Chemical and Rheological Characteristics of Thermally Stable Kraft Lignin Polycondensates Analyzed by Dielectric Properties

Le Dai Duong,[a] Nguyen Dang Luong,[b] Nguyen Thi Thanh Binh,[c] In-Kyung Park,[c] Seong Hoon Lee[d],Dea Sik Kim,[d] Yong Sang Lee,[e] Young Kwan Lee,[f] Byung Woo Kim,[f] Kwang Ho Kim,[g] Ho KyuYoon,[g] Ju Ho Yun,[h] and Jae-Do Nam[a,c,]*

In light of the difficulties and disagreements in determining the property-processing structure relations of lignin-based polymers, dielectric analysis was used to identify the thermal and rheological characteristics of a lignin-based polycondensate and the pristine lignin. Using dielectric analysis, the pristine lignin with M_w=6000 g/mol, was clearly identified as giving the wet glass transition temperature ($T_{g,wet}$) and the evolution of gases (*i.e.*, burning) at around 80 °C to 125 °C followed by subsequent cross-linking reactions over 150 °C to give the dry glass transition temperature ($T_{g,dry}$) of lignin at around 130 °C to 140 °C. Connecting the lignin macromers using sequential condensation reactions with caprolactone and sebacoyl chloride, the lignin based polycaprolactone (LigPCL) polycondensates were synthesized as a thermoplastic polymer composed of lignin macromers and aliphatic polyester chains with M_w=10500 g/mol. The synthesized LigPCL presented good thermal stability and rheological melting behavior without evolving odor or fumes. In particular, the $T_{2\%}$ (defined at 2% of weight loss) of the LigPCL and pristine lignin were 200 °C and 80 °C, respectively. The melt viscosity was measured at 10^3Pa·s at 120 °C, ensuring facile melt-blending processing with various commodity polymers to be used in eco-friendly polymer composite development.

Keywords: Lignin; Polycondensate; Polycaprolactone; Biodegradable polymer; Eco-friendly

Contact information: a: Department of Energy Science, Sungkyunkwan University, Suwon, South Korea; b: Polymer Technology, Department of Biotechnology and Chemical Technology, Aalto University, School of Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland; c: Department of Polymer Science and Engineering, Sungkyunkwan University, Suwon, South Korea; d: Hyundai Motors Company, South Korea; e: Sogang University, South Korea; f: Department of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea; g: Department of Materials Science Engineering, Korea University, Seoul 136-713, South Korea; h: Korea Automotive Technology Institute, South Korea;
**Corresponding author: jdnam@skku.edu*

INTRODUCTION

Lignin is an amorphous and cross-linked aromatic polymer providing the tissues of vascular plants with strength and rigidity. Tremendous amounts of kraft lignin or *black liquor* (*ca*. 30 million tons/year) are produced as a by-product of the pulping industry and mostly burnt as fuel, although it is one of the most useful abundant biopolymer resources (Sarkanen and Ludwig 1971; Hatakeyama and Hatakeyama 2004; Argyropoulos and Menachem 1997). Nowadays, biodegradable materials that do not contribute to a build-up of atmospheric CO_2 are inevitably required in all sectors of industry, such as the automobile, construction, and electronics industries. Moreover, the pristine lignin may be used as a novel, appropriate, and renewable feedstock (Luong *et al.* 2011; Stewart 2008; Pouteau *et al.* 2003). Relative to its potential use in common processing methods, however, lignin demonstrates a lack of thermal stability and shows no viscous flow by nature, which precludes its direct use in industrial applications. For example, the pristine lignin evolves odor and fumes when it is heated over ca. 80 ^{o}C because the molecular weight of lignin extracted from pulp-industry waste is relatively low, ranging from 10^2 g/mol to 10^3 g/mol, and the pristine lignin unavoidably contains various volatile molecules and water (Kirk Othmer 2005). These small molecules and water are associated with the processing-property-structure relation of the pristine lignin because they are strongly restrained by the hydrophilic group of lignin and behave as a part of plasticizing molecules (Hatakeyama and Hatakeyama 2004) to influence the mobility of lignin macromers. Accordingly, the physicochemical transitions of lignin, [*e.g.*, glass transition temperature (T_g)], are substantially influenced by the presence of water or small molecules.

Stemming from its unstable and heterogeneous nature, even the T_g of lignin is not agreed upon among researchers, giving different values for different pre-treatment, isolation, thermal-history, or measurement techniques such as DSC, IR spectrometry, optical density, viscoelastic modulus, NMR, and WAXS measurement conditions (Hatakeyama and Hatakeyama 2004; Feldman *et al*. 1986; Hatakeyama and Hatakeyama 2011; Hatakeyama *et al*. 2002). This lack of agreement is due to the fact that the glass transition and the evolution of volatile organic compounds contained in the pristine lignin may occur simultaneously when lignin is heated over 80 ^{o}C during measurement (Hatakeyama and Hatakeyama 2004; Vazquez *et al*. 1995). As a result, the $T_{g,dry}$, which may be defined as being measured after the heat treatment of the pristine lignin (usually up to around 200 ^{o}C), was reported at around 130 ^{o}C to 160 ^{o}C (Hatakeyama and Hatakeyama 2004; Hatakeyama and Hatakeyama 2011; Hatakeyama *et al*. 2002). However, it should be mentioned that there is a strong possibility that lignin could not only undergo volatilization of small molecules, but also crosslinking reactions simultaneously during the heat treatment due to the presence of lignin reactive sites. Consequently, the $T_{g,wet}$, which may be defined as being measured before the heat treatment, does not accord well with different researchers due to differences in sample preparation and thermal history (Hatakeyama and Hatakeyama 2004). Recently, a dielectric multi-flexing technique has proved its capability of identifying the overlapping thermal transitions of lignin-based polymer systems, and this technique has not yet been used to analyze the pristine lignin (Nguyen Thi *et al.* 2009). This technique is considered very appropriate to analyze the obliterated transitions and reactions of the lignin-based materials.

