Probing Structural Dynamics of Lignin-Derived Covalent Adaptable Networks Using SAXS and WAXS

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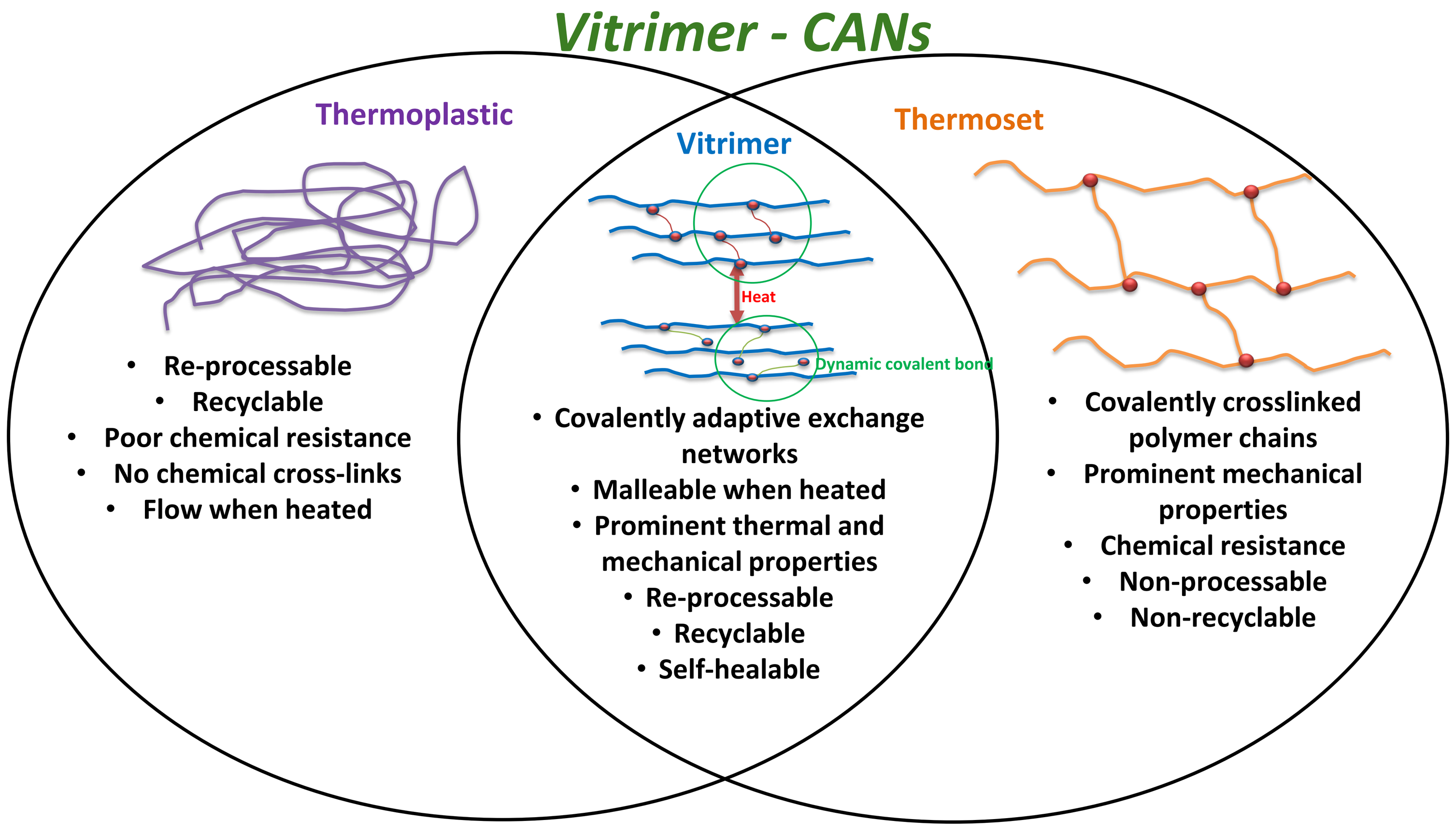
Abstract

