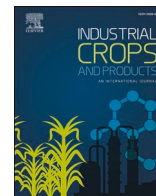# Glass transition temperature and mechanical damping of spruce lignin plasticized with methylimidazolium-based ionic liquids

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Short communication

Glass transition temperature and mechanical damping of spruce lignin plasticized with methylimidazolium-based ionic liquids

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ABSTRACT

An isolated spruce lignin was plasticized with methylimidazolium-based ionic liquids (ILs) with varying cations and anions and the glass transition temperature (T_g) and mechanical damping of the blends were determined with dynamic mechanical analysis (DMA). The T_g was found to decrease for all blends. The mechanical damping, however, was found to be maintained or decreased upon plasticization, indicating a maintained or increased mechanical rigidity. Only a combination that included the sterically hindered, strongly hydrogen-bond-accepting anion acetate increased mechanical damping.

1. Introduction

Ionic liquids (ILs) are increasingly being used in wood, biomass, and biopolymer processing (Khoo et al., 2021). The main reason for this is their high swelling and solvating ability of biopolymers. This ability is primarily attributed to their capacity to disrupt hydrogen bonds (HB) and other strong secondary interactions (Singh, 2022). Lignin is a notoriously difficult polymer to dissolve and process, and thus, IL applications in lignin processing are highly interesting.

ILs have been used to pulp or pretreat lignocellulosic biomass, chemically modify lignin and form lignin-containing composite materials (Szalaty et al., 2020). In many of these applications, the glass transition of lignin is critical. In pulping it is crucial to process above the glass transition temperature (T_g) of lignin as it promotes softening, diffusion and, in the case of delignification, reaction – this is true for both traditional pulping (Back and Salmén, 1982; Irvine, 1985) and pretreatments with ILs (Li et al., 2011; Marks and Viell, 2022; Yang et al., 2023). Water acts as a plasticizer for lignin, but only up to a few weight percent. Therefore, the T_g-lowering effect of ILs on lignin is of importance. However, no studies have yet directly examined the thermomechanical behaviour of pure lignin plasticized by ILs.

There is a knowledge gap in how ILs affects the thermoplastic properties of lignin. In synthetic polymers, ILs tend to lower the T_g to the same degree as traditional plasticizers, but the dynamical moduli are

retained or lowered to a lesser degree for some blends (Rahman and Brazel, 2006; Scott et al., 2003). The reason for this has been proposed to be due to strong secondary interactions with IL. These findings suggest that there could be combinations of cations and anions that are less optimal for lignin as well. To properly apply IL to lignocellulosic processing, a better understanding of how lignin responds to IL plasticization and which combinations of anions and cations that might be suitable for a given application is needed.

Plasticization of biopolymers can be said to occur by two interconnected mechanisms: increasing the distances between polymer chains and disrupting strong secondary interactions (Vieira et al., 2011). Methylimidazolium-based IL have been shown to partake in both HB and π-π interactions with lignin: anions accept H, cations donate H, and the conjugated unit of the cation interacts with the lignin aromatic ring (Hart et al., 2015; Singh, 2022; Zhang et al., 2017; Zubeltzu et al., 2020). The distances between plasticized polymer chains, and consequently their mobility, will be affected by the ability of the ILs to form new secondary interactions with lignin and by the steric impact of the cations and anions themselves.

This study evaluates, for the first time, the effect of ILs with varying compositions on the T_g and mechanical damping behaviour of isolated spruce lignin. Dynamic mechanical analysis (DMA) was used to assess how varying the anion and cation influence the thermophysical properties of lignin. Given that lignins are not self-supporting, measurements

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were conducted using a powder sample holder, which has been shown to be an effective tool for studying lignocellulosic materials (Henrik-Klemens et al., 2024; Ou et al., 2015).

