Epoxy Resins Derived from the Renewable Gallic Acid and Phytic Acid for Food Cans Coating

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Research Overview and Objectives

With this work, the PI aims to synthesize new thermoset materials in this project using bio-based building blocks extracted from soybean byproducts. The new bio-based epoxy resins will be constructed by incorporating Gallic Acid (GA), Phytic Acid (PA), and 1,3-Propanediol (PD), with a focus on applications related to internal can coatings intended for food packaging. GA from soybean milk residue was once again selected as a building block due to its bio-based availability, multifunctionality, rigidity, and antioxidant and non-toxic properties. This rigid aromatic unit can be substituted for the harmful fossil fuel-based aromatic monomers commonly used in food and beverage can coatings, such as Bisphenol A (BPA). PA, a well-known non-toxic compound, can also be extracted from soybeans in high quantities during the soymilk and biofuel production processes. This compound forms stable complexes by chelating to minerals, making it beneficial for anticorrosion applications; therefore, PA will be used for its anti-corrosive characteristics and as a soybean-derived epoxy hardener. PD, a safe bio-based compound, will also be utilized to further modify the resin's thermal and mechanical properties by imparting additional flexibility into the crosslinked network.

The PI aims to design new thermosets as alternative materials to fossil fuel-based resins for canned food coating applications at the University of North Dakota's (UND's) Chemical Engineering Department. These polymers contain non-toxic building blocks and can be substituted for the potentially carcinogenic BPA materials in food packaging applications. These designed materials are composed of naturally occurring components that may pose a low risk to human health in the event of resin degradation and monomer release. The project objectives are encapsulated in discrete tasks below.

Task 1 – Tetraglycidyl ether of gallic acid (TEGA) synthesis

[1] PI

[2] Co-I

GA-based monomer synthesis will be tested using two well-established synthetic approaches (**Figure 1**). The synthetic routes will be compared in terms of the monomer's production cost, yield, and purity. Approach 1: GA will be reacted with an excess of epichlorohydrin in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB) using a one-step synthetic approach[9]. Afterward, a sodium hydroxide solution (20%, w/w) will be added to the reaction mixture under vigorous stirring to obtain the target monomer. Approach 2: A GA- based monomer will be reacted with allyl bromide in the two-step synthetic method[10]. The allylated product will then be transformed into its tetraglycidyl ether using *m*-chloroperbenzoic acid and triethyl amine as a catalyst.

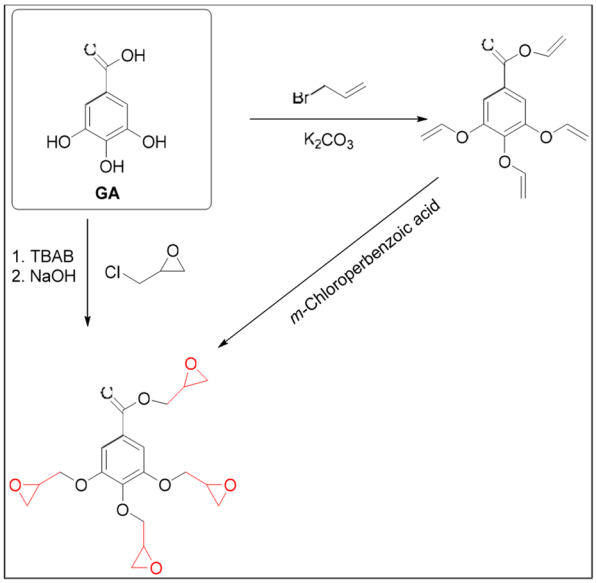

Figure 1 - Synthetic approach of tetraglycidyl ether of gallic acid (TEGA)

Task 2 – Diglycidyl ether of 1,3-propanediol (DEPD) synthesis

Similarly to Task 1, diglycidyl ether of 1,3-propanediol will be synthesized via one- and two-step synthetic approaches. Both approaches will be tested to compare the monomer's production cost, purity, and percentage yield (**Figure 2**).

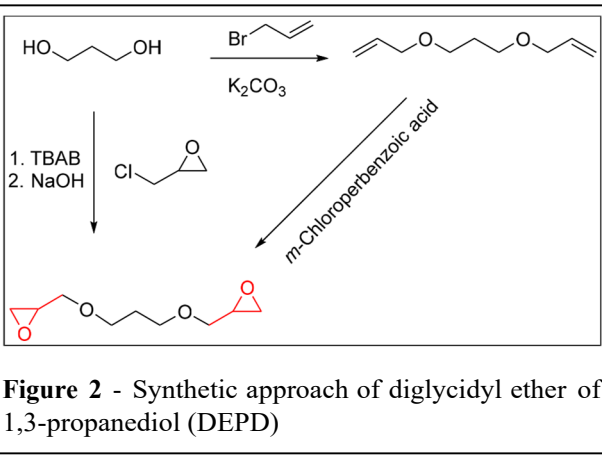

Figure 2 - Synthetic approach of diglycidyl ether of 1,3-propanediol (DEPD)

Task 3 – Soybean-derived epoxy resin synthesis

The bio-based epoxy resin will be synthesized by mixing different ratios of TEGA and DEPD with PA. The molar ratio of the PA to epoxy groups will be varied, and the thermal curing step will be tested at temperatures ranging from 50 to 140°C (**Figure 3**).

