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Dynamic Mechanical Analysis of Plasticized and Esterified Native, Residual, and Technical Lignins: Compatibility and Glass Transition

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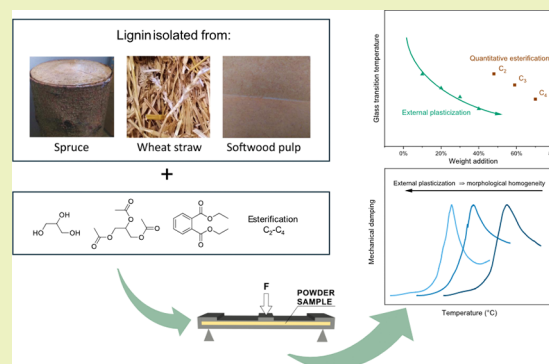
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ABSTRACT: The high glass transition temperature (T_g), stiffness, and poor flow properties of lignin are obstacles to lignin and lignocellulose utilization in thermoplastic applications. Two commonly applied methods to modify the viscoelastic properties of polymers are external plasticization, which involves physically blending them with low-molecular-weight additives, and internal plasticization, which involves covalently attaching side chains. However, most studies on lignin plasticization have focused on either technical, low-molecular-weight lignin or native, in situ lignin, with few efforts to bridge this gap. This study aims to determine if different lignin structures are susceptible to different modes of plasticization and how the plasticizer affects the phase morphology of the blends. Four lignins (softwood kraft lignin and lignin isolated from wheat straw, Norway spruce xylem, and residual softwood kraft pulp lignin) were plasticized with three external plasticizers (glycerol, triacetin, and diethyl phthalate) with different functionalities. The four lignins were in parallel internally plasticized by esterification with short-chain fatty acids (acetic, propionic, and butyric acid). The T_g and phase morphology of the modified lignins were studied by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Apart from phase separation in some lignin plasticizer blends, each plasticizer demonstrated similar efficiency (T_g depression) across all lignins, suggesting that the structure of the plasticizer, rather than the lignin structure, plays a more significant role in determining the outcome. Aprotic plasticizers were generally more efficient than protic per molar unit, and the magnitude of their mechanical dampening was also smaller over the glass transition, likely due to a decrease in the hydrogen bond density of the system. External plasticization was also found to narrow the width of the glass transition, indicating the formation of a morphologically more homogeneous material with less local T_g s than the pure lignin, whereas esterification broadened it somewhat.

KEYWORDS: lignin, lignocellulose, dynamic mechanical analysis, glass transition, plasticization, esterification, acetylation, differential scanning calorimetry



INTRODUCTION

Lignin is an abundant biopolymer and is present in many industrially important biomasses. In pulping, lignin has traditionally been seen as an obstacle to overcome. Still, as more emphasis is put on finding biobased alternatives to fossil raw materials, efforts to utilize lignin have increased.^{1–3} The relatively low environmental impact of lignin-containing pulp has also spurred interest in using high-yield pulps.⁴

Lignin in untreated biomass (native lignin), in pulp (residual lignin), and lignin isolated during pulping (technical lignin), have different molecular weights and structures and consequently different T_g s, but unless the molecular weight is very low, they are commonly found in the 150–250 °C span.^{5,6} The high T_g originates from the aromatic rings in the polymer backbone and strong inter- and intramolecular interactions, which also makes them brittle with poor flow properties.⁷

The high T_g and brittleness of lignin often call for some kind of plasticization before use. Water is used to soften lignin and

other wood components in traditional woodworking and pulping.⁸ In molding pulp, water also plays an important role.⁹ However, the T_g -depressing effect of water on lignin is limited with a cutoff point at a few weight percent.^{5,10} For technical lignins, such as kraft and organosolv lignin, many different plasticization strategies have been developed, based on both external (physical blend) and internal (covalently bonded side chains) plasticization, which surpass the effect of water.^{7,10}

Many different external plasticizers have been found to lower the T_g of technical lignin, provided they have some polarity.^{11–14} Plasticizers act as spacers between polymer

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Table 1. Yield, Molecular Weight, and OH Content of Lignins^a

sample	yield (%)	M_n (kg/mol) ^d	M_w (kg/mol) ^d	aliphatic	OH content (mmol/g) ^e			
					5-substituted	G noncondensed	H	COOH
spruce EMAL ^b (SL)	60 ^c	3.8	27.5	7.7	0.5	1.1	0.1	0.1
wheat straw EMAL (WL)	68 ^c	3.1	15.7	8.7	0.3	0.9	0.7	0.2
pulp EMAL (PL)	47 ^c	5.8	77.3	4.8	1.6	1.4	0.1	0.4
softwood kraft lignin (KL)		1.6	12.2	2.4	2.6	2.6	0.2	0.4

^aFor experimental details, see previous publication. ^bEnzymatic mild acidolysis lignin (EMAL). ^cYield = mass of extract/mass of Klason and acid-soluble lignin of biomass. ^dDetermined with size-exclusion chromatography and pullulan standards and should therefore be seen as relative within the study, as this method undervalues the molecular weight. ^eDetermined with ³¹P NMR.

chains, causing an increase in the free volume and hence a reduction of the T_g . For OH-containing polymers, such as lignin, breaking inter and intramolecular hydrogen bonds is important, which explains the effect of water on the relatively hydrophobic lignin.^{10,15} The most efficient plasticizers for both technical and in situ native lignin are often found to be aprotic,^{10,16–18} meaning that they can only accept hydrogen bonding. The reason for this has not been elucidated, but the density of these secondary interactions likely plays a role, as protic plasticizers will be able to engage in more hydrogen bonding with lignin.

Another factor to consider is the phase morphology of the blends. The cohesive energy difference and specific interactions between plasticizer and polymer have a large effect on the distribution of plasticizer in the matrix. This will in turn affect properties such as processability, stability, and permeability. Poor dispersion of plasticizers in polymers leads to broad glass transitions, poor barrier properties, and in the long term, phase separation and migration.¹⁹

Dynamic mechanical analysis (DMA), a highly sensitive method, has been used to study the compatibility of plasticizers in synthetic polymers since the mid-20th century,²⁰ but has so far not been applied for this purpose on isolated lignins. DMA is also useful as the mechanical properties of polymers change more drastically over the glass transition than the calorimetric properties. The T_g of lignin is not always detectable with DSC,²¹ and powder sample holder for DMA has proven useful for studying the T_g of high molecular-weight lignins.⁶

As the demand for biosourced products increases, plasticizing a wide variety of lignins is important.⁹ Native, residual, and technical lignins vary in chemical and molecular structure,^{22,23} which would be expected to lead to different plasticization outcomes; however, external lignin plasticization has mainly been applied to either technical or native in situ lignins.

