

# High Molecular-Weight Thermoplastic Polymerization of Kraft Lignin Macromers with Diisocyanate

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A high molecular-weight thermoplastic lignin-based polymer was successfully synthesized by adjusting the degree of polymerization while inducing linear growth of lignin macromers via methylene diphenyldiisocyanate. The thermoplastic lignin-urethane polymer was desirably achieved in a narrow range of reaction conditions of 2.5 to 3.5 h at 80 °C in this study, and the molecular weight of the resulting lignin-based polyurethanes (LigPU) reached as high as 912,000 g/mole, which is far above any reported values of lignin-based polymer derivatives. The thermal stability of LigPU was greatly improved by the urethane polymerization, giving the initial degradation temperature ( $T_{2\%}$ ) at 204 °C, which should be compared with  $T_{2\%} = 104$  °C of the pristine lignin. This was due to the fact that the OH groups in the lignin macromers, having low bond-dissociation energy, were replaced by the urethane bonds. In dielectric analysis, the synthesized LigPU exhibited a softening transition at 175 °C corresponding to a combinatorial dual process of the dry  $T_{g,dry}$  of the lignin macromers and the softening of methylenediphenyl urethane chains. This work clearly demonstrated that a high molecular weight of thermoplastic LigPU could be desirably synthesized, broadening the lignin application for value added and eco-friendly products through common melt processes of polymer blend or composites.

*Keywords:* Lignin; Lignin-based polyurethane; Eco-friendly; Dielectric analysis; Glass transition temperature

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## INTRODUCTION

Lignin is the most abundant and renewable organic resource next to cellulose as a potential raw material for being unitized in polymer blends and composites (Feldman *et al.* 1986). The structure of lignin is a three-dimensionally crosslinked phenylpropanoid polymer linked by ether bonds between monomeric phenylpropane units. Lignin constitutes 20 to 30% of the weight of wood (Bonnini *et al.* 2005). Since there is a low decomposition temperature of lignin at around 80 to 120 °C (Kubo and Kadla 2008), the blending temperature has to be kept as low as possible when using synthetic polymers including PP, PE, epoxy, *etc.* (Pouteau *et al.* 2004). In order to enhance thermal stability,

lignin has been chemically modified by various methods using -OH groups in lignin via deacetylation, esterification, urethane reactions, *etc.* (Feldman *et al.* 1986; Yoshida *et al.* 1987). However, most lignin by-products in the pulping industry are not used desirably as value-added materials, but are still wasted by being burnt as fuel (Lora and Glasser 2002). Wide utilization of lignin for higher-value applications is limited by the crosslinked thermosetting nature of lignin macromers, its poor thermal stability, and low molecular weight (*ca.* 2000 to 4000 g/mol) (Fenner and Lephard 1981). Thus, there is a need to achieve high molecular-weight thermoplastic lignin-based polymers ensuring melt processes at elevated temperatures (Bonini *et al.* 2005; Binh *et al.* 2009; Evtuguin *et al.* 1998).

The glass transition temperatures and bond-dissociation temperatures of the pristine lignin, usually measured in the form of wood, are practically low at around 80 °C to 120 °C ( $T_{g,wet}$ ), above which odors and fumes usually are released. In this temperature region, the pristine lignin macromers are softened, resulting in a major reduction in the elastic modulus (Salmen 1984), and the thermal dissociation is accelerated by the formation of phenolic radicals from OH groups in lignin (Velmurugan *et al.* 2009). If the pristine lignin is to be thermally processed at elevated temperatures, their  $T_g$  and thermal stability should be enhanced (Jain and Glasser 1993; Wu *et al.* 2002; Nadji *et al.* 2005). Although some progress has been made on these issues through various polymerization techniques incorporating lignin macromers in polycaprolactone (Hatakeyama *et al.* 2002), polyester (Hatakeyama *et al.* 2002), polyurethanes (Evtuguin *et al.* 1998; Hatakeyama *et al.* 2002; Yoshida *et al.* 1990; Nakamura *et al.* 1992), phenolics (Feldman *et al.* 1986), urea (Feldman *et al.* 1986) *etc.*, the thermoplastic nature and molecular weight were not clearly confirmed (Nakamura *et al.* 1992; Thring *et al.* 1997). Since the pristine lignin contains multiple OH groups, *ca.*>10/mer, it is difficult to avoid the crosslinking reactions completely in these polymerization reactions to achieve high molecular-weight thermoplastic lignin-based polymers (Hatakeyama and Hatakeyama 2011). Therefore, it is believed that a fundamental understanding of the processing-property-structure relationship of the lignin-based polymerization is needed to enable the development of thermoplastic lignin-based polymers.

