Effect of Lignocellulose Nanofibril and Polymeric Methylene Diphenyl Diisocyanate Addition on Plasticized Lignin/Polycaprolactone Composites

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Kraft lignin was plasticized with ε-caprolactone *via* twin-screw extrusion at 150 °C, and its glass transition temperature was decreased from 155 to 96 °C. The lignin or plasticized lignin (p-lignin)/polycaprolactone (PCL) composites with and without lignocellulose nanofibril (LCNF) or polymeric methylene diphenyl diisocyanate (pMDI) were prepared, and their properties were compared. The p-lignin was better dispersed in the PCL than neat lignin, and the p-lignin/PCL composites exhibited a homogenous fractured surface despite the addition of LCNF. An increase in the lignin or p-lignin content decreased the tensile strength and elastic moduli but increased the melt flow index (MFI). With the addition of pMDI and LCNF, the tensile properties and MFI improved and declined, respectively. The strength improvement by pMDI and LCNF was better in the p-lignin/PCL composite than in the lignin/PCL composite.

Keywords: Plasticized lignin; Composite; Lignocellulose nanofibril; Polymeric methylene diphenyl diisocyanate

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INTRODUCTION

Bio-based plastics can be prepared from natural polymers, such as starch, cellulose, lignin, and protein (Cui *et al*. 2013; Belhassen *et al*. 2014; Spiridon *et al.* 2015; Garrido *et al*. 2016; Graupner *et al*. 2016; Nagy *et al.* 2018). Most of these plastics are biodegradable and compostable. Many studies on the development of bio-based plastics have focused on replacing synthetic plastics obtained from petroleum (Siracusa *et al.* 2008; Karamanlioglu *et al.* 2017).

Recently, lignin has gained increasing attention as a raw material for carbon fiber and bioplastics (Baker *et al*. 2012; Baker and Rials 2013; Hilburg *et al*. 2014; Akato *et al.* 2015; Tran *et al*. 2016; Kun and Pukánszky 2017). Lignin accounts for up to 30% of the dry mass of lignocellulose and is usually obtained as a byproduct in the pulping industry. It is generally used as a solid fuel in pulping plant operations (Vishtal and Kraslawski 2011; Saito *et al*. 2012; Kang *et al*. 2013). Despite its advantages such as its low cost, low density, biodegradability, and low toxicity, the utilization of lignin for bioplastics has been limited due to its low strength, brittleness, and poor thermal flowability (Sahoo *et al*. 2013; Sen *et al*. 2015).

Many plasticizers have been used to lower the glass transition temperature (T_g) of lignin to improve its thermal flowability (Bouajila *et al.* 2006; Stelte *et al.* 2012; Sen *et al*. 2015; Wang *et al*. 2016). The plasticizers increase the free volume by spacing polymer chains and the mobility of the chain segments, resulting in a decrease in the T_g and melt viscosity (Wang *et al.* 2016). Feldman *et al.* (2003) plasticized organosolv lignin with 30 phr of plasticizers, including diethylene glycol dibenzoate, butyl benzyl phthalate, and tricresyl phosphate. The T_g of lignin decreased from 97 °C to 35 °C, 38 °C, and 53 °C, respectively. Bouajila *et al*. (2006) also studied the effect of plasticizers such as water, ε-caprolactone, ethylene glycol, vanillin, ethylene carbonate, and ferulic acid on the T_g of kraft lignin (KL). They reported that the T_g (160 °C) decreased with increasing plasticizer content for all samples, with the variation depending on the plasticizer.

Thermoflowable composites of thermoplastics and lignin have also been developed. Liu *et al.* (2016) prepared enzymatic hydrolysis lignin (EHL)/high-density polyethylene (HDPE) composites with mass fractions of 40%, 50%, 60%, and 70% for the EHL using a twin-screw extruder at 160 °C to 185 °C. The tensile strength decreased with increasing EHL content. Ye *et al.* (2017) prepared lignosulfonate or desulfonated lignosulfonate/ polylactic acid (PLA) composites from a dichloromethane solution *via* a casting method. Furthermore, as the lignin content increased, the tensile strength and Young’s moduli of both composites decreased. This was due to the poor mechanical properties of lignin itself. Further, its poor adhesion with polymers remains an issue.

The increase in the interaction between lignin and other matrix polymers is also important. Using a coupling agent such as an isocyanate coupling agent can improve the interfacial adhesion. Lee and Wang (2006) investigated the effect of lysine-diisocyanate (LDI) on the properties of bamboo-fiber-reinforced PLA and polybutylene succinate (PBS) composites. They reported that the LDI formed urethane linkages between the bamboo fiber and polymers, which improved the tensile strength of the composites. Sahoo *et al.* (2013) also reported the effect of adding polymeric methylene diphenyl diisocyanate (pMDI) on the properties of PBS/lignin/switchgrass (50/25/25) composites. The addition of pMDI improved the tensile properties due to the urethane linkage formed by the reaction of the –NCO group of pMDI and the hydroxyl group of the lignin, switchgrass, and PBS.