This study aims to determine whether different types of lignin exhibit varying levels of plasticizer compatibility and efficiency, and if they respond differently to different external and internal plasticization treatments. Softwood kraft lignin (KL) and lignin isolated from Norway spruce (SL), wheat straw (WL), and high-yield softwood kraft pulp (PL) were plasticized internally and externally and thermoplastic properties evaluated. Three external plasticizers were chosen for their disparity in functionality: glycerol (GLY), triacetin (TA), and diethyl phthalate (DEP) (see Figure S1 for molecular structure of plasticizers). GLY is a triol with the capacity to donate and accept hydrogen bonds, whereas TA and DEP are aprotic and can only accept hydrogen bonds. DEP is furthermore an electron-deficient aromatic, with potential for donor-accepting

interactions with the electron-rich lignin aromatics, and could consequently compete with internal π - π bonds.²⁴ The lignins were also internally plasticized, by quantitative esterification of OH groups with acetic, propionic, and butyric anhydride. The T_g and phase morphology of these blends and lignin esters were studied with DMA and differential scanning calorimetry (DSC). The high sensitivity of DMA allowed for a detailed study of the mechanical damping profiles of the blends, whereas DSC was used to study phase separation.

MATERIALS AND METHODS

Materials. The following chemicals were used as received: acetic, propionic, and butyric anhydride (Sigma-Aldrich, $\geq 99\%$); chloroform (Sigma-Aldrich, $\geq 99\%$); diethyl phthalate (DEP) (Sigma-Aldrich, 99.5%); glycerol (GLY) (Sigma-Aldrich, $\geq 99.0\%$); methanol (Thermo Scientific, $\geq 99\%$); pyridine (Scharlab, 99.5%, anhydrous); triacetin (TA) (Sigma-Aldrich, 99%). Softwood kraft lignin (KL) from the LignoBoost process was provided by a Swedish pulp mill. Never-dried unbleached softwood kraft pulp (13 wt % lignin content) was kindly supplied by Stora Enso AB (Karlstad, Sweden). The pulp and the kraft lignin were made from Norway spruce (*Picea abies*) and pine (*Pinus sylvestris*), but with unknown ratios. Wheat straw (*Triticum aestivum*) and Norway spruce (*Picea abies*) xylem was sourced in Sweden.

Lignin Isolation. WL, SL and PL were isolated according to the enzymatic mild acidolysis lignin (EMAL) protocol, which isolates lignin at high yield with little apparent degradation (depolymerization and condensation).^{25,26} The isolation process and the isolated lignins in this study has been described and characterized in a previous publication.⁶ The yield of isolation, molecular weight, and the OH content determined with ³¹P NMR are found in Table 1.

Lignin Esterification. The lignins were esterified with acetic, propionic, and butyric anhydride, respectively, in pyridine at room temperature under a nitrogen atmosphere and stirring for 24 h. Lignin (250 mg) was dissolved in 50 mL of pyridine, after which a 20-mol equiv of anhydride (of the total OH in the lignins) was added. All esterifications were performed once. The procedure was adopted from Månsson²⁸ for quantitative acetylation. The reaction was terminated by adding methanol. The acetylated lignins were collected by rotary evaporation. The propionated and butylated lignin were isolated by first removing volatile compounds with rotary evaporation at 50 °C. The propionic and butyric acids were then removed by liquid-liquid extraction with deionized water and chloroform (10:90 mL). The extraction was repeated until the extraction liquid was neutral and no liquid remained after rotor evaporation. All esterified lignins were then dried in a vacuum oven at 50 °C overnight to evaporate any remaining acid or pyridine.

Degree of Esterification Determined by FTIR and ³¹P NMR. Attenuated total reflectance Fourier transform IR (ATR-FTIR) measurements of the esterified lignins were recorded with a Spectrum One FTIR Spectrometer (PerkinElmer instruments). Absorbance was recorded in the range of 4000–400 cm^{-1} with 32 scans and a resolution of 4.0 cm^{-1} . All samples were measured 5 times, and the spectra were averaged, background subtracted using a moving average

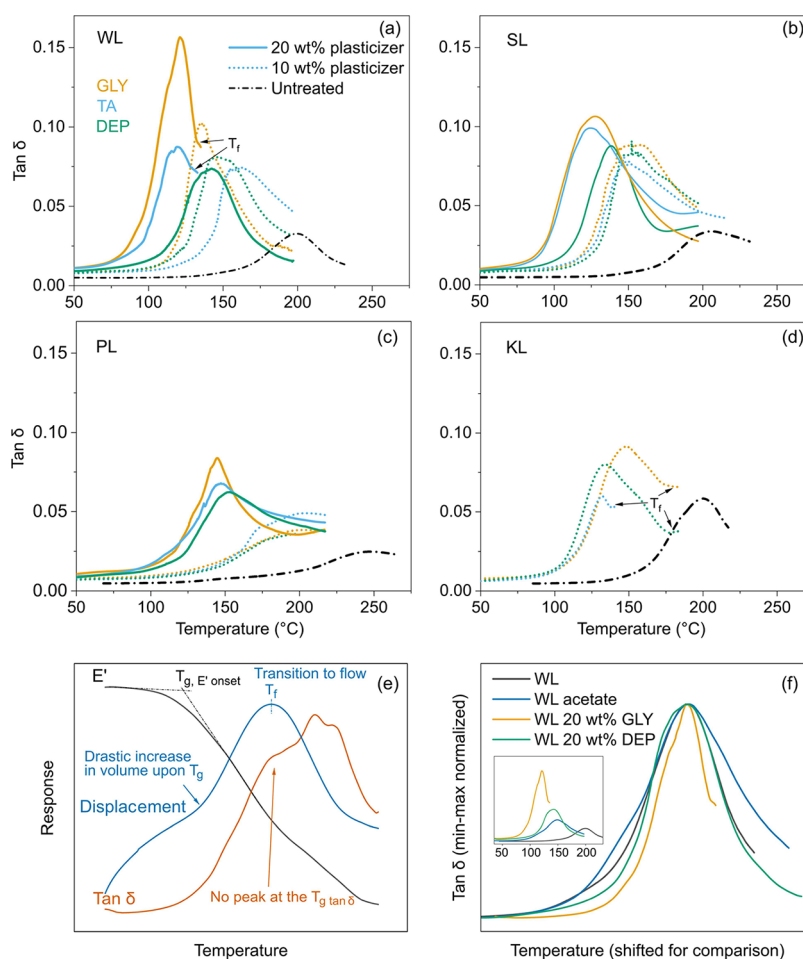


Figure 1. (a–d) $\tan \delta$ thermographs of plasticized lignin. The legend in panel (a), refers only to panels (a–d). T_f refers to the temperature where the blend starts to flow, which is illustrated in the DMA curves of WL 30 wt % GLY in panel (e), together with the determination of T_g E' onset. (f) Width of the glass transition in $\tan \delta$ with the temperature shifted for clarity. Inset shows the unscaled curves.

algorithm, and normalized to the aromatic stretching at 1600 cm^{-1} using SpectraGryph 1.2.