Among various polymerization methods with lignin macromers, the lignin-based urethane polymerization has been investigated using different diisocyanates, different reaction conditions, and different ratios of functionalities (Bonini *et al.* 2005; Yoshida *et al.* 1987; Evtuguin *et al.* 1998; Nakamura *et al.* 1992; Thring *et al.* 1992; Hatakeyama and Hatakeyama 2011). The ratio of -N=C=O to -OH in lignin was investigated by measuring  $T_g$  of the lignin-based polyurethane (Thring *et al.* 1992), but only a few previous studies have reported the thermoplastic nature or molecular weight of the resulting polymers, *e.g.*, 15,096 g/mol (Bonini *et al.* 2005) and 39,000 g/mol (Yoshida *et al.* 1987), using tetrahydrofuran (THF) as a solvent for GPC measurement. Using oligoethylene oxidediisocyanate at the polymerization temperature of 60 °C for 8 h, the glass transition temperature of the resulting lignin-based polyurethane was measured within a range from -45 °C to -28 °C, which may well be in the liquid state at the room temperature (Evtuguin *et al.* 1998). In addition, the weight loss (2 wt%) of the above lignin derivative occurred at around 95 °C to 130 °C, which is not high enough for practical application of blending in melt processing.

Since the lignin macromers contain multiple functionalities of -OH (>10/mer), the lignin-based polyurethanes (LigPU) could be easily cross-linked during polymerization, depending on reaction conditions and the activities of diisocyanate. The cross-linked

LigPU would have thermosetting characteristics that would preclude its melt-processing. Herein, the focus was on identifying the specific reaction conditions for synthesizing thermoplastic LigPU derivatives at high molecular weights ( $M_w$ ). Using methylene diphenyldiisocyanate and kraft lignin macromers, it was found that the molecular weight of LigPU was critically affected by the reaction time and temperature in a sensitive way, beyond which it became either a low molecular-weight LigPU or a three-dimensionally crosslinked one.

## EXPERIMENTAL

### Materials

The black liquor containing lignin was obtained from Moorim P&P, South Korea; the company used a broad range of leaf trees imported from Vietnam and Thailand. The N,N-dimethylacetamide (DMAc) ( $C_4H_9NO$ ) (99%) was obtained from Junsei Co., Japan. Methylene diphenyldiisocyanate (MDI) (98.0%) was supplied by Sigma-Aldrich Co., USA. Stannous octoate (2-ethylhexanoic acid tin (II) salt) (95%) was purchased Sigma-Aldrich Co., USA. Deionized (DI) water was used in all experiments.

### Extraction of Kraft Lignin from Black Liquor.

For the extraction of kraft lignin from black liquor, 1400 mL of pristine black liquor (pH=12) was mixed with 250 mL DI water and purged with carbon dioxide gas for around 3 h at 60 °C (Luong *et al.* 2011). After treating with 2000 mL of 0.2 M sulfuric acid, the pH of the solution was reduced to 9, and thereupon the lignin began to precipitate. In the next step, 1000 mL of 0.2 M alum was quickly added to reduce the pH to around 4 with vigorous mechanical stirring at room temperature. The precipitate was then washed, filtered, and vacuum-dried (Luong *et al.* 2011).

### Synthesis of Kraft Lignin-Based Polyurethane

Extracted lignin in the amount of 10 g was dissolved in 350 mL DMAc at 50 °C for 40 min. MDI was added drop-wise in 100 mL of DMAc (15 wt%) and the NCO/OH ratio was adjusted to 1.0, which was calculated based on the molecular weight and chemical structure of methylene diphenyldiisocyanate and the lignin. The MDI/DMAc mixture was then added to the lignin solution at room temperature. Subsequently, the stannous octoate (0.01 wt%) was added slowly to the above mixture under vigorous stirring (Bonini *et al.* 2005). The reaction mixture was held at 80 °C for 2.5 h, 3.0 h, and 3.5 h with mechanical stirring. The mixture was then cooled down to room temperature, washed several times with a mixture of acetone and DI water to remove impurities, and finally, freeze-dried to a constant mass.

### FTIR Spectroscopy

The FT-IR was analyzed using a Bruker IFS-66/S spectrometer, within the range 4500 to 500  $cm^{-1}$ .

### Thermogravimetry Analysis

The weight loss was measured within a temperature range from 40 °C to 600 °C at a heating rate of 10 °C/min in  $N_2$  using a TGA- 2050, TA Instrument Inc. The pristine

lignin and LigPU samples were heated to 80 °C for 24 h and kept in the environmental condition for 24 h before measurements.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was studied with a DSC TA291 from 40 °C to 350 °C at a heating rate of 10 °C/min in an N<sub>2</sub> environment.

### Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to measure the molecular weight of LigPU using AT-400 (Ltd NS2001P). The column set was calibrated using polystyrene (PS) standards in DMAc solvent. The DMAc flow rate was 1mL/min. Operation of the chromatograph was controlled by original computer software Multichro™ data by Yullin Technology.

