Synthesis and Characterization of Thermoplastic Polyurethane (TPU) from Bio-based Polyester Polyol

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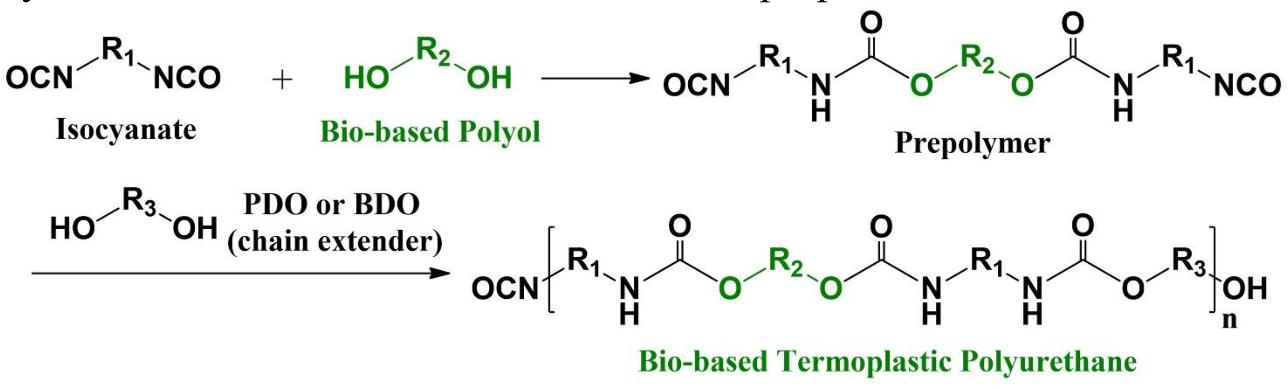
Abstract. Efforts to replace petrochemical-based polymers with biomass-derived polyols have been widely pursued across various industries.[1-5] This study focuses on the synthesis of thermoplastic polyurethane (TPU) by substituting petrochemical-based polyols with bio-based polyester polyols and investigates the resulting material's physical properties. The incorporation of bio-based polyols contributes to low-carbon technology within the context of TPU production. In this work, TPU synthesised with bio-based polyols demonstrated comparable physical properties to those formulated with petrochemical-derived polyols. The study also examined the influence of bio-polyol content on the mechanical and thermal properties of TPU. Mechanical properties, including hardness, tensile strength, and elongation, were evaluated, while thermal characteristics were analysed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The findings indicate that TPU synthesised from bio-based polyols exhibits similar performance to conventional petrochemical-based TPU, with variations in properties depending on the bio-polyol content. This study highlights the potential of bio-based polyols in TPU synthesis, advancing the development of low-carbon technology.



Introduction

- **Toward Sustainable High-Elasticity Materials: Utilizing Bio-Based Polyols for Eco-Conscious TPU Development**
  - Carbon neutrality demands alternative materials to replace petrochemical-based polymers.
  - Bio-based polyols derived from biomass enable the synthesis of sustainable thermoplastic polyurethane (TPU) with reduced carbon emissions.
  - TPU with varying bio-polyol contents was synthesized and analyzed to evaluate its potential as a sustainable high-performance material.
  - Mechanical and thermal properties were assessed to confirm feasibility for industrial applications.

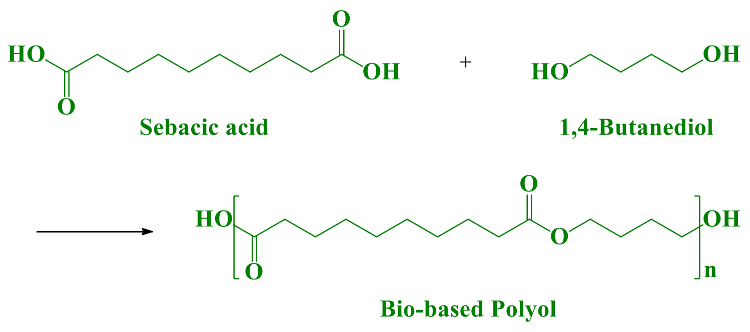
Objective

- **To develop bio-based TPU with high bio-content while maintaining mechanical and thermal performance**
  - TPU was synthesized using bio-based polyester polyols to substitute petroleum-based polyols.
  - The study investigates how increasing bio-polyol content affects hard segment ratio, phase behavior, and material properties.
  - The goal is to establish bio-based TPU as a competitive solution for mobility, industrial, and textile applications.