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point of approximately 60 °C and a T_g of approximately -60 °C (Ermeydan *et al.* 2014; Carmona *et al.* 2015). As PCL can be hydrolyzed in the human body, it has received tremendous attention as a material for application in pharmaceutical and biomedical engineering (Ermeydan *et al*. 2014; Yari *et al.* 2016). The PCL produced by the ring-opening polymerization of ε-caprolactone has hydroxyl and carboxyl groups at the terminal. Thus, both terminal groups of the PCL can be linked with the phenolic hydroxyl group of lignin with the reaction of MDI. Cateto *et al*. (2011) proposed that three-dimensional networks were formed between lignin and PCL due to the addition of MDI, and the formation of lignin-based polyurethanes was monitored with different hydroxyl concentrations of lignin and PCL. The isocyanate concentration of MDI was measured using Fourier transform infrared spectroscopy (Cateto *et al*. 2011). They reported that the isocyanate conversion for the networks decreased as the lignin content and molecular weight of the PCL increased. The addition of the isocyanate coupling agent is expected to improve the properties of the lignin-based PCL composite.

In this context, the approach of the research team to improve the mechanical properties and thermo-flowability of lignin/PCL composite has been to use lignocellulose nanofibril (LCNF) as a reinforcing filler and plasticize lignin using ε-caprolactone. Lignocellulose nanofibril containing hydrophobic lignin has a better affinity for hydrophobic polymers and is thus expected to strengthen the lignin-based composite due to improvement of its interfacial adhesion. As LCNF has outstanding physicomechanical properties such as low density, large specific surface area, high thermal stability, and high strength comparable to glass fiber, aramid fiber, and carbon fiber, it has great potential as a reinforcing filler for the composite (Jonoobi *et al.* 2010; Lee *et al.* 2010; Jang *et al*. 2013; Ziaei-tabari *et al*. 2017). In this study, the effect of lignin plasticization and the addition of LCNF and pMDI on the dispersity, mechanical properties, and thermal flow properties of the composites were investigated.

EXPERIMENTAL

Materials

Polycaprolactone (PCL, M_w: 75,000 to 95,000) was purchased from Sigma-Aldrich Co. (St. Louis, MO, USA), and the ε-caprolactone used for the plasticization of lignin was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The lignocellulose (*Liriodendron tulipifera* L.) used for the preparation of LCNF was obtained from the Experimental Forest of Kangwon National University (Chuncheon, South Korea). The pMDI was obtained from Kumho Mitsui Chemicals Co. (Seoul, Republic of Korea).

Preparation of KL

The KL used in this study was isolated from black liquor using the following method (Kim *et al.* 2015). The black liquor was produced from a range of Southeast-Asian hardwood chips provided by Moorim Pulp and Paper Co. (Ulsan, Republic of Korea). After adjusting the pH of the black liquor to ~2.0 using a concentrated HCl solution, the precipitated lignin was recovered by filtration. This precipitate was repeatedly washed with fluent deionized water and then dried at 60 °C in an oven for two weeks.

Methods

Preparation of LCNF

The wood powder used for the preparation of LCNF was suspended at 5.0 wt.% (3,000 mL) and then subjected to wet disk-milling (WDM, MKCA6-2, Masuko Sangyo Co., Ltd, Kawaguchi, Japan). The rotational speed was set at 1,800 rpm, and the clearance between the upper and lower disks was reduced to between 80 μm and 150 μm from the zero point, at which the disks would begin to rub. The defibrillation process was repeated 15 times.

Plasticization of lignin

The KL was placed in a vacuum-dryer at 40 °C for 48 h and then mixed with ε-caprolactone with a weight ratio of 80/20 (lignin/ε-caprolactone). The mixture was subjected to a twin-screw extruder (BA-11, Bautek Co., Pocheon, Republic of Korea) with an L/D ratio of 40. Lignin plasticization was performed at 150 °C with a screw speed of 50 rpm, and the extruding operation was repeated three times for complete plasticization.

Preparation of lignin or p-lignin/PCL composite

The lignin and p-lignin were mixed with PCL with a ratio of 10/90, 30/70, and 50/50 (the lignin or p-lignin/PCL). The lignin for the p-lignin/PCL blends was prepared *via* twin-screw extrusion at 140 °C with a screw speed of 50 rpm. The LCNF-reinforced composite was produced using the following method. The lignin or p-lignin (15 g) was added to 1.25 wt.%, 2.50 wt.%, and 5.00 wt.% LCNF suspensions (200 g), having a solid weight of 2.5 g, 5.0 g, and 10 g, respectively. After stirring at 300 rpm for 12 h, the suspensions were frozen rapidly in a cold trap at -50 °C and freeze-dried at -55 °C for 48 h using a freeze dryer (FDB-5502, Operon, Republic of Korea). By adding the PCL to the freeze-dried mixture, the LCNF content was controlled to 5 phr, 10 phr, and 20 phr based on the weight of lignin or p-lignin/PCL blends. Subsequently, the LCNF-reinforced composites were prepared *via* twin-screw extrusion at 140 °C and 50 rpm. In addition, to investigate the effect of the addition of a coupling agent, pMDI of 1 phr and 3 phr was added during the extrusion.