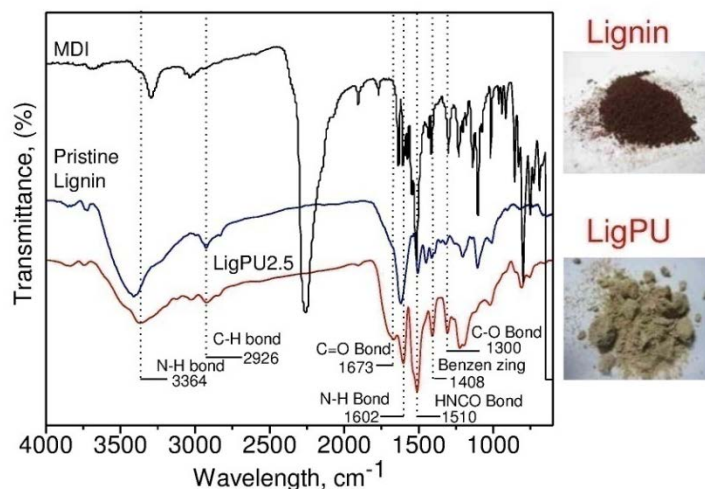
### Dielectric Analysis

The glass transition temperatures were determined using dielectric spectrometer (Novocontrol GmbH, CONCEPT 40) at different frequencies in 10 Hz to 10000 Hz from 25 °C to 220 °C at a heating rate of 3 °C/min in nitrogen.

## RESULTS AND DISCUSSION

### Chemical Structure and Molecular Weight of LigPU

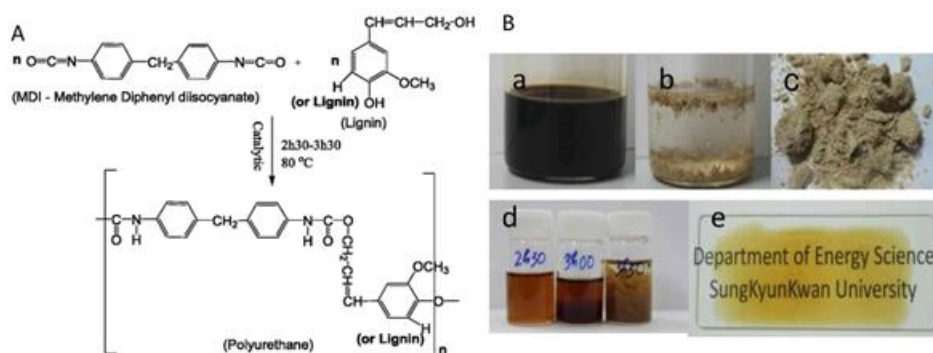
The LigPU samples synthesized in different conditions are summarized in Table 1. Figure 1 compares the FT-IR spectra of the pristine lignin, MDI, and the synthesized lignin-based polyurethane polymerized at 80 °C for 2.5 h (LigPU2.5). As can be seen clearly, three IR spectra show a medium-weak peak of the benzene ring vibration at 1408 cm<sup>-1</sup>. The peak at 1673 cm<sup>-1</sup> in LigPU2.5 spectra represents the stretching of the C=O bond in urethane groups (-NHCOO-) and ester groups, and the peak at 1602 cm<sup>-1</sup> is assigned the N-H bond stretching of urethane groups. Thus, it is confirmed that the -OH groups in lignin macromers reacted preferentially with isocyanate to form urethane chains.



**Fig. 1.** FT-IR spectra of the MDI and pristine lignin compared with the synthesized LigPU2.5 and camera pictures of pristine lignin and LigPU at room temperature

The peak at  $2926\text{ cm}^{-1}$  corresponds to the C-H bond stretching of methyl or methylene groups; this peak also appears in the spectra of both pristine lignin and synthesized LigPU2.5. The strong and broad peak at  $3364\text{ cm}^{-1}$  in LigPU2.5 spectra is a characteristic peak of N-H groups.