- This study explores the structural evolution of lignin-derived supramolecular polymers within covalent adaptable networks (CANs) using in-situ small- and wide-angle X-ray scattering (SAXS and WAXS). CANs, a promising class of reconfigurable materials, rely on dynamic crosslinking to enable recyclability and mechanical adaptability.
- SAXS is employed to track nanoscale changes in network topology, including the rearrangement of crosslink domains during mechanical deformation and thermal reprocessing. Simultaneously, WAXS is employed to investigate molecular packing, capturing interchain distance variations and local structural ordering within the adaptable matrix.
- Temperature-resolved SAXS/WAXS are crucial for optimizing material design, ensuring recyclability and sustainability in applications such as recyclable coatings, self-healing polymers, and high-performance composites. This work bridges fundamental structure-property relationships with practical applications, contributing to the advancement of circular polymer systems for sustainable material innovation.

Introduction

Vitrimer - CANs



- Lignin, an abundant and renewable aromatic polymer, provides a sustainable route for creating CANs via imine chemistry.
- Understanding the structure–property relationships across scales is critical, especially when tuning crosslink density by varying lignin content.
- This study investigates how increasing lignin content (10–50 wt%) affects the nanoscale and molecular-level structure using Small- and Wide-Angle X-ray Scattering (SAXS/WAXS) at the application and processing temperature.

Objective

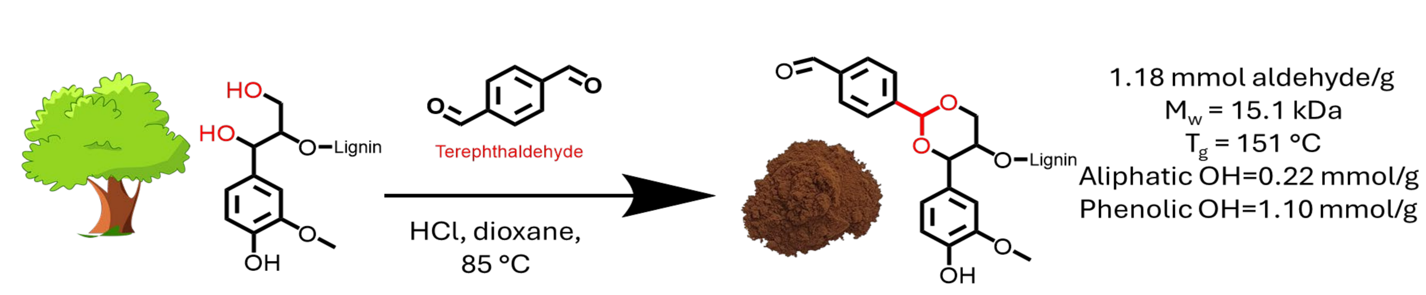
- To use SAXS and WAXS to probe:
  - Nano-domain formation (SAXS)
  - Short-range molecular packing (WAXS)
- To correlate structural features with thermal and mechanical performance.

