Acid-Catalyzed Solvolysis of Softwood Using Polyethylene Glycol Monomethyl Ether to Produce Functional Lignin Derivatives

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Glycol lignins (GLs) produced through acid-catalyzed solvolysis of softwood meal using glycols, such as polyethylene glycol (PEG), have been used for the development of functional materials. In this study, GLs with various physical and chemical properties were synthesized *via* solvolysis with monomethyl ethers of polyethylene glycol (MPEG), such as MPEG-n4 and MPEG-n8. The effects of the reaction time and temperature on the yield, molecular weight, and thermal properties of MPEG-lignin were studied. The yield of MPEG-lignin increased with the solvolysis time. Acid-catalyzed solvolysis using MPEG-n4 occurred faster than that using MPEG-n8. Higher reaction temperature resulted in a higher yield of MPEG-lignin with a higher glass transition temperature (T_g) and viscous thermal flow temperature (T_f). The T_g and T_f of MPEG-lignins increased with the solvolysis time. The MPEG-lignins synthesized at higher reaction temperatures showed a relatively strong carbonyl absorbance band in the infrared spectra, which was ascribed to decomposed sugar derivatives.

INTRODUCTION

Lignin is one of the major components of plant cell walls and the most abundant renewable aromatic polymer (Eudes *et al.* 2014). Technical lignin, such as kraft lignin, is obtained as a byproduct of the kraft pulping process (Duval and Lawoko 2014). LignoBoost (Tomani 2010) and LignoForce (Kouisni *et al.* 2016) are systems that efficiently recover kraft lignin from the black liquor obtained in the kraft pulping process. Kraft lignin has been used as a solid biofuel (Tomani 2010) and raw material for resins, particularly as a copolymer of phenol–formaldehyde adhesives (Olivares *et al.* 1988). However, the use of kraft lignin is limited because of the presence of sulfur in its macromolecular structure (Lora and Glasser 2002; Gomes *et al.* 2014). Organosolv process is one of sulfur-free pulping processes and a promising alternative to kraft pulping (Lora and Glasser 2002). Organosolv pulping is the process of lignin extraction from wood chips by organic solvents or their aqueous solutions (Zhao *et al.* 2009). Organosolv delignification with variety of organic solvents was previously investigated (Johansson *et al.* 1987). Delignification using both low-boiling points solvents, such as ethanol, methanol, and butanol (Aronovsky and Gortner 1936; Johansson *et al.* 1987), and high-boiling point solvents, such as ethylene glycol (Jiménez *et al.* 2008), phenol (Jiménez *et al.* 1997), 1,4-butanediol (Li *at el.* 2015), and 1,3-butanediol (Kishimoto and Sano 2003)

has been reported. The use of high-boiling point solvents enables cooking under atmospheric pressure (Takata *et al.* 2016). We have previously reported the solvolysis of wood with polyethylene glycol (PEG) under atmospheric pressure to produce lignin-PEG derivatives (Glycol lignin: GL) (Nge *et al.* 2016, 2018). We reported the chemical structure of GL that had PEG-modified structure of lignin derivatives (Nge *et al.* 2018).

Glycol lignin has viscous thermal flow properties because of the effect of PEG chains grafted on GL. Various GL-based materials, such as flexible electronic substrate films (Takahashi *et al.* 2017), elastomeric epoxy resins (Ono *et al.* 2019), and heat-resistant insulation films (Suzuki *et al.* 2019), have been developed. Fiber-reinforced plastics (FRP), such as glass FRPs and carbon FRPs, with GL used as a part of the FRP matrix resin have been developed. These FRPs with GL have been applied in automobile parts and woofer units of high-resolution omnidirectional speakers (Nge *et al.* 2021).

The chemical and physical properties of GLs were controlled by the type of PEG with different chain length (Nge *et al.* 2018). The properties of GLs could be improved by studying solvolysis with various potential solvolysis reagents. In this study, two types of polyethylene glycol monomethyl ether (MPEG), in which one end of PEG is methoxylated, were used as the solvolysis reagents. The chemical and physical properties of the products (MPEG-lignin) were studied.

EXPERIMENTAL

Preparation of MPEG-Lignin

Figure 1 shows the schematics of the preparation of MPEG-lignin. Solvolysis solvents were prepared by the addition of 0.3 wt% of concentrated sulfuric acid to the two types of MPEG with different chain lengths (MPEG-n4 and MPEG-n8, Nippon Nyukazai Co., Ltd., Tokyo, Japan). Oven-dried (105 °C) Japanese cedar softwood meal (*Cryptomeria japonica*; 1 g; average particle size of 0.4 mm) was loaded in a test tube as reaction vessel with 5 g of the solvolysis solvent. The reaction mixture was mechanically stirred in a preheated oil bath to initiate the reaction. The acid-catalyzed solvolysis was performed at 120, 130, 140, 150, and 160 °C for 30 to 120 min under atmospheric pressure. The reaction vessel was then immersed in an ice water bath to quench the reaction. Then, approximately 30 mL of 0.1 M aqueous NaOH solution was added to the reaction vessel. The solvolysis product was subjected to centrifugation at 3300 rpm for 20 min to carry out a solid-liquid separation. The solid residues were washed three times with distilled water and dried at 105 °C overnight. The liquid part was adjusted to pH 2 using 1.5 M aqueous H_2SO_4 under stirring to isolate MPEG-lignin, which precipitates in acidic environments. The MPEG-lignin precipitates were collected by centrifugation at 3300 rpm for 20 min, followed by successive washing with distilled water. The washed precipitates were air-dried at 25°C, followed by vacuum drying at room temperature (25±3 °C), yielding fine MPEG-lignin powders. The yield of MPEG-lignin was calculated on a dry wood basis (Eq. 1).