Since lignin is thermally unstable and thermosetting in nature, it cannot be melt-processed in its natural form. In order to broaden its applications, it is highly desirable to impose the thermoplastic nature as well as good thermal stability to the lignin derivatives, which would allow polymer blending or composite processes at elevated temperatures around 150 ^{o}C to 250 ^{o}C. In this sense, various reaction routes have been reported for the modification of lignin macromers as summarized in the following references (Sarkanen and Ludwig 1971; Hatakeyama and Hatakeyama 2004; Feldman *et al.* 1986; Hatakeyama *et al.* 2003; Evtugin and Gandini1996; Yoshida *et al.* 1987; Bonini *et al.* 2005; Nguyen Thi *et al.* 2009). Options include reactions via caprolactone (*CL*) (Hatakeyama and Hatakeyama 2004; Feldman *et al.* 1986; Hatakeyama *et al.* 2002), isocyanate (Feldman *et al.* 1986; Hatakeyama *et al.* 2002; Yoshida *et al.* 1987; Bonini *et al.* 2005), phenolics (Feldman *et al.* 1986), urea formaldehyde (Feldman *et al.* 1986), *etc*. Although the synthesis routes of lignin derivatives are reported, the thermoplastic characteristics of the lignin derivatives, (*e.g.,* viscosity or softening), *etc.*, have not yet been clearly identified particularly in light of the melt-processing window. This is seemingly due to the fact that the developed lignin derivatives are thermosetting and the softening transition is overlapped with the additional crosslinking reactions at elevated temperatures. Moreover, the lignin-derivatives may be practically thermosetting polymers because the number of hydroxide groups in pristine lignin molecules is more than 10. Thus, the crosslinking reaction would be unavoidable (Berry and Viswanathan 2002). Consequently, the fundamental understanding of chemorheological characteristics of thermoplastic lignin derivatives should be investigated for lignin to be used as a renewable feedstock in large-scale applications.

Polyesterification of lignin macromonomers with diacid chlorides in the presence of glycols was reported to give crosslinked polyesters, which have no viscous flow even at high temperatures (Evtugin *et al.* 1996; Zhao-Xia and Alessandro1991; Berry and Viswanathan 2002). Considering the number of -OH functionality in a lignin macromolecule, *ca*. 10, there is great possibility that the resulting lignin polyester would be easily crosslinked to become thermosets (Berry and Viswanathan 2002). Lignin has been polymerized with caprolactone, giving lignin-based polycaprolactone (LigPCL), followed by a subsequent polymerization with diisocyanate, giving LigPCL-based polyurethane (Hatakeyama *et al.* 2002). Controlling the ratio of functionalities for lignin and caprolactone, different properties of LigPCL-based polyurethane are reported. However, it is not clear whether the *CL* monomers are polymerized by themselves or with lignin macromers since the measured T_g is very low, ranging from -30 °C to -70 °C, which seems to be the T_g of homopolymerized polycaprolactone (PCL). It should be mentioned that the viscous-flow characteristics of the resulting polymer or the rheological properties have not been clearly reported.

In this study, we selectively activated the appropriate amount of -OH groups in lignin using ε-caprolactone, and subsequently polymerized the resulting lignin derivative with a diacid chloride in order to induce a linear or quasi-linear growth of the lignin derivative. The crosslinking reaction was also minimized by using triethylamine as a catalyst. Compared with the pristine lignin, the chemorheological transitions of the developed LigPCL polycondensate were thoroughly investigated. In particular, the overlapped transitions of $T_{g,wet}$, $T_{g,dry}$, volatilization, and high-temperature crosslinking reactions of the pristine lignin were clearly identified using dielectric analysis. The viscosity measurement demonstrates that the resulting lignin-based polycondensate exhibitsa thermoplastic nature and can be used for most thermoplastic blending and composite processes.

EXPERIMENTAL

Materials

The black liquor was a commercial byproduct received from Moorim P&P, South Korea; the company used a broad range of leaf trees imported from Vietnam and Thailand. Sebacoyl chloride (*SC*) ($C_{10}H_{16}O_2Cl_2$) and ε-caprolactone (*CL*) ($C_6H_{10}O_2$) (99%) were purchased from Sigma-Aldrich Co., USA. N, N-dimethylacetamide (DMAc) (99%) was supplied by Junsei Co., Japan. Triethylamine (TEA) (99%) was obtained from Sam Chun Co., South Korea. Deionized (*DI*) water was used in all experiments.

Extraction of Kraft Lignin from Black Liquor

In our previous paper, lignin was extracted successfully from black liquor by precipitation with an aluminum potassium sulfate dodecahydrate alum solution (Luong *et al.* 2011). 1000 mL of pristine black liquor (pH=12) was purged with carbon dioxide gas for around 30 min at 60 °C. After treating it with carbon dioxide gas, the pH of the solution was reduced to 9 and thereupon the lignin began to precipitate. In the next step, 5000 mL of 0.2 M alum was quickly added to reduce the pH to 4 with vigorous mechanical stirring at room temperature. The precipitate was then washed, filtered, and vacuum-dried (Luong *et al.* 2011).