Materials & Methods

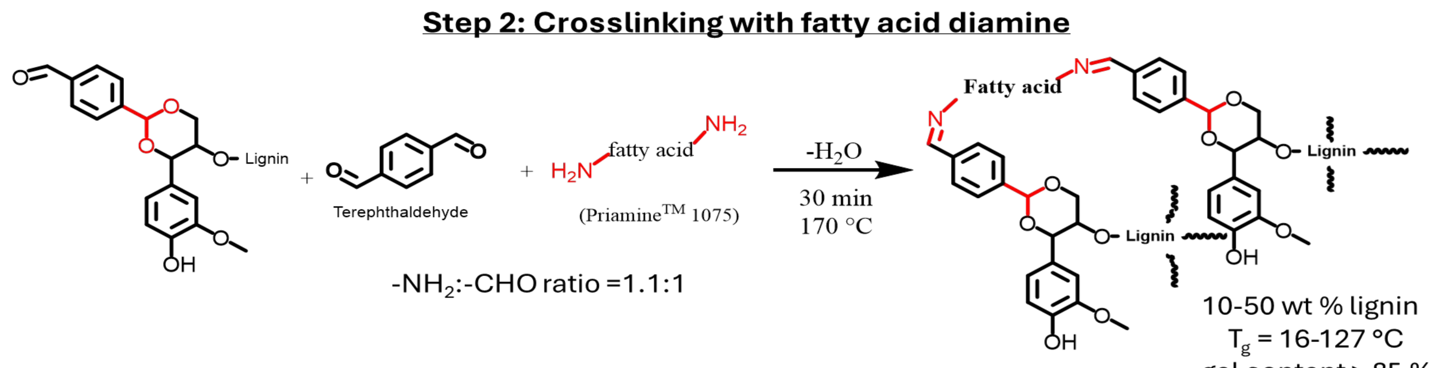
- **Formulation:** LP1 to LP5 with 10–50 wt % aldehyde-modified lignin, crosslinked with Priamine™ 1075.
- **Processing**: Hot-pressed at 170 °C under 40 bar to form dense vitrimer samples.
- **SAXS/WAXS:** Measured in transmission mode.
- **SAXS range**: $0.05 < q < 8$ nm^{-1}
- **WAXS range**: $6 < q < 24$ nm^{-1}

Preparation of Vitrimer

Step 1: Aldehyde modification of lignin

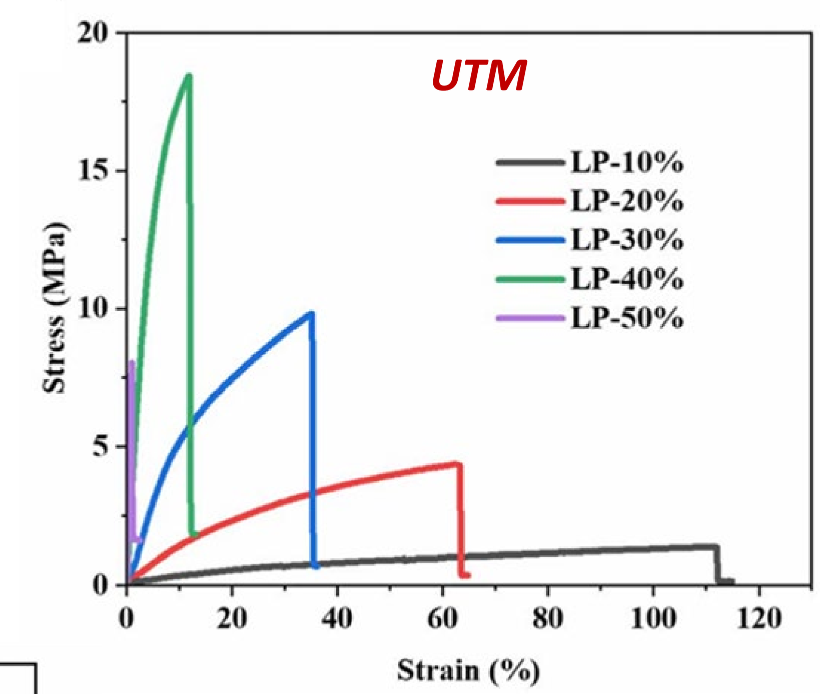


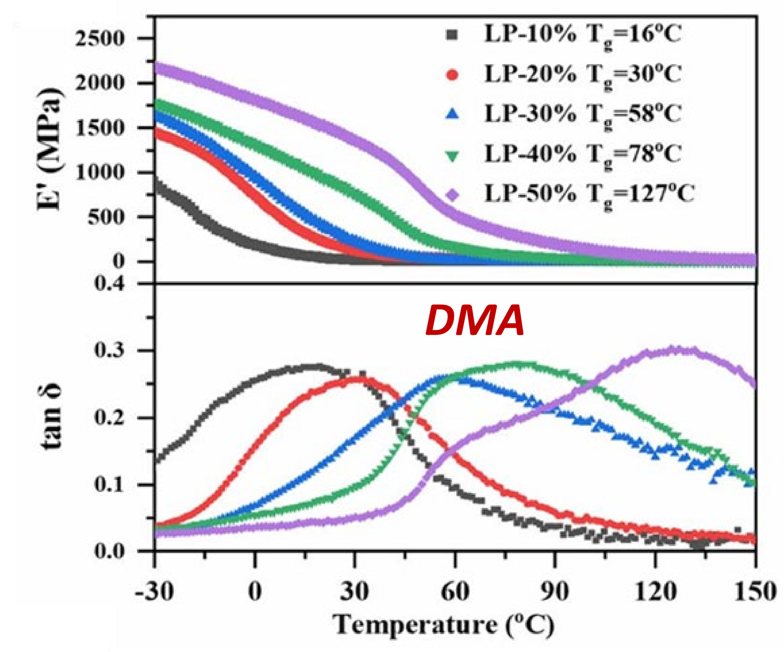
Step 2: Crosslinking with fatty acid diamine



