

North Dakota Soybean Council

Mid-year Report-June 2024

Title: Polyethylene Terephthalate (PET)-Analogue from Soybean Gallic Acid.

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Objectives: We proposed using green polymers developed at UND, chemical engineering department to aid in PET plastic replacement and serves as new green plastics through:

1. Reacting soybean GA with ethylene glycol.
2. Reacting soybean GA with glycerol.
3. Creating a simple solvent-free method using non-toxic starting materials.

Tasks:

1. Synthesize new green plastics from soybean gallic acid reaction with ethylene glycol.
2. Synthesize new green plastics from soybean gallic acid reaction with glycerol.
3. Characterize the new polymer resulting from “1” in terms of DSC and TGA, to study the thermal behavior, an important property in various applications. In addition, chemically characterize the synthesized polymer from “1” in terms of FTIR and NMR analysis.
4. Characterize the new polymer resulting from “2” in terms of DSC and TGA, to study the thermal behavior, an important property in various applications. In addition, chemically characterize the synthesized polymer from “2” in terms of FTIR and NMR analysis.
5. Test the biological /antibacterial activity of both polymers from “1” and “2” to assess the possibility of medical/pharmaceutical/coating application.
6. Test the developed polymers 3D printability to produce complex shapes that could be utilized in different applications.

Summary: Project Overview and Progress Update

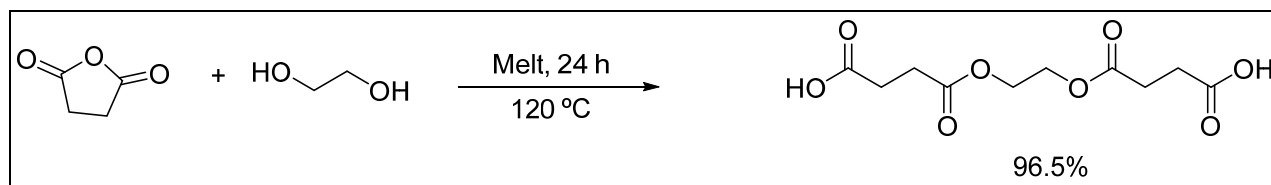
The project's main goal is to use waste byproducts from processing soybeans as the primary reactant in developing environmentally friendly substitutes for polyethylene terephthalate (PET), a widely recognized coating polymeric used in various applications. As indicated in the Mid-year report, the PI's team has successfully synthesized the soybean-derived PET analogue. However, challenges related to the final products' solubility, scalability and commercial-scale production have remained unresolved. We therefore redesigned the synthetic approach to incorporate succinate units in the polymer backbone structure to enhance the final product's chemical and thermal properties, degradability and heat re-processability. The synthetic approach involves first reacting gallic acid (GA) with an excess amount of epichlorohydrin (ECH) to obtain GA-based glycidylated monomer in moderate yield. Ethylene glycol and succinic anhydride were reacted in the melt in 1:2 molar ratio to obtain ethylene glycol bis(acid ester) monomer in high yield (96.5%). A mixture of the GA-based glycidylated monomer and diester diacid monomer was thermally cured in the presence of the transesterification catalyst, $Zn(acac)_2$, at different curing temperatures and different monomers ratios.

Progress of Work and Results to Date

Monomers Synthesis

Monomer 1: Ethylene glycol bis(acid ester)

At first, ethylene glycol was alcoholysized with succinic anhydride to obtain ethylene glycol bis(acid ester) (Scheme 1), the monomer was synthesized in the melt and was obtained in high purity and high yield.



Scheme 1: Synthesis of Ethylene glycol Diacid Diester

Chemical characterization of ethylene glycol bis(acid ester) structure was performed by 1H and ^{13}C NMR spectroscopy. Figure 1 a and b display the 1H and ^{13}C NMR ethylene glycol bis(acid ester), respectively.