Synthesis of Lignin-Based Polycaprolactone Polycondensate (LigPCL polycondensate)

Extracted lignin in the amount of 2.5 g was dissolved in 22.5 mL of DMAc at 50 °C for 30 min. Based on the molecular weights of *CL* (114 g/mol) and a lignin repeating unit (180 g/mol), which correspond to coniferyl alcohol (Kirk-Othmer 2005), the molar ratio of *CL* to -OH groups in lignin, $[CL]/[\mathrm{OH}]_{\mathrm{lignin}}$, was fixed at 5 in this study. *CL* was added to the lignin solution at room temperature and then held at 130 °C for 17 h to synthesize the LigPCL. Subsequently, based on the molecular weight of 239 g/mol for *SC*, the molar ratio of $\text{-COCl}_{(SC)}$ to $\text{-OH}_{(\mathrm{lignin})}$, $[\mathrm{COCl}]/[\mathrm{OH}]_{\mathrm{lignin}}$, was fixed at 2. *SC* was dissolved in DMAc (20 wt%) and mixed with the synthesized LigPCL mixture at room temperature. The TEA (TEA/*SC* molar ratio of 1) was then added slowly to the above mixture under vigorous stirring. Subsequently, the reaction mixture was held at 120 °C for 12 h under mechanical stirring. The final polymerization mixture was then filtered and washed with water several times. The precipitate was finally collected by filtering and was dried.

FTIR Spectroscopy

The infrared (FTIR) spectra of the lignin and LigPCL polycondensate were analyzed using a Bruker IFS-66/S spectrometer.

Thermogravimetry Analysis

The weight loss behavior was measured by a thermogravimetric analyzer (TGA-2050, TA Instrument Inc.) from 50 °C to 700 °C in N_2 at a heating rate of 10 °C/min. The pristine lignin and LigPCL samples were heated to 70 °C for 24 h and kept in the environmental condition for 24 h before measurements.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed with a DSC 6100 (SEICO) from -100 °C to 300 °C at a heating rate of 10°C/min in an N_2 environment.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to measure the molecular weights of lignin using Agilent 1100S. The column set was calibrated by the use of monodisperse poly (methyl methacrylate) (PMMA) standards in THF solvent.

Dielectric Analysis

The glass transition temperatures were determined using a dielectric analysis (DEA) spectrometer (Novocontrol GmbH, CONCEPT 40) at different frequencies of 10

Hz to 10000 Hz from 25 °C to 220 °C at a heating rate of 3 °C/min in a nitrogen gas flow.

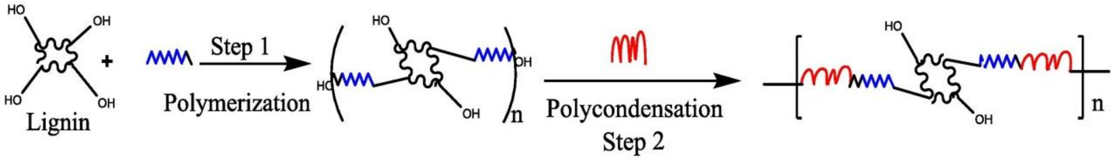
Viscosity

The viscosity was measured by using MCR300 from 30 °C to 200 °C at a heating rate of 5 °C/min. The measurement was carried out by a plate-plate measurement system PP 25 (Φ=25 mm) with thick setting of 1 mm, and the shear rate increased from 1 to 100 s^{-1}.

RESULTS AND DISCUSSION

Reaction Route of LigPCL Polycondensates

As shown in Scheme 1, the LigPCL is synthesized by the ring-opening polymerization of ε-caprolactone with the hydroxyl groups in the lignin macromonomers (Hatakeyama *et al.* 2002), where the hydroxyl groups in the lignin macromolecules act as initiating agents for the ring-opening reaction of the cyclic ε-caprolactone monomers. In addition, the OH of CL is more active than pristine lignin because of the stereoscopic hindrance stemming from the alkyl and benzene groups, the caprolactone reaction enhances the mobility of pristine lignin molecules and increase the inter-molecular distance of OH groups. The resulting lignin-*CL* polycondensate undergoes the polycondensation reaction with -COCl groups in sebacoyl chloride while being catalyzed by triethylamine. The key in this sequential reaction is to induce a linear growth of lignin macromers while minimizing the crosslinking reaction with *SC*. Therefore, the selective capping of -OH groups in lignin macromers with *CL* is needed to give *ca.* two hydroxyl groups remaining in the lignin macromers after *CL* capping; this is also one of the key steps to control the reaction conditions when the PCL end groups are further connected with *SC* to give linear or quasi-linear lignin polycondensates.



Scheme 1. Schematic synthesis route of the LigPCL through the polymerization with ε-caprolactone (step 1) and the polycondensation reaction between LigPCL and sebacoyl chloride catalyzed by triethylamine (step 2)

Thermal Stability

Figure 1 compares the TGA thermograms (Fig. 1A) and weight loss derivative curves (Fig. 1B) of the pristine lignin and the synthesized LigPCL polycondensate. In order to compare the thermal stability in the early stage of weight loss, the $T_{2\%}$ was defined as the temperature at which the weight loss of 2% occurs. It is believed that $T_{2\%}$ is important because lignin usually evolves odor or fume accompanied by weight loss in the early stage of weight loss (Zhao-Xia *et al.* 1991). In this study, the $T_{2\%}$ of the pristine lignin was measured at 80 °C, while that of the synthesized LigPCL polycondensate was 200 °C. Likewise, at the 200 °C weight loss of the pristine lignin was decreased 6% while the LigPCL only 2%. This shows that the synthesized LigPCL polycondensate had substantially improved thermal stability allowing common polymer and composite melt processes to be used at around 180 °C to 200 °C. It is believed that the low molecular weight lignin molecules are desirably connected in the LigPCL polycondensate to form larger molecules. In addition, the hydrophilic nature of the pristine lignin substantially decreased through the condensation reactions of hydroxide groups in lignin, which results in a minimal amount of evolution regarding water in LigPCL. The final TGA residue of the LigPCL polycondensate was lower than that of the pristine lignin because PLC was included in the LigPCL polycondensate chains.