The ILs in this study were selected to have anions with a range in basicity (i.e. HB accepting potential) with [CH₃COO]⁻ being the most basic anion, Cl⁻ intermediate and [HSO₄]⁻ the least basic based on the pK (BHX) scale (Galland et al., 2022). The hypothesis for this selection was that higher basicity anions would be better at competing with lignin-lignin HB and consequently increase the mobility of the polymers chains. The cations were chosen to have aliphatic side chains of different lengths and position. While larger plasticizer side chains generally create more effective spacing between polymer chains, a study on lignin solubilization found that bulky side chains can also hinder the accessibility of lignin to the imidazolium aromatic unit (Hart et al., 2015). Thus, there is balance to be found between spacing efficiency and accessibility.

2. Method

A spruce lignin, isolated using the enzymatic mild acidolysis lignin (EMAL) protocol, which isolates lignin of high yield and little degradation (Wu and Argyropoulos, 2003), was used in this study to be representative of native softwood lignin. The isolation process and characterization of the lignin used in this study can be found in (Henrik-Klemens et al., 2024). The lignin was plasticized by adding the IL in a methanol solution, which was allowed to evaporate slowly after 24 h of impregnation. An evaluation of this plasticization procedure is described in more detail in (Henrik-Klemens et al., 2025). The lignin was plasticized to 15 wt% with [Bmim]⁺ (1-*n*-butyl-3-methylimidazolium) with [CH₃COO]⁻, Cl⁻ and [HSO₄]⁻ as anions and with [Emim]⁺ (1-*n*-etyl-3-methylimidazolium), [Bm₂im]⁺ (1-*n*-butyl-2,3-dimethylimidazolium), [Hmim]⁺ (1-*n*-hexyl-3-methylimidazolium) with Cl⁻ as anion (Fig. 1). Lignin plasticized with 10 wt% triacetin was included as a reference. All chemicals were used as received from Sigma-Aldrich. The samples were heated at 120 °C for 5 min right before analysis to remove any remaining methanol or moisture. This heating step has been shown to increase the T_g of pure lignin with ~5 °C, most likely due to water loss, as no exothermic reactions was detected at 120 °C using differential scanning calorimetry (Henrik-Klemens et al., 2024).

The samples were analysed with a powder sample holder for DMA in a Q800 (TA instruments), where pure lignin was run between 25 and 250 °C and the plasticized lignin between 25 and 200 °C with a heating rate of 3 °C/min and a frequency of deformation of 1 Hz. 30 mg of lignin blend was loaded at a time, and each blend was run in triplicates. The moduli values are non-absolute, as the steel sample holder is bent contributing to the force reading and because powders do not have well-defined geometric factors; however, as the tan δ is calculated from the phase lag, these values are more easily compared. The T_g was determined as the $T_{\tan \delta\, max}$.

3. Results and discussion

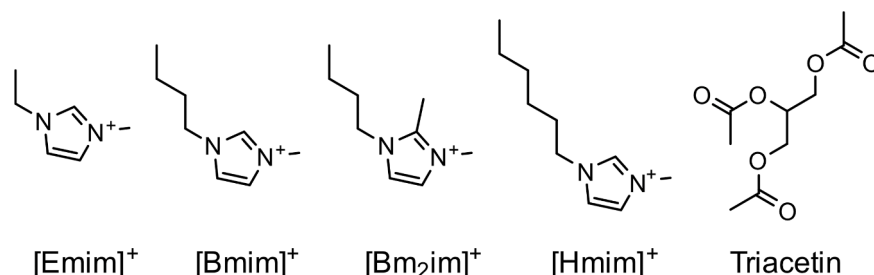The mechanical damping profiles of the lignin blends are found in

Fig. 2. The tan δ is a measure of the ratio between viscous and elastic response to stress in a material, with higher values indicating more viscous movements, i.e. more mechanical damping (Menard, 1999). At low temperatures, tan δ in lignin blends is slightly higher than for untreated lignin, which suggests an increased mobility in the polymer glass. Likewise, the tan δ_{max}, one of the definitions of the T_g, is seen to occur at lower temperatures for all blends. However, the magnitude at the maximum is either unchanged or lower for all blends, except for [Bmim][CH₃COO] and triacetin. This would entail that the moduli, and consequently the molecular mobility, over the glass transition is not significantly changed from the unplasticized state. This effect contradicts the anticipated outcome of plasticization but aligns with the previously reported maintained or comparatively less reduced moduli values for certain blends of ILs with poly(vinyl chloride) and poly (methyl methacrylate) (Rahman and Brazel, 2006; Scott et al., 2003).