Morphological observation

To prepare the LCNF sample for morphological observation, the solvent exchange of LCNF was carried out using the following method. The LCNF suspensions were diluted to 0.001 wt.% and then sonicated using an ultrasonicator (VCX130PB, Sonics & Materials, Inc., Newtown, CT, USA) for 1 min. The suspensions were vacuum-filtrated on a polytetrafluoroethylene membrane filter with a pore size of 0.2 µm (ADVANTEC®, Toyo Roshi Kaisha, Ltd., Niigata, Japan) using a vacuum pump (N8203FT, KNF Neuberger Inc., Freiburg, Germany). The membrane filter with filtrated LCNF was immersed in tert-butyl alcohol for 30 min. This immersing procedure was repeated thrice to completely exchange water with tert-butyl alcohol. The LCNF was freeze-dried at -55 °C for 3 h to prevent the aggregation of the fibrils. The freeze-dried LCNF sample and fractured lignin or plasticized lignin/PCL composites were coated with iridium using a high-vacuum sputter coater (EM ACE600, Leica Microsystems, Ltd., Wetzlar, Germany). The coating thickness was approximately 2 nm. The morphologies were observed using a scanning electron microscope (SEM, S-4800, Hitachi, Ltd., Tokyo, Japan) at the Central Laboratory of Kangwon National University (Chuncheon, South Korea).

Differential scanning calorimetry (DSC) testing

DSC measurement was conducted with a differential scanning calorimeter (SDT Q600, TA instruments, Inc., New castle, DE, USA) to determine the T_g of lignin and p-lignin. The samples (5 mg to 10 mg) were heated on an aluminum pan under a nitrogen gas purge (100 mL/min). Scanning temperatures ranged from 25 °C to 170 °C, with a heating rate of 1 °C/min.

Tensile testing

The prepared lignin or plasticized lignin/PCL composites were hot-pressed at 150 °C for 1 min for sheet formation. For tensile testing, the specimens were cut from the sheet according to the Type V dimensions described by American Society for Testing and Materials (ASTM) D638 standard and maintained in a thermohygrostat at 25 °C and a relative humidity of 65% to standardize the effect of relative humidity on the tensile properties. Tensile testing was conducted using a universal testing machine (H50K, Hounsfield Test Equipment, Redhill, U.K.) at a cross-head speed of 10 mm/min with a specimen span length of 50 mm. At least nine specimens of each sample were tested, and the average values were obtained.

Melt flow index (MFI)

The MFI and melt viscosities of the composites were measured with a melt flow indexer (MFI 4050, Rhopoint Instruments, Ltd., Hastings, U.K.). The sample was preheated in a vessel for 2 min at 150 °C. Subsequently, the samples were measured using a die with a 2.09 mm diameter and a load cell of 2.16 kg. The measurement distance was set at 25.4 mm, and the MFI and melt viscosity were calculated automatically by the software of the melt flow indexer.

RESULTS AND DISCUSSION

Characteristics of LCNF and p-Lignin

Figure 1 (a) shows the SEM micrograph of LCNF prepared *via* WDM 15 times. There were thick fibers with diameters of 100 nm to 200 nm alongside 20-nm-thick fibers. The authors' previous study reported that the non-uniform morphology of LCNF was due to the existence of lignin, which impedes defibrillation (Park *et al.* 2015, 2017). Figure 1 (b) indicates that the nanoscale lignin particles came together to form micron-scale particle aggregates. The lignin plasticized with 25% ε-caprolactone at 150 °C showed a clean and smooth surface without any lignin particles (Fig. 1 (c)).

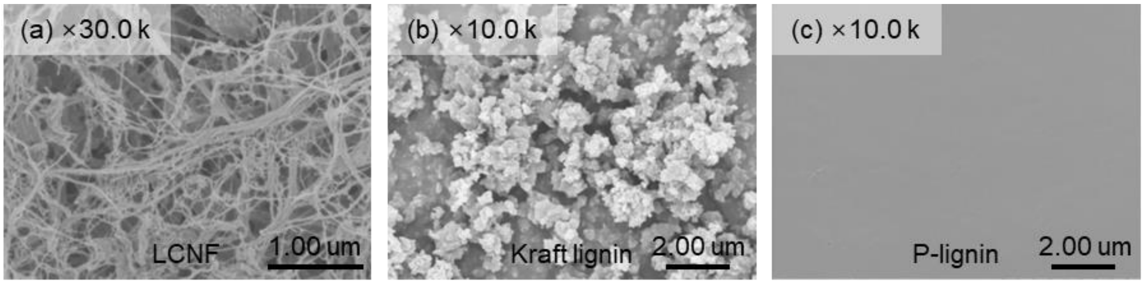


Fig. 1. SEM micrographs of LCNF (a), lignin (b), and p-lignin (c)

The T_g of lignin is known to be between 90 °C to 180 °C depending on its molecular structure and weight (Bouajila *et al*. 2006; Wang *et al.* 2016). Figure 2 shows the DSC thermogram of lignin and p-lignin. The T_g of lignin was found to be 155 °C, and it was decreased to 96 °C *via* plasticization.

