North Dakota Soybean Council

Mid-year Report-December 2023

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 overall aim of the project is to contribute to the development of eco-friendly alternatives to polyethylene terephthalate (PET), a widely known critical polymeric precursor in various applications, utilizing the waste byproducts from soybean processing as the main co-reactants in the development process. The development process is to advance the synthesis method utilizing a convenient, low cost, and solvent-free approach which will render the production process scalable and commercially competitive. Thus far, we have already synthesized and characterized one of the two proposed PET-analogue polymers, accounting for 50% of the overall project outcomes. We have completed tasks 1&3 while simultaneously working and making progress on tasks 2,4, 5 and 6. We have successfully optimized the reaction conditions of a synthesis process that eventually lead to the production of a new green PET-analogue polymer #1. The green polymer was produced by reacting soybean gallic acid with ethylene glycol in the presence of DMAP as a catalyst. The reaction yield was improved and amounted to 72% through the polymerization process. The obtained brown dark product was analyzed by FTIR, H-NMR, and ^{13}C-NMR, confirming the chemical structure thereby the successful synthesis of the PET-analogue polymer. We have also assessed and found that the polymer product is soluble in both polar and non-polar solvents, making it suitable for various applications.

Up to Date Progress Results

Polymer Synthesis Procedure

Gallic acid (1.0 g) was completely dissolved in 10 ml ethanol at 70º C before slowly adding ethylene glycol. A small amount of 4-Dimethylaminopyridine (DMAP) (0.02 g) was added to the solution, and the reaction was left for nine hours. The pure product was obtained without column chromatography (brown dark product), Yield of 72% (Figure 1).

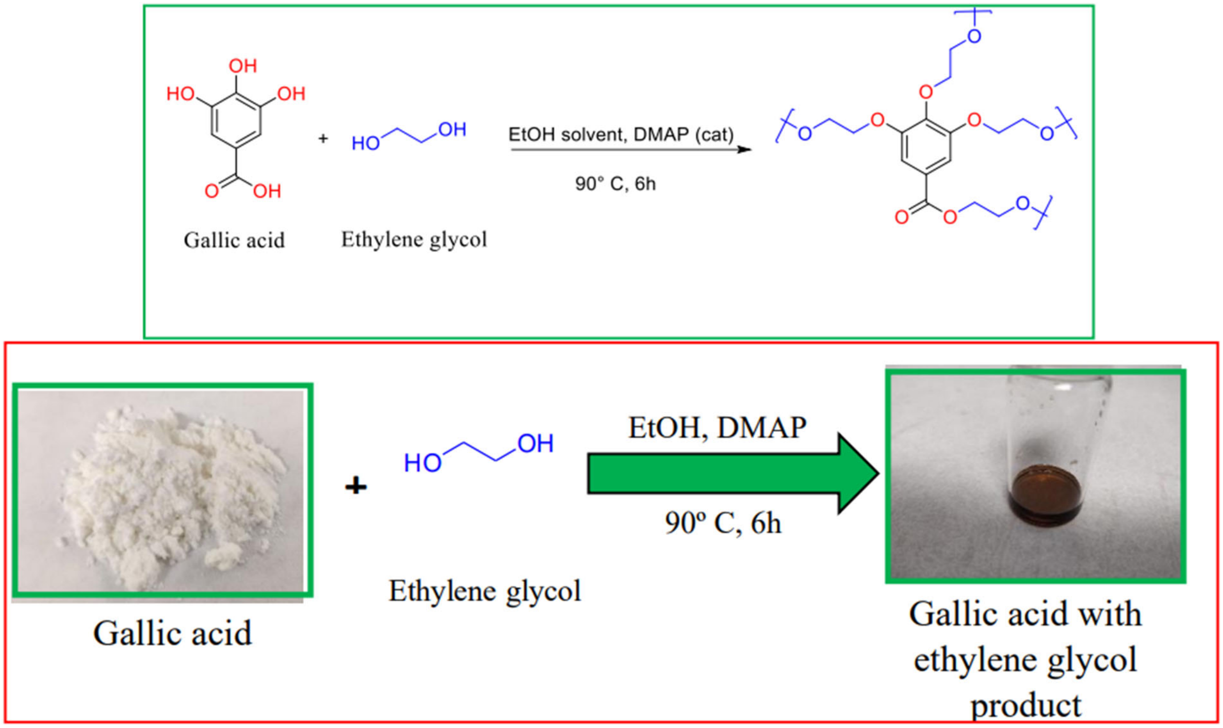

Figure 1:Schematics of the PET-analogue polymer#1 synthesis.

