMPA/(LL+PTMG) was set at 1.5/1. The non-volatile content of WPUs was 30%. Prior to resin synthesis, polyol was removed to a glass reactor and dried in a vacuum oven at 50 °C for 2 h. During pre-polymerization, DMPA with the weight of DMAc and IPDI were added and reacted under a N_2 atmosphere at 80 °C with constant stirring of 150 rpm. In the reaction, according to ASTM-D2572, NCO content was measured at the synthesized period. The end reaction time depended on a theoretical value of NCO content. TEA was added to undergo neutralization at 50 °C for 0.5 h, followed by adding deionized water with a stirring rate of 400 rpm. Eventually, EDA or 1,4-BD were added to undergo a chain extending reaction for 30 min, followed by stirring at room temperature overnight. The weight percentages of the components are shown in Table 1.

2.4 Characterization of WPU suspensions

A rotary viscometer (Brookfield, DV-E), surface tension meter (FACE CBVP-A3), and pH meter (Suntex SP-701) determined viscosity, pH value, and surface tension of WPU suspensions, respectively, at 25 ± 2 °C. In addition, the suspension was diluted with double the amount of deionized water. A dynamic light scattering analyzer (DLS; Malvern Zetasizer Nano-ZS) measured the particle size of WPU suspension.

2.5 Preparation of WPU films

Films were prepared by casting WPU suspensions into a box with polytetrafluoroethylene coating, and then dehydrated at room temperature for seven days. Specimens were then moved to oven at 70 °C for 2 h. Films were ca. 0.2 mm thick.

2.6 Characteristics of WPU films

Functional groups of WPU film were determined directly using Fourier-transform infrared spectroscopy (FTIR; PerkinElmer spectrum 100) by attenuated total reflectance. Samples were scanned 16 times within a spectral range of 650–4000 cm^{-1} at a resolution of 8 cm^{-1}. WPU films with the dimension of 15 × 50 mm were immersed in distilled water for 3 h and the swelling ratio was calculated by the following equation: $(W_1 - W_0)/W_1$; where W_0 and W_1 are the weights of films before and after water immersion, respectively. Water- and solvent-resistance were measured by immersing the WPU films in distilled water and ethyl acetate for one day. Weight retention was calculated by $W_3/W_2 \times 100$; where W_2 and W_3 are the weight of dried specimens before and after immersion treatment. Three repetitions were completed for each sample. According to ASTM D 638, tensile strength of the WPU films was measured by a universal strength testing machine (Shimadzu EZ Test-500N) under a loading speed of 5 mm/min. Three repetitions were performed for each condition. The viscoelastic behavior of the WPU films with a tensile mode was measured by a Dynamic mechanical analyzer (DMA) (Perkin-Elmer, DMA 8000). The specimens were heated from −90 to 70 °C at the rate of 2 °C/min and set frequency as 1 Hz. Thermal degradation was measured by a Thermogravimetric analyzer (TGA) (Perkin-Elmer; Pyris 1) from 50 °C to 750 °C with a heating rate of 10 °C/min under N_2 gas.

3 Results and discussion

3.1 Properties of WPU suspensions

Table 2 shows the properties of WPU suspensions prepared with different conditions. WPU suspensions prepared with 1,4-BD as the chain extender had a pH value of 6.7, while those prepared with EDA had weak basic suspensions. All of the WPU suspensions were in a low viscosity liquid with a non-volatile content of 30%. However, using the mixture of PTMG/LL as the polyol feedstock had a higher viscosity than that using PTMG only. Using EDA as the chain extender had viscosity higher than that with 1,4-BD. WPU suspensions had a surface tension between 37.4 dyne/cm and 40.0 dyne/cm. These values were lower than that of pure water (ca. 73 dyne/cm) because the WPU molecules were suspended particles that disperse in the aqueous phase, which may destroy the intermolecular attraction of water molecules and lead to lower surface tension. The hydrophobicity of the LL was higher than PTMG, and the LL-EPU and LL-BPU were difficult to align on the surface, so their surface tensions were slightly higher than EPU and BPU (Yen et al. 2006).

Table 1: Weight percentage of raw materials used in WPU suspensions.