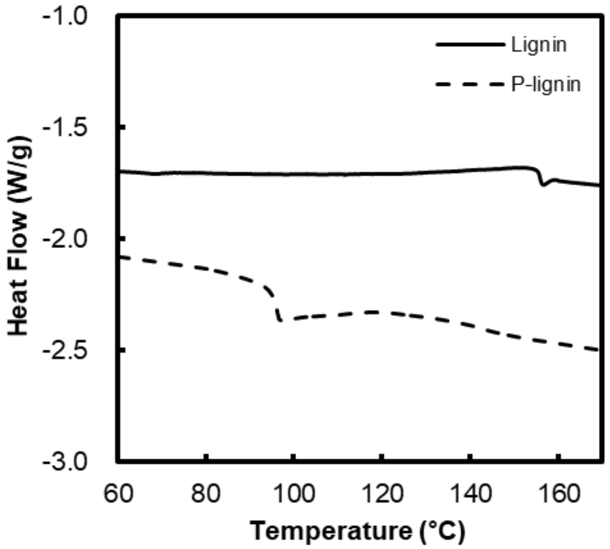


Fig. 2. DSC thermograms of lignin and P- lignin

Morphologies of Lignin or p-lignin/PCL Composites

Figure 3 displays the fractured surface of lignin or p-lignin/PCL blends with different lignin or p-lignin contents. In the lignin/PCL blends, lignin particles were observed, and their numbers increased remarkably with increasing lignin content. In particular, for the blend with 50% lignin content, large cavities caused by the removal of lignin particles during breaking were observed. In polymer blends, immiscibility can generally occur in a phase-separated structure if the polymers have low interfacial adhesion. It has been reported that only a few polymers including poly(ethylene oxide), polyethylene terephthalate, and poly(*N*-vinyl pyrrolidone) are miscible with lignin (Wang *et al*. 2016). Hu *et al.* (2014) stated that, in SEM images of the lignin/HDPE composites, cavities and cracks between unmodified lignin particles and HDPE were observed due to the weak interfacial adhesion between the lignin and HDPE.

However, p-lignin/PCL blends showed clean and smooth fractured surfaces. Although the PCL was immiscible with lignin, the plasticization made the lignin disperse well. Teramoto *et al*. (2009) reported the miscibility of organosolv lignin derivatives such as acetate, propionate, butyrate, valerate, and PCL by phase separation behavior using an atomic force microscope. They concluded that the esterification of lignin can improve its compatibility with PCL. The ε-caprolactone used as a plasticizer in this study can esterify lignin during the plasticization process at high temperature, which may improve its compatibility with PCL.

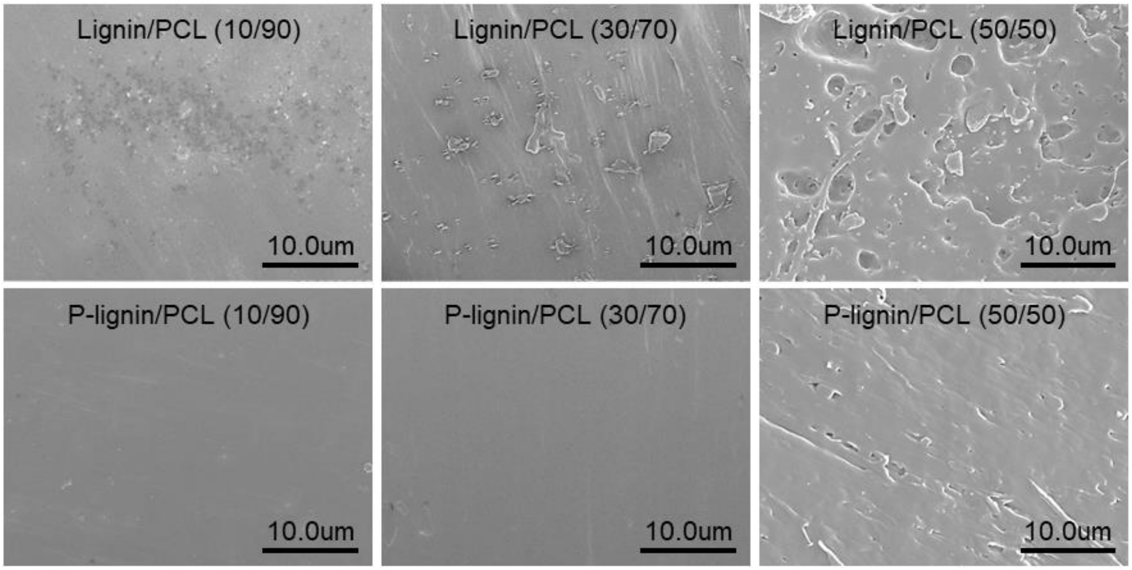


Fig. 3. SEM micrographs of the fractured surface of the lignin or p-lignin/PCL blends

Figure 4 shows the morphological characterization of the fractured surface of the lignin/PCL (30/70) composites with different LCNF and pMDI contents. A rougher surface was observed in the LCNF-reinforced composites without pMDI, and the composites with pMDI showed a comparatively smooth surface, indicating better dispersion of LCNF in the lignin matrix due to the coupling effect of the pMDI.