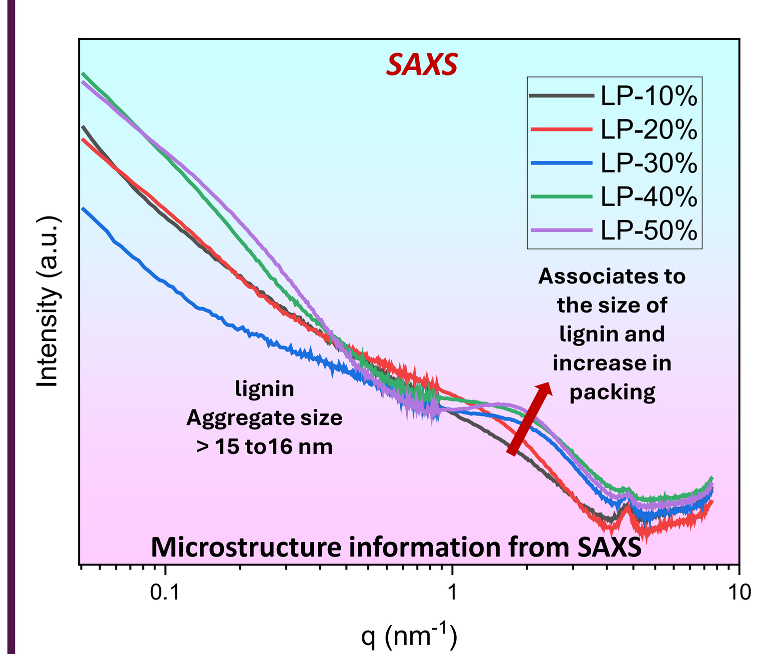
Results & Discussion

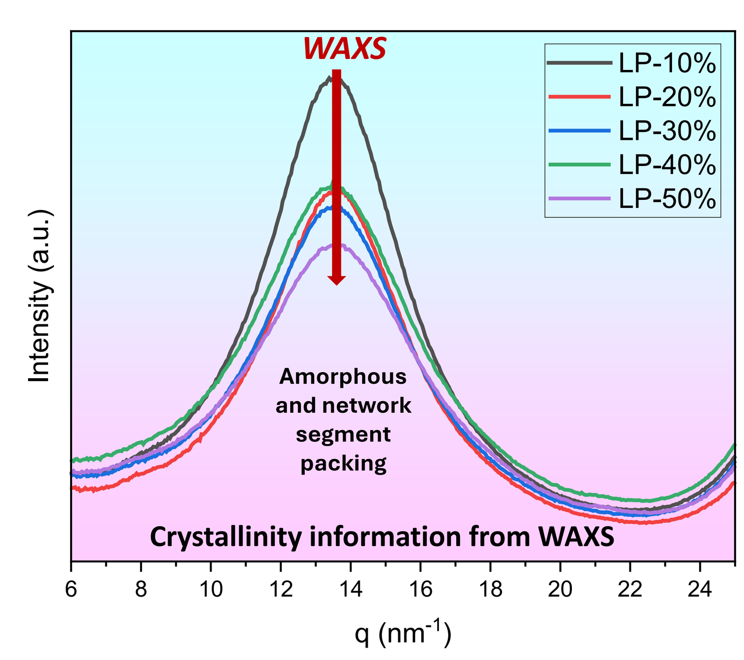
- **Increase in Tensile Strength & Modulus** → Lignin reinforces network; better stress transfer.
- **Decrease in Elongation at Break** → Reduced ductility due to rigid/filler-like lignin zones.
- UTM- Universal Testing Machine