From examining the pristine lignin material, the thermal history or heat treatment changes the physicochemical states of the pristine lignin, which is clearly demonstrated in Figs. 1C and 1D. Comparing the pristine lignin samples before and after the thermal treatment at 200 °C, the C-OH stretching peaks at 1264 cm^{-1} and 1022 (primary alcohol) cm^{-1} disappear and the peaks at 1110 cm^{-1}, which can be ascribed to the C-O-C ether bond, appear after the thermal treatment. The color of the samples also changes from brown to black. In addition, the pristine lignin dissolves well in DMAc, but the thermal-treated lignin does not. Overall, it is clearly shown that the pristine lignin sample is three-dimensionally crosslinked by the thermal treatment at 200 °C, seemingly through the homopolymerization of -OH groups in lignin macromers to form the ether linkage, as displayed in Fig. 1D and 1C. Figure 1demonstrates that the pristine lignin cannot be thermal-processed over 100 °C because fumes are generated and the lignin molecules could become crosslinked.

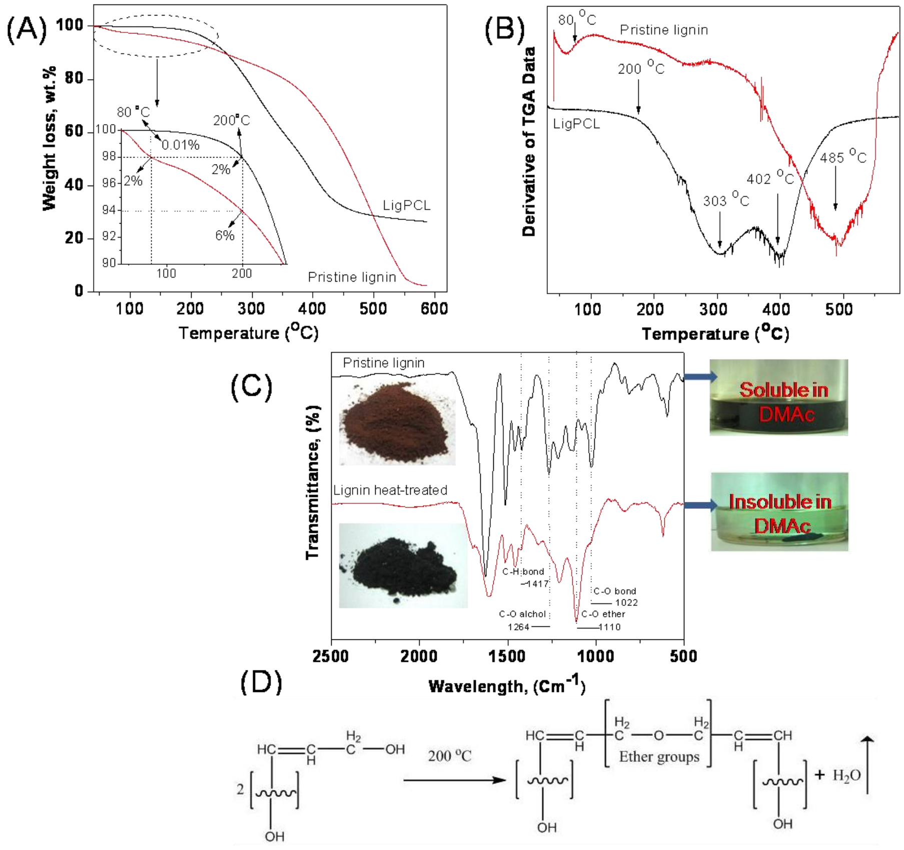


Fig. 1. TGA thermograms of weight loss (A) and their derivatives (B), comparing the pristine lignin and the synthesized LigPCL polycondensate. The FT-IR spectra of the pristine lignin at room temperature at 30 °C compared with the lignin treated at 200 °C (C), and crosslinking reaction of pristine lignin (D).

Dielectric Properties of Pristine Lignin

The physicochemical transition of the pristine lignin is further investigated in Fig. 2 using a dielectric analysis multiplexing technique, which allows the obliterated and overlapped transitions to be analyzed in a sensitive way that cannot usually be achieved by way of other analysis techniques (Nguyen Thi *et al.* 2009; Song *et al.* 2007; Senturia and Sheppard 1986). In dielectric analysis, the current obtained when a sinusoidal voltage (the excitation) is applied in an alternating electric field gives a complex form that can be separated from the conductivity and capacitive components referred to as the permittivity (ε') and dielectric loss (ε'') (Nguyen Thi *et al.* 2009). The experimental results are usually shown in plots of permittivity (ε') and dielectric loss (ε'') as a function of frequency with temperature as a parameter, or as a function of temperature with frequency as a parameter. Such data has been generated for many polymeric materials, for which much has been learned about the molecular motions in polymer, relaxation, transition mechanisms, and morphological (Mijovic *et al.* 1993). According to the Debye function, ε'' corresponds to the amount of energy required to align the dipoles or the movement of ions, while ε' represents the total alignment of the dipoles to the electric field. The quantities ε' and ε'' are then calculated from this measured amplitude and phase change, which can be expressed as follows (Song *et al.* 2007; Maffezzoli *et al.* 1994),

$$\varepsilon' = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{1+2\pi f\tau} \tag{1}$$

$$\varepsilon'' = \frac{(\varepsilon_r - \varepsilon_u)2\pi f\tau}{1+(2\pi f\tau)^2} + \frac{\sigma}{2\pi f\varepsilon_o} \tag{2}$$