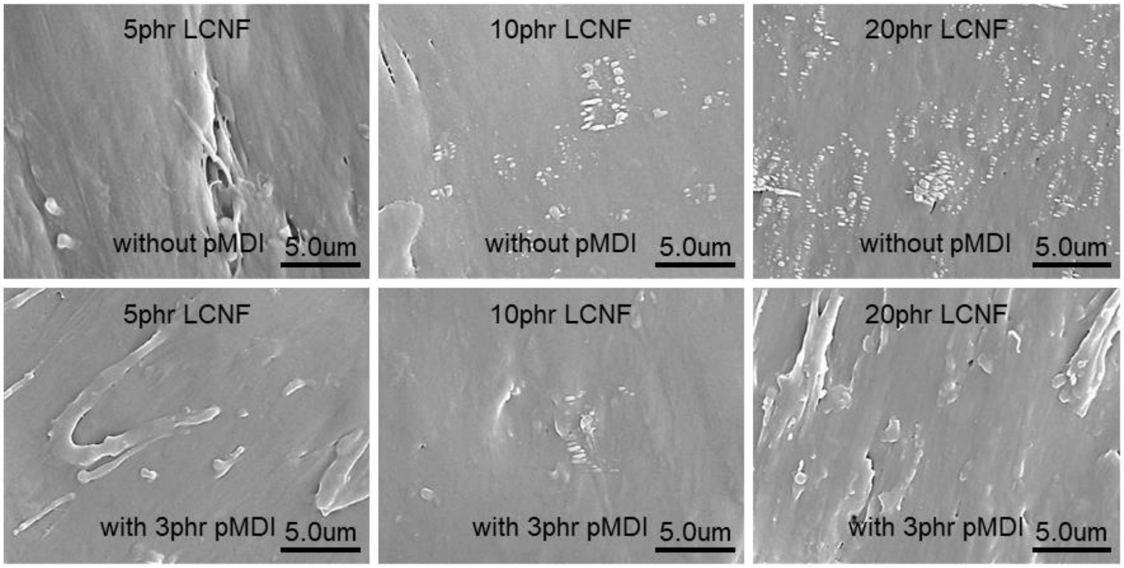


Fig. 4. SEM micrographs of the fractured surface of LCNF-reinforced lignin/PCL composite with and without pMDI

Figure 5 shows the SEM micrographs of the fractured surface of LCNF-reinforced p-lignin/PCL (30/70) composites. Unlike the morphologies of LCNF-reinforced lignin/PCL composites (Fig. 4), a highly smooth and homogeneous phase appeared in all of the composites. Even in the composite with 20% LCNF content without pMDI, a clean fractured surface was observed, showing better dispersion of p-lignin than neat lignin.

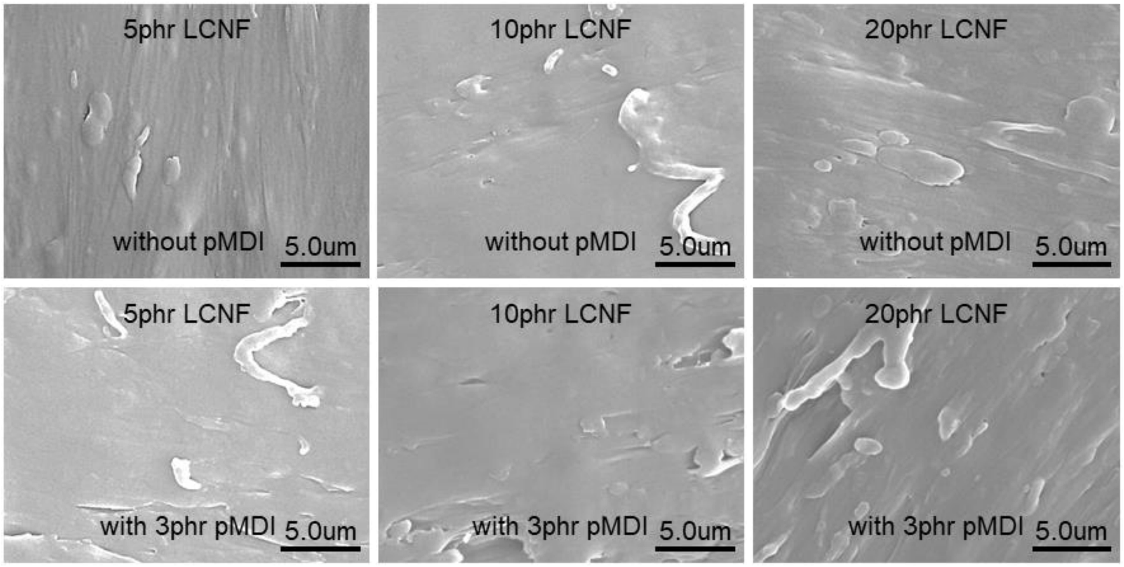


Fig. 5. SEM micrographs of the fractured surface of LCNF-reinforced p-lignin/PCL composites with and without pMDI