Figure. Target application fields.

Experimental

Bio-based polyester polyol



Method

- Polyols and an isocyanate were mixed at a specified ratio and stirred at 80 °C for 1 h to form a prepolymer.
- The mixture was vacuum-dried at 90 °C to remove residual moisture.
- After cooling to 45 °C, a chain extender was added.
- The reaction was terminated upon reaching a noticeable increase in viscosity.
- The mixture was transferred into a mold and post-cured at 80 °C overnight.

Table. Materials compositions

	Materials	Mw [g/mol]	Bio-TPU 0% [mol]	Bio-TPU 20% [mol]	Bio-TPU 40% [mol]	Bio-TPU 60% [mol]	Bio-TPU 80% [mol]	Bio-TPU 100% [mol]
Polyol	PTMG	1,000	0.08	0.064	0.048	0.032	0.016	0
	Bio Polyol	603	0	0.016	0.032	0.048	0.064	0.08
Isocyanate	4.4`-MDI	250.25	0.16	0.16	0.16	0.16	0.16	0.16
Chain extender	1,4-BDO	101.19	0.08	0.08	0.08	0.08	0.08	0.08
HS(wt/%)			38	40	42	44	47	50

Materials

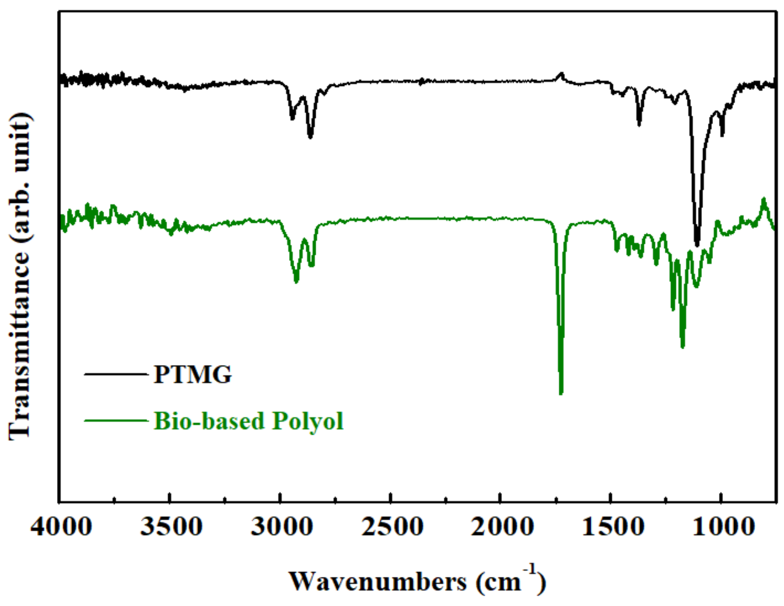


Figure. Comparison of FT-IR spectra between petroleum-derived PTMG and a bio-based polyester-type polyol.

Characterizations

Chemical structure analysis

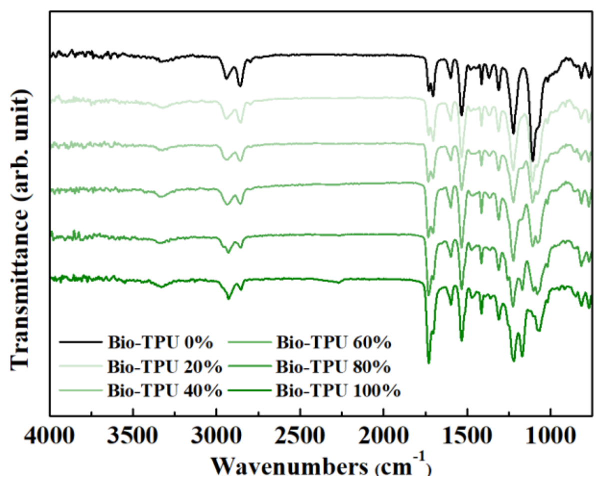


Figure. FT-IR spectra of TPU samples synthesized with different bio-based polyol contents. As the bio-polyol content increases, characteristic peak intensities grow, indicating effective incorporation into the polymer network.

