PNNL-30668

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1.0 Introduction

Fiber-reinforced composite materials are increasingly used to replace heavy metal components in transportation applications for lightweighting purposes. Polymer matrix materials used in automotive parts, such as epoxies, nylons, and polypropylenes, are almost all produced from fossil fuels. Higher performance thermoset composites are generally not repairable and lower-cost thermoplastic composites do not have enough performance to replace steel. Vitrimers are a new class of polymer materials with long shelf life, low waste in production, ease of processing, and repairability that have the potential to break through the high-cost thermoset/low-performance thermoplastic barrier to vehicle light-weighting. Vitrimers also exhibit easier chemical recyclability than conventional thermosets with reversible chemical crosslinking that enables reprocessing of scrap from production and end of life components.

Vitrimers are a new class of engineered plastics that are weldable, repairable and recyclable like thermoplastics but have high mechanical properties like thermosets. Bio-based vitrimers have only recently been reported in the academic[1] and patent literature. These materials represent an unusual opportunity to meet both VTO light-weighting targets for low-density, high performance materials and BETO sustainability targets for value-added high-volume applications of bio-fuel byproducts. Also, PNNL researchers have previously demonstrated a process to convert CO_2 into potential vitrimer precursors. Washington State University (WSU) success in demonstration of bio-based vitrimers and recent steps toward commercialization of petroleum-based vitrimers support the opportunity for PNNL success in development of sustainable vitrimer materials for recyclable, high-performance fiber-reinforced composites for the transportation sectors.

In this work, two approaches are taken in collaboration with WSU towards development of sustainable vitrimer materials: the CO_2-based approach and the bio-based approach. In the CO_2-based approach, we developed a novel vitrimer chemistry based on earlier PNNL achievements in CO_2-derived polycarbonates. A multifunctional polyol is selected to react with polycarbonate through ring-opening polymerization with a special in-house catalyst developed for improved conversion efficiency. Molecular structure is tuned for optimal processing properties and performance (e.g., viscosity, transition temperatures). As for the bio-based approach, a fully bio-based hydroxyl-terminated hyperbranched prepolymer (HBP) is developed via catalyst-free polycondensation of renewable feedstocks. Various characterization techniques and benchtop demonstration are implemented to verify vitrimer chemistry and characteristics.

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[1] *Macromolecules* 2018, 51, 15, 5577–5585

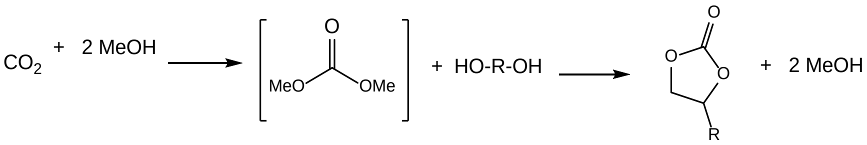
2.0 Results and Accomplishments

2.1 CO_2-based Approach

The design of CO_2 vitrimers in this work involves three steps, each with its own advantages, leading to many architectural possibilities of vitrimer materials. CO_2 is first converted to a cyclic carbonate. This conversion has been well known as a common way of producing cyclic carbonates in an industrial setting. The second step is polymerization of the cyclic carbonate into a highly branched prepolymer which can crosslink to attain high mechanical performance in the third step. Note that some of the key chemistry details are replaced by generic terms as we pursue intellectual property protection for this work.

Step 1: Preparation of cyclic carbonate from CO_2 and diols

The reaction of diols and CO_2-derived dimethyl carbonate (an industrially established process) allows the formation of versatile cyclic carbonates.



In this work, we have demonstrated the preparation of cyclic carbonates from three different bio-based alcohols using a special in-house catalyst (containing KNO_3 and Hydrotalcite; referred to as K/hydrotalcite subsequently). The results are shown in the table below. We found that the yield of cyclic carbonate is dependent on the structure of the alcohol used for conversion.