Tensile Properties of Lignin or p-Lignin/PCL Composite

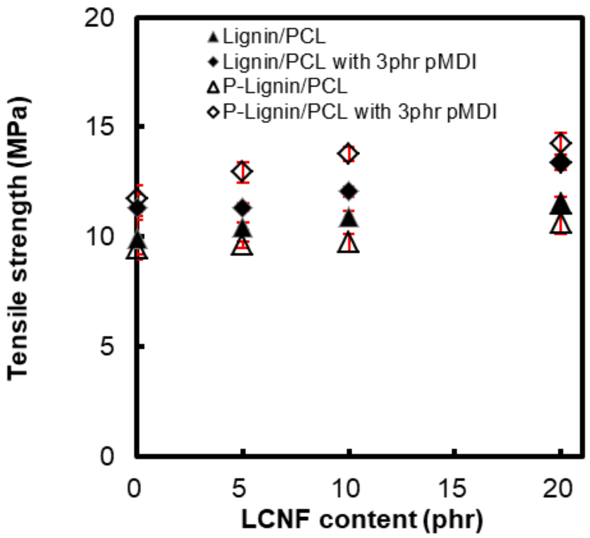
Table 1 presents the tensile strengths, elastic moduli, and elongation at break results of the lignin or p-lignin/PCL blends with different lignin and pMDI contents. The tensile strength of the blends without pMDI decreased with increasing lignin or p-lignin content. The decrease in the tensile strength of blends due to the addition of lignin is a general phenomenon in incompatible blends. Spiridon *et al.* (2015) also reported that increases in lignin content decreased the tensile strength of lignin/PLA composites, which was due to the low strength of lignin itself and the weak interfacial adhesion between the lignin and matrix polymers. Teramoto *et al.* (2009) also reported that the tensile strength of the esterified lignin/PCL composites decreased as the content of the esterified lignin increased from 25% to 50%. However, esterified organosolv lignins have good compatibility with PCL. Moreover, they stated that the elastic modulus increased with increasing esterified lignin content. This phenomenon was also observed in this study. The elastic moduli of the lignin or p-lignin/PCL blends increased as the lignin content increased. The PCL is a flexible polymer with low elastic modulus and high elongation similar to rubber. As the elastic modulus of the lignin is approximately 2.0 GPa to 6.7 GPa (Youssefian and Rahbar 2015), the addition of lignin can increase the elastic modulus and decrease the elongation at break in the blend. Nitz *et al.* (2001) also stated that the elastic moduli of the lignin/PCL composites increased from 400 MPa to 1175 MPa, and the strain decreased from above 520% to 5% as the lignin content in the composite increased to 70 wt.%.

The addition of pMDI improved the tensile strength and elastic moduli of both lignin and p-lignin/PCL (30/70) blends. In addition, the tensile strength of the p-lignin/PCL (30/70) blend without pMDI was lower than that of the lignin/PCL (30/70) blend. However, there was no remarkable difference in the tensile strength of both blends with pMDI.

Table 1. Tensile Properties of Lignin or p-Lignin/PCL blend with and without pMDI

	Composition of Lignin or P-lignin/PCL Blends			Tensile Strength (MPa)	Elastic Modulus (MPa)	Elongation at Break (%)
	Lignin or p-lignin (wt%)	PCL (wt%)	pMDI (phr)			
PCL	-	100	-	9.9 ± 0.3	171 ± 9	938 ± 48
Lignin/PCL	10	90	-	9.9 ± 0.5	231 ± 12	796 ± 105
	30	70	-	9.7 ± 1.0	274 ± 58	680 ± 107
	30	70	1	11.4 ± 0.3	331 ± 17	450 ± 20
	30	70	3	11.6 ± 0.7	446 ± 56	410 ± 70
	50	50	-	8.3 ± 0.6	362 ± 32	510 ± 80
P-lignin/PCL	10	90	-	9.0 ± 0.8	187 ± 24	863 ± 84
	30	70	-	8.4 ± 0.3	251 ± 31	750 ± 142
	30	70	1	11.8 ± 0.8	283 ± 34	596 ± 93
	30	70	3	11.9 ± 0.6	328 ± 21	490 ± 67
	50	50	-	7.8 ± 0.9	281 ± 59	650 ± 90

The LCNF containing lignin on its surface may be more suitable as a reinforcing filler for lignin-based composites due to its better compatibility with lignin than with CNFs without lignin. Figure 6 shows the effect of the addition of LCNF on the tensile properties of lignin or p-lignin/PCL (30/70) composites. For all composites, the tensile strength and elastic modulus increased with the increase in the LCNF content. Iwamoto *et al*. (2014) reported the reinforcing effect of LCNF on PP (polypropylene) composite, finding that the addition of LCNF improved the flexural stiffness and impact strength of the composite. The increases of tensile strength and elastic modulus were greater in the composite with pMDI than in that without the pMDI.