Where ε_r and ε_u are the unrelaxed and relaxed permittivity, respectively. The relaxed permittivity determines the maximum dipolar alignment with the given temperature and chemical state (Senturia and Sheppard 1986), σ is the ionic conductivity, ε_o is the absolute permittivity of free space (ε_o=8.85.10^{-12} F/m), τ is the molecular relaxation time, and f is the frequency (Hz) (Nguyen Thi *et al.* 2009; Song *et al.* 2007). In the case where the dipole term may be neglected since ionic movement is dominant, then ε'' can be used to calculate the ionic conductivity:

$$\sigma = 2\pi f\varepsilon''\varepsilon_o \tag{3}$$

According to Equation (3), the ionic conductivity usually shows a frequency-dependent dipolar behavior in solid-state transitions such as T_g, but exhibits a frequency-independent feature when the ions are free to move in the liquid state, (*e.g.*, the onset of viscous flow or viscosity minimum) (Song *et al.* 2007; Senturia and Sheppard 1986; Maffezzoli *et al.* 1994).

Figure 2 presents ε' and ε'' of the pristine lignin sample measured at various frequencies, 10 Hz-10000 Hz, as functions of temperature under a dynamic heating condition at 3 ^{o}C/min. Clearly, ε' and ε'' of the pristine lignin in Figs. 2A and 2B strongly depend on frequencies due to viscoelastic characteristics of polymers. It should be addressed that the peak positions of ε' and ε'' measured at difference frequencies appear at the same temperature, which is not the case with most polymer systems, because a typical T_g of polymer shows a frequency dependence due to the viscoelastic nature of polymer. It is considered that the molecular weight of the pristine lignin, M_w=6000 g/mol, is not high enough to exhibit long-range molecular relaxation. Figures 2A and 2B show two peaks composed of four regions in ε' and ε'', which are quite unusual in most synthetic polymers. In the first region in $50^{o}C < T < 100\ ^{o}C$, ε' increases from 2 to 6 in a large extent with temperature, which is believed to be the $T_{g,wet}$ of the pristine lignin centered at 79 ^{o}C, taken from the midpoint of the transition. Thus $T_{g,wet}$ agrees with the previous studied of wood T_g in the wet status (Ursula 2007; Salmen 1982), which is not heat-treated before measurement. As indicated in Fig. 1, the evaporation of water and low-M_w molecules also occurs in this transition of $T_{g,wet}$.

It is interesting to note that ε' and ε'' decreased with temperature in the second region, $100\ ^{o}C < T < 125\ ^{o}C$, which is not usually observed in reversible transition of most polymer systems. More specifically, the decreasing behavior of ε' with temperature indicates that the pristine lignin is stiffened with increasing temperature, which should accompany, for example, chemical reactions or the removal of plasticizing molecules. As we observed in the TGA analysis (Fig. 1), the pristine lignin gradually loses weight in the range 50 ^{o}C to 150 ^{o}C due to the evaporation of water and low molecular-weight lignin molecules. Accordingly, the ε' and ε'' in $100\ ^{o}C < T < 125\ ^{o}C$ may be ascribed to lignin stiffening through the elimination of plasticizing molecules of water and low molecular-weight lignin molecules.

When the pristine lignin was further heated, ε' and ε'' increased again in the range 125 ^{o}C to 155 ^{o}C, clearly indicating that the lignin sample was softened again. We believe that this can be ascribed to the $T_{g,dry}$ of the pristine lignin corresponding to the typical thermal relaxation of dried lignin molecules after the plasticizing molecules are removed. Taking the midpoint of the transition, the $T_{g,dry}$ may be identified as 138 ^{o}C. The $T_{g,dry}$ measured in this study agrees well with the literature values as references (Hatakeyama 2002; Kues 2007; Salmen 1982). Afterwards, ε' and ε'' decreased again with temperature ranging between 155 ^{o}C and 220 ^{o}C, meaning that the material stiffened as temperature increased. It is believed that this transition is considered to be a crosslinking homopolymerization reaction of the lignin -OH groups, which were already discussed in Figs. 1C and 1D. Overall, the pristine lignin exhibited two glass transition temperatures at $T_{g,wet}$=79 ^{o}C and $T_{g,dry}$=138 ^{o}C, which is in agreement with the literature values measured in different heat-treatment conditions (Hatakeyama 2002).

Figure 2C shows the ionic conductivity of the pristine lignin plotted as a function of temperature. When the material is in a solid state, the ionic conductivity usually exhibits a frequency-dependent feature due to the molecular relaxation. On the other hand, when the material is in a liquid state, the ionic moieties (*e.g.*, water) are allowed to move freely through the media, resulting in the frequency-independent feature as described in Equation (3). Figure 2C shows the glass state in *ca*. $T < 60\ ^{o}C$, where the ionic conductivity is strongly dependent on frequencies since the pristine lignin is in the typical solid state. After further heating, it merges together in the $T_{g,wet}$ region ($60\ ^{o}C < T < 80\ ^{o}C$) becoming frequency-independent. In this $T_{g,wet}$ region, it is believed that there exists a substantial amount of molecular mobility of the pristine lignin and, thus, the ionic (or electronic) moieties and water molecules could move easily under the electrical potential. At temperatures over the $T_{g,wet}$, the ionic conductivity became frequency-dependent, seemingly due to the molecular evolution and crosslinking reactions, which agrees well with previous discussions in Figs. 2A, 2B, and Fig. 1.