Fractional components (%) = [Obtained products (g) / Wood meal (g)] × 100   (1)

All MPEG-lignin samples were stored in a desiccator for further analysis. Control experiments involving solvolysis reactions with PEG200 and PEG400 as solvents at 140 °C for 90 min, were also performed (Nge *et al.* 2016) for comparison.
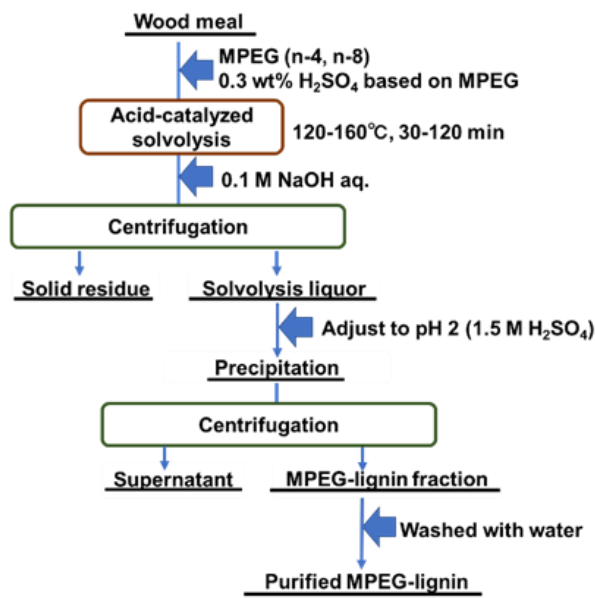
Fig. 1. Schematics of the preparation of MPEG-lignin

Characterization of MPEG-Lignin

Klason lignin analysis

Klason lignin analysis was performed according to the standard NREL procedure (Sluiter *et al.* 2008) with minor modification (Nge *et al.* 2018). Acidic solution filtrate was diluted to an appropriate concentration, and its absorbance at 205 nm was measured using a UV spectrophotometer (Shimadzu Corporation, Kyoto, Japan). Acid-soluble lignin content was determined using the absorbance constant of 110 dm^3 g^{-1} cm^{-1} (Dence 1992; Nge *et al.* 2018). All analyses were performed in duplicate for each sample, and the average values are reported.

Attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectroscopy

The ATR-FTIR spectra were recorded using a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific, Madison, WI, USA) equipped with an ATR accessory, a single ctystal diamond top plate. Vacuum-dried MPEG-lignin and solid residue samples were used for spectra collection and were scanned from 4000 to 400 cm^{-1} wavelength region with an accumulation of 32 scans at a resolution of 4 cm^{-1}. The band intensity of aromatic skeletal vibrations (aromatic ring C=C–C stretching) at 1510 cm^{-1} was used as an internal reference to normalize all MPEG-lignin spectra after ATR correction and baseline adjustment. The C–O stretching of cellulose and hemicelluloses at 1060 cm^{-1} was used for the normalization of solid residue spectra.

Size exclusion chromatography (SEC)

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity of MPEG-lignin samples were determined using a Prominence LC-20AD (Shimadzu Corporation, Kyoto, Japan) system equipped with a UV (280 nm), refractive index detector, and a sequence of two styrene-divinyl benzene gels columns: Shodex KD-804 and KD-802. The measurement was performed under the same conditions of previous research (Nge *et al.* 2016, 2018). High-performance liquid chromatography-grade *N,N*-dimethyl formamide containing 10 mM LiBr was used as the eluent at a flow

rate of 1.0 mL min^{-1} and 40 °C. Fluka PEG/poly(ethylene oxide) standard ReadyCal sets (Sigma-Aldrich Japan G. K., Tokyo, Japan) were used for molecular mass calibration. The standard and test samples were completely dissolved in the eluent and filtered through a 0.20 µm polytetrafluoroethylene syringe filter (ADVENTEC) prior to injection into the system.

Thermomechanical analysis (TMA)

The TMA was performed on TMA Q400 (TA Instruments-Waters LLC, New Castle, DE, USA) under a nitrogen flow rate of 100 mL min^{-1}. Vacuum-dried MPEG-lignin sample (approximately 6 mg) was loaded in a platinum pan, and the sample surface was covered with an aluminum lid. The sample was heated from room temperature to 200 or 220 °C at a heating rate of 5 °C min^{-1} under an applied load of 0.05 N. Using TA universal analysis software, the glass transition temperature (T_g) and viscous thermal flow temperature (T_f) were determined at the first and second transition points in TMA profiles, respectively.

Thermogravimetric analysis (TGA)

The TGA was conducted using a TGA Q500 (TA Instruments-Waters LLC, New Castle, DE, USA) under a nitrogen flow rate of 60 mL min^{-1} in the sample chamber and 40 mL min^{-1} in the balance chamber. Approximately 7 mg of MPEG-lignin powder was initially heated to 105 °C at 10 °C min^{-1} and kept isothermally for 20 min, followed by heating to 850 °C at 10 °C min^{-1}. Using TA universal analysis software, the decomposition starting temperature (T_{dst}) and maximum thermal decomposition temperature (T_{dmax}) were estimated from TGA profiles as temperatures corresponding to 5 wt% and maximum weight loss.