Quantification of hydroxyl groups with ^{31}P NMR was conducted according to Balakshin and Capanema²⁹ with the internal standard endo-*N*-Hydroxy-5-norbornene-2,3-dicarboximide (Sigma-Aldrich) and the phosphorylation reagent 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Sigma-Aldrich). Measurements were conducted between 1 and 3 h after the addition of the reagent. The NMR spectra were recorded on a Bruker Avance NEO spectrometer 600 MHz utilizing inverse gate detection and a 90° pulse width. The times of acquisition and relaxation were 1.0 and 5.0 s, respectively, and 256 scans were measured. Background subtraction was performed using a linear function. The spectra were chemical shift calibrated using the anhydride product at 132.2 ppm. The degree of esterification was determined by calculating the fraction of OH groups available for phosphorylation before and after esterification.

Lignin Plasticization. Lignins (200 mg) were plasticized in glass vials by adding the plasticizer (20 wt %) in methanol solution with a glass syringe, stirring the blend, and sealing the vial. The lid was removed after 24 h and the methanol was allowed to evaporate slowly for 48 h, after which the samples were put in a vacuum oven at 100 mbar at 40°C for 1 h to remove the last methanol. No weight loss was found when pure plasticizer was subjected to the same conditions. The samples were then stored in a desiccator to avoid moisture uptake.

The T_g of the blends were predicted for kraft lignin using the Fox equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (1)$$

where w_1 and w_2 are the weight fractions and $T_{g,1}$ and $T_{g,2}$ are the glass transition temperatures of the two components.^{30,31}

DMA Measurements. A Q800 from TA Instruments equipped with a dual cantilever clamp and a powder sample holder was used to perform DMA measurements. The measurements were carried out with a heating rate of $3^\circ\text{C}/\text{min}$ and an amplitude of deformation of $5\ \mu\text{m}$. The temperature range for the measurements was 20°C to 50 – 70°C over T_g of the samples. A deformation frequency of 1 Hz was employed for all measurements, and duplicates were measured for each sample. The error of the duplicate measurements was calculated as the difference divided by 2. The moduli values are nonabsolute when conducting DMA with the powder sample holder, partly due to the steel parts bending and partly because powders do not have well-defined geometric factors; however, as the $\tan \delta$ is calculated from the phase lag, no normalization has been performed except when stated.

DSC Measurements. T_g of KL and KL-plasticizer blends were determined with a DSC 2 STARe system from Mettler Toledo. Each sample was run in triplicate, with an approximate weight of 10 mg in aluminum crucibles with a pinhole in the lid. The samples underwent two consecutive heating ramps, starting from 50°C below to 50°C over the T_g with a heating rate of $10^\circ\text{C}/\text{min}$. A cooling ramp of $10^\circ\text{C}/\text{min}$ was applied between the two heating ramps, with a 3 min isothermal between each step. The inflection point in the second run was used to determine the T_g . To determine if phase separation had occurred between lignin and plasticizer, the occurrence of a T_g of the plasticizer was examined in the manner described above but using a

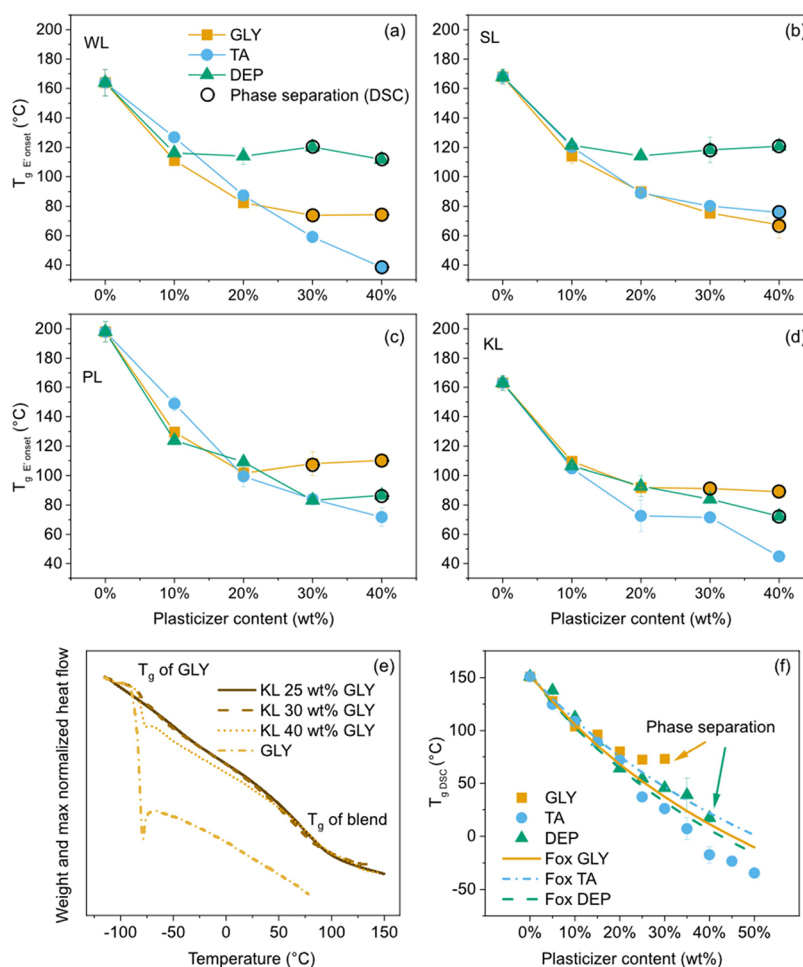


Figure 2. (a–d) T_g determined with DMA as a function of plasticizer content. (e) Weight- and max-normalized DSC graph illustrating the phase separation of GLY from KL. (f) T_g of KL determined by DSC as a function of plasticizer content. The predicted T_g s for the blends calculated with the Fox equation (eq 1) have also been plotted.

liquid-nitrogen-cooled system (DSC 250, TA Instruments). All samples with a plasticizer content of 20 wt % or higher were analyzed in this manner. As the T_g of KL-TA blends at high loadings were very low, the liquid-nitrogen-cooled system was also used to confirm the accuracy of the T_g determination (see Figure S4b).