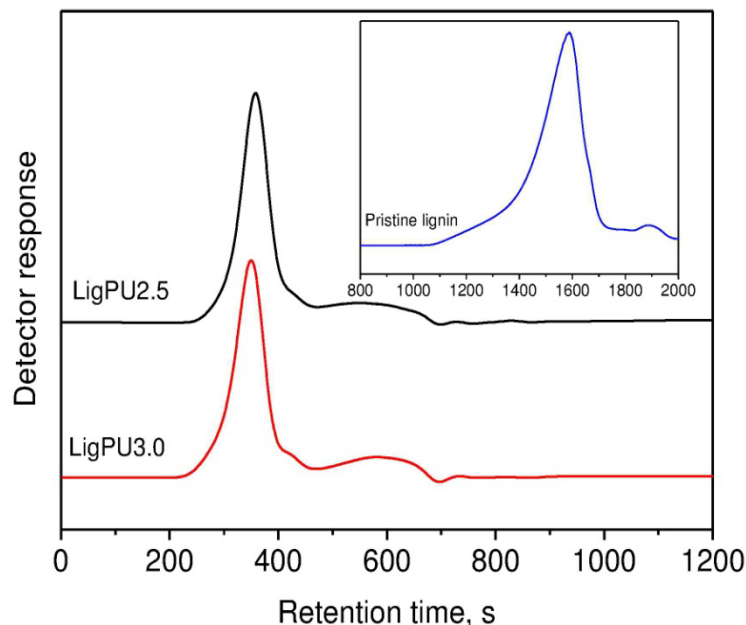
The spectrum of the synthesized LigPU2.5 shows a strong peak of a C-O bond at  $1300\text{ cm}^{-1}$ , which is regarded as formation of the NHCOO bond. In addition, the peak at  $1510\text{ cm}^{-1}$  is attributed to the complicated vibrations including H-N-C=O amide II combined motions, which confirms that the urethane reaction took place successfully between the OH groups in lignin and CNO groups in methylene diphenyldiisocyanate (Bonini *et al.* 2005). Figure 1 also shows photo images of the pristine lignin and the LigPU2.5 powder. As can be seen, the pristine lignin was dark brown but LigPU2.5 was light brown.



**Fig. 2.** (A) Schematic chemical structure of polyurethane derived from pristine lignin; (B), (a) camera images of reaction mixture, (b) lignin-based polyurethane precipitated in water after washing, (c) dried polyurethane powder, (d) shows the dissolved LigPU in DMAc, in which 2h30, 3h00, and 3h30 correspond to LigPU2.5, LigPU3.0, and LigPU3.5 samples, respectively, and (e) LigPU film formed by spin coating from 5 wt% DMAc solution

Figure 2A exhibits the synthesis pathway of LigPU, where the -OH groups in lignin react with the -CNO groups of MDI to create new urethane bonds and, therefore, the lignin macromer units are connected together. Figure 2B-a shows the black-colored mixture of kraft lignin and MDI before polymerization. After polymerization, the synthesized lignin-based polyurethane becomes a pale-brown color as precipitated by washing with water/acetone solution (Fig. 2B-b). Then, the precipitate was finally collected by filtering and drying to become the pale brown powder, as shown in Fig. 2B-c. Figure 2B-d shows three bottles of the LigPU 2.5, LigPU3.0, and LigPU3.5 dissolved in DMAc, each exhibiting completely-, partially-, or hardly-dissolved status of solutions, respectively. This demonstrates that the solubility of synthesized LigPU samples is inversely proportional to polymerization time or molecular weight.

The LigPU solution (5 wt%) was spin-coated on a glass substrate exhibiting a yellow transparent thin film (Fig. 2B-e). This confirms that the thermoplastic LigPU was successfully synthesized, allowing the solution-based thermoplastic wet processes. It is believed that this could open a new era of lignin application for being used widely as biodegradable eco-friendly thermoplastic materials.



**Fig. 3.** GPC of the pristine lignin compared with the LigPU2.5 and LigPU3.0

Table 1 summarizes the molecular weight results for pristine lignin and synthesized LigPU materials. The pristine lignin showed  $M_w$  and  $M_n$  at 5400 g/mol and 1800 g/mol, respectively, which gave a  $M_w/M_n$  (MWD) ratio of 2.8. With the LigPU2.5 synthesized at 80 °C for 2.5 h, the  $M_w$  and  $M_n$  were changed to 724,000 g/mol and 588,000 g/mol with MWD of 1.2, respectively. For 3.0 h, the  $M_w$  and  $M_n$  of the LigPU3.0 increased to be 912,000 g/mol and 694,000 g/mol, respectively, giving an MWD value of 1.3, as confirmed by the GPC eluograms (Fig. 3). When the reaction time was extended to 3.5 h, the synthesized LigPU3.5 did not dissolve in any solvents, demonstrating that the lignin macromers were cross-linked to become a three-dimensionally connected thermoset polymer.