RESULTS AND DISCUSSION

Yield of Fractional Components

The GL prepared *via* acid-catalyzed solvolysis using MPEG-n4 and MPEG-n8 solvents are denoted as MPEG-n4-lignin and MPEG-n8-lignin, respectively. Figure 2(a) shows the yields of MPEG-n4-lignin and MPEG-n8-lignin and the corresponding solid residues as a function of solvolysis reaction time. The yield of MPEG-lignin fractions gradually increased with increasing solvolysis time. Accordingly, the amount of solid residue decreased with solvolysis time. The yields of MPEG-n4-lignin at 30, 60, 90, and 120 min were 18.2±0.1%, 22.8±0.6%, 24.8±0.6%, and 26.6±0.4%, respectively. The yields of MPEG-n8-lignin at 30, 60, 90, and 120 min were 9.8±0.7%, 18.1±1.0%, 21.4±0.6%, and 23.7±0.4%, respectively. Thus, the yield of MPEG-n4-lignin was generally higher than that of MPEG-n8-lignin. These results suggest that the molecular weight of the solvolysis reagent affects the rate of solvolysis, which in turn impacts the product yield. The molecular weights of MPEG-n4 (M_W = 208) and MPEG-n8 (M_W = 384) were approximately similar to those of PEG200 and PEG400, respectively. In a control experiment, the yields of PEG-lignins prepared from PEG200 (25.8 ±1.4%) and PEG400 (19.3 ±0.1%) solvolysis system under the same reaction conditions (at 140°C for 90 min) showed similar values with those of MPEG-lignins. In the authors' previous study (Nge *et al.* 2016) on the acid-catalyzed PEG solvolysis, the yield of GL in solvolysis with PEG200 was higher than that in solvolysis with PEG400. The acid-catalyzed MPEG solvolysis in

the present study showed a similar trend. Although the reaction rate differed between MPEG-n4 and MPEG-n8, the yield of MPEG-lignin showed similar tendencies in both cases: it increased until 90 min and then leveled off (Fig. 2(a)). Thus, 90 min was chosen as the optimum solvolysis time for subsequent studies of the effect of reaction temperature on the physical and chemical properties of MPEG-lignin.

The effect of reaction temperature was studied at 120, 130, 140, 150, and 160 °C for 90 min. Figure 2(b) shows the fractional components of the wood meal as a function of solvolysis temperature for both MPEG solvents. The amount of solid residue decreased with increasing reaction temperature.

The yields of MPEG-n4-lignin at 120, 130, 140, 150, and 160 °C were 11.9%, 21.1±0.8%, 24.8±0.6%, 28.4±2.0%, and 44.1±9.2%, respectively. The yields of MPEG-n8-lignin at 120, 130, 140, 150, and 160 °C were 2.5%, 11.3±1.1%, 21.4±0.6%, 27.2±0.5%, and 40.8±6.8%, respectively. For both solvolysis reagents, the yield of MPEG-lignin increases with reaction temperature. The yield of MPEG-lignin at 120 °C was rather low, indicating that 120 °C is not sufficient for the solvolysis of wood. Therefore, MPEG-lignins obtained at 120 °C were not characterized. For both MPEG-n4-lignin and MPEG-n8-lignin, the yields at 140 and 150 °C were comparable, whereas the yield at 160 °C was considerably higher.
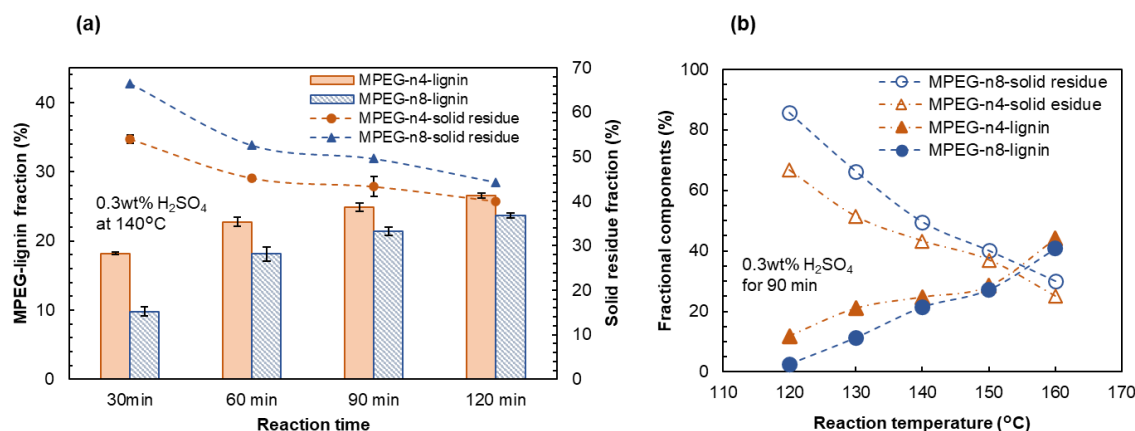

Fig. 2. (a) Yields of MPEG-lignins and solid residues as a function of reaction time; and (b) Yields of MPEG-lignins and solid residues as a function of reaction temperature

Characterization of MPEG-Lignins

Klason lignin analysis

Figure 3 shows the Klason lignin contents of MPEG-lignins and corresponding solid residues calculated based on the Klason lignin content of the wood meal. The Klason lignin content of wood meal used in this study was 32.9%.