LL/PTMG	Weight percentage (%)							
(OH/OH)[a]	PTMG	LL	DMPA	DMAc	IPDI	TEA	EDA (1,4-BD)	Water
0/1	18.2	0.0	1.9	3.7	8.1	1.1	0.7	66.3
1/1	11.7	2.6	2.4	4.8	10.6	1.5	1.0	65.2

[a]Molar ratio of OH/OH for LL and PTMG.

Table 2: Properties of WPU suspensions.

Code of resin	Chain extender	PTMG/LL (−OH/−OH)[a]	pH	Viscosity[b] (cps)	Surface tension[b] (dyne/cm)	Average particle size (nm)
EPU	EDA	1/0	8.6	19.3	37.4	44
LL-EPU	EDA	1/1	9.6	67.1	40.0	246
BPU	1,4-BD	1/0	6.7	5.5	38.5	48
LL-BPU	1,4-BD	1/1	6.7	10.6	40.0	205

[a]The molar ratio of −OH/−OH for PTMG and LL. [b]With 30% non-volatile content and measured at 25 °C.

DLS analysis showed WPU suspensions prepared with the mixture of PTMG/LL had an average particle size much larger than those prepared with PTMG only. The former had a value of over 205 nm, while the latter was below 48 nm because LL had a polyhydroxy-structure and the polyfunctionality (Yamada et al. 2001, 2007), making it easier to form side chains and even a three-dimensional network in the local structure during the pre-polymerization. Figure 1 shows the size distribution of WPU suspensions prepared under different conditions. EPU and BPU had a similar particle size distribution, with most of the particles below 100 nm. In contrast, LL-EPU and LL-BPU had a bimodal particle size distribution, with particles between 100 and 1000 nm. This may be due to the existence of the network structure and high molecular weight of LL-based WPUs, as mentioned above, giving the pre-polymers higher viscosity and less dispersion in water. The results showed an uneven dispersed of the pre-polymer molecules suspense in the aqueous phase and forming some larger particles.
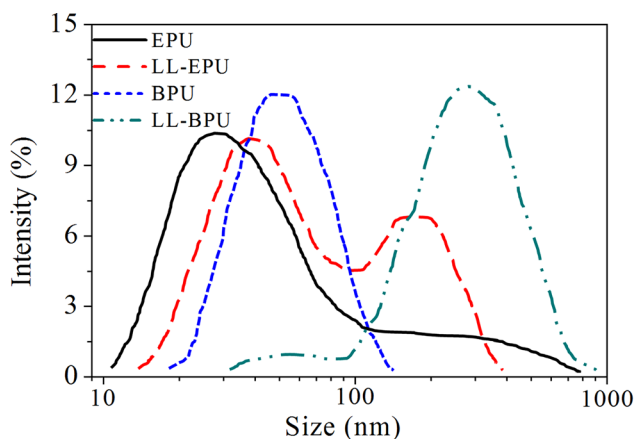
3.2 FTIR spectra of WPU films

Figure 2 shows FT-IR spectra of WPU films prepared under different conditions. The broad absorption band at around 3319 cm^{-1} and the sharp peak at 1702 cm^{-1} were attributed to the stretching vibration of N−H and C=O in the structure of urethane, respectively. Peaks at 1564 and 1237 cm^{-1} were identified as the characteristic absorption peaks of amide II (C−N−H) and amide III (N−C=O), respectively. The weak peak at 773 cm^{-1} was attributed to the out-of-plane bending vibration of COO for urethane. Peaks at 2927 and 2855 cm^{-1} were attributed to the asymmetric and symmetrical stretching vibration of CH$_2$, respectively. Peaks at 1459 and 1364 cm^{-1} were due to their bending vibration, while 1306 cm^{-1} was due to the twist vibration of CH$_2$. The sharp peak at 1104 cm^{-1} was attributed to the stretching vibration of C−O−C in PTMG (Król et al. 2015; Pérez-Limiñana et al. 2005; Yu et al. 2008).