**Table 1.** Molecular Weight ( $M_w$ ), Molecule Number ( $M_n$ ), and Molecular Weight Distribution (MWD) of the Pristine Lignin and the Synthesized LigPU2.5, LigPU3.0, LigPU3.5

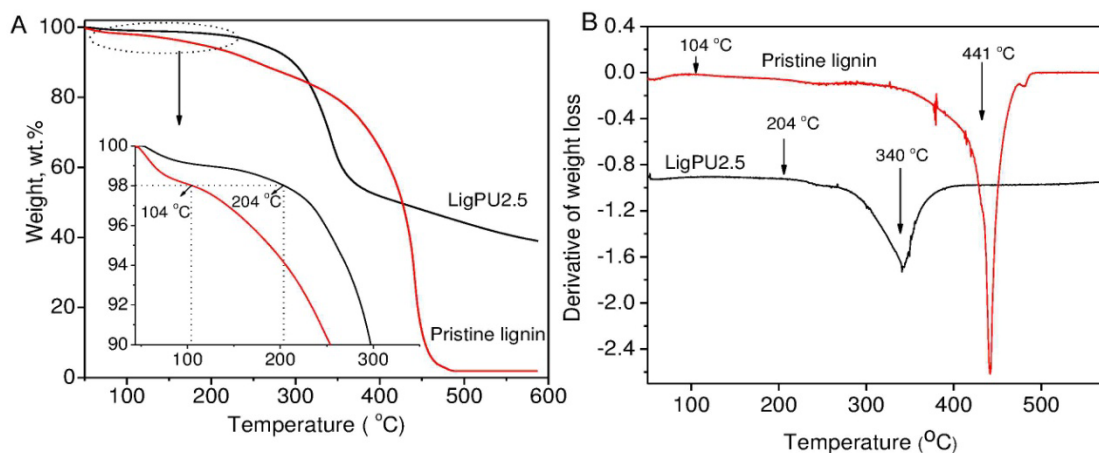
Samples	Time reaction (h)	$M_w$ (g/mol)	$M_n$ (g/mol)	MWD ( $M_w/M_n$ )
Lignin	-	5400	1800	2.8
LigPU2.5	2.5	724000	588000	1.2
LigPU3.0	3.0	912000	694000	1.3
LigPU3.5	3.5	N/A (Insoluble)	N/A (Insoluble)	N/A

Note that the polymerization temperature 80 °C for all samples.

### Thermal Stability

Figure 4 compares the TGA thermograms and the derivative curves of the pristine lignin and LigPU2.5. In order to compare the thermal stability of the pristine lignin and the LigPU2.5, in this study, the initial decomposition temperature ( $T_{2\%}$ ) is defined as the temperature where 2% weight loss occurs. Figure 4A clearly shows that the initial

decomposition temperatures of the pristine lignin and LigPU2.5 (2 wt%) were 104 °C and 204 °C, respectively. This means that the synthesized LigPU2.5 had a superior thermal stability compared to the pristine lignin.



**Fig. 4.** TGA thermograms of weight loss (A) and their derivatives (B) comparing the pristine lignin and the synthesized LigPU2.5

The derivative spectra in Fig. 4B show that the maximum rate of thermal decomposition was at 441 °C with 71% and 340 °C with 20% of weight loss for the pristine lignin and the synthesized LigPU2.5, respectively. This suggests that the lignin macromers efficiently participated in the process of the numerous crosslinking and condensing reactions to form a high-molecular polymer. Furthermore, when the temperature reached over 400 °C, the pristine lignin lost more than 95% of its weight, but LigPU2.5 maintained over 50% of its weight (Table 2). This significant difference also indicates that the synthesized LigPU2.5 had a substantially improved thermal stability. Overall, it is confirmed that common melt processes of polymers and composites can be carried out with LigPU because the thermal stability is ensured in the processing temperatures around 200 °C.

**Table 2.** Thermal Decomposition Temperatures Based on Weight Loss Analyzed by TGA Thermograms Comparing Pristine Lignin and LigPU2.5

Samples	$T_{2\%}$	$T_{10\%}$	$T_{max}$	$W_{max}$
LigPU2.5	204 °C	299 °C	463 °C	47%
Lignin	104 °C	254 °C	463 °C	95%

\* $T_{2\%}$  and  $T_{10\%}$  represent the temperature where there is 2% and 10% weight loss, respectively;  $T_{max}$  is the temperature corresponding to the maximum rate of weight loss;  $W_{max}$  is weight loss (%).

### Effect of Permittivity on the Thermal Properties of LigPU

Figure 5A shows DSC thermograms of the pristine lignin and LigPU2.5. In spite of repeated DSC experiments, the glass transition temperatures were not clearly identified, but several broad valleys and vague transitions were observed, some of which were not often reproducible in the repeated DSC experiments. This seems to be due to the nature