The Klason lignin contents of MPEG-n4-lignin and MPEG-n8-lignin prepared at 130 °C were 49.0% and 23.3%, respectively, while the corresponding solid residues were 18.8% and 47.8%. Thus, at 130 °C, the Klason lignin content of MPEG-n4-lignin was higher than that of MPEG-n8-lignin. The MPEG-n4-lignin obtained at 140 °C showed 65.1% Klason lignin content, which was higher than that of MPEG-n8-lignin (50.5%) obtained at the same reaction temperature. The corresponding solid residues were 8.1% and 18.8%. The Klason lignin content of MPEG-n4-lignin prepared at 150 °C (67.2%) was close to that at 140 °C. In contrast, the MPEG-n8-lignin prepared at 150 °C showed a Klason lignin content of 68.8%, which also was considerably higher than that at 140 °C

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and was close to that of MPEG-n4-lignin prepared at 150 °C. The solid residues of MPEG-n4-lignin and MPEG-n8-lignin prepared at 150 °C were 6.9% and 13.6%, respectively. At a reaction temperature of 160 °C, the Klason lignin contents of both MPEG-n4-lignin and MPEG-n8-lignin were high, 140.8% and 83.2%, respectively. Notably, the Klason lignin content of MPEG-n4-lignin exceeded 100%, suggesting that the Klason lignin fraction may contain insoluble products such as decomposed sugar derivatives. The corresponding solid residues of MPEG-n4-lignin and MPEG-n8-lignin were 5.9% and 16.2%. Only small amounts of acid-soluble lignin were detected: 0.33% to 0.53% in MPEG-n4-lignin samples, with corresponding solid residues of 0.28% to 0.38%, and 0.47% to 0.64% in MPEG-n8-lignin samples, with corresponding solid residues of 0.36% to 0.46%.
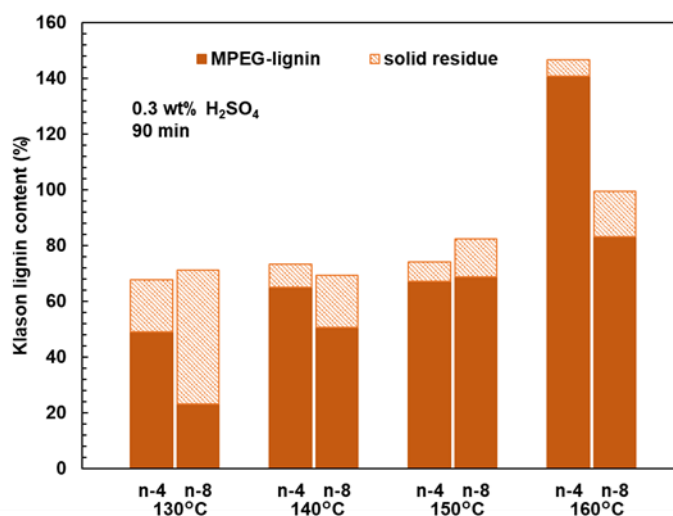

Fig. 3. Klason lignin content distributions of MPEG-lignins based on the Klason lignin content of wood meal

ATR-FTIR spectroscopy

ATR-FTIR spectra of MPEG-n4, milled wood lignin (MWL) extracted from Japanese cedar wood meal (Nge *et al.* 2020), and MPEG-n4-lignin prepared at 140 °C for 90 min are shown in Fig. 4(a). The absorbances at 2873, 1352, 1113, and 941 cm^{-1} observed in MPEG-n4 spectra correspond to symmetric C–H stretching of methylene groups, CH_2 wagging, C–O stretching, and CH_2 rocking vibration, respectively. In particular, the C–O stretching vibration at 1113 cm^{-1} showed a strong intensity. The absorbances at around 3400 cm^{-1} (O–H stretching), 2937 cm^{-1} (C–H stretching), 1594 cm^{-1} (aromatic ring C=C–C stretching), 1510 cm^{-1} (aromatic ring C=C–C stretching), 1462 cm^{-1} (C–H deformation), 1269 cm^{-1} (G-ring breathing with C=O stretching), and 1140 cm^{-1} (aromatic C–H deformation) are the characteristic absorbance of lignin polymer in MWL (Faix *et al.* 1992; Shi *et al.* 2012; Nge *et al.* 2020). Compared with MWL spectrum, the appearance of two strong peaks at 1132 cm^{-1} (C–O–C stretching of ether) and 1093 cm^{-1} (C–O deformation in secondary alcohol and ether) in addition to absorbance at 2879 cm^{-1} (C–H stretching), 1354 cm^{-1} (CH_2 wagging), and 947 cm^{-1} (CH_2 rocking) corresponding to MPEG-n4 were observed in MPEG-lignins. This result suggests the introduction of MPEG moieties into the lignin macromolecules.

Figure 4(b) shows the ATR-FTIR spectra of MPEG-n4-lignins. The ATR-FTIR spectra of MPEG-lignin prepared at 160 °C is similar to those of MPEG-lignins obtained under other conditions, with a notable difference observed at 1707 cm^{-1}. The strong

absorbance at 1707 cm^{-1} suggests the presence of a carbonyl structure. It is generally assumed that MPEG-lignin prepared at high reaction temperatures might contain carbonyls from decomposed sugar derivatives (Alekhina *et al.* 2015; Martín-Sampedro *et al.* 2019). The ATR-FTIR spectra of the corresponding solid residues of MPEG-n4-lignins are shown in Fig. 4(c). Because these solid residues are cellulose-rich, the most distinct absorbance at 1061 cm^{-1} corresponded to C–O stretching of cellulose and hemicellulose polymers (Shi *et al.* 2012). The spectra of the solid residue obtained at 130 °C showed the absorbance at 1275 to 1279 and 1510 cm^{-1}, which were the characteristic bands of lignin (Fig. 4(c)). These bands exhibit higher intensities at 130 °C than at higher temperatures (140 to 160 °C). This suggests that a considerable amount of lignin remained in the solid residue at 130 °C.