RESULTS AND DISCUSSION

Externally Plasticized Lignins. This study aims to elucidate the impact of lignin and plasticizer structure on the plasticization of lignin. For this purpose, four different lignins were studied. The high yield and purity protocol of EMAL was used to isolate lignin from Norway spruce (SL), wheat straw (WL) and softwood kraft pulp (PL). Additionally, a softwood kraft lignin (KL) refined with the Lignoboost process was acquired.

The molecular differences of the lignins are reflected in the content of Table 1, where KL has the lowest molecular weight and the highest phenolic content, while SL and WL have intermediate molecular weights and the highest aliphatic OH content. PL is intermediate in OH content but has the highest molecular weight. Likewise, KL and PL have higher contents of 5-substituted lignin structures (such as 5–5' and 4–O–5' linkages), which are results of condensation reactions during pulping. Further discussion of the molecular structure and their impact on the T_g can be found in our previous publication.⁶

The glass transitions of lignins are broad compared to synthetic polymers,^{6,32} likely due to the inherent heterogeneity in lignin structure and composition. The glass transition of plasticized polymers typically broadens due to the increase in compositional heterogeneity.^{33–39} However, upon plasticization of the lignins, the transitions did not broaden further (Figure 1a–d), but rather narrow down, especially with 20 wt % plasticizer. Based on the temperature difference between the $\tan \delta$ maximum and the $\tan \delta$ onset, the transitions narrow with around 10–50% (Figure S2). This would indicate that lignins form a more morphologically homogeneous material upon plasticization with less local environments (local T_g s). TA gave the narrowest transitions in all lignins except WL, indicating that TA is highly compatible with many lignin structures.

As the moduli values in this study are nonabsolute, the crossover point from more elastic to more viscous ($E'' > E'$) cannot be determined. The point when the material becomes liquid-like in the sample holder is still detectable, as $\tan \delta$ starts to increase, and the displacement reading of the instrument shows that the pocket is being pressed together – i.e., the sample is flowing out. These transitions have been illustrated in Figure 1e, and the transitions are marked T_f in Figure 1a–d. The low molecular-weight KL has a greater tendency to start to flow (see Figure S3 for KL-GLY blends), even at low plasticizer concentrations, likely due to the small amounts of

entanglements. This, unfortunately, hinders the determination of the T_g at E'' and $\tan \delta$ maximum, values that indicate the center of the transition. That is why the T_g in this study is determined as the onset of the decline in E'' , as the material does not start to flow at this stage of the transition. Another limitation brought on by the flow is that samples with a plasticizer content higher than 40 wt % could not be loaded in the powder pocket, as they started to flow at room temperatures.

In Figure 2a–d, the onset of the T_g in E' is plotted as a function of plasticizer content. At 10 wt % the outcome appears to be uniform: TA performs slightly worse for WL and PL, but otherwise the plasticizers are equally efficient in reducing the T_g of the specific lignins. This suggests that each plasticizer forms similar structures across all lignins, or at the very least, no superior conformation arises from any specific combination.

When comparing lignins with 10 wt % plasticizer content, the T_g reduction is similar between SL, WL and KL (approximately 60 °C), while the T_g for PL drops 80 °C with GLY and DEP. The reason for this could be that the high molecular-weight PL, with its relative lack of mobile chain ends, is mobilized to a greater extent by adding small diffusing plasticizers.

GLY has about half the molecular weight relative to the other two plasticizers, and as a consequence, the molar content is twice as high at the same weight content. In this view, the molar performance of GLY is much worse. The molar content and size of plasticizers are important, as a higher amount of functional groups will compete better with polymer–polymer interactions and introduce more free volume, but also as smaller molecular plasticizers tend to blend better in many polymer systems.^{19,40–42} The poor molar performance of GLY could be due to the fact that, unlike the other two plasticizers, it can both donate and accept hydrogen bonds and therefore maintain the hydrogen bond density in the system. This phenomenon, the hydrogen-bond bridging of protic plasticizers, has been observed in both synthetic and biobased systems and tends to lead to mechanically stronger or stiffer materials and less efficient T_g reduction.^{43–45} Thus, GLY appears to lower the T_g by increasing the free volume but not necessarily by decreasing hydrogen bonding in the system.

Another indication of the effect of the strong interactions of GLY is the height of the $\tan \delta$ maximum. The $\tan \delta$ values increase with the addition of plasticizers due to a shift in the ratio of viscous to elastic resistance to deformation of the material (E''/E'), i.e. the material becomes more mobile. GLY generally produces higher peaks in both $\tan \delta$ and E'' than the other plasticizers, meaning that the viscous resistance to deformation is increased during the glass transition. Pure GLY has a higher viscosity than TA and DEP, due to its high hydrogen bond capability, and it is therefore not surprising that it also infers this viscosity on the GLY-lignin blends.

DEP is generally not more efficient in lowering the T_g than TA. It appears that aromatic interactions do not occur between lignin and DEP, or that aromatic interactions in lignin are weaker than internal hydrogen bonding and therefore less relevant when hydrogen-accepting plasticizers are added. Following from the latter, it is also possible that the formation of lignin-plasticizer hydrogen bonds disrupts lignin–lignin aromatic interactions, as they would be highly conformation-dependent.

The T_g values start to plateau at higher plasticizer contents. This behavior indicates phase separation. To determine if the plasticizer had separated from the lignins, the materials were subjected to DSC analysis. An individual T_g for the plasticizer is evidence of it having formed its own phase (shown in Figure 2f), and the occurrence of phase separation has been marked with circles in Figure 2a–d. Phase separation occurs at different concentrations for the different lignins. The two isolated native lignins have a low miscibility with DEP, whereas the two more condensed lignins (KL and PL) phase separate at lower concentrations with GLY. TA is the most compatible plasticizer with all of the lignins, and no phase separation was detected for KL and PL.