Figure 1: Size distribution of WPU suspensions. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with 1,4-BD.
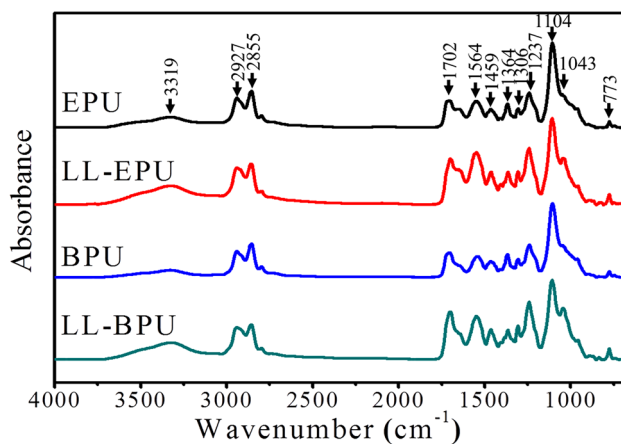

Figure 2: FT-IR spectra of WPU films. Numbers with arrows represented wavenumbers of the absorption peaks position of WPU films. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with1,4-BD. Weight percentages of PTMG and IPDI were 18.2 and 8.1% in EPU and BPU suspensions. Weight percentages of PTMG, LL and IPDI were 11.7 and 2.6 and 10.6% in LL-EPU and BPU suspensions.

When EDA was used as the chain extender, the urea structure was formed due to the reaction between the amine group of EDA and the NCO group of isocyanate. This can enhance the hydrogen bond and made the C=O stretching vibration shift to a lower wavenumber band. Delpech and Miranda (2012) also noted that the absorption of the C=O stretching vibration separated into two peaks due to the hydrogen bond. As can be seen, in addition to the peak of 1702 cm^{-1}, a peak at 1646 cm^{-1} that was attributed to the urea structure can be found for the EPU and LL-EPU that used EDA as the chain extender. However, for the BPU and LL-BPU that used 1,4-BD as the chain extender, the signal appearing around 1646 cm^{-1} showed a shoulder but not a clear peak. This shoulder may be attributed to the C=O stretching vibration of allophanate formed from the excess isocyanate reaction with a secondary amine in urethane during pre-polymerization. Further, the peak at 1043 cm^{-1} attributed to the C–O–C stretching vibration of lignin can be found for LL-EPU and LL-BPU, indicating lignin had been introduced into the structure of WPU (Boeriu et al. 2004).

3.3 Water- and solvent-resistance of WPU films

Table 3 shows the water-resistance and solvent-resistance of WPU films made with different conditions. The swelling ratio can be an index for hydrophilicity the films, with greater the hydrophilicity leading to more efficient penetration of water within the film. Comparing the chain extenders, the EPU and LL-EPU using EDA as the chain extender had a higher swelling ratio and lower weight retention following water immersion but higher weight retention of ethyl acetate immersion than those with 1,4-BD as the chain extender. This may be due to the higher proportion of urea structure in WPU films using EDA as the chain extender, which provided a stronger hydrogen bond between the molecular chains. Therefore, ethyl acetate could not easily penetrate the films, resulting in higher weight retention after the dissolving test. However, the stronger hydrogen bond gave the films better hydrophilicity, allowing more water molecules to penetrate the film and make it more easily to swell and separate. The results in a higher swelling ratio had lower weight retention following water immersion.

The WPUs prepared with a mixture of PTMG and LL had higher swelling ratio and lower weight retention following water immersion than those prepared with PTMG only since LL was a complex composition containing polyhydroxy groups. Some of the unreacted hydrophilic

Table 3: Water-resistance and solvent-resistance of WPU films.

Code of resin	Swelling ratio[a]	Weight retention (%)	
		Water[b]	Ethyl acetate[b]
EPU	0.21	57.3	91.9
LL-EPU	1.18	21.6	82.5
BPU	0.11	81.0	79.1
LL-BPU	0.73	49.6	81.8

[a]Following water immersion. [b]Following water and ethyl acetate immersion.

hydroxyl groups may persist in the WPU film, leading to more water absorption in the film. In addition, LL had components that cannot react with NCO groups and dissolve during the dissolving test (Zou et al. 2009).