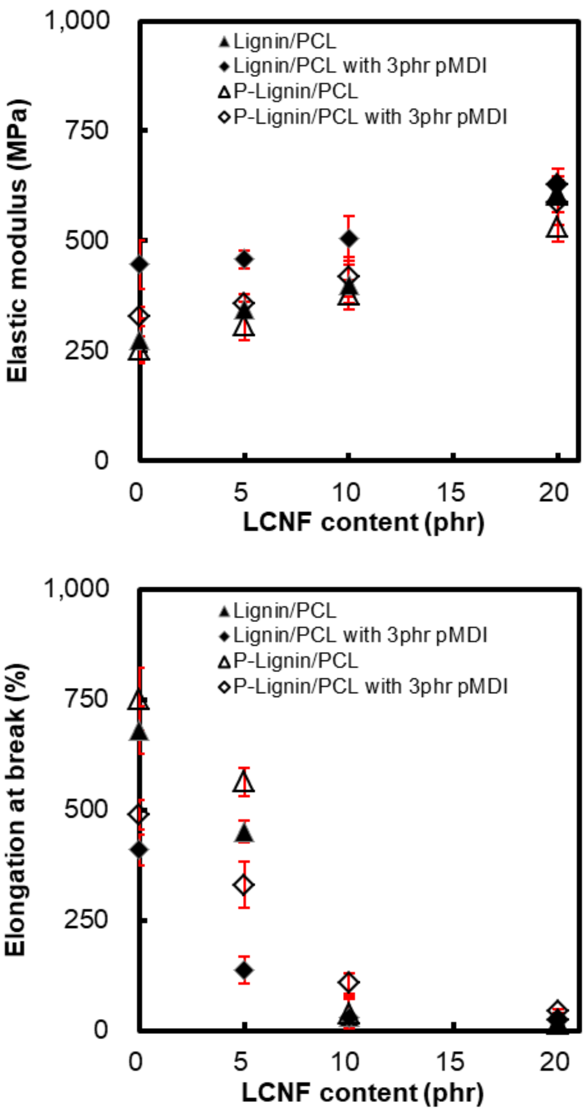


Fig. 6. The tensile properties of LCNF-reinforced lignin or p-lignin/PCL (30/70) composite with and without pMDI

The pMDI improved the interfacial adhesion between the LCNF and PCL and that between the lignin or p-lignin and PCL due to its coupling effect. Jang *et al.* (2014) also reported that the addition of pMDI improved the tensile strengths and elastic moduli of PBS/CNF composites. In p-lignin/PCL composites, the enhancement of the strength properties by adding the pMDI and LCNF was more prominent. As the better dispersibility caused by plasticization increased the interface area of lignin molecules, the chance of forming urethane linkages increased. Further, the elongation at break decreased with increasing LCNF content for all composites.

Melt-flowability of Lignin or p-Lignin/PCL Composites

The MFI and melt viscosity of the lignin or p-lignin/PCL (30/70) blends with different lignin contents were measured at 150 °C under a load of 2.16 kg, as shown in Fig. 7. As the lignin content increased, the MFI and melt viscosity of the lignin/PCL blend increased and decreased, respectively. However, when 50% lignin was added, the

MFI and melt viscosity decreased and increased, respectively. As lignin cannot be melted or fused, excessive addition of lignin can deteriorate the melt flow properties of the blends. Klapiszewski *et al.* (2016) reported that the addition of lignin to PP increased the MFI of PP/lignin (90/10) composite, showing better thermoflowability. Mousavioun *et al.* (2013) also reported that the addition of 10% and 30% lignin lowered the viscosity of pure poly(hydroxybutyrate) (PHB), but the addition of more than 60% of lignin increased the melt viscosity of pure PHB, showing more than 10 times higher viscosity. Plasticization of lignin improved the thermoflowability of p-lignin/PCL blends, yielding high MFI and low melt viscosity.