The miscibility with and dissolution of lignin is not easily predicted. Hansen solubility parameters (HSP) can often only give an indication, but cannot fully predict the solubility of lignin.^{46,47} There are many different estimations of the HSP for lignins, both experimental and theoretical, for both native and technical lignins.⁴⁸ The total HSP typically fall between 20 and 30 MPa^{1/2}, with native lignins in the higher end and kraft lignins in the lower—mainly due to the lower polarity and hydrogen bonding capacity of kraft lignin.

Two different lignin-HSP models were selected to predict the miscibility of the plasticizers by calculating the relative energy distance (eq S1). The two models were selected to reflect the spread in molecular structure of the investigated lignins: one is an alkali lignin representing a condensed lignin rich in phenol, and one is a milled wood lignin, representing an isolated native lignin rich in alcohol, both determined through the Hansen dissolution method.

The calculated relative energy distance (see Table S1) of TA and DEP gave values below 1 for alkali lignin indicating partial miscibility, whereas GLY had a value just over 2 indicating immiscibility. For milled wood lignin, all the plasticizers had values slightly below 2. HSP could predict the partial miscibility of some of the plasticizers, but it could not predict the better overall performance of TA and the poor performance of DEP with WL and SL.

KL plasticized with TA does not phase separate at 40 wt %, and it also appears to become more efficient at higher loading. However, it was not possible to load 50 wt % samples in the DMA as the material was too soft at room temperature. To explore the plasticization of KL in more detail, DSC measurements were conducted on KL samples from 0 to 50 wt % plasticizer with 5 wt % intervals (Figure 2f for T_g versus plasticizer content, Figure S4 for second heating curves). Unlike the higher molecular weight lignins, the T_g of plasticized KL was detectable throughout the concentration series.

The DSC-determined T_g s were successively lower than the T_g s determined with DMA. This is not uncommon in the literature.^{49–51} One reason is the difference in experimental time frames, not only due to varying heating rates but also because DMA introduces a frequency-dependent observation time through the periodic strain, complicating direct comparisons.⁵² Another reason is that DSC and DMA detect different changes upon heating. DSC detects the change in heat capacity (ΔC_p), which is sensitive to the glass-forming properties and molar content, whereas DMA detects changes in the mechanical properties. Compared to low molecular-weight plasticizers, polymers have low molar content and are hard glass formers, meaning that the change in ΔC_p will be relatively small.⁵³ Most likely, the change in ΔC_p of the

plasticizers is detected before the change in mechanical properties is registered with DMA.

The general trend observed for plasticized KL is the same in both DMA and DSC. GLY plateaus at low concentrations, DEP still has a declining curve upon phase separation, and TA has a continuous T_g depression with increasing plasticizer content. Also, no phase separation was detected at 50 wt % TA.

In previous studies on the plasticization of lignin,^{10,11} T_g versus composition curves often appear discontinuous, meaning that they do not follow an additive relationship, such as Fox or Gordon–Taylor-based models. These nonmonotonic behaviors indicate that interactions between polymer and plasticizer are changing. This is often interpreted as the plasticizer going from mainly interacting with the polymer, to having more interactions with itself. If the break in the curve leads to a reduced rate of change, this is often interpreted as the plasticizer starts to distribute itself more heterogeneously within the matrix, leading to poorer plasticization performance.^{33,54} In a recent study⁵⁵ where starch was plasticized with GLY, an increased rate of T_g decline was observed above 20 wt %. Based on molecular dynamics simulation, the authors hypothesized that the increased rate was due to the formation of plasticized regions that start to move cooperatively. They describe it as percolating paths formed when the plasticizer volume is high enough.

As the T_g of the pure plasticizers could be determined with DSC, the Fox equation can be used to model the data. All plasticizer blends follow the model up to a content of approximately 20 wt %, but at higher concentrations, GLY starts to phase separate, and TA achieves higher efficiency. In the case of blends leading up to phase separation, it appears reasonable to assign the declining efficiency to a poorer dispersity of plasticizers in the system. Conversely, TA is soluble in KL over the whole concentration range, so the hypothesis, that at a certain plasticizer volume, a new better-plasticized supramolecular structure has formed, also appears reasonable. The same phenomena are not seen in the other lignins studied with DMA. This could be due to that the break-off point occurs above 40 wt %, or the poorer solubility of the plasticizers, either due to poor interactions which lowers the enthalpy gain, but also due to their much higher molecular weight, which lowers the entropy gain.

Internally Plasticized Lignins. Esterification of lignin can introduce free volume as the side chains hinder close packing of the material. A higher content of side chains, either in terms of length or number, typically increases the amount of free volume in polymers, unless the fraction of side chains becomes so large that they dissolve into each other and increase intermolecular interactions.^{56,57} Esterification also weakens the secondary interactions of lignin, as OH groups are substituted by ester groups. There is some experimental evidence that aliphatic OH partakes in stronger intermolecular interactions in lignin than phenolic OH, as the latter instead interacts with methoxy groups on the same ring,⁵⁸ which suggests that native lignins would have a greater T_g -depression upon esterification.

The lignins in this study were esterified with linear C_{2-4} esters to investigate the effect of esterifying lignins with different OH groups, and to investigate how esterification compares to external plasticization in terms of efficiency for lignins of different structures. Esterification was confirmed with FTIR, showing a reduction in OH stretching by a factor of 10, and with ³¹P NMR, which only detects 1–5% of the original

OH content after esterification (Figure S3 and Table S2). The samples can therefore be considered to be close to quantitatively esterified. Between 0 and 4 wt % of acid residue from the anhydride reaction was found in the samples in the ³¹P NMR analysis. This residue might lower the T_g somewhat but compared to a quantitative esterification (weight increase of 50–70%), the effect is likely negligible.