CO2-based agent	Bio-based alcohol	Catalyst	Product	Yield
Dimethyl carbonate	Alcohol A	K/hydrotalcite	Cyclic carbonate A	97%
	Alcohol B	K/hydrotalcite	Cyclic carbonate B	87%
	Alcohol C	K/hydrotalcite	Cyclic carbonate C	70%

Step 2: Cyclic carbonate to highly branched pre-polymer (HBP)

The prepolymer is formulated from the select cyclic carbonate and alcohol through catalytic transesterification. For this step, cyclic carbonate C was selected as the building unit for the HBP due to its additional hydroxyl group. This could play an important role in determining the mechanical performance of the final product, because the extra hydroxyl group allows formation of a highly branch product. ^1H NMR was used to examine the resulting chemistry (data not shown).

We varied the ratio of cyclic carbonate C to alcohol as well as the catalyst load to pursue an HBP with desired structure and functionality. The optimal reaction condition in our study was determined to consist of a carbonate-alcohol molar ratio of 10:1 and a 2 mol% load of titanium isopropoxide (TTIP) catalyst.

Step 3: Highly branched pre-polymer to vitrimer

The hydroxyl groups in the HBP are crosslinked with isocyanate to form urethane linkages, resulting in networked polymers. Two distinct isocyanates are considered in this work: an aryl diisocyanate, 4-4-methylene diphenyl isocyanate (MDI) and aliphatic one, hexamethylene diisocyanate (HDI). The size and chain rigidity/flexibility of the crosslinker molecule are considered to largely affect the molecular weight and molecular arrangement of the final polymer. This could further affect the occurrence of transesterification, when appropriate conditions are present, and thereby affect a critical vitrimer performance parameter – the ability of matrix to be formed again after cure (reformability). Fourier transform infrared spectroscopy (FTIR) was employed to confirm that all isocyanates reacted, and urethane bonds formed, as showed in Figure 1.

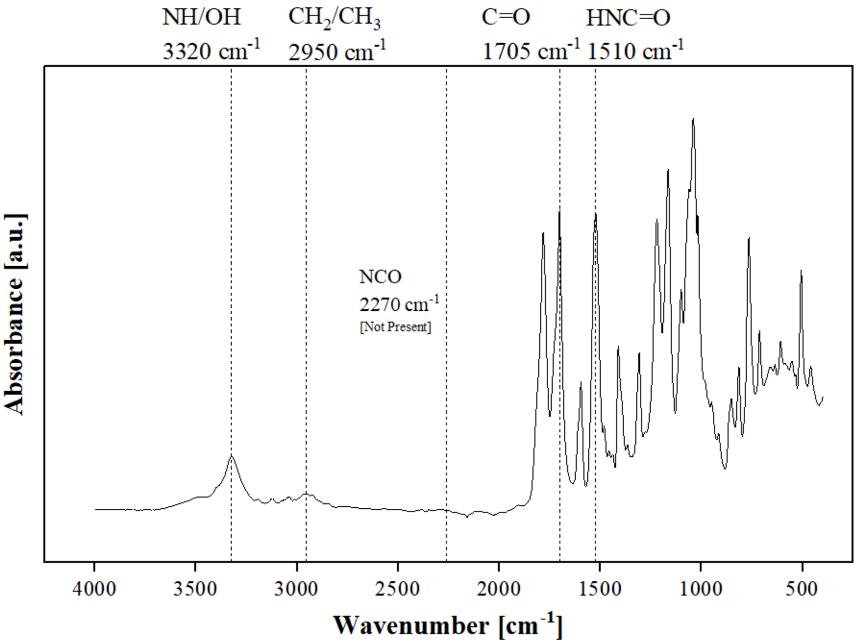


Figure 1. Representative FTIR of MDI-derived vitrimer.

We also measured the viscosity and shear modulus of both HDI- and MDI-derived vitrimers. The results suggest that the HDI-derived vitrimer have a viscosity at 10,000 cps (as viscous as honey) after the vitrimer transition temperature is reached. The MDI-derived vitrimer settles around 20,000 cps in viscosity due to its more rigid molecular structure. Further, reformability of a CO_2-based vitrimer sample made from MDI is validated in a benchtop demonstration experiment where cured polymer is reformed into a bar geometry upon heating.