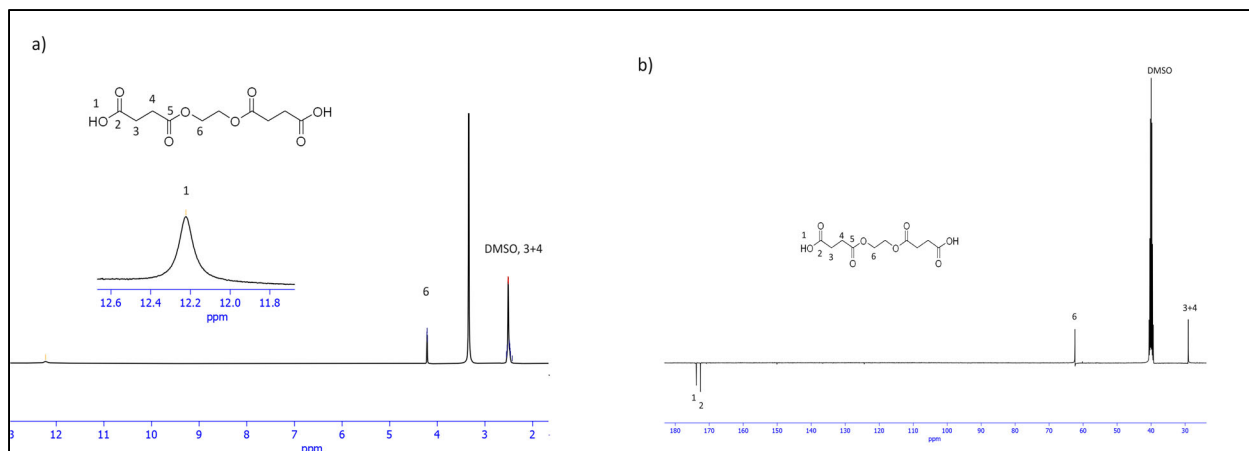
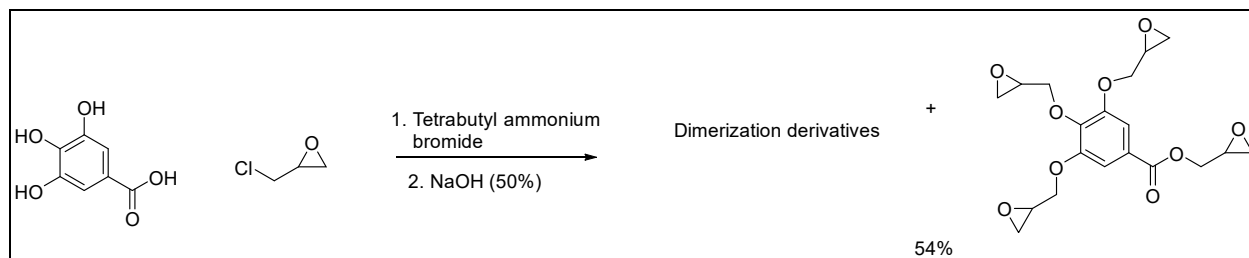


Figure 1: NMR spectra of monomer 1

Monomer 2: GA-based glycidylated monomer

As shown in Scheme 2, GA was reacted with an excess of epichlorohydrin (ECH) in the presence of the phase transfer catalyst tetrabutylammonium bromide (TBAB). ECH was selected as a glycerol-derived building block because, through ring-opening polymerization, it indirectly incorporates a glycerol unit into the polymer backbone. The reaction progress was monitored by measuring the Epoxy Equivalent Weight (EEW) using hydrochloric acid/acetone and cresol red/thymol mixture as an indicator.



Scheme 3: Synthesis of GA-based glycidylated monomer

Additionally, the formation of the tetraglycidylated derivative of gallic acid was confirmed by the ^1H NMR spectroscopy. Figure 2 A and B display the ^1H NMR spectra of GA and GA-based glycidylated monomer, respectively. In the ^1H NMR spectra, the characteristic signals for phenolic and carboxyl hydroxyl protons in GA (around 9 ppm and 12.3 ppm, respectively) were not observed in GA-based glycidylated monomer, whereas numerous aliphatic signals from oxirane groups were identified.

