PacifiCan-MMRI Accelerating Circular Economy (ACE) TechBrief Report

Project title: Using CO2 incorporation and lignin to polyol conversion to develop sustainable bio-based non-isocyanate polyurethane rigid foams

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Introduction & Background:

Polyurethane (PU) rigid foam is a highly versatile and efficient insulation material used in various applications, including construction, refrigeration, and automotive industries. It is created by the reaction of polyols and isocyanates, forming a closed-cell structure that provides excellent thermal insulation, mechanical strength, and moisture resistance The use of PU rigid foam is growing at a rapid rate regarding their lightweight, excellent strength-to-weight ratio and great thermal energy performance. Currently, the vast majority of rigid foam insulation materials, including rigid foam board and spray foam, are produced from petrochemical feedstocks [1]. As such, they are produced from non-renewable and toxic isocyanate sources, emit significant greenhouse gas (GHG) emissions during manufacturing and are difficult to recycle at the end of life [2].

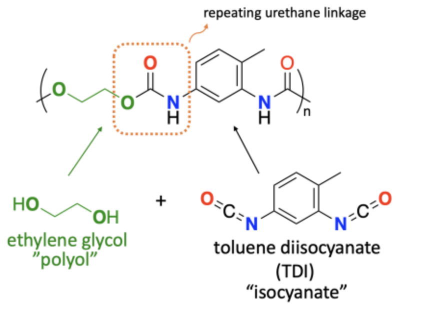

Figure 1. Commercial Polyurethanes. Urethane bonds can be formed by combining an alcohol (-OH) with an isocyanate. Polyurethanes can then be made by combining polyol and diisocyanate.

This research proposed a methodology for producing bio-based non-isocyanate polyurethane (NIPU) through lignin or recycled polyethylene terephthalate (PET) plastics to replace traditional PU rigid foam produced through a hazardous process from toxic materials such as isocyanates and phosgene [3]. Lignin can be used as a sustainable source of Polyol with benefits such as utilizing waste chemicals in the pulp and paper industry, approaching bio-based non-isocyanate polyurethanes, and promoting sustainable synthesis of chemicals from renewable resources.

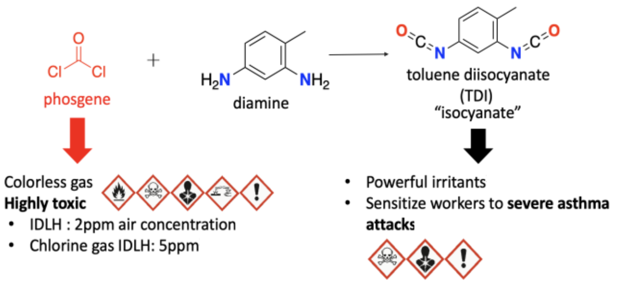

Figure 2. Dangers of Isocyanate Polyurethanes [4], [5].

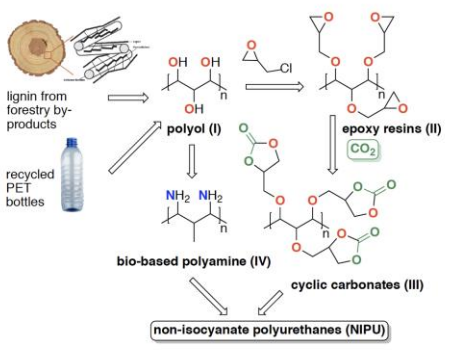

Figure 3. Overview of the proposed methodology for producing NIPU.

Figure 3 summarizes the overall objectives of the research. The proposed methodology involved the curing of polyfunctional cyclic carbonates with polyfunctional amines to develop NIPUs. Five-membered cyclic carbonates can be generated readily from bioderived epoxy resins (generated from the catalytic epoxidation of vegetable oils) by chemical fixation with carbon dioxide, and the polyamines can be generated from the catalytic amination of bio polyols. Therefore, the general methodology for the research involved the use of bio-polyols to generate 100% bio-based NIPU thermoplastics by polyaddition of difunctional bio-based cyclic carbonates with difunctional bio-base diamines, reinforced with forest product filaments.

Relevance to Circular Economy:

This research aligned with the circular economy by proposing the replacement of toxic, non-renewable PU with bio-based NIPU derived from wood waste products such as lignin and recycled PET plastics. It aimed to waste valorization, reduce GHG emissions, and enhance recyclability while incorporating carbon capture in production. By utilizing renewable resources and closing material loops, this research was dedicated to supporting sustainable development and eco-friendly manufacturing.