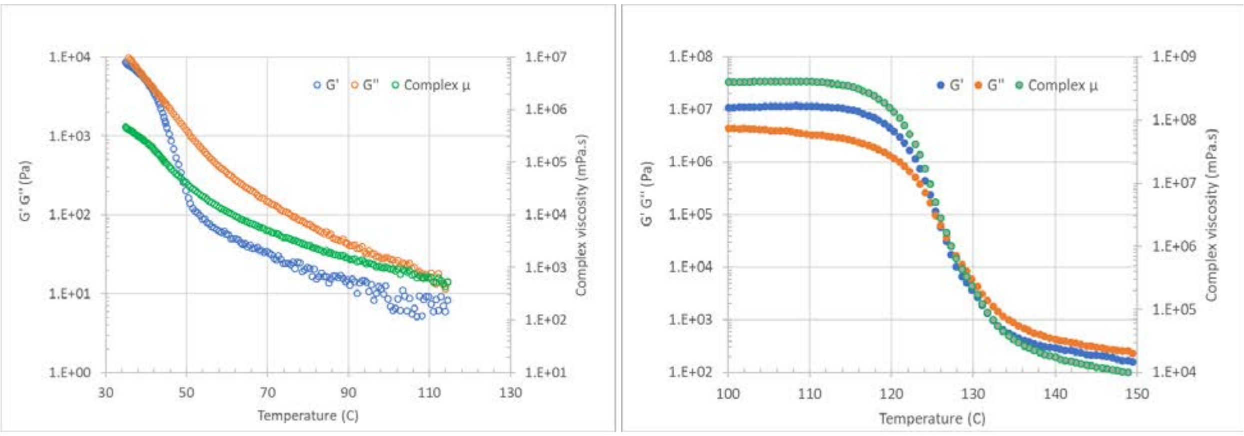


Figure 2. Viscosity and shear modulus of HDI- (left) and MDI-derived (right) vitrimers.

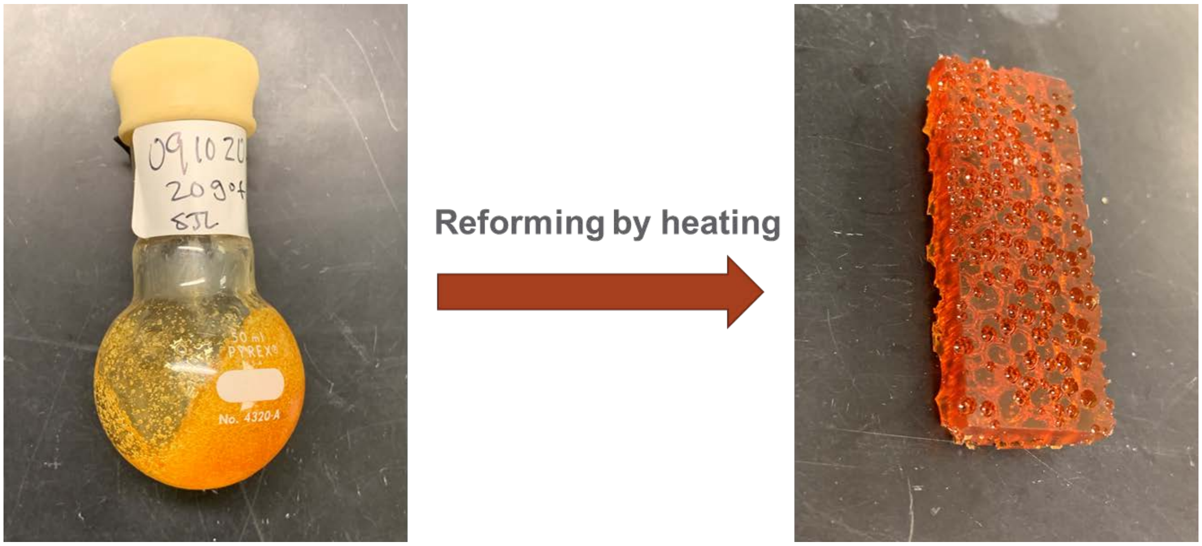


Figure 3. Benchtop demonstration of CO_2-based vitrimer. Vitrimer (malleable thermoset) is formed/cured in a reaction flask shown on the left and reformed into a bar shape upon heating.