A large variation in the reduction in T_g for quantitative acetylation is found for technical lignins in the literature (25–65 °C).^{10,59–61} It is not clear why there are such large discrepancies. Some studies may have wrongly assumed quantitative acetylation, without sufficient characterization, or that there might be problems with solvent and acid impurities. The relationship between the degree of acetylation and T_g has been found to have a nonlinear decay¹⁰ and longer side chains of the esters reduce the T_g to a larger extent, but with a declining trend.^{59–61}

In this study, acetylation appears equally efficient for all lignins (Figure 3) with a drop of about 60–70 °C. This would

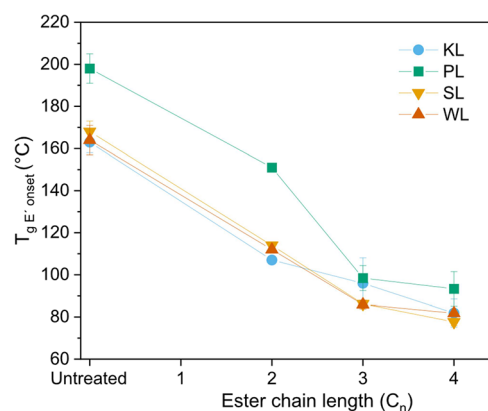


Figure 3. T_g as a function of ester chain length.

indicate that substituting phenolic and aliphatic OH groups are comparable in reducing the T_g , as the total OH contents of softwood lignins are close to identical. Between C_2 and C_3 the slopes start to deviate. SL and WL have similar molecular weights and behave alike. PL, which has a much higher molecular weight, had its T_g reduced to a larger extent. KL, with the lowest molecular weight, had the flattest curve. When going from C_3 to C_4 , the lines flatten, except for KL which continues on the same linear trajectory. A study on low molecular-weight lignins also found a linear relationship between ester chain length and T_g for C_{2-4} .⁶¹ Lignins of different molecular weights appear to respond differently to esterification, with higher molecular weight lignins benefiting more from longer side chains; however further experiments are needed to clarify this relationship.

Internal plasticization did not lead to a reduction in the width of the glass transition as was seen with external plasticization (Figure 1f), except for PL acetate. That the fixed position of the new side chains does not increase the spatial homogeneity is not surprising. It is common that introducing aliphatic side chains, to both synthetic and biopolymers, leads to the formation of side chain clusters.^{62–64} Clusters have not necessarily formed in the lignins in this study, but the phenomena illustrate the nondynamic nature of internal plasticization.

The mass increase of completely acetylated lignins (based on 8–10 OH mmol/g) would be approximately 50 wt %, which roughly equals a 1 °C reduction in T_g per wt % added for all the lignins in the study. This value for the external plasticization is closer to 3–4 °C/wt %. Propylation and butylation have a similar reduction of 1–1.5 °C/wt %. Thus, the atomic efficiency for esterification was very poor as compared to external plasticization. As both the degree of esterification¹⁰ and the amount of external plasticizer added reduced the T_g with an hyperbolic decline, a lower degree of modification would likely not change this difference in efficiency greatly.

CONCLUSIONS

The T_g -depression and compatibility of lignins with various structures with three different plasticizers and three types of esterifications were evaluated utilizing DSC and powder-holder DMA. The solubility of the plasticizers varied between the different lignins but the hypothesis that various lignin structures would exhibit varying susceptibilities to different mechanisms of external plasticization was not supported. Each plasticizer demonstrated similar efficiency across all lignins, suggesting the formation of similar lignin-plasticizer structures. Based on the HSP for milled wood lignin and alkali lignin, it was not possible to predict but only indicate suitable plasticizers. GLY, a hydrogen donating and accepting plasticizer, had a poor molar efficiency in reducing the T_g as well as high mechanical damping over the glass transition, compared to the plasticizers that could only accept hydrogen bonding. It would then appear as if reducing the hydrogen bond density of the system with aprotic plasticizers decreases both the T_g and the viscosity to a larger extent, which would be more beneficial for thermoplastic processing. Plasticizers were found to not only reduce the T_g of lignin but also be able to narrow down the glass transition width, which indicates a decrease in morphological heterogeneity.

Internal plasticization was found to be less efficient in reducing the T_g per weight unit added, and it did not generally reduce the width of the glass transition. External plasticization strategies therefore appear to be superior for the thermoplastic processing of lignin: they are resource-efficient and increase the uniformity of the phase change.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c08391>.

Molecular structure of plasticizers; Hansen solubility parameters and relative energy differences calculated for lignin blends; width of glass transitions; example FTIR and ³¹P NMR spectra of esterified lignins; and degree of esterification determined by ³¹P NMR (PDF)

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Notes

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REFERENCES

- Upton, B. M.; Kasko, A. M. Strategies for the Conversion of Lignin to High-Value Polymeric Materials: Review and Perspective. *Chem. Rev.* **2016**, *116* (4), 2275–2306.
- Chio, C.; Sain, M.; Qin, W. Lignin utilization: A review of lignin depolymerization from various aspects. *Renewable and Sustainable Energy Reviews* **2019**, *107*, 232–249.
- Moreno, A.; Sipponen, M. H. Lignin-based smart materials: a roadmap to processing and synthesis for current and future applications. *Materials Horizons* **2020**, *7* (9), 2237–2257.
- Oliaei, E.; Lindström, T.; Berglund, L. A. Sustainable Development of Hot-Pressed All-Lignocellulose Composites—Comparing Wood Fibers and Nanofibers. *Polymers* **2021**, *13* (16), 2747.
- Back, E.; Salmén, L. Glass transitions of wood components hold implications for molding and pulping processes. *TAPPI J.* **1982**, *65* (7), 107–110.
- Henrik-Klemens, Å.; Caputo, F.; Ghaffari, R.; Westman, G.; Edlund, U.; Olsson, L.; Larsson, A. The glass transition temperature of isolated native, residual, and technical lignin. *Holzforschung* **2024**, *78* (4), 216–230.
- Wang, C.; Kelley, S. S.; Venditti, R. A. Lignin-Based Thermoplastic Materials. *ChemSusChem* **2016**, *9* (8), 770–783.
- Börcsök, Z.; Pásztor, Z. The role of lignin in wood working processes using elevated temperatures: an abbreviated literature survey. *European Journal of Wood and Wood Products* **2021**, *79* (3), 511–526.
- Zhang, Y.; Duan, C.; Bokka, S. K.; He, Z.; Ni, Y. Molded fiber and pulp products as green and sustainable alternatives to plastics: A

mini review. *Journal of Bioresources and Bioproducts* **2022**, *7* (1), 14–25.

(10) Bouajila, J.; Dole, P.; Joly, C.; Limare, A. Some laws of a lignin plasticization. *J. Appl. Polym. Sci.* **2006**, *102* (2), 1445–1451.

(11) Ayoub, A.; Treasure, T.; Hansen, L.; Nypelö, T.; Jameel, H.; Khan, S.; Chang, H.-M.; Hubbe, M. A.; Venditti, R. A. Effect of plasticizers and polymer blends for processing softwood kraft lignin as carbon fiber precursors. *Cellulose* **2021**, *28* (2), 1039–1053.

(12) Banu, D.; El-Aghoury, A.; Feldman, D. Contributions to characterization of poly(vinyl chloride)–lignin blends. *J. Appl. Polym. Sci.* **2006**, *101* (5), 2732–2748.