3.4 Mechanical properties of WPU films

Mechanical properties of polymers can be classified into five categories based on the moduli, i.e., (a) soft and weak, (b) hard and brittle, (c) soft and tough, (d) hard and strong, and (e) hard and tough (Carraher Jr and Seymour 1984). Figure 3 displays the stress–strain curves of WPU films made from different WPUs and Table 4 had their tensile properties. The EPU film prepared with EDA as a chain extender showed hard and tough characteristics, with tensile strength and elongation at breaking of 14.8 MPa and 2326%, respectively. In contrast, the BPU film prepared with 1,4-BD as the chain extender was soft and tough, with low tensile stress though the breaking does not occur, even when elongation reaches 3700%, the detection limit of the equipment. This was because the EDA was a diamine that can provide the film a higher proportion of urea structure as well as a stronger hydrogen bond between the molecular chains. Therefore, using EDA as the chain extender gave the EPU film higher tensile strength (Delpech and Coutinho 2000).

When LL replaced part of the PTMG, the breaking elongation of LL-EPU and LL-BPU films significantly decreased but their modulus greatly increased, indicating that adding LL made the films hard and brittle. This can be attributed to the aromatic ring and polyhydroxy groups in LL, which provided the rigid structure and local cross-linking. DMA results also indicated that when soft segments of LL-EPU and LL-BPU appeared the rigidity was higher than the EPU and BPU. LL made the films more rigid but also leads to lower tensile deformation capability. In addition, the non-uniform internal stress distribution due to the heterogeneous structure within the film would also cause fracturing to occur at a lower degree of deformation
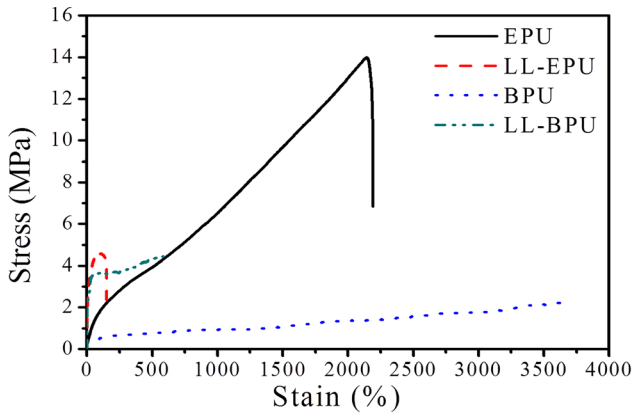
Figure 3: Stress–strain curves of WPU films. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with1,4-BD.

Table 4: Tensile properties of WPU films.

Code of resin	Strength (MPa)	Modulus (MPa)	Elongation at breaking (%)	Energy (J)
EPU	14.8 ± 1.7	3.3 ± 0.7	2330 ± 140	1.65 ± 0.28
LL-EPU	5.3 ± 0.5	16.4 ± 6.4	140 ± 20	0.05 ± 0.01
BPU	⏤[a]	1.3 ± 0.2	⏤[a]	⏤[a]
LL-BPU	6.8 ± 0.4	31.0 ± 4.8	610 ± 4	0.32 ± 0.02

[a]The samples do not break under the maximum elongation capability of the instrument.

(Ciobanu et al. 2004). Further, LL contained some components that cannot react with isocyanate (Zou et al. 2009), which would form as a shortcoming position in the interior of WPU films and accelerate damage at lower stress and strain.

3.5 DMA thermal analysis of WPU films

Figure 4 shows the DMA curves of WPU films prepared under different conditions. According to Figure 4A, the storage modulus of all WPU films decreased with higher temperature, indicating that molecular chains in the film have thermal activity. The significant reduction in storage modulus occurred at temperatures between –80 and –60 °C, indicating that a phase transition in the films occurred within this temperature range.

Comparing the properties of WPU films prepared with different chain extenders, using EDA as a chain extender gave the films higher storage modulus than those with 1,4-BD at a temperature lower than –50 °C. Comparing the neat PU and LL-containing PU films, the curves of storage

modulus for LL-EPU and LL-BPU showed a rubbery plateau following the phase transition, indicating the thermal activity at this temperature region would be decreased. However, a second phase transition was found when the temperature reached 30 °C. Conversely, the storage modulus for neat PU films, EPU and BPU, continuously declined after the temperature over the first phase transition, indicating they had a semi-crystalline structure. Therefore, a sliding motion occurred between the crystalline regions at a higher temperature and caused the storage modulus to decrease continuously (Sánchez-Adsuar et al. 2000).