Methodology:

This research proposed to approach NIPUs by replacing toxic isocyanate components in polyurethanes using bio-based building blocks through the following steps:

1. Conversion of bio polyols to epoxy resins, cyclic carbonates, and polyamines.

a) *Bio-polyols to bio-based epoxy resins:* Bio-polyols, derived from lignin or recycled PET, are modified into epoxy resins [6]. To this end, the oxidation of unsaturated compounds like plant oils and terpene derivatives using various catalytic epoxidation processes can be applied. In addition, polyols can be treated with epichlorohydrin, derived from glycerol, which is a by-product of bio-diesel production and comprises a promising route to bio-based epoxy resins.

b) *Bio-based epoxy resins to cyclic Carbonate Synthesis:* Epoxy resins are converted into cyclic carbonates using carbon dioxide [1].

c) *Bio-Based Polyamines:* These amines act as curing agents for the synthesis of NIPU from bio-oil-based cyclic carbonates [1].

2. Coupling Reactions: The reaction between cyclic carbonates and polyamines forms NIPUs. Reactivity depends on the amine structure, and catalysts improve efficiency at elevated temperatures (>70°C).

3. Rigid PU Foam Formation: The next phase involves scaling up foam production [7] using microfibril cellulose fibre (MFC), which has high tensile strength as a toughening agent to strengthen NIPU foams.

4. Materials and Flammability Testing: The final stage involves testing the mechanical and fire-resistant properties of the developed materials.

Conclusion

This research proposed a methodology for environmentally friendly NIPU rigid foam boards using recycled and bio-based polyols with modified additives. The new materials are expected to partially replace petroleum-based polyols, which dominate the global market.

Additionally, the final foam boards are expected to consist of over 60% bio-based materials, primarily sourced from Canadian forest residues. It aimed to explore polyols derived from Canadian lignin. The formulation allowed for incorporating cellulose or lignin-based carbon filament resin, further enhancing the bio-based content.

The new materials are also designed to provide strong thermal resistance and are projected to be 20% more cost-effective than existing petroleum-based alternatives. Additionally, they are expected to be significantly more fire-resistant, taking at least twice as long to ignite.

Finally, these bio-based rigid foam boards are expected to be compatible with existing industrial foam production machinery, ensuring a smooth transition for manufacturers.

References:

1- Maisonneuve, L.; Lamarzelle, O.; Rix, E.; Grau, E.; Cramail, H., Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s. Chem. Rev. 2015, 115, 12407-12439, 10.1021/acs.chemrev.5b00355.

2- Brugsch, H. G.; Elkins, H. B., Toluene di-isocyanate (TDI) toxicity. N. Engl. J. Med. 1963, 268, 353, 10.1056/nejm196302142680705.

3- Akindoyo, J. O.; Beg, M. D. H.; Ghazali, S.; Islam, M. R.; Jeyaratnam, N.; Yuvaraj, A. R., Polyurethane types, synthesis and applications - a review. RSC Adv. 2016, 6, 114453-114482, 10.1039/c6ra14525f.

4- Immediately Dangerous To Life or Health (IDLH) Values. https://www.cdc.gov/niosh/idlh/intridl4.html (accessed Feb 9, 2023)

5- Isocyanates.https://www.cdc.gov/niosh/topics/isocyanates/default.html#:~:text=Isocyanates%20are%20a%20family%20of,repair%2C%20and%20building%20insulation%20materials. (accessed Feb 9, 2023)

6- Cateto, C. A.; Barreiro, M. F.; Rodrigues, A. E.; Belgacem, M. N., Optimization Study of Lignin Oxypropylation in View of the Preparation of Polyurethane Rigid Foams. Ind. Eng. Chem. Res. 2009, 48, 2583-2589, 10.1021/ie801251r.

7- Marcovich, N. E.; Auad, M. L.; Bellesi, N. E.; Nutt, S. R.; Aranguren, M. I., Cellulose micro/nanocrystals reinforced polyurethane. J. Mater. Res. 2006, 21, 870-881, 10.1557/jmr.2006.0105.

ACE project funding provided by: Pacific Economic Development Canada; NRC Industrial Research Assistance Program; NSERC CRSNG; Mitacs; The University of British Columbia

Document # MMRI-13032025