(13) Milotskiy, R.; Szabó, L.; Takahashi, K.; Bliard, C. Chemical Modification of Plasticized Lignins Using Reactive Extrusion. *Frontiers in Chemistry* **2019**, *7*, 633.

(14) Sakata, I.; Senju, R. Thermoplastic behavior of lignin with various synthetic plasticizers. *J. Appl. Polym. Sci.* **1975**, *19* (10), 2799–2810.

(15) Vural, D.; Gainaru, C.; O'Neill, H.; Pu, Y.; Smith, M. D.; Parks, J. M.; Pingali, S. V.; Mamontov, E.; Davison, B. H.; Sokolov, A. P.; et al. Impact of hydration and temperature history on the structure and dynamics of lignin. *Green Chem.* **2018**, *20* (7), 1602–1611.

(16) Sadoh, T. Viscoelastic properties of wood in swelling systems. *Wood Science and Technology* **1981**, *15* (1), 57–66.

(17) Miyoshi, Y.; Sakae, A.; Arimura, N.; Kojiro, K.; Furuta, Y. Temperature dependences of the dynamic viscoelastic properties of wood and acetylated wood swollen by water or organic liquids. *Journal of Wood Science* **2018**, *64* (2), 157–163.

(18) Chowdhury, S.; Frazier, C. E. Thermorheological Complexity and Fragility in Plasticized Lignocellulose. *Biomacromolecules* **2013**, *14* (4), 1166–1173.

(19) Immergut, E. H.; Mark, H. F. Principles of Plasticization. In *Plasticization and Plasticizer Processes, Advances in Chemistry*; American Chemical Society, 1965; Vol. 48, pp 1–26.

(20) Nielsen, L. E.; Buchdahl, R.; Levreault, R. Mechanical and Electrical Properties of Plasticized Vinyl Chloride Compositions. *J. Appl. Phys.* **1950**, *21* (6), 607–614.

(21) Souto, F.; Calado, V. Mystifications and misconceptions of lignin: revisiting understandings. *Green Chem.* **2022**, *24* (21), 8172–8192.

(22) Crestini, C.; Lange, H.; Sette, M.; Argyropoulos, D. S. On the structure of softwood kraft lignin. *Green Chem.* **2017**, *19* (17), 4104–4121.

(23) Froass, P. M.; Ragauskas, A. J.; Jiang, J.-E. Chemical Structure of Residual Lignin from Kraft Pulp. *Journal of Wood Chemistry and Technology* **1996**, *16* (4), 347–365.

(24) Martinez, C. R.; Iverson, B. L. Rethinking the term “pi-stacking. *Chemical Science* **2012**, *3* (7), 2191–2201.

(25) Jääskeläinen, A. S.; Sun, Y.; Argyropoulos, D. S.; Tamminen, T.; Hortling, B. The effect of isolation method on the chemical structure of residual lignin. *Wood Science and Technology* **2003**, *37* (2), 91–102.

(26) Guerra, A.; Filpponen, I.; Lucia, L. A.; Saquing, C.; Baumberger, S.; Argyropoulos, D. S. Toward a Better Understanding of the Lignin Isolation Process from Wood. *J. Agric. Food Chem.* **2006**, *54* (16), 5939–5947.

(27) Zinovyev, G.; Sulaeva, I.; Podzimek, S.; Rössner, D.; Kilpeläinen, I.; Sumerskii, I.; Rosenau, T.; Potthast, A. Getting Closer to Absolute Molar Masses of Technical Lignins. *ChemSusChem* **2018**, *11* (18), 3259–3268.

(28) Månsson, P. Quantitative Determination of Phenolic and Total Hydroxyl Groups in Lignins. *Holzforchung* **1983**, *37* (3), 143–146.

(29) Balakshin, M.; Capanema, E. On the Quantification of Lignin Hydroxyl Groups With 31P and 13C NMR Spectroscopy. *Journal of Wood Chemistry and Technology* **2015**, *35* (3), 220–237.

(30) Fox, T. G.; Loshaek, S. Influence of molecular weight and degree of crosslinking on the specific volume and glass temperature of polymers. *J. Polym. Sci.* **1955**, *15* (80), 371–390.

(31) Sperling, L. H. *Introduction to physical polymer science*; Wiley: 2006.

(32) Karaaslan, M. A.; Cho, M.; Liu, L.-Y.; Wang, H.; Rennecker, S. Refining the Properties of Softwood Kraft Lignin with Acetone: Effect of Solvent Fractionation on the Thermomechanical Behavior of Electrospun Fibers. *ACS Sustainable Chem. Eng.* **2021**, *9* (1), 458–470.

(33) Vilics, T.; Schneider, H. A.; Manovicu, V.; Manovicu, I. A new approach to PVC-plasticizer interaction by using a Tg concentration power equation. *Polymer* **1997**, *38* (8), 1865–1870.

(34) Huang, H.-H.; Yorkgitis, E. M.; Wilkes, G. L. A morphological study on the plasticization of poly(vinyl chloride) by diethylhexyl succinate and Dibutyl Phthalate. *Journal of Macromolecular Science, Part B* **1993**, *32* (2), 163–181.

(35) Ren, Z.; Dong, L.; Yang, Y. Dynamic mechanical and thermal properties of plasticized poly(lactic acid). *J. Appl. Polym. Sci.* **2006**, *101* (3), 1583–1590.

(36) Mok, M. M.; Kim, J.; Torkelson, J. M. Gradient copolymers with broad glass transition temperature regions: Design of purely interphase compositions for damping applications. *J. Polym. Sci., Part B: Polym. Phys.* **2008**, *46* (1), 48–58.

(37) Ljungberg, N.; Colombini, D.; Wesslén, B. Plasticization of poly(lactic acid) with oligomeric malonate esteramides: Dynamic mechanical and thermal film properties. *J. Appl. Polym. Sci.* **2005**, *96* (4), 992–1002.

(38) Boughalmi, R.; Jarray, J.; Larbi, F. B. C.; Dubault, A.; Halary, J. L. Molecular Analysis of the Mechanical Behavior of Plasticized Amorphous Polymer. *Oil Gas Sci. Technol. Rev. l'IFP* **2006**, *61* (6), 725–733.

(39) Zhang, L.; Wang, X.-F.; Liu, H.; Yu, L.; Wang, Y.; Simon, G. P.; Qian, J. Effect of plasticizers on microstructure, compatibility and mechanical property of hydroxypropyl methylcellulose/hydroxypropyl starch blends. *Int. J. Biol. Macromol.* **2018**, *119*, 141–148.