All cations paired with Cl⁻ have a similarly low tan δ_{max}; however, upon varying the anions, the situation changes, with either an increase or decrease in mechanical damping. [Bmim][CH₃COO] increases the mechanical damping over the glass transition whereas [Bmim]Cl and [Bmim][HSO₄] maintain or decrease it. [CH₃COO]⁻ is the strongest HB acceptor, which might explain the increased mobility: it is the most efficient at disrupting lignin-lignin HB. Even so, it does not help explain the lower mobility of [Bmim]Cl and [Bmim][HSO₄].

A decrease in T_g but an increase in mechanical rigidity (i.e. resistance to deformation) is often observed for blends of plasticizers and polymers that partake in strong HB (Song and Wang, 2020; Stukalin et al., 2010; Özeren et al., 2020). This phenomenon can be explained by the formation of HB bridges between polymer chains and plasticizers, which provide additional space for the polymer to move (lower T_g), while maintaining the energy barrier of chains slipping past each other (maintained rigidity). Cl⁻ and [HSO₄]⁻ can participate in several HB simultaneously, whereas [CH₃COO]⁻ is sterically hindered from network formation by its methyl group. It is therefore possible, that [CH₃COO]⁻ competes more efficiently with lignin-lignin HB but does not form HB bridges, leading to a reduction in both T_g and rigidity.

The change in T_g is relatively uniform (Fig. 3) and is not far from values found for traditional plasticizers for lignin as seen in previous publications (Ayoub et al., 2021; Bouajila et al., 2006) or compared to the triacetin reference. The large standard deviation of [Emim]Cl is likely due to heterogeneity of the blend, as there is no indication of error in the individual measurements. Among the cations paired with Cl⁻, [Bmim]Cl stands out with the largest ΔT_g, although not significantly different from [Emim]Cl based on a *t*-test (95 % confidence interval). It could be that [Bmim]Cl, and possibly [Emim]Cl, perform better due to an effective balance between access to the imidazolium aromatic unit and their ability to space the polymer chains, as was found in a previous NMR study (Hart et al., 2015).

Among the anions paired with [Bmim]⁺, [Bmim]Cl and [Bmim] [HSO₄] stand out with a significantly higher and a lower depression in T_g as compared to [Bmim][CH₃COO], respectively. That [HSO₄]⁻ performs worse was to be expected with its low basicity, but that Cl⁻ performs better than [CH₃COO]⁻ is unexpected. The declining order T_g $_{[Bmim]Cl} > T_g$ $_{[Bmim][CH3COO]} > T_{g[Bmim][HSO4]}$ follows the order of the