Figure 2D shows the DSC thermograms of pristine lignin after heat treatment at different temperatures and LigPCL polycondensates. The pristine lignin shows a broad exothermic peak, which seems to include $T_{g,wet}$, evolution of low molecules, $T_{g,dry}$, and crosslinking reactions together. The exothermic peak is substantially decreased when the pristine lignin is heat-treated at 100 °C because the small molecules are eliminated by the heat treatment. When the pristine lignin is heat-treated at 200 °C, $T_{g,dry}$ is measured at 118 °C, which agrees well with the dielectric analysis.

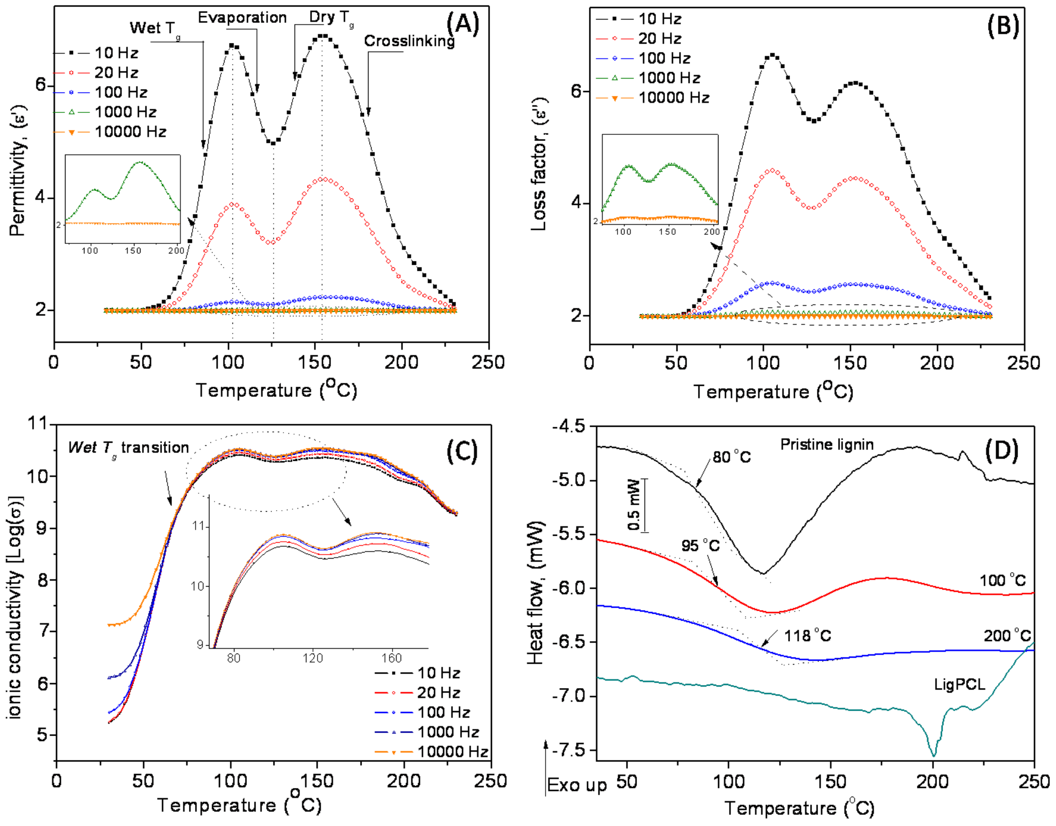


Fig. 2. Dielectric responses of permittivity (A), loss factor (B), and ionic conductivity (C) of pristine lignin. DSC thermograms of the pristine lignin, lignin heat treated at 100 °C, 200 °C, and the synthesized LigPCL polycondensate (D).

FT-IR and Molecular Weight of LigPCL Polycondensate

Figure 3A compares the IR spectra of the pristine lignin and synthesized LigPCL polycondensate. Both IR spectra show several medium-weak and multiple bands of the benzene ring at 1416 cm^{-1}, 1464 cm^{-1}, 1508 cm^{-1}, and 1630 cm^{-1}. The peak at 2931 cm^{-1} is regarded as the C-H bond stretching of methyl or methylene groups, and the peak at 1128 cm^{-1} is assigned to the C-O bond stretching of ether or ester groups. These peaks appear in the spectra of both the pristine lignin and the LigPCL polycondensate. The strong and broad peak at 3440 cm^{-1} is the characteristic peak of the O-H groups or phenolic compounds in the pristine lignin and the LigPCL polycondensate. The spectra of the LigPCL polycondensate shows two strong peaks corresponding to the C=O bond at 1768 $cm^{-1}$and 1705 cm^{-1}, which indicates the formation of ester groups in the LigPCL polycondensate by the esterification reaction, thus confirming Scheme1.

The molecular weights of the pristine lignin and the LigPCL polycondensate can be seen in Fig. 3B and Table 1, which summarize the weight average molecular weight (M_w), the number average molecular weight (M_n), and the molecular weight distributions (MWD =M_w/M_n). The pristine lignin has M_w and M_n values of 6000 g/mol and 3700 g/mol, respectively, with a MWD of 1.6. After the polycondensation reaction, the M_w and the M_n of the LigPCL polycondensate were increased to 10500 g/mol and 7300 g/mol, respectively, with a narrowed MWD of 1.4.