2.2 Bio-based Approach

A fully bio-based hydroxyl-terminated hyperbranched prepolymer (HBP) is synthesized from the polycondensation of renewable feedstocks glycerol and itaconic acid. After reaction, the double bond from itaconic acid was preserved, to be used for further crosslinking. The stoichiometric ratio of glycerol to itaconic acid was carefully controlled so that the resulting HBP possesses abundant -OH groups and ester linkages, essential to enable catalyst-free efficient dynamic transesterification in the system. Due to the high viscosity of HBP, biobased isosorbide methacrylate (IM) was synthesized and used as a reactive diluent. The addition of rigid monomer IM also increased the thermal and mechanical performance of the polymer. To control the crosslink density, 2-hydroxyethyl methacrylate (HEMA) was added as a second reactive diluent. By adjusting the weight ratio of HBP/IM/HEMA, the performance of the resulting polymer can then be tuned. Rheology testing and differential scanning calorimetry (DSC) are used to characterize the resulting polymers.

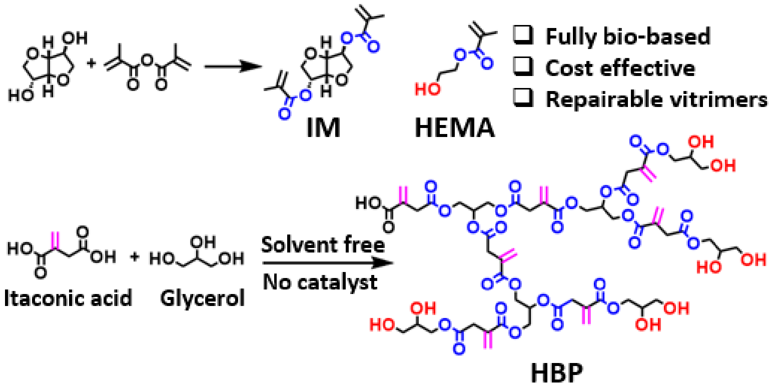


Figure 4. Synthetic scheme of bio-based vitrimer from glycerol and itaconic acid.

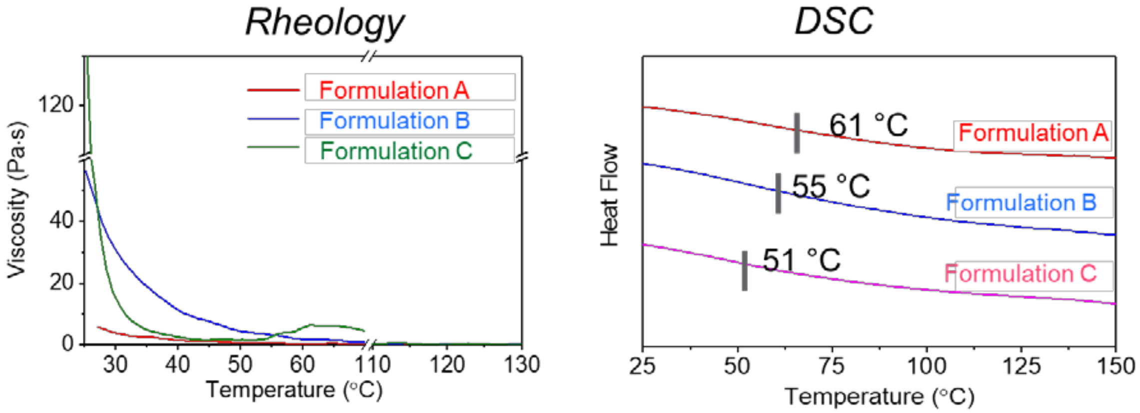


Figure 5. Characterization results of three bio-based vitrimer formulations.