As mentioned in the results of Klason lignin analysis, high Klason lignin contents in the samples prepared at 160 °C, suggest that the determined Klason lignin content may have included decomposed sugar-derived compounds.
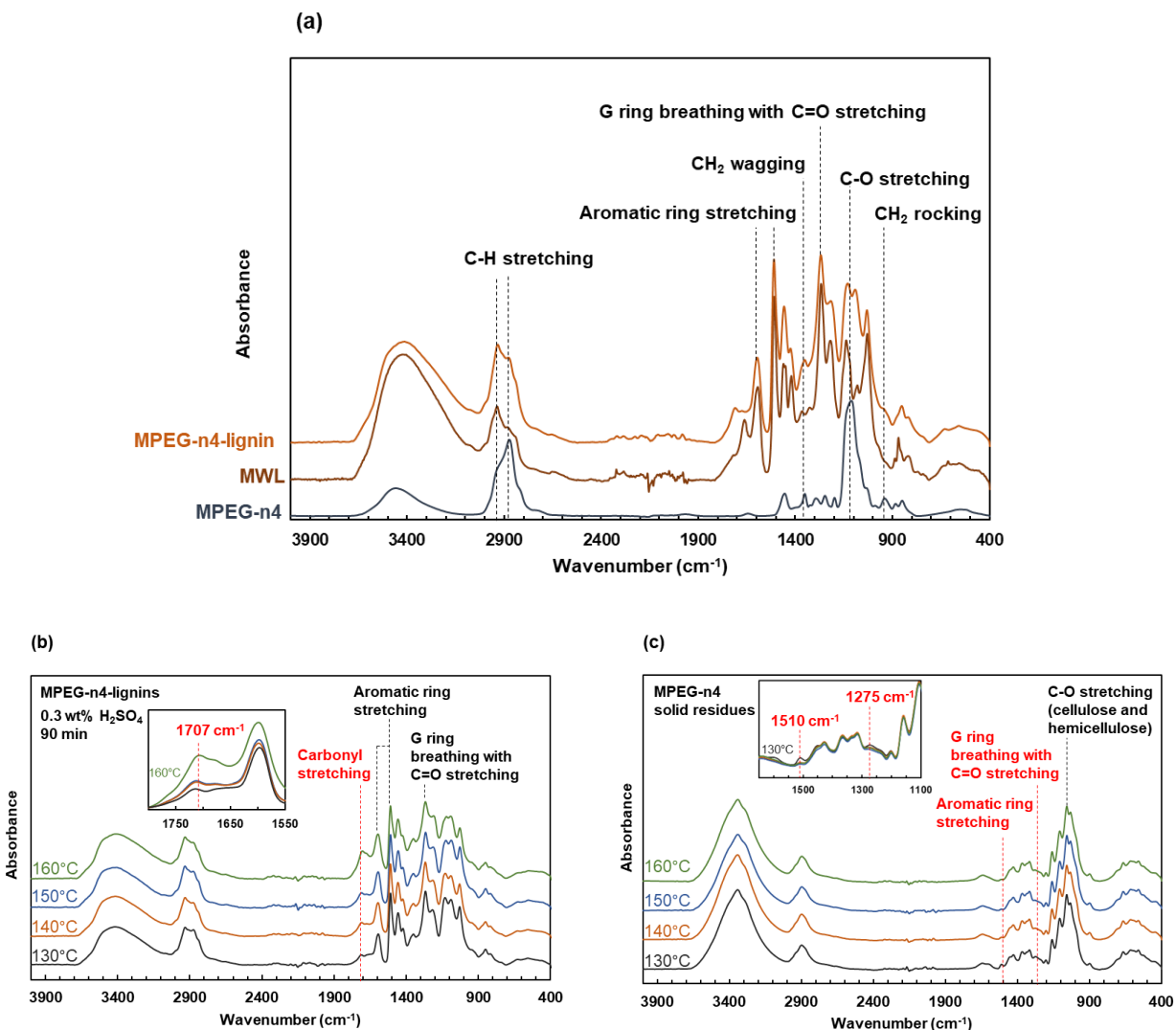

Fig. 4. (a) ATR-FTIR spectra of MPEG-n4, milled wood lignin (MWL) extracted from Japanese cedar wood meal, and MPEG-n4-lignin prepared at 140 °C for 90 min; (b) ATR-FTIR spectra of MPEG-n4-lignins; (c) ATR-FTIR spectra of MPEG-n4 solid residues

SEC analysis

Table 1 shows the result of SEC analysis. The M_w values of MPEG-n4-lignins decreased with the increase in reaction temperature from 130 to 150 °C. At the same time, the M_w of MPEG-n4-lignin at 160 °C was slightly higher than that at 150 °C. A similar trend was observed for MPEG-n8-lignin. The M_w values decreased with increasing reaction temperature until 150 °C. Notably, the molecular weights of MPEG-n4-lignin and MPEG-n8-lignin obtained at 140 °C and 90 min were lower than those of GLs obtained under the same conditions using PEG200 and PEG400, solvents with molecular masses similar to those of MPEG-n4 and MPEG-n8 (Nge *et al.* 2016, 2018).