According to Figure 4B, except for BPU, there were two tan δ peaks, indicating a two-phase structure within the film. The peak appearing at the low-temperature side and high-temperature side were attributed to the glass phase transition of soft segments and the motion of hard segments domain. Yen et al. (2003) pointed out having more urea structure in PU resin increases intermolecular hydrogen bond strength and the obvious phase separation. The peak at the low-temperature side was attributed to the glass phase transition of soft segments. The films of EPU and BPU had similar peak temperatures and peak heights, indicating that the kind of chain extender did not influence thermal activity of soft segments. However, the peak height clearly decreased and the peak width narrowed for LL-containing PU films, indicating that LL-containing PU films had higher rigidity and the soft segments thermal activity was limited.

The peak at the high-temperature side was attributed to the motion of hard segments domain. Comparing EPU and BPU, the former had a peak at ca. 40 °C, but the values of tan δ for BPU rose steadily increased temperature. This may be due to EPU using EDA as a chain extender having hard segments with a higher proportion of urea structure and stronger hydrogen bonds. Conversely, the hard segments of BPU were mainly composed of urethane with a weaker hydrogen bond than that of urea. Therefore, the thermal activity of hard segments increased with higher temperature, resulting in a continuous increase of the tan δ value, rather than the formation of a peak (Yen et al. 2003).

Table 5 shows the relevant parameters of the tan δ peak. The peak temperature of the phase transition of soft segments for LL-EPU and LL-BPU appeared lower than that of EPU and BPU. This reveals that when LL was introduced, the thermal activity of soft segments becomes more susceptible to temperature. However, the influence of LL on the hard segments was not significant. Comparing the peak height, LL-EPU and LL-BPU peak heights were lower for the phase transition of soft segments than those of EPU and BPU. This indicated that the addition of LL caused an
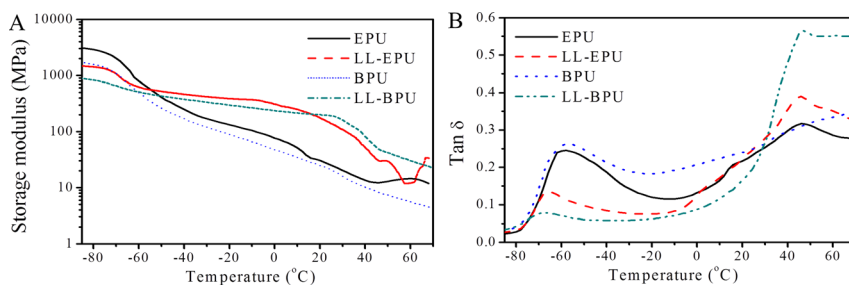
Figure 4: DMA curves of WPU films. (A) storage modulus, (B) tan δ. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with 1,4-BD.

intermolecular hydrogen bond structure that can limit the thermal activity of the soft segments and increase the rigidity of soft segments (Luo et al. 2013). However, they had a higher peak height at a high temperature, which is attributed to the phase transition of hard segments than that of EPU. These results may contribute to the regularity of the arrangement of the molecular chains being affected by the existence of LL, which increases the intermolecular distance and reduces the rigidity of the hard segments.

3.6 TGA thermal analysis of WPU films

In this study, the NCO/OH mole ratio was set at 1.6/1.0 during the pre-polymerization stage. Except for the structure of urethane, the excessive NCO would result in the formation of partial allophanate and isocyanurate in pre-polymers. When EDA was used as the chain extender, the structure of urea and biuret was formed. Whereas, if 1,4-BD was used as the chain extender, the prepared WPUs were mainly composed of a urethane structure. Ravey and Pearce (1997) and Krämer et al. (2010) pointed out the urea structure had the highest thermal stability, followed by the urethane structure, while the allophanate and biuret structures had lower thermal resistance.

Figure 5 shows the TG and DTG curves of WPU films. All WPU films showed rapid thermal degradation at temperatures between 250 and 400 °C, with similar thermal degradation behavior. However, EPU and LL-EPU had less

weight loss at temperatures lower than 250 °C than that of BPU and LL-BPU, indicating the use of EDA as the chain extender can give WPUs better thermal stability. In addition, the weight losses of LL-EPU and LL-BPU were higher than EPU and BPU, respectively. This was because some of the low molecular weight compounds existed in LL, which did not participate in the crosslink reaction and can be gasified at a lower temperature (Zou et al. 2009).