We also investigated the vitrimer behaviors of the polymers. The abundant -OH groups and ester linkages in the resin ensure an efficient dynamic transesterification reaction, which in turn endows reparability and reprocessability to the polymers. First, the stress relaxation behavior was measured using a rheometer. At 200 °C, the cured polymers relaxed to 37% of the initial stress at ~3200s without a catalyst. Second, the self-healing of scratched polymer films was monitored using an optical microscope. After heating for 10 min at 200 °C with an axial force of 5.0 N, the scratch recovered by ~30%. Lastly, when cured polymer powders were employed in hot-pressing, ground polymer powders were recompressed into complete films, indicating good reprocessability.

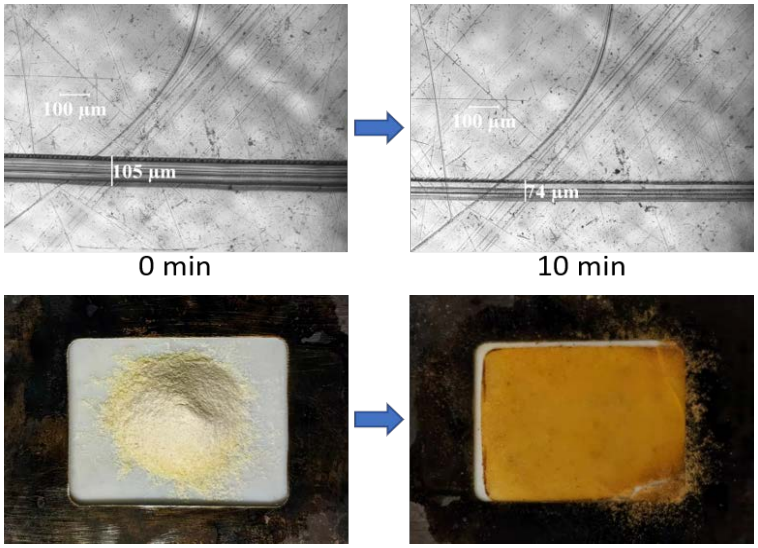


Figure 6. Repairability and reprocessability demonstration of bio-based vitrimer samples.

One bio-based vitrimer formulation is further prepared into fiber-reinforced composites by impregnating with fiberglass mats. 1 wt.% azobisisobutyronitrile (AIBN) is used for curing at 75 °C for 3 hours, followed by a post-curing at 100 °C for 2 hours and 160 °C for 1 hour. Adequate mixing is needed before curing for optimal results. Images of the composites prepared are shown in Figure 7.

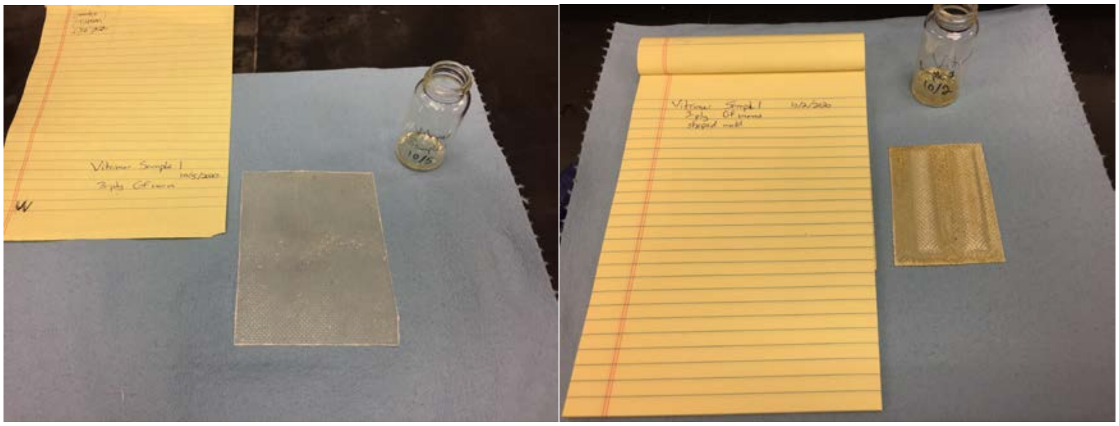


Figure 7. Fiberglass reinforced bio-based vitrimer composites.

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