Table 1. Weight Average Molecular Weight (M_w), Number Average Molecular Weight (M_n), and Molecular Weight Distribution (MWD) Analyzed by GPC for the Pristine Lignin and the Synthesized LigPCL Polycondensate

Samples	M_w (g/mol)	M_n (g/mol)	MWD (M_w/M_n)
Lignin	6000	3700	1.6
LigPCL polycondensate	10500	7300	1.4

The GPC chromatogram in Fig. 3B compares the pristine lignin and the LigPCL polycondensate.

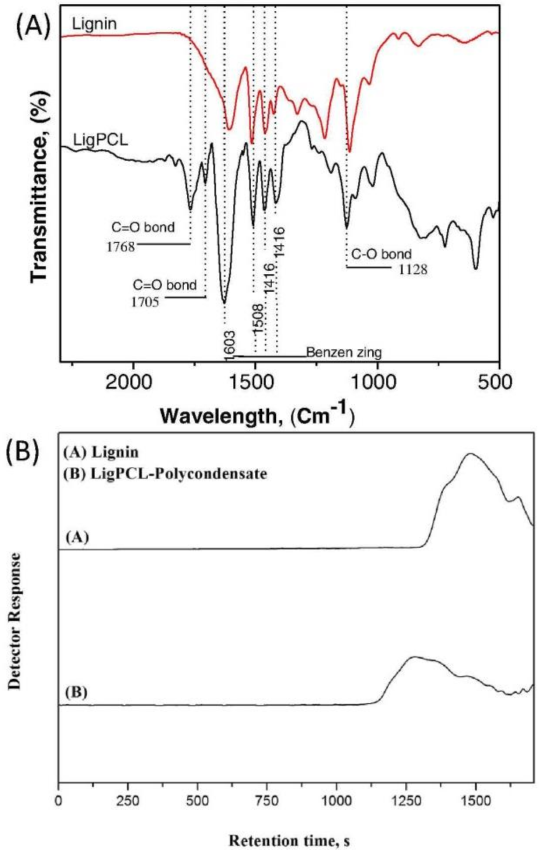


Fig. 3. FT-IR spectra and GPC thermograms of the pristine lignin (A) and the synthesized LigPCL polycondensate (B)

The pristine lignin does not seem to taper off over the retention time of 1700 sec, exhibiting several peaks seemingly because the small molecules are included in the natural lignin. The elution time of the LigPCL polycondensate was shorter than that of the pristine lignin, indicating that the molecular weight of the LigPCL polycondensate was increased by the polyesterification reactions.

Dielectric Properties of LigPCL Polycondensate

Dielectric analysis of LigPCL polycondensate is shown in Figs. 4A and 4B. The measurements were made at different frequencies ranging from 10 Hz to 10000 Hz. Figures 4A and 4B show that *ε*' and *ε*" of LigPCL polycondensate were completely different from the pristine lignin in Figs. 2A and 2B. The LigPCL polycondensate shows a single transition in a relatively broad range of temperature of 125 ^{o}C <*T*< 160 ^{o}C, exhibiting a large increment of *ε*' and *ε*" from 2.2 to 6.7 with temperature. The broad range of transition temperature is likely to stem from the nature of the lignin macromers. The extent of the increment for *ε*' and *ε*' of the synthesized LigPCL may be regarded as the glass transition and the subsequent solid-to-liquid transition of molecular softening, which is usually observed in most amorphous thermoplastics. Since the glass transition of the lignin segment and the softening of the PCL segment take place in the same temperature range, this transition would rather be regarded a softening transition of thermoplastic LigPCL.

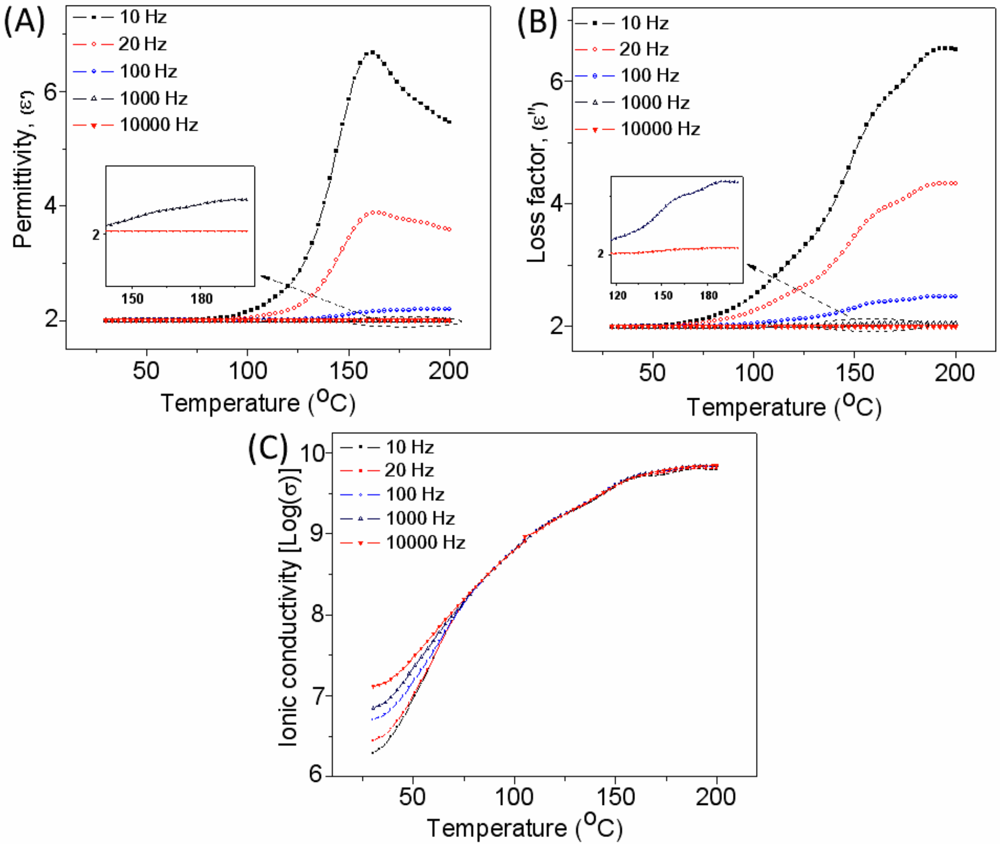


Fig. 4. Dielectric responses of permittivity (A), loss factor (B), and ionic conductivity (C) of LigPCL measured at different frequencies as a function of temperature at a heating rate of 3 ^{o}C/min as the glass transition peak.