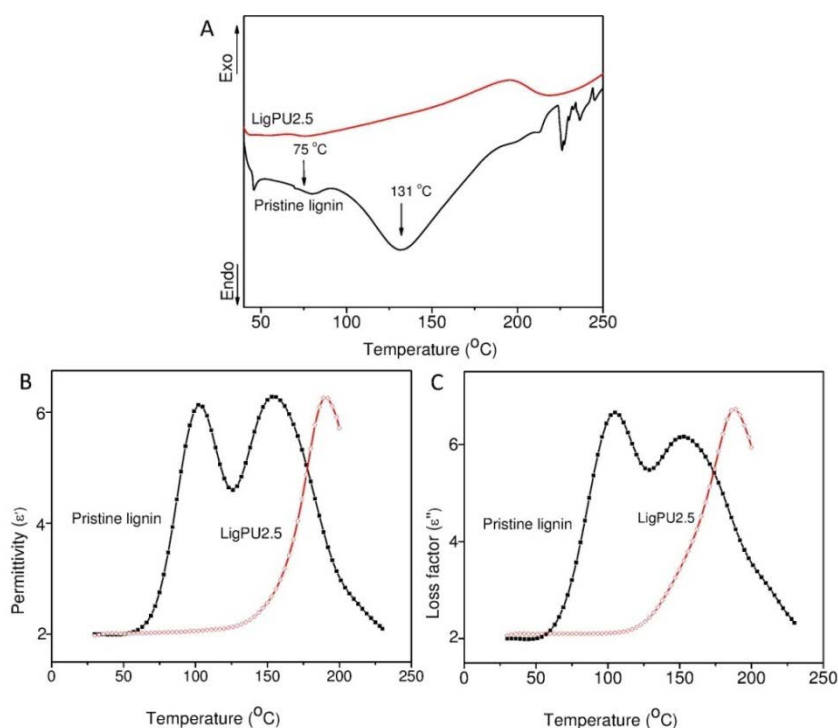
of the randomly distributed functional groups and conformational or configurationally irregularity of lignin macromers (Song *et al.* 2007).

For this reason, dielectric analysis was used to determine the glass transition temperature of the synthesized LigPU2.5; the dielectric response is very sensitive for a wide range of frequencies (Binh *et al.* 2009; Song *et al.* 2007; Duong *et al.* 2013). In dielectric analysis, a sinusoidal voltage is applied to create an alternating electric field, and the defined current is expressed in a complex form ( $\epsilon$ ), that can be separated from the conductivity and capacitive components denoted as the permittivity ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ), respectively. According to the Debye equation,  $\epsilon'$  exposes the amount of the alignment of the dipoles or the movement of ions, while  $\epsilon''$  indicates the total energy required to align the dipoles of the movement of ions;  $\epsilon'$  and  $\epsilon''$  may be expressed as follows (Song *et al.* 2007):

$$\epsilon' = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{1 + 2\pi f \tau} \quad (1)$$

$$\epsilon'' = \frac{(\epsilon_r - \epsilon_u)2\pi f \tau}{1 + (2\pi f \tau)^2} + \frac{\sigma}{2\pi f \epsilon_0} \quad (2)$$

where  $\epsilon_0$  is the absolute permittivity of free space,  $\epsilon_u$  and  $\epsilon_r$  are the unrelaxed and relaxed permittivity, respectively,  $\tau$  is the molecular relaxation time,  $\sigma$  is the ionic conductivity, and  $f$  is the frequency (Hz).



**Fig. 5.** DSC thermograms of the pristine lignin and the LigPU2.5 (A), dielectric responses of permittivity (B) and loss factor (C) measured at 10 Hz frequency as a function of temperature at a heating rate (3 °C/min). Note that the  $\epsilon'$  and  $\epsilon''$  of pristine lignin in Fig. 5B and 5C were reproduced from our previous in work (Duong *et al.* 2013) for a clear comparison with LigPU2.5 polymers.



The DEA analysis data of the pristine lignin was reported in a previous paper (Duong *et al.* 2013), and herein it was reproduced for comparison with the LigPU. Figure 4 shows the permittivity ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) at 10 Hz comparing the pristine lignin (Duong *et al.* 2013) and the synthesized LigPU2.5. As can be confirmed,  $\epsilon'$  and  $\epsilon''$  of LigPU2.5 were completely different from that of the pristine lignin. The LigPU2.5 presents a single transition in a relatively broad range of temperature of 150 °C to 200 °C (centered at 175 °C), exhibiting a large increment for  $\epsilon'$  and  $\epsilon''$  from 2.0 to 6.4 with the temperature. It is believed that this transition corresponds to the typical thermal relaxation of molecular softening, which is usually observed in most amorphous thermoplastic polymers. Taking the midpoint of the softening transition temperature of the synthesized LigPU2.5, the softening temperature may be regarded as 175 °C. Afterwards,  $\epsilon'$  and  $\epsilon''$  decreased with the temperature ranging between 200 °C and 250 °C, meaning that the material became stiffened as temperature increased.