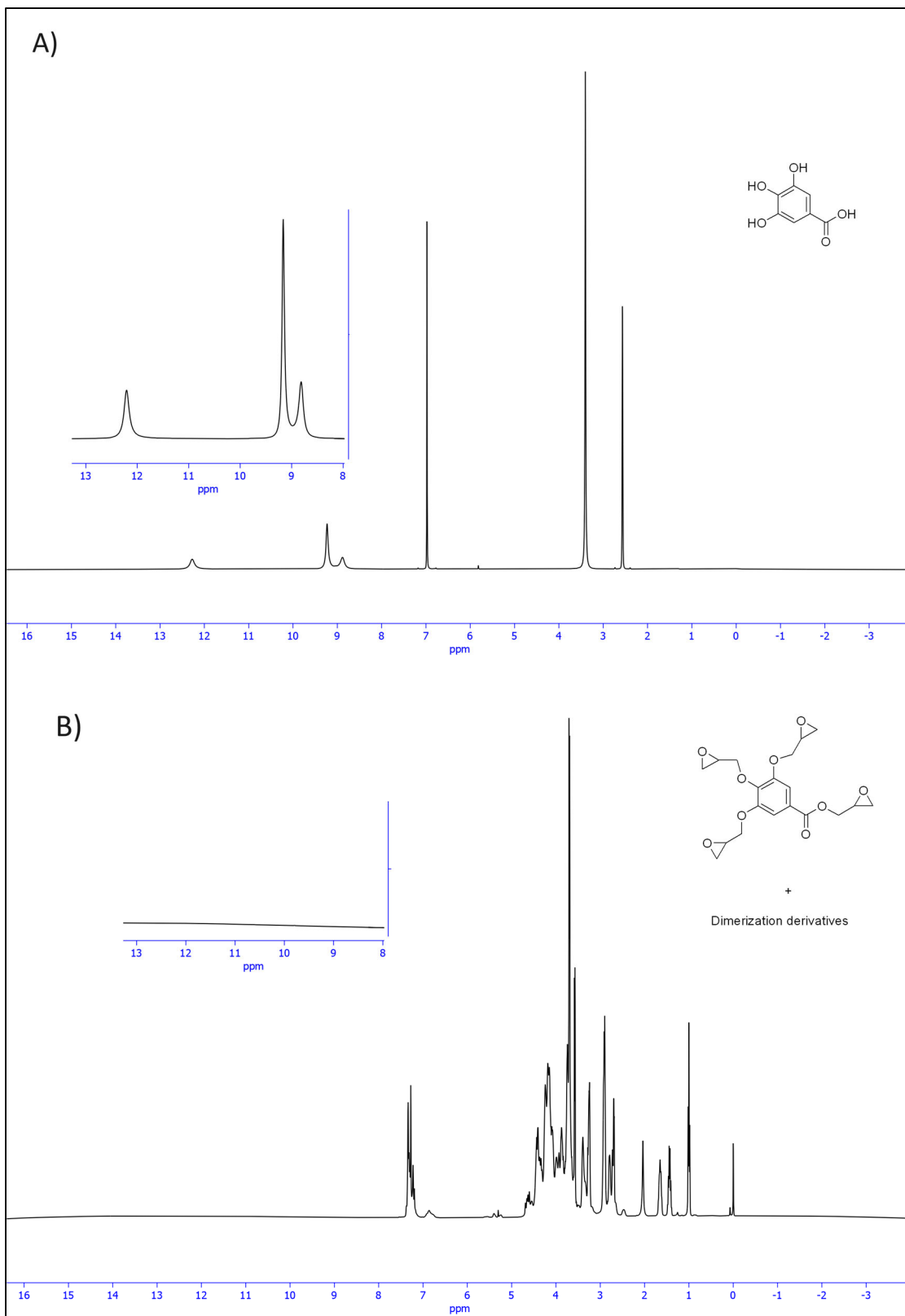


Figure 2: ^1H NMR spectra of A) GA and B) GA-based glycidylated monomer

Polyester epoxy synthesis

The synthesis of the bio-based PET analogue was achieved by mixing monomers 1 and 2 with a catalytic amount of $\text{Zn}(\text{acac})_2$ catalyst and a small volume of ethanol. This mixture was degassed at room temperature to remove the solvent, poured into a silicon mold, and degassed for 60 min at 50 °C to ensure the elimination of entrapped air before curing. The oxirane rings in the GA-based glycidylated monomer react with the active hydrogen atoms of diacid diester monomer and convert the liquid epoxy mixture into a solid, insoluble, crosslinked bio-based resin. The polymerization reaction was tested using different monomers' equivalent weights and different catalyst ratios. The thermal curing reaction was carried out by heating the mixture for 2 h at 120 °C, 2 h at 140 °C, and 16 h at 160 °C.