The midpoint of the transition at 143 °C may be regarded as the representative viscous softening of the synthesized LigPCL. Over 160 °C, it is interesting to note that ε' and ε'' of the LigPCL polycondensate started decreasing with temperature seemingly due to additional crosslinking and or chain growth reactions. The ionic conductivity of LigPCL in Fig. 4C presents a typical dipole relaxation in the glass state, $T < 90$ °C, exhibiting a frequency-dependent behavior and, then, the ionic conductivity became frequency-independent, indicating that the LigPCL is lignified at temperatures above 90 °C. It is believed that the glass transition and softening process take place in the LigPCL condensates, which can hardly be separated due to the large amount of ionic moieties or radicals for ionic conductance to be dominant.

Figure 5A shows the viscosity of the LigPCL polycondensate. The measurements were made at different frequencies ranging from 1 rad/s to 100 rad/s. The viscosity decreases with increasing temperature showed the thermoplastic nature of the synthesized LigPCL polycondensate. At 40 °C to 120 °C, the viscosity decreased drastically with increasing temperature, and then, the viscosity reached a low stable value at around 10^2 mPa·s over 160 °C. In addition, Fig. 5B shows the physical appearance of pristine lignin and LigPCL polycondensate in the heated states at 200 °C. The pristine lignin remained solid during heating with a color change. On the other hand, the LigPCL condensates became liquid at 200 °C, exhibiting its thermoplastic nature. This result confirms that the LigPCL condensate is thermally stable and becomes a thermoplastic polymer melt at around 200 °C without evolving fumes. We believe that it could open new era of lignin for being used widely as eco-friendly sustainable materials.

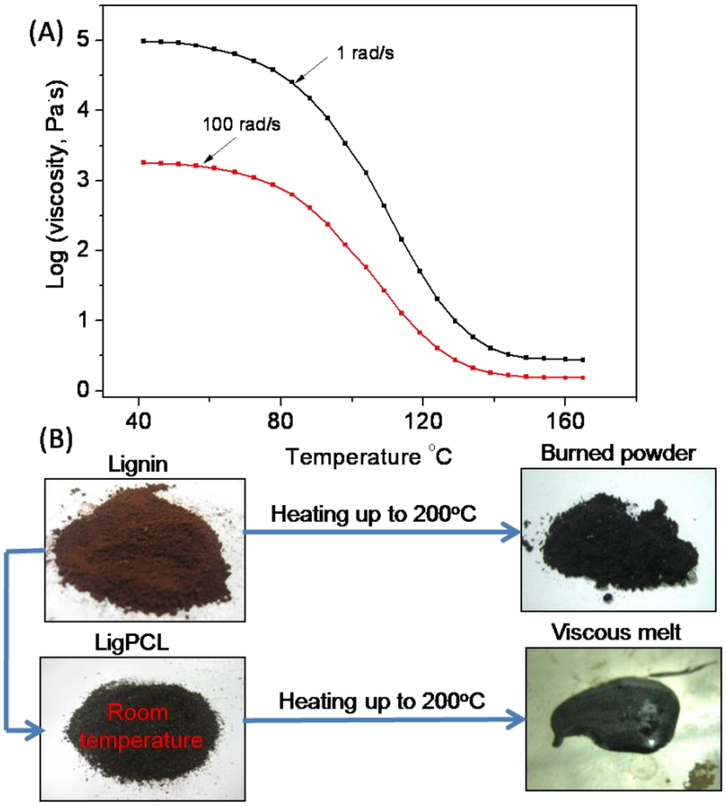


Fig. 5. Viscosity of LigPCL polycondensate (A) measured at different frequencies and digital images of the pristine lignin, pristine lignin after heating at 200 °C, the LigPCL polycondensate after drying and heating at 200 °C (B).

The developed synthetic route of LigPCL allows the lignin-based systems to contain soft segments of polycaprolactone in the main chains, which could be very useful in molecular design and composite applications in the lignin-based polymer systems. The synthesized LigPCL exhibited an increased molecular weight and improved thermal stability, allowing polymer-melt processing to be carried out up to 200 °C. The developed lignin system shows potential uses as eco-friendly polymers and composites most likely through compatibilization of natural fillers and synthetic polymers.

CONCLUSIONS

1. This study successfully demonstrated that Kraft lignin has two glass transition temperatures of T_g: $T_{g,wet}$ at 79 °C without heat treatment and $T_{g,dry}$ at 138 °C after heat treatment.
2. Kraft lignins could automatically become crosslinked under elevated temperatures. A kraft lignin-based polycaprolactone polycondensate was successfully synthesized by the polycondensate reactions of the LigPCL with sebacoyl chloride in the presence of TEA as a catalyst.
3. The developed polycondensate showed improved thermal stability compared to the pristine lignin, especially in the temperature regime of typical melt processing. In particular, the LigPCL could be melt-processed, which could allow for many applications in green composites.

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