Characterization Results

^{1} H-NMR spectrum of the product showed a new peak doublet at 2.98 ppm when compared with the spectrum of gallic acid, resulting from ethylene glycol interaction and reaction with gallic acid. In addition, the disappearance of the carboxylic acid peak, usually appearing at 12.20 ppm, in the product spectra confirms that the reaction proceeded to completion (Figure 2).

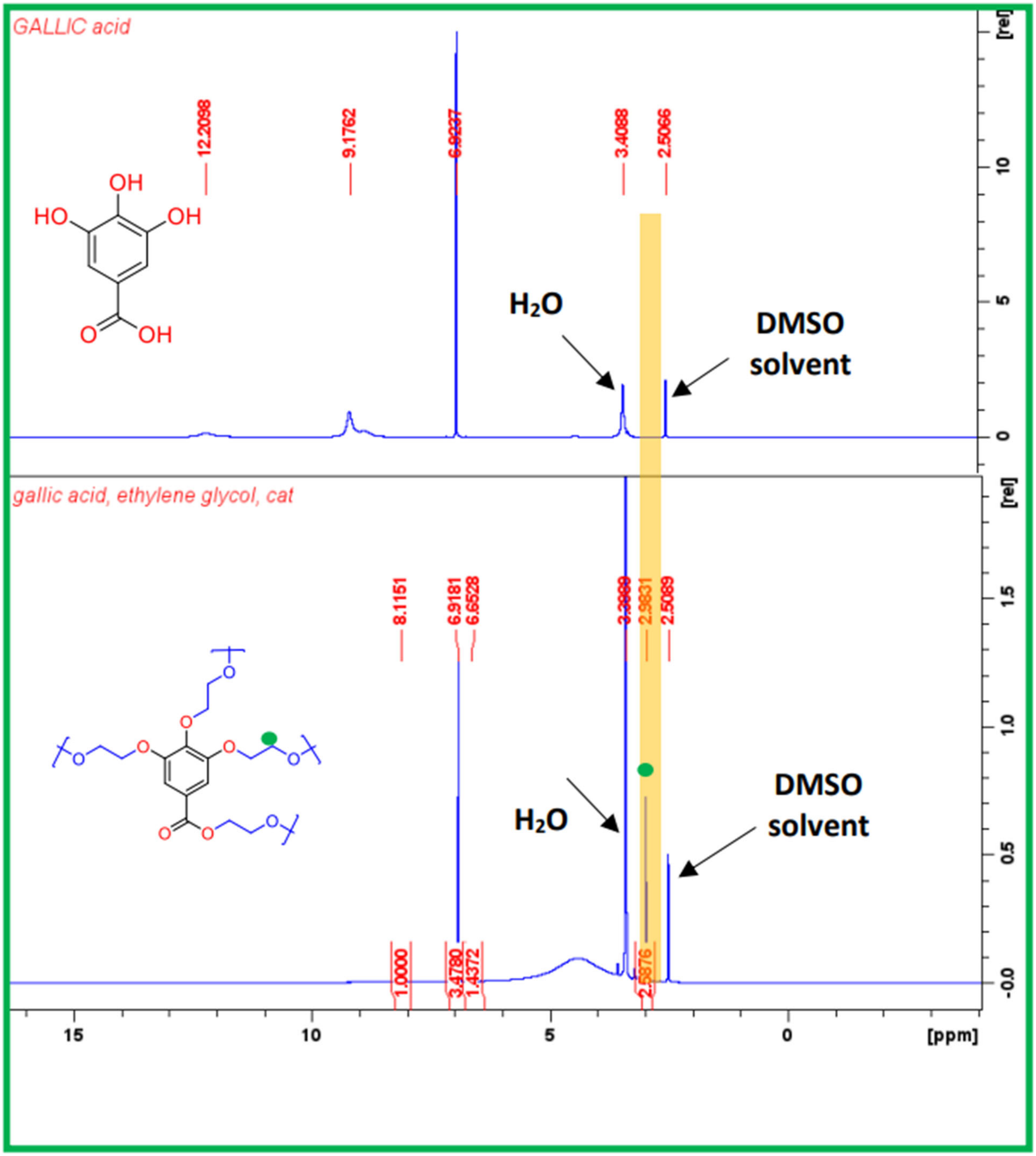

Figure 2: [1] HNMR spectra of gallic acid, compared to the polymer product.