In addition, the details of the physicochemical changes in the lignin-polyurethanes can be examined by using the complex electric modulus (CEM). In this analysis method, the complex electric modulus ( $M^*$ ) is derived from the complex dielectric constant ( $\epsilon^*$ ) as follows (Song *et al.* 2007; Maffezzoli *et al.* 1994),

$$\epsilon^* = \epsilon' + j\epsilon'' \quad (3)$$

$$M^* = M' + jM'' \quad (4)$$

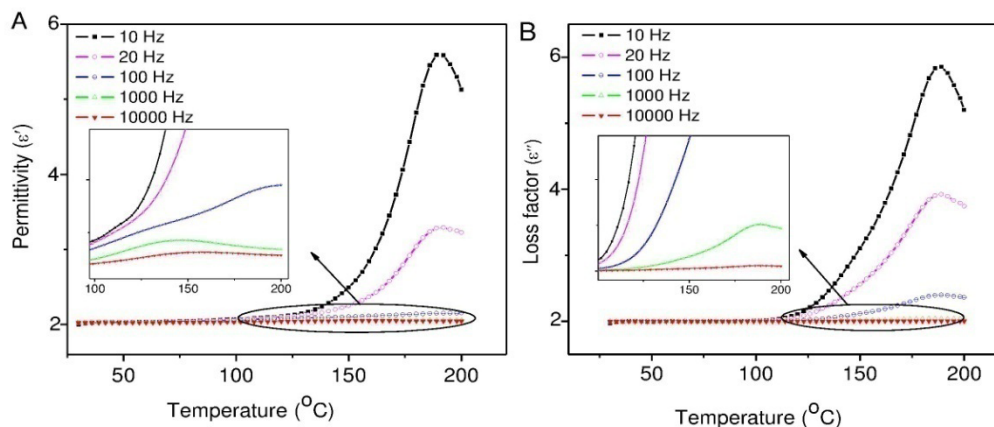
where  $M'$  and  $M''$  are the real part and the imaginary part, respectively. These are under the complex electric modulus can be expressed as:

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (5)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (6)$$

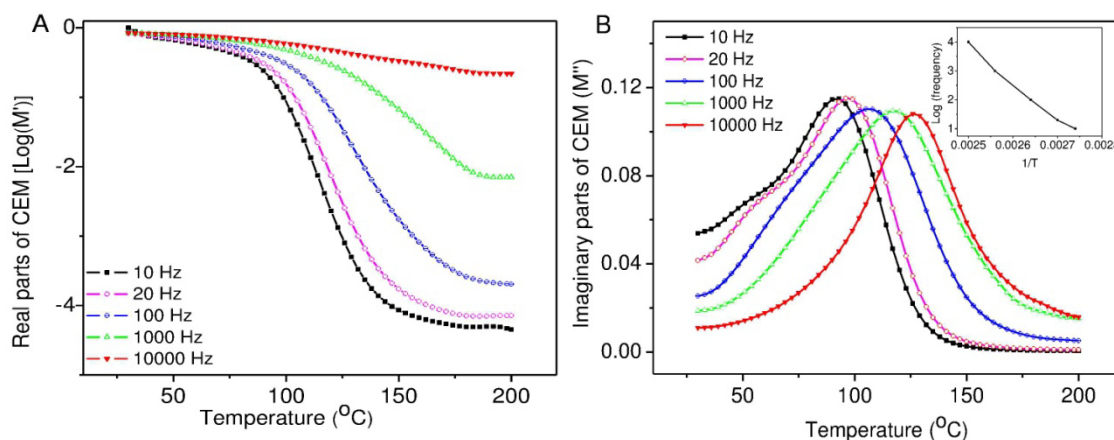
The real part of the CEM ( $M'$ ) operates like a mechanical elastic modulus and the imaginary part CEM ( $M''$ ) like a mechanical storage modulus as a function of temperature (Binh *et al.* 2009). Accordingly,  $M'$  usually decreases with increasing temperature, providing an abrupt inclining change at the transitions. For this reason  $M'$  is often used for analysis of the complicated and overlapped transitions of the inner most layers of polymers (Song *et al.* 2007).

Figures 6A and 6B show  $\epsilon'$  and  $\epsilon''$  of LigPU2.5 as a function of temperature at different frequencies ranging from 10 Hz to 10000 Hz under the dynamic heating conditions. In Figs. 6A and 6B, the transitions or peaks appear at different positions at different frequencies due to the viscoelastic nature of the LigPU polymer, which confirm the dependence of softening temperature on frequency due to the viscoelastic nature. It is considered that the molecular weight of LigPU2.5,  $M_w=724,000$  g/mol is high enough to exhibit long-range molecular relaxation (Duong *et al.* 2013). Over 190 °C, it is interesting to note that  $\epsilon'$  and  $\epsilon''$  of LigPU2.5 began to decrease with temperature, seemingly due to additional crosslinking. In fact, Figs. 6A and 6B support the results in Figs. 5B and 5C, presenting the softening temperature represented by different frequencies.