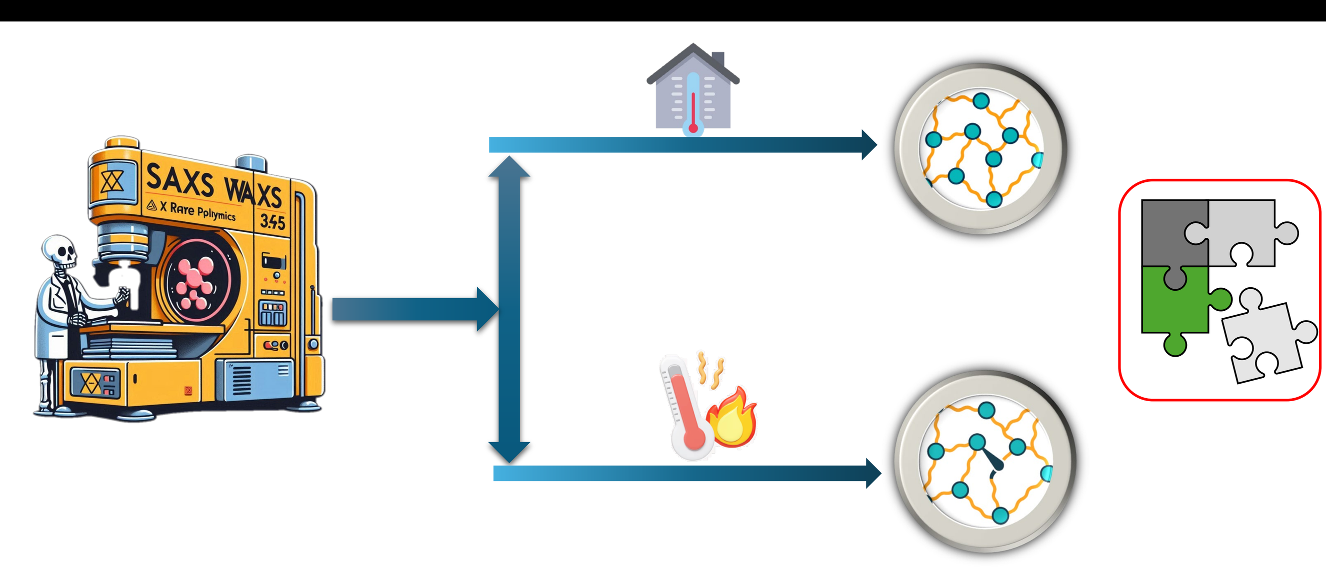
- ↑ **Storage Modulus & Tg** → Rigid lignin domains restrict mobility, increase thermal stiffness.
- ↑ **Broader tan δ** → Indicates phase heterogeneity and lignin-induced microdomains.
- **Hypothesis**: Lignin forms multifunctional crosslinks + stiff microphases → stiff but less extensible CANs.
- DMA – Dynamic Mechanical Analyzer





Future-work

Probing a network structure during transition temperature of vitrimer using X-ray scattering analysis



Concluding Remarks

- WAXS at room temperature shows a broad amorphous peak at 14.5 nm^{-1}. The peak intensity reduces with increase in lignin %.
- SAXS explains a lignin's network and size characteristic that matches with the dynamic and mechanical properties of material. es.
- The X-ray scattering analysis at transition temperature compared to room analysis at room temperature will give more information such as network structure and phase separation.

References

Liu, J., & Bernaerts, K. V. (2024). Preparation of lignin-based imine vitrimers and their potential application as repairable, self-cleaning, removable and degradable coatings. Journal of Materials Chemistry A, 12, 2959–2971. https://doi.org/10.1039/D3TA06338K

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