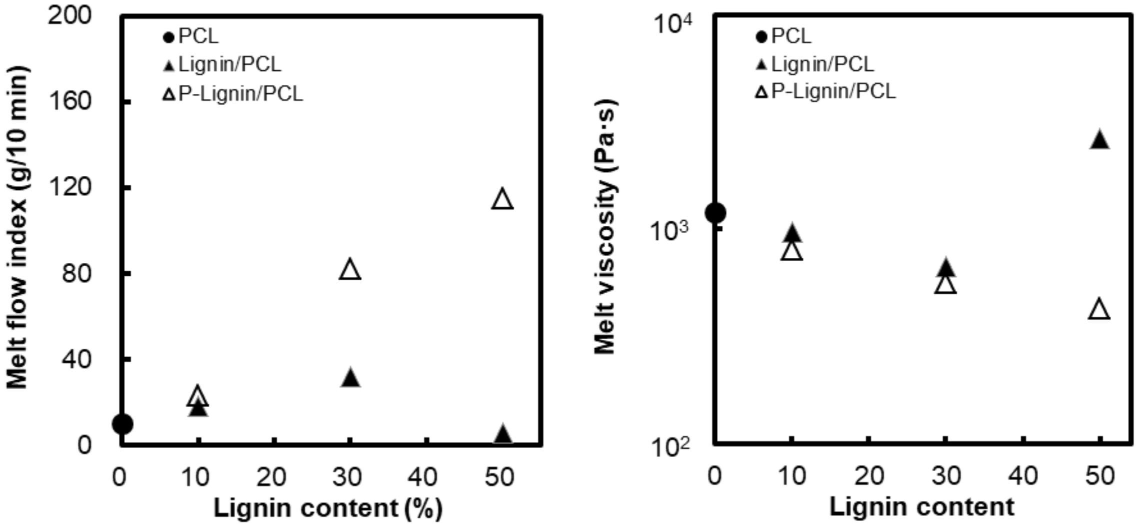


Fig. 7. The MFI and melt viscosity of PCL and lignin or p-lignin/PCL (30/70) blends without pMDI and LCNF

The effect of the addition of LCNF and pMDI on the MFI and melt viscosity of the lignin or p-lignin/PCL (30/70) composites was also investigated (Fig. 8). The p-lignin/PCL composite without pMDI had extremely high MFI, indicating good flowability. The better dispersibility of the p-lignin in PCL discussed above may result in desirable melt flow characteristics. However, MFI declined rapidly with the addition of 5% LCNF and did not change remarkably with further addition of LCNF, resulting in an increase in the melt viscosity. The addition of pMDI decreased the MFI and increased the melt viscosity, which may have been due to the improved interfacial adhesion between the polymers due to the coupling effect of pMDI. Liu *et al*. (2015) reported that the viscosity of the PBS/lignin composites increased with the addition of the silane coupling agent.

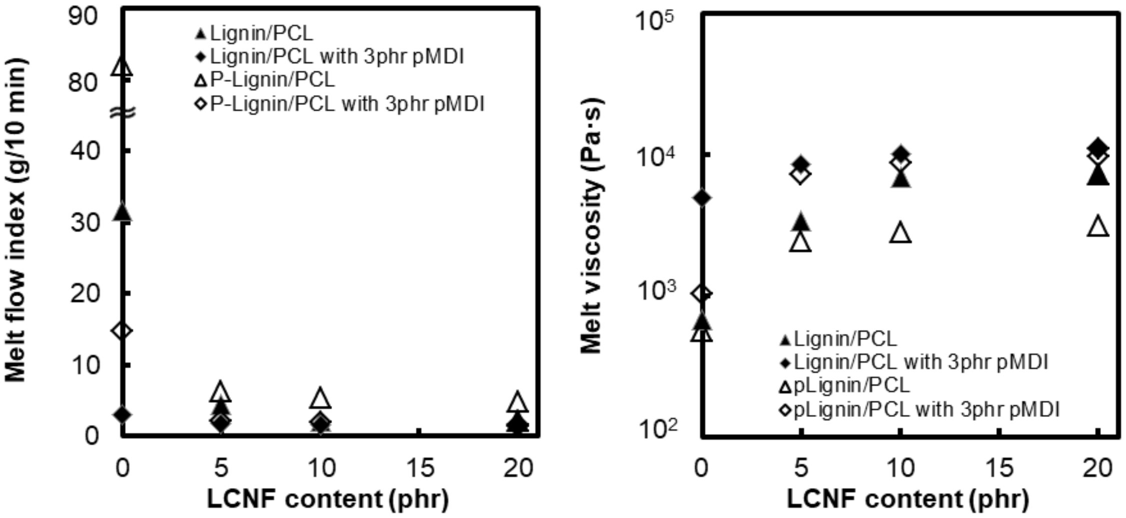


Fig. 8. The MFI and melt viscosity of PCL and lignin or p-lignin/PCL (30/70) composite with pMDI and LCNF

CONCLUSIONS

1. The effects of plasticization of lignin and the addition of lignocellulose nanofibril (LCNF) and polymeric methylene diphenyl diisocyanate (pMDI) on the properties of lignin/polycaprolactone (PCL) blends were investigated. The p-lignin was better dispersed in PCL than neat lignin, showing a smooth and homogenous fractured surface.
2. Increases in the lignin or p-lignin content resulted in decreases in the tensile strength and elastic moduli of the lignin or p-lignin/PCL blends. However, the tensile properties improved with the addition of pMDI and LCNF in both composites.
3. The melt flow index (MFI) increased with increasing in lignin or p-lignin content and was higher in the p-lignin/PCL blend than in the lignin/PCL blend. The addition of pMDI and LCNF reduced the thermal flowability of the composites.

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