Table 1. Number-Average Molecular Weight (M_n), Weight-Average Molecular Weight (M_w), and Polydispersity (PD) of GL (0.3 wt% H_2SO_4, 90 min)

System		M_n	M_w	PD
PEG200	140 °C	1563	4132	2.6
MPEG-n4	130 °C	1422	3811	2.7
MPEG-n4	140 °C	1263	3150	2.5
MPEG-n4	150 °C	1184	2844	2.4
MPEG-n4	160 °C	1174	3088	2.6
PEG400	140 °C	1618	4865	3.0
MPEG-n8	130 °C	1361	3812	2.8
MPEG-n8	140 °C	1268	3116	2.5
MPEG-n8	150 °C	1231	3037	2.5
MPEG-n8	160 °C	1254	3358	2.7

TMA results

The changes in the volume of MPEG-lignins were recorded as the distance moved by the probe in the TMA analysis. Figure 5(a) shows the TMA profiles of MPEG-n4-lignins as a function of reaction temperature. All MPEG-n4-lignins showed two distinct inflection points related to two volume changes. The former represents the glass transition temperature (T_g), and the latter corresponds to the viscous thermal flow temperature (T_f). Notably, the TMA analysis methodology used in the present study is the same as used in the authors' previous study on PEG solvolysis (Nge *at el.* 2016, 2018). The T_g and T_f values of MPEG-n4-lignin obtained at the reaction temperature of 130 °C were 98 °C and 139 °C, respectively, and the values increased with increasing reaction temperature. The MPEG-n8-lignins showed a trend similar to that for the MPEG-n4-lignins (Fig. 5(b)). The T_g and T_f values of MPEG-n8-lignin prepared at a reaction temperature of 130 °C were 72 °C and 122 °C, respectively. Furthermore, both T_g and T_f of MPEG-n8-lignins also increased with reaction temperature; however, the T_g and T_f of MPEG-n4-lignins (with a shorter polymer chain) are higher than those of the MPEG-n8-lignins (with a longer polymer chain).

As discussed above, the Klason lignin content also increased with reaction temperature (Fig. 3). Thus, the amount of introduced MPEG decreased with increasing reaction temperature. Therefore, MPEG-lignins prepared at higher reaction temperatures are expected to have higher proportions of aromatic structures, leading to high T_g and T_f. Therefore, lower T_g and T_f of MPEG-n8-lignins compared to those of MPEG-n4-lignins were supported by the Klason lignin content being lower in MPEG-n8-lignins than in MPEG-n4-lignins.
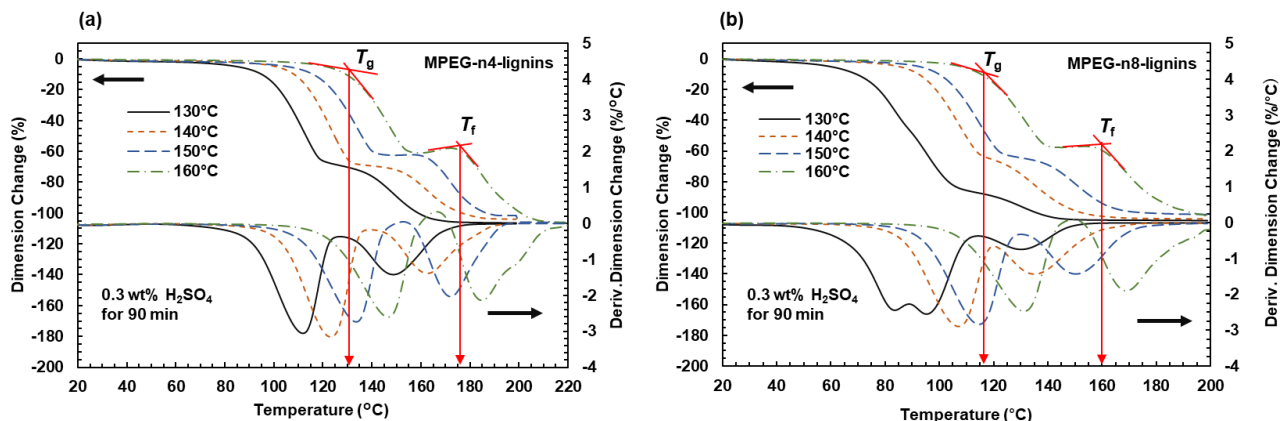
Fig. 5. (a)TMA profiles of MPEG-n4-lignins as a function of reaction temperature; and (b) TMA profiles of MPEG-n8-lignins as a function of rection temperature

TGA results

Figure 6(a) shows the TGA profiles of MPEG-n4-lignins. All MPEG-lignins showed similar T_{dmax} of about 360 °C.

The T_{dst} of MPEG-n4-lignin obtained at a reaction temperature of 130 °C was 244 °C, and the T_{dst} of MPEG-n4-lignins prepared at 140, 150, and 160 °C were in the range of 252 to 257 °C. The char residues at 800 °C for MPEG-n4-lignins prepared at 130, 140, and 150 °C were in the range of 32% to 34%. At the same time, that for MPEG-n4-lignin obtained at 160 °C was 42%.