[13] C NMR spectrum of product exhibited the emergence of a new peak at 63.24 ppm, contrasting the gallic acid spectrum. This new peak can be attributed to the presence of ethylene glycol in the gallic acid ethylene compound. Additionally, carboxylic acid has a shaft of 167.93 ppm to 168.101 ppm due to ethylene glycol reacting with gallic acid (Figure 3).

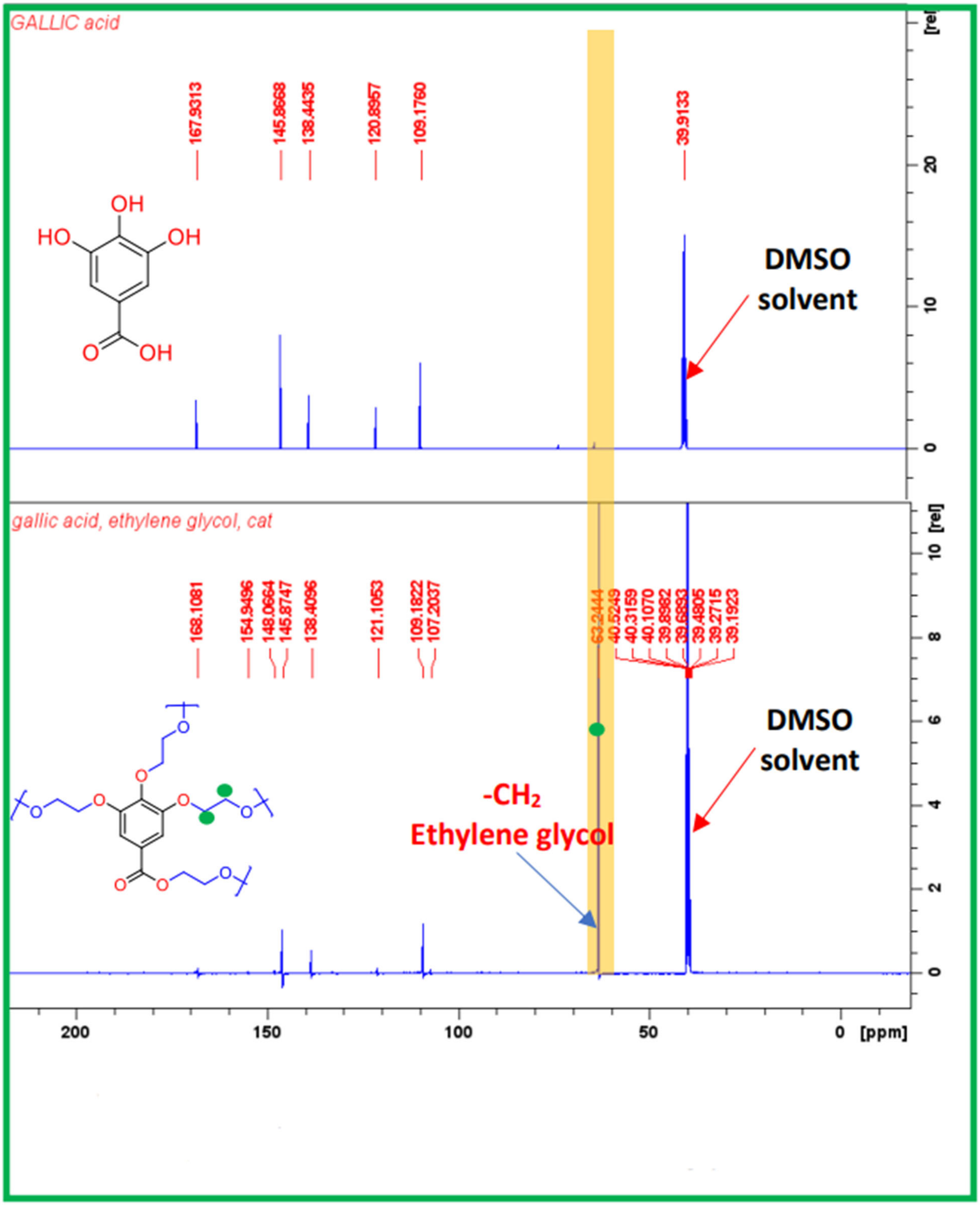

Figure 3: ^{13}C HNMR spectra of gallic acid, compared to the polymer product.

The FTIR spectra in Figure 4 indicate that the product had a new peak around 3499.05 cm^{-1}, which correspond to the stretching vibration of the hydroxyl group. The peak at 1093.26 cm^{-1} was attributed to the C-O groups, while the peak at 1665.06 cm^{-1} was attributed to the C=C groups. The peak at 1739.61 cm-1 (C=O, stretching). Generally, esters are less stable than their corresponding carboxylic acids due to their lower resonance stabilization. The stretching vibration peak of the benzene ring C=C groups was 1427.67 cm-1.