Fig. 1. Molecular structures of the ionic liquid cations and of triacetin.
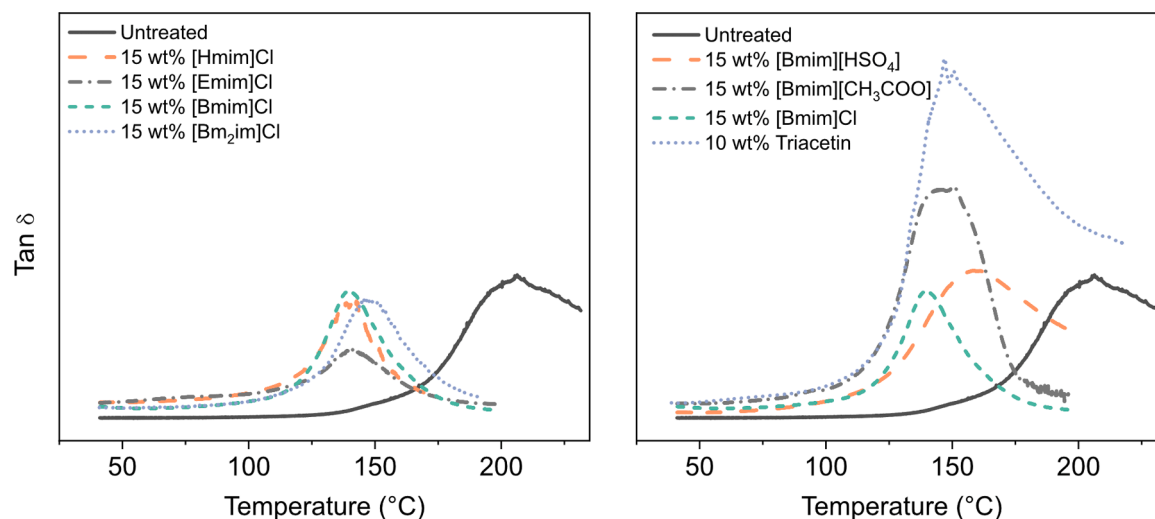
Fig. 2. Representative DMA thermographs of spruce lignin plasticized with ionic liquids with different cations (left) and anions (right). The two graphs have the same y- and x-axis scaling and range.
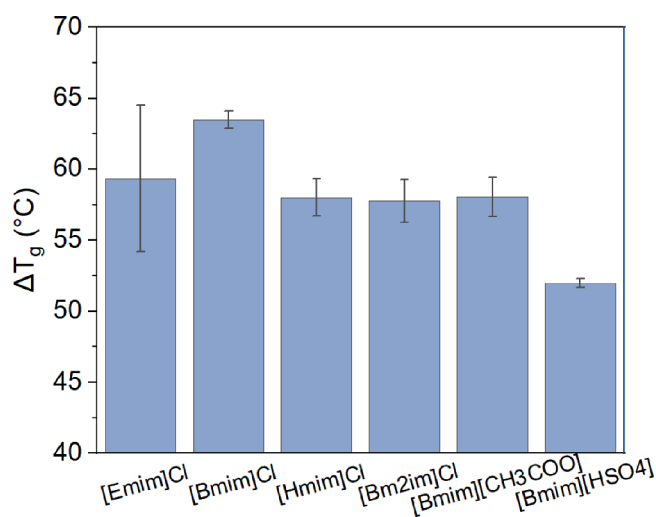
Fig. 3. The change in T_g with 15 wt% ionic liquid. The error bars are the standard deviation based on triplicate measurements.

molar masses of the anions. That is, per weight per cent added, there will be more Cl^-, which might help to explain its higher efficiency.

4. Conclusions

ILs are used with lignin-containing materials in a wide range of applications involving thermal processing; however, their influence on the thermomechanical properties of isolated lignin is not known. In this work, an isolated native spruce lignin was plasticized with methylimidazolium-based ILs of varying cations and anions and the blends were evaluated using DMA. All ILs lowered the T_g of lignin but not all increased the mechanical damping, which would have been expected upon plasticization. The basicity of the anion was more important than the chain length of the cation, affecting both the T_g as well as the mechanical properties – likely due to the high H-bonding potential of anions with lignin. In fact, only a combination with the sterically restricted and highly basic anion, $[CH_3COO]^-$, was found to increase the mechanical damping. These findings suggest that ILs of high anion basicity and steric hindrance should be selected to allow pulping and pretreatments of lignocellulose at lower temperatures.

CRediT authorship contribution statement

Larsson Anette: Writing – review & editing, Funding acquisition, Conceptualization. **Haraguchi Shuichi:** Writing – review & editing, Investigation. **Ghaffari Roujin:** Writing – review & editing, Investigation, Conceptualization. **Henrik-Klemens Åke:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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