Mechanical properties

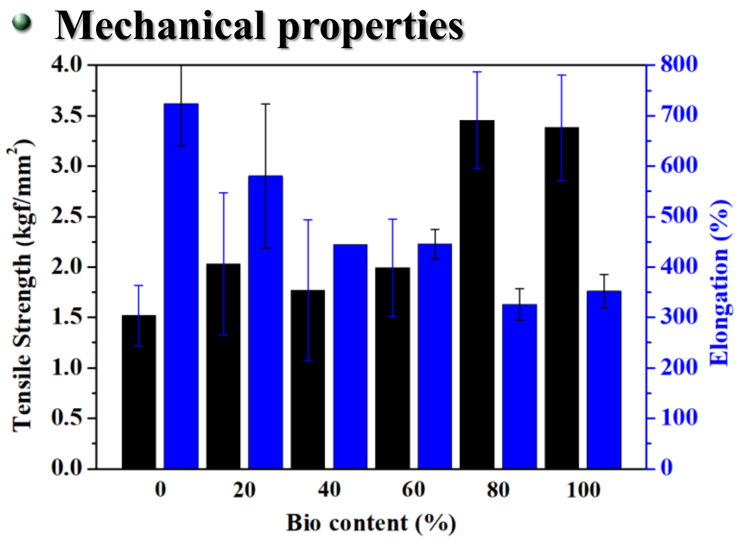
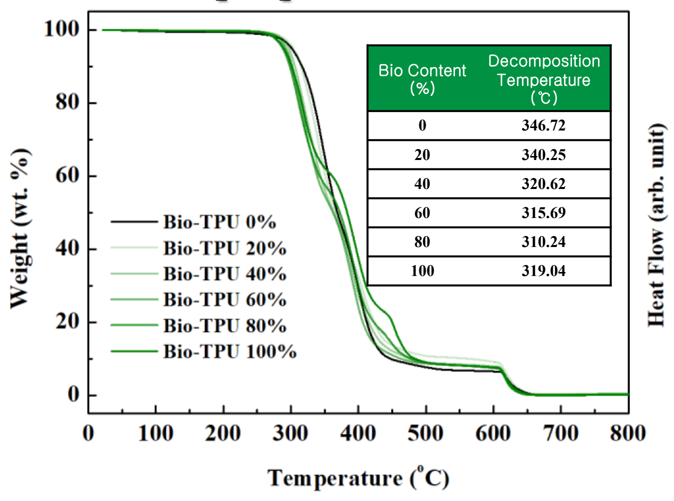


Figure. Mechanical properties of TPU with varying bio-polyol content. Increased bio-content led to lower tensile strength and higher elongation due to the rise in hard segment ratio from lower molecular weight bio-polyols.

Thermal properties



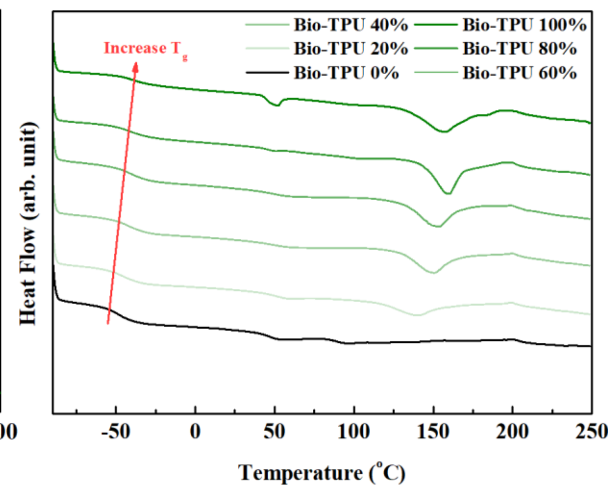


Figure. Thermal analysis results (left: TGA, right: DSC) of TPU with varying bio-polyol content. As bio-content increased, decomposition temperature decreased due to the lower thermal stability of bio-based segments, while Tg shifted higher, reflecting increased hard segment content and enhanced phase separation. Bio-polyol incorporation thus affected both thermal stability and chain mobility.

Conclusions

- **Thermoplastic polyurethane (TPU) was successfully synthesized by partially replacing petrochemical polyols with bio-based polyester polyols.**
- **FT-IR analysis confirmed the effective incorporation of bio-based polyols into the polymer structure.**
- **Mechanical testing showed that increasing bio-content led to reduced tensile strength but improved elongation, attributed to the rise in hard segment content due to the lower molecular weight of bio-polyols.**
- **Thermal analysis revealed that higher bio-content decreased decomposition temperature while increasing Tg, reflecting changes in segmental structure and phase separation.**
- **These results demonstrate the potential of bio-based polyols for producing sustainable TPU materials with tunable properties.**

Reference

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