Figure 6(b) shows the TGA profiles of MPEG-n8-lignins. The T_{dst} of MPEG-n8-lignin prepared at 130 °C was 248 °C, which was slightly higher than the corresponding value for MPEG-n4-lignin. Consequently, the determined T_{dst} of 260 to 264 °C for the MPEG-n8-lignins obtained at 140 to 160 °C are higher than those of MPEG-n4-lignins prepared at the same temperatures. These results suggest that MPEG-n8-lignins have better thermal stability than MPEG-n4-lignins. The char residue of MPEG-n8-lignins at 800 °C is at the range of 31% to 39%.
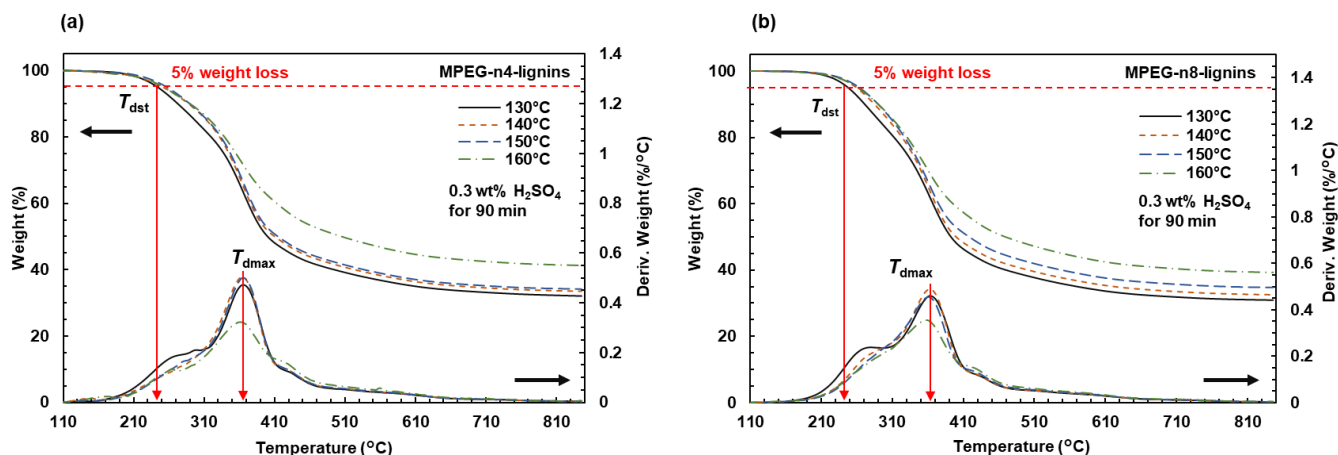

Fig. 6. (a) TGA profiles of MPEG-n4-lignins as a function of rection temperature; and (b) TGA profiles of MPEG-n8-lignins function of rection temperature

CONCLUSIONS

1. Considerable amounts of polyethylene glycol monomethyl ether (MPEG)-lignins were produced *via* an acid-catalyzed solvolysis of softwood meal in the presence of MPEGs.

2. The solvolysis of wood meal using MPEG-n4 proceeded faster than that using MPEG-n8.

3. MPEG-lignins prepared at higher reaction temperatures showed higher glass transition temperature (T_g) and viscous thermal flow temperature (T_f).

4. MPEG-lignins prepared at higher reaction temperatures exhibited larger carbonyl structure contents, which might be attributed to the decomposition of wood sugars.

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REFERENCES CITED

Alekhina, M., Ershova, O., Ebert, A., Heikkinen, S., and Sixta, H. (2015). "Softwood kraft lignin for value-added applications: Fractionation and structural characterization," *Ind. Crops Prod.* 66, 220-228. DOI: 10.1016/j.indcrop.2014.12.021

Aronovsky, S. I., and Gortner, R. A. (1936). "The cooking process, IX, Pulping wood with alcohols and other organic reagents," *Ind. Eng. Chem. Res.* 28(11), 1270-1276. DOI: 10.1021/ie50323a009

Dence, C. W. (1992). "The determination of lignin," in: *Springer Series in Wood Science, Methods in Lignin Chemistry*, C. W. Dence and S. Y. Lin (eds.), Springer, Berlin, Germany, pp. 33-62.

Duval, A., and Lawoko, M. (2014). "A review on lignin-based polymeric, micro- and nano-structured materials," *Reactive and Functional Polymers* 85, 78-96. DOI: 10.1016/j.reactfunctpolym.2014.09.017

Eudes, A., Liang, Y., Mitra, P., and Loqué, D. (2014). "Lignin bioengineering," *Curr. Opin. Biotechnol.* 26, 189-198. DOI: 10.1016/j.copbio.2014.01.002

Faix, O. (1992). "Fourier transform infrared spectroscopy," in: *Springer Series in Wood Science, Methods in Lignin Chemistry*, C. W. Dence and S. Y. Lin (eds.), Springer, Berlin, Germany, pp. 83-110.

Gomes, F. J. B., Santos, F. A., Colodette, J. L., Demuner, I. F., and Batalha, L. A. R. (2014). "Literature review on biorefinery processes integrated to the pulp industry," *Nat. Resour.* 5(9), 419-432. DOI: 10.4236/nr.2014.59039

Jiménez, L., De La Torre, M. J., Maestre, F., Ferrer, J. L., and Pérez, I. (1997). "Organosolv pulping of wheat straw by use of phenol," *Bioresource Technol.* 60(3), 199-205. DOI: 10.1016/S0960-8524(97)00028-X

Jiménez, L., Pérez, A., De La Torre, M. J., Rodríguez, A., and Angulo, V. (2008). "Ethyleneglycol pulp from tagasaste," *Bioresource Technol.* 99(7), 2170-2176. DOI: 10.1016/j.biortech.2007.05.044

Johansson, A., Aaltonen, O., and Ylinen, P. (1987). "Organosolv pulping – Methods and pulp properties," *Biomass* 13(1), 45-65. DOI: 10.1016/0144-4565(87)90071-0