(40) Sothernvit, R.; Krochta, J. M. Plasticizer effect on mechanical properties of β -lactoglobulin films. *Journal of Food Engineering* **2001**, *50* (3), 149–155.

(41) Cuq, B.; Gontard, N.; Cuq, J.-L.; Guilbert, S. Selected Functional Properties of Fish Myofibrillar Protein-Based Films As Affected by Hydrophilic Plasticizers. *J. Agric. Food Chem.* **1997**, *45* (3), 622–626.

(42) Taghizadeh, A.; Favis, B. D. Effect of high molecular weight plasticizers on the gelatinization of starch under static and shear conditions. *Carbohydr. Polym.* **2013**, *92* (2), 1799–1808.

(43) Song, P.; Wang, H. High-Performance Polymeric Materials through Hydrogen-Bond Cross-Linking. *Adv. Mater.* **2020**, *32* (18), No. 1901244.

(44) Stukalin, E. B.; Douglas, J. F.; Freed, K. F. Plasticization and antiplasticization of polymer melts diluted by low molar mass species. *J. Chem. Phys.* **2010**, *132* (8), No. 084504.

(45) Özeren, H. D.; Guivier, M.; Olsson, R. T.; Nilsson, F.; Hedenqvist, M. S. Ranking Plasticizers for Polymers with Atomistic Simulations: PVT, Mechanical Properties, and the Role of Hydrogen Bonding in Thermoplastic Starch. *ACS Applied Polymer Materials* **2020**, *2* (5), 2016–2026.

(46) Vermaas, J. V.; Crowley, M. F.; Beckham, G. T. Molecular Lignin Solubility and Structure in Organic Solvents. *ACS Sustainable Chem. Eng.* **2020**, *8* (48), 17839–17850.

(47) Sameni, J.; Krigstin, S.; Sain, M. Solubility of lignin and acetylated lignin in organic solvents. *BioResources* **2017**, *12* (1), 1548–1565.

(48) Ma, Q.; Yu, C.; Zhou, Y.; Hu, D.; Chen, J.; Zhang, X. A review on the calculation and application of lignin Hansen solubility parameters. *Int. J. Biol. Macromol.* **2024**, *256*, No. 128506.

(49) Rials, T. G.; Glasser, W. G. Multiphase materials with lignin. VI. Effect of cellulose derivative structure on blend morphology with lignin. *Wood Fiber Sci.* **1989**, *21* (1), 80–90.

(50) Fadda, H. M.; Khanna, M.; Santos, J. C.; Osman, D.; Gaisford, S.; Basit, A. W. The use of dynamic mechanical analysis (DMA) to evaluate plasticization of acrylic polymer films under simulated gastrointestinal conditions. *Eur. J. Pharm. Biopharm.* **2010**, *76* (3), 493–497.

(51) Gutierrez-Villarreal, M. H.; Rodríguez-Velazquez, J. The effect of citrate esters as plasticizers on the thermal and mechanical properties of poly(methyl methacrylate). *J. Appl. Polym. Sci.* **2007**, *105* (4), 2370–2375.

(52) Gracia-Fernández, C. A.; Gómez-Barreiro, S.; López-Beceiro, J.; Tarrío Saavedra, J.; Naya, S.; Artiaga, R. Comparative study of the dynamic glass transition temperature by DMA and TMDSC. *Polym. Test.* **2010**, *29* (8), 1002–1006.

(53) Wu, G.; Liu, Y.; Shi, G. New Experimental Evidence for Thermodynamic Links to the Kinetic Fragility of Glass-Forming Polymers. *Macromolecules* **2021**, *54* (12), 5595–5606.

(54) Roy, S. K.; Brown, G. R.; St-pierre, L. E. The Influence of Thermodynamic Interactions on the Glass Transition of Poly (Vinyl Chloride)-Benzylbutylphthalate Mixtures. *International Journal of Polymeric Materials and Polymeric Biomaterials* **1983**, *10* (1), 13–20.

(55) Özeren, H. D.; Olsson, R. T.; Nilsson, F.; Hedenqvist, M. S. Prediction of plasticization in a real biopolymer system (starch) using molecular dynamics simulations. *Materials & Design* **2020**, *187*, No. 108387.

(56) Qi, C.; Zhang, S.; Wu, Y.; Li, H.; Wang, G.; Huai, G.; Wang, T.; Ma, J. A study on free-volume properties of styrene-acrylic ester type copolymers. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37* (17), 2476–2485.

(57) Sen, B. O.; Cetin, S.; Yahşi, U.; Soykan, U. Role of free volume in mechanical behaviors of side chain lcp grafted products of high density polyethylene. *Journal of Polymer Research* **2021**, *28* (8), 313.

(58) Kubo, S.; Kadla, J. F. Hydrogen Bonding in Lignin: A Fourier Transform Infrared Model Compound Study. *Biomacromolecules* **2005**, *6* (5), 2815–2821.

(59) Koivu, K. A. Y.; Sadeghifar, H.; Nousiainen, P. A.; Argyropoulos, D. S.; Sipilä, J. Effect of Fatty Acid Esterification on the Thermal Properties of Softwood Kraft Lignin. *ACS Sustainable Chem. Eng.* **2016**, *4* (10), 5238–5247.

(60) Glasser, W. G.; Jain, R. K. Lignin Derivatives. I. Alkanoates. *Holzforschung* **1993**, *47* (3), 225–233.

(61) Fox, S. C.; McDonald, A. G. Chemical and thermal characterization of three industrial lignins and their corresponding lignin esters. *BioResources* **2010**, *5* (2), 990–1009.

(62) Janewithayapun, R.; Hedenqvist, M. S.; Cousin, F.; Idström, A.; Evenäs, L.; Lopez-Sanchez, P.; Westman, G.; Larsson, A.; Ström, A. Nanostructures of etherified arabinoxylans and the effect of arabinose content on material properties. *Carbohydr. Polym.* **2024**, *331*, No. 121846.

(63) Beiner, M.; Huth, H. Nanophase separation and hindered glass transition in side-chain polymers. *Nat. Mater.* **2003**, *2* (9), 595–599.

(64) Chen, X.; Zheng, N.; Wang, Q.; Liu, L.; Men, Y. Effect of synthetic pathways on the phase transition and side-chain crystallization behavior of alkyl-substituted cellulose ethers. *Polym. Chem.* **2014**, *5* (13), 4105–4114.