The bio-based epoxy resin was synthesized by reacting monomers 1 and 2 at stoichiometric ratios of 1:1, 1:0.75, and 1:2 for their functional groups, respectively. During the curing reaction, the oxirane rings of the epoxy monomer react with the active hydrogen atoms in the ethylene glycol bis(acid ester) monomer forming the crosslinked bio-based resin. Differential Scanning Calorimetry (DSC) was employed to ascertain the optimal curing temperature range of the polymer and to analyze the effects of zinc catalyst and reactants' ratios on the product's thermal behavior.

Figure 3 displays the DSC curves and the characteristic temperatures of the curing system at heating rates 20 °C/min. It can be seen that the temperature range of the exothermic reaction is large, and the peak temperature of the curing reaction is at 112 °C, the DSC thermogram also indicates the occurrence of two curing mechanisms due to the presence of two types of oxirane rings.

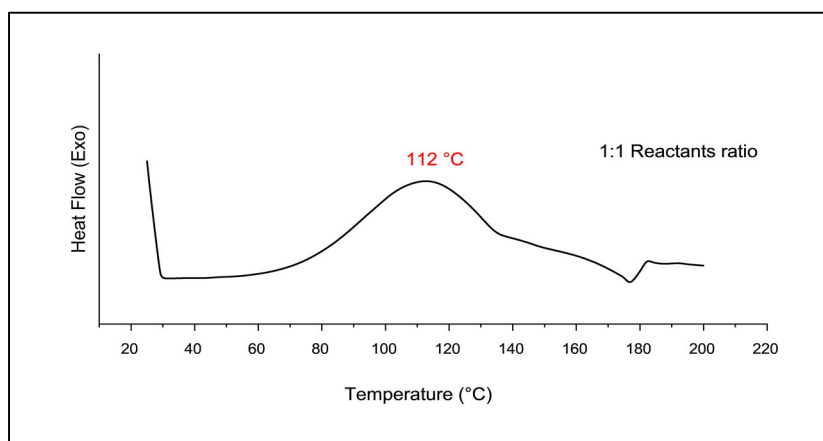


Figure 3: The DSC curves of curing system

The influence of the monomer ratios was also investigated using differential scanning calorimetry (DSC) at functional groups stoichiometric ratio of 1:1, 1:0.75, and 1:2 for monomer 1 to monomer 2, respectively. As depicted in Figure 4, changing the ratio of the reactants results in the formation of resins with different glass transition temperatures (T_g). Given that the T_g of PET ranges from 67 to 81°C, the weight equivalent monomer ratio of 1:1 was chosen to ensure the thermal properties of the resulting material align with those of PET.