Kishimoto, T., and Sano, Y. (2003). "Delignification mechanism during high-boiling solvent pulping. IV. Effect of a reducing sugar on the degradation of guaiacylglycerol-beta-guaiacyl ether," *J. Wood Chem. Technol.* 23(3-4), 233-248. DOI: 10.1081/WCT-120026931

Kouisni, L., Gagbe, A., Maki, K., Holt-Hindle, P., and Paleologou, M. (2016). "LignoForce system for the recovery of lignin from black liquor: Feedstock options, odor profile, and product characterization," *ACS Sustainable Chem. Eng.* 4(10), 5152-5159. DOI: 10.1021/acssuschemeng.6b00907

Li, Y., Jia, H., Ruxianguli, R., Yin, H., and Zhang, Q. (2015). "Extraction of lignin from wheat straw by catalysts in 1,4-butanediol medium under atmospheric pressure," *BioResources* 10(1), 1085-1098. DOI: 10.15376/biores.10.1.1085-1098

Lora, J. H., and Glasser, W. G. (2002). "Recent industrial applications of lignin: A platform for renewable aromatic polymeric materials," *Green Chem. Sustainable Technol.* 10(2), 39-48. DOI: 10.1023/A:1021070006895

Martín-Sampedro, R., Santos, J. I., Fillat, Ú., Wicklein, B., Eugenio, M. E., and Ibarra, D. (2019). "Characterization of lignins from *Populus alba* L. generated as by-products in different transformation processes: Kraft pulping, organosolv and acid hydrolysis," *Int. J. Biol. Macromol.* 126, 18-29. DOI: 10.1016/j.ijbiomac.2018.12.158

Nge, T. T., Takata, E., Takahashi, S., and Yamada, T. (2016). "Isolation and thermal characterization of softwood-derived lignin with thermal flow properties," *ACS Sustainable Chem. Eng.* 4(5), 2861-2868. DOI: 10.1021/acssuschemeng.6b00447

Nge, T. T., Tobimatsu, Y., Takahashi, S., Takata, E., Yamamura, M., Miyagawa, Y., Ikeda, T., Umezawa, T., and Yamada, T. (2018). "Isolation and characterization of polyethylene glycol (PEG)-modified glycol lignin via PEG solvolysis of softwood biomass in a large-scale batch reactor," *ACS Sustainable Chem. Eng.* 6(6), 7841-7848. DOI: 10.1021/acssuschemeng.8b00965

Nge, T. T., Tobimatsu, Y., Yamamura, M., Takahashi, S., Takata, E., Umezawa, T., and Yamada, T. (2020). "Effect of heat treatment on the chemical structure and thermal properties of softwood-derived glycol lignin," *Molecules* 25(5), article 1167. DOI: 10.3390/molecules25051167

Nge, T. T., Yamada, T., Tobimatsu, Y., Yamamura, M., Ishii, R., Tanaike, O., and Ebina, T. (2021). "Fractionation and characterization of glycol lignins by stepwise-pH precipitation of Japanese cedar/poly(ethylene glycol) solvolysis liquor," *ACS Sustainable Chem. Eng.* 9(2), 756-764. DOI: 10.1021/acssuschemeng.0c06892

Olivares, M., Guzmán, J. A., Natho, A., and Saavedra, A. (1988). "Kraft lignin utilization in adhesives," *Wood Sci. Technol.* 22(2), 157-165. DOI: 10.1007/BF00355851

Ono, K., Tanaike, O., Ishii, R., Nakamura, T., Shikinaka, K., Ebina, T., Nge, T. T., and Yamada, T. (2019). "Solvent-free fabrication of an elastomeric epoxy resin using glycol lignin from Japanese cedar," *ACS Omega* 4(17), 17251-17256. DOI: 10.1021/acsomega.9b01884

Shi, J., Xing, D., and Li, J. (2012). "FTIR studies of the changes in wood chemistry from wood forming tissue under inclined treatment," *Energy Procedia* 16(Part B), 758-762. DOI: 10.1016/j.egypro.2012.01.122

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., and Crocker, D. (2008). *Determination of Structural Carbohydrates and Lignin in Biomass* (NREL/TP-510-42618), *LAP*, National Renewable Energy Laboratory, Golden, CO, USA.

Suzuki, A., Shikinaka, K., Ishii, R., Yoshida, H., Ebina, T., Ishida, T., Nge, T. T., and Yamada, T. (2019). "Heat-resistant insulation film containing clay and wood components," *Appl. Clay Sci.* 180, article 105189. DOI: 10.1016/j.clay.2019.105189

Takahashi, K., Ishii, R., Nakamura, T., Suzuki, A., Ebina, T., Yoshida, M., Kubota, M., Nge, T. T., and Yamada, T. (2017). "Flexible electronic substrate film fabricated using natural clay and wood components with cross-linking polymer," *Adv. Mater.* 29(17), article 1606512. DOI: 10.1002/adma.201606512

Takata, E., Nge, T. T., Takahashi, S., Ohashi, Y., and Yamada, T. (2016). "Acidic solvolysis of softwood in recycled polyethylene glycol system," *BioResources* 11(2), 4446-4458. DOI: 10.15376/biores.11.2.4446-4458

Tomani, P. (2010). "The Lignoboost process," *Cellul. Chem. Technol.* 44(1-3), 53-58.

Zhao, X., Cheng, K., and Liu, D. (2009). "Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis," *Appl. Microbiol. Biotechnol.* 82(5), 815-827. DOI: 10.1007/s00253-009-1883-1