There were two peaks of the thermal degradation rate for EPU, as shown in the DTG curve. A distinct peak appeared at temperatures between 200 and 450 °C and another weaker peak appeared above 500 °C, which were attributed to the thermal degradation of urethane and polyol skeleton, respectively (Cervantes-Uc et al. 2009). There were two shoulders at the low-temperature side, which were attributed to the thermal degradation of allophanate and biuret. Compared with the other three resins, EPU had the highest peak temperature. This was because using EDA as the chain extender gave WPU the structure of urea, so WPU has higher crystallinity and thermal stability (Delpech and Coutinho 2000). Nevertheless, there was only one shoulder for BPU, due to the lack of the biuret structure when 1,4-BD was used as the chain extender. The shoulder was replaced by a peak for LL-EPU and LL-BPU, indicating that thermal resistance at low temperatures would be decreased by adding LL. However, a new shoulder appeared at a temperature over 400 °C, which was assumed to be the thermal degradation of the lignin, the component with higher heat-resistance (Wang et al. 2010).

Table 5: Parameters of the peak of tan δ for WPU films.

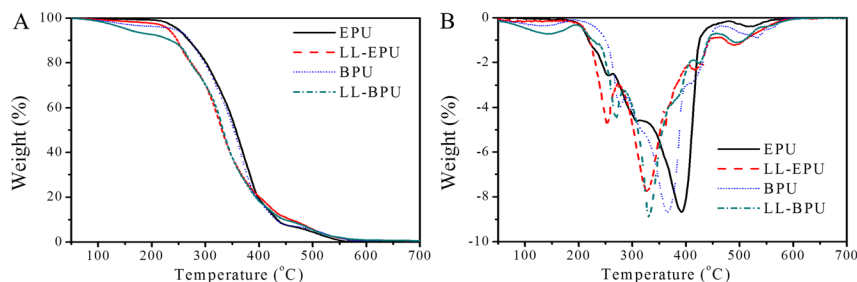| Code of resin	Peak at low temperature				Peak at high temperature			
	Onset temp. (°C)	Peak temp. (°C)	Peak height	Peak width (°C)	Onset temp. (°C)	Peak temp. (°C)	Peak height	Peak width (°C)
EPU	−75	−59	0.115	52	−23	46	0.199	77
LL-EPU	−78	−65	0.082	35	−36	48	0.295	75
BPU	−76	−56	0.226	15	−23	−	−	−
LL-BPU	−80	−68	0.050	13	−21	46	0.543	73

Figure 5: TG and DTG curve of WPU films. (A) TG, (B) DTG. EPU and LL-EPU were synthesized from PTMG and PTMG/LL mixture with EDA. BPU and LL-BPU were synthesized from PTMG and PTMG/LL mixture with 1,4-BD.

4 Conclusions

This study prepared WPU suspensions by reacting PTMG and PTMG/LL with IPDI and using EDA and 1,4-BD as chain extenders. The results showed WPU suspensions using 1,4-BD and EDA as chain extenders were weakly acidic and weakly alkaline, respectively. WPU suspensions prepared with PTMG/LL as the raw material had higher viscosity and larger average particle dimensions than those with PTMG along. FTIR analysis showed WPU films prepared with EDA as the chain extender had urethane, urea, and allophanate structures. However, only urethane and allophanate were formed for those with 1,4-BD as the chain extender. The stress–strain relationship showed EPU and BPU had hard-tough and soft-tough behavior, respectively. When PTMG/LL was used as the raw material, WPU films prepared with the characteristic were hard and brittle, with had high modulus with low breaking elongation. DMA analysis showed a two-phase structure within the films of EPU, LL-EPU, and LL-BPU. Addition of LL mainly affected the thermal activity of soft segments, making the film became with LL more rigid. Thermal degradation of WPU films mainly occurred at temperatures between 250 and 400 °C. Using EDA as the chain extender gave WPU films better heat-resistance than that with 1,4-BD.

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