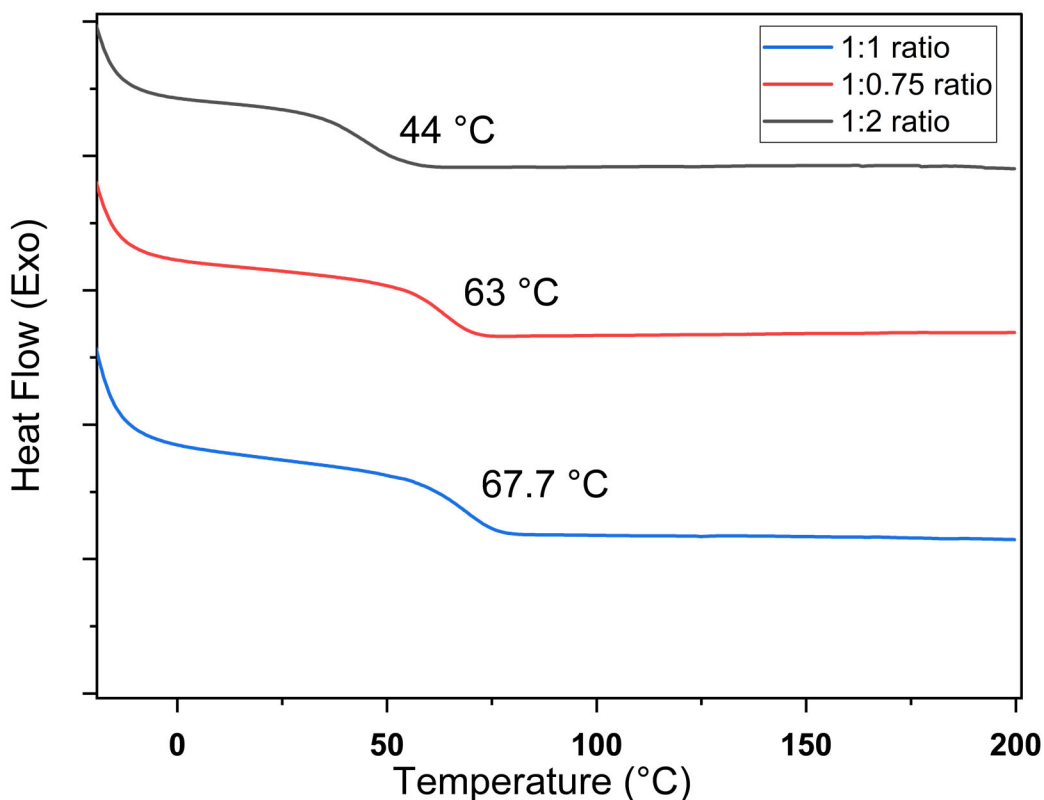


Figure 4: The DSC thermograms of

The spectral characterization of the polymer structure was achieved by means of FTIR. As depicted in Figure 5, the FTIR spectrum of the polyester epoxy shows the main characteristic absorption bands of the ester group (1730 cm^{-1}), aromatic ring ($1590, 1148\text{ cm}^{-1}$), the aliphatic and aromatic C–H stretching vibration ($2960\text{--}2870\text{ cm}^{-1}$) and the hydroxyl group ($3500\text{--}3200\text{ cm}^{-1}$). Additionally, the absence of the oxirane ring absorption band at 910 cm^{-1} indicates the completion of the curing reaction.

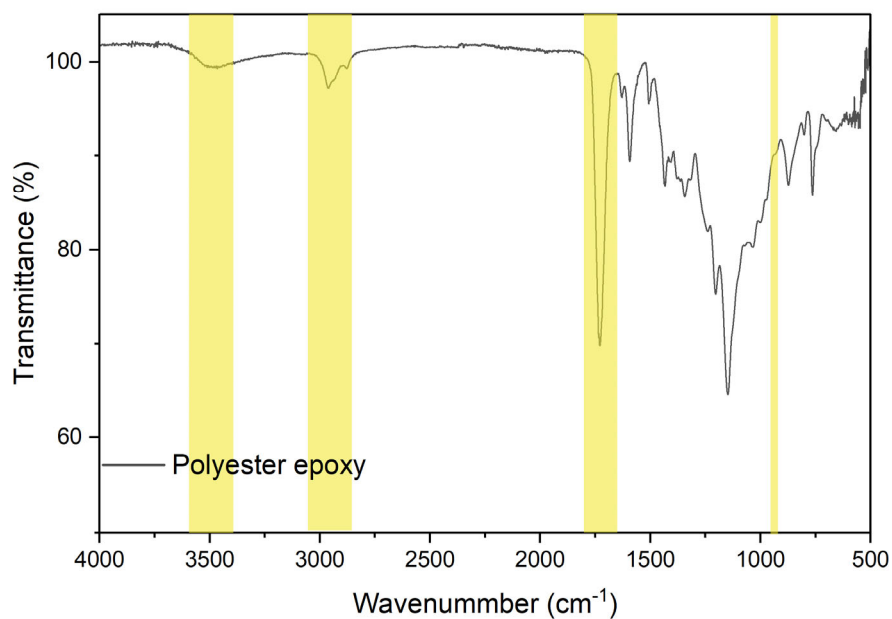


Figure 5: FTIR spectrum of the bio-based polymer

Work to Be Completed

The development and characterization of the second PET-analogue polymer is to be completed over the next few months. The following tasks related to both PET-analogue are to be completed as well:

1. Thermal properties investigation through TGA.
2. Testing the biological /antibacterial activity of both polymers.
3. Testing the 3D printability of both polymers.