**Fig. 6.** Dielectric responses of LigPU2.5 in (A) permittivity and (B) loss factor measured at different frequencies as a function of temperature at a heating rate (3 °C/min)

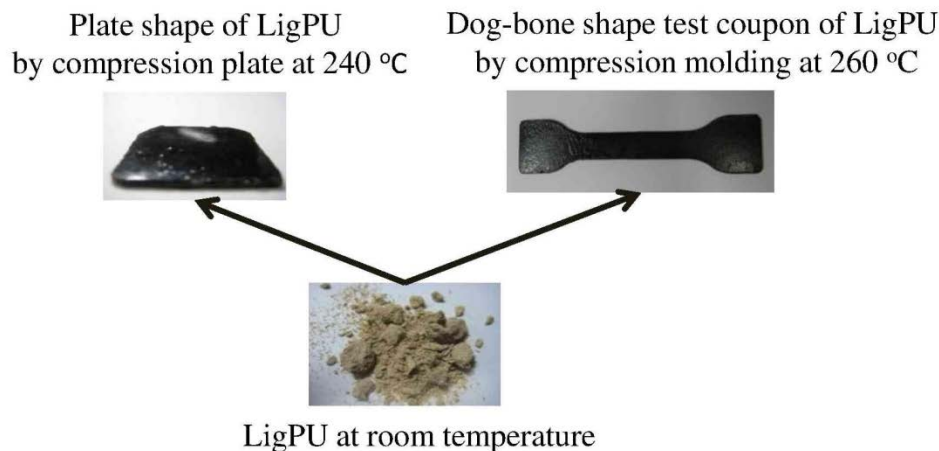
The glass transition or softening transition temperature has been measured by  $\epsilon'$  and  $\epsilon''$  and further analyzed to calculate the energy of activation for the given relaxation processes (Duong *et al.* 2013; Mijovic *et al.* 1993).



**Fig. 7.** (A) Real parts of CEM ( $M'$ ) and (B) imaginary parts of CEM ( $M''$ ) measured at different frequencies as a function of temperature at a heating rate (3 °C/min). The inset shows Arrhenius plot of the  $M''$  peaks, indicating an activation energy of 103.9 kJ/mol.

The transitions and peaks in  $\epsilon'$  and  $\epsilon''$  can be analyzed more clearly using CEM (Song *et al.* 2007), which exhibits similar features to complex modulus. Figure 7A presents  $M'$  of LigPU2.5 at different frequencies ranging between 10 Hz to 10000 Hz. It can be clearly seen that  $M'$  was decreased by several orders of magnitude with temperature from 150 °C to 200 °C, giving an inflection point at around 175 °C, which may be regarded as the softening temperature of the synthesized LigPU2.5. In addition,  $M''$  in Fig. 7B clearly shows the softening transition as peaks appearing at different positions at different frequencies due to the viscoelastic nature of the LigPU2.5. The inset in Fig. 7B shows the Arrhenius plot in the peak temperature of  $M''$  versus frequency, which can be ascribed to the temperature dependence of the viscoelastic relaxation rate of the LigPU2.5. The observed activation energy was 103.9 kJ/mol, which corresponds to

the median value of the energy barrier that has to be passed over during the softening transition temperature (Song *et al.* 2007).



**Fig. 8.** LigPU molded as a plate and dog-bone shape parts each compression-molded at 240 °C and 260 °C, respectively.

In Fig. 8, the melt processing could be used to form the synthesized polymer into various shapes at temperatures ranging from 240 °C to 260 °C without any emission of irritating vapors or odor. This clearly demonstrates that various products could be produced using traditional polymer molding processes including injection molding. This was ensured by the fact that the LigPU was thermally stable and thermoplastic in nature, which could be melt-processed at around 240 °C. As can be seen, the color of the LigPU was pale brown in powder, and it turned dark brown in melt or molded product over 240 °C. It is believed that the developed LigPU could find various applications as green materials through various melt polymer processes.

Overall, the synthesized lignin-based polyurethane showed thermoplastic characteristics in solvent solubility and softening transition temperature at around 175 °C measured in dielectric analysis. The synthesized LigPU exhibited a high molecular weight and improved thermal stability ensuring polymer thermal processing over 200 °C. It is believed that developed methodology and the LigPU can be employed in various applications of eco-friendly coating, thermoplastic blending/compounding, and composite fabrication.

## CONCLUSIONS

The molecular weight of the synthesized lignin-based polyurethanes could be controlled by polymerization conditions of time and temperature. In this experiment the results showed that a molecular weight of LigPU from 724000 g/mol to 912000 g/mol was achieved. The initial decomposition temperature of the synthesized LigPU2.5 was increased up to 204 °C. The polymerization condition of the kraft lignin with MDI was 2.5 h to 3.0 h at 80 °C.

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