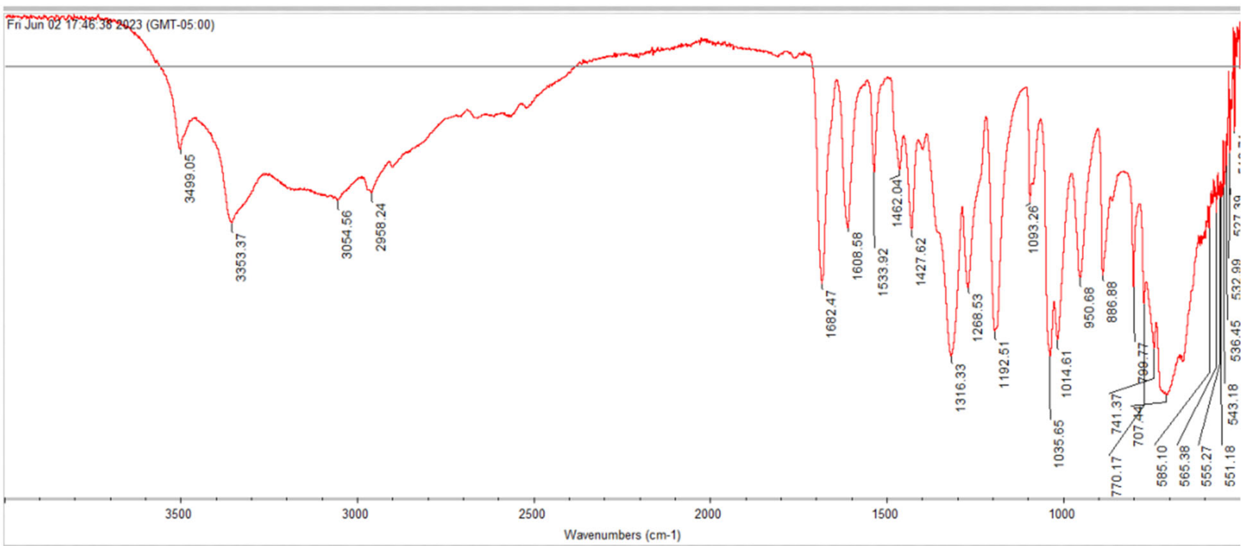

Figure 4:FTIR spectra of gallic acid, compared to the polymer product.

Solubility

The solubility of the polymer product was evaluated in polar and non-polar solvents. The polymer was found to be soluble in both solvent types as shown in table 1.

Table 1:Polar and nonpolar solvents where the polymer product was soluble.

Polar solvents	**Nonpolar solvents**
Water	Hexene
Acetone	Toluene
N, N-dimethylformamide	Chloroform
Pyridine	

Work to Be Completed

The development and characterization of the second PET-analogue polymer is to be completed over the next few months. The development is to be carried out by reacting soybean gallic acid with glycerol followed by characterization to confirm the chemical structure. The following tasks related to both PET-analogue 1 and PET- analogue 2 are to be completed as well:

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