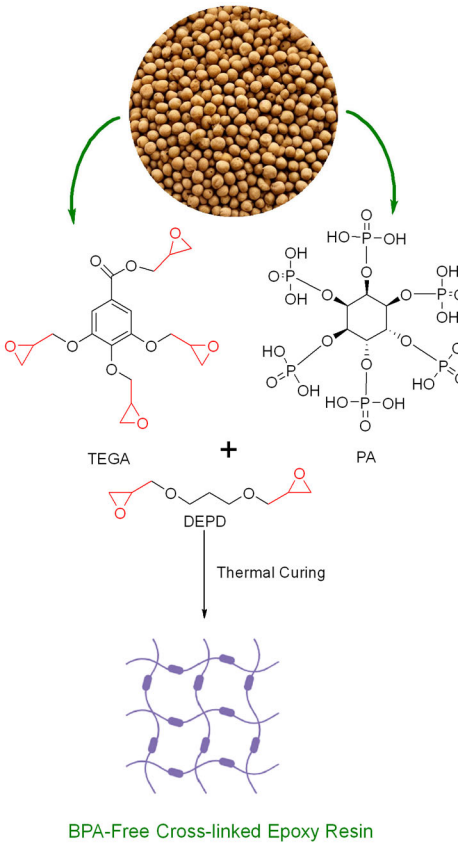

Figure 3 - Synthesis of soybean derived epoxy resin

Task 4 – Thermal behavior and spectral characterization

The synthesized monomers will be characterized using nuclear magnetic resonance (^{1}H and ^{13}C NMR) and infrared (IR) spectroscopy. The new epoxy resins will be characterized using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and infrared (IR) spectroscopy. The resin's thermal properties will be tuned by varying the TEGA/DEPD ratios. Additionally, the influence of the curing conditions (time, temperature, humidity) on the material's thermal stability will be explored.

Task 5 – Mechanical properties and anticorrosion behavior

Dynamic Mechanical Analysis will be used to study the thermosets' stress relaxation behavior, and a mechanical testing machine will be used to measure the tensile properties. Similarly to the previous task, the influence of the monomers' molar ratio and curing conditions on the mechanical properties will be investigated. Additionally, the anticorrosion behavior of the developed coating materials will be investigated using salt spray testing and adhesion testing.

Completed Work: Deliverables and/or Milestones

For Task 1, tetra-allylated gallic acid (AGA) was synthesized at high yield of 82% in preparation as a feedstock to synthesize tetraglycidyl ether gallic acid (TEGA).

Gallic acid glycidylation was achieved through a two-step chemical synthesis process. First, the hydroxyl groups of gallic acid were allylated with the assistance of an alkaline catalyst, resulting in tetra-allylated gallic acid (AGA). In the second step, the double bonds in AGA were epoxidized to produce a mixture of glycidylated gallic acid derivatives. The allylation was carried out using various synthetic reagents and optimized reaction conditions to achieve a high yield of the tetra-allylated AGA monomer. Several reaction protocols from the literature were tested and refined to optimize the yield (**Table 1**). The choice of solvent, reaction temperature, and the molar ratios of reagents were carefully varied and controlled to determine the optimal conditions for the allylation step.

TEGA was then synthesized and, among the mono- di-, and tri-byproducts, the desired tetraglycidyl ether gallic acid synthesis was achieved with a yield of 80% (**Figure 4**)

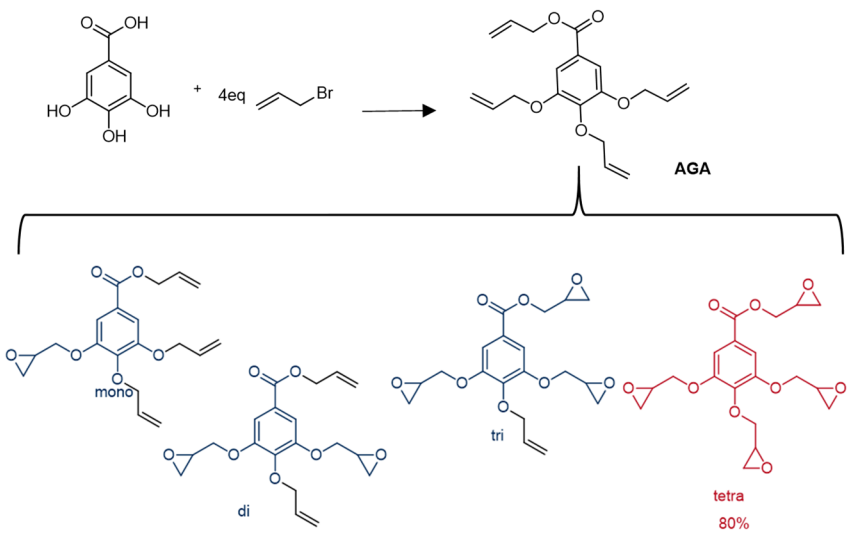

Figure 4 – TEGA synthesis yield amongst potential byproducts

Table 1 – AGA reaction optimization chart

Entry	solvent		K_2CO_3	temperature	AGA(tetra)	Time (H)
1	DMF	4	4	r.t	41%	48
2	Acetone	8	8	70°C (reflux)	60 %	24
3	Acetone	10	8	70°C (reflux)	82 %	24
4	NET_3/Pyridine	12	12	r.t	30%(mixed)	48

Progress of Work and Results to Date

As this is the first progress report, the completed work listed above is also the progress/results to date.

Work to be Completed

The next steps are applying lessons learned in Task 1 to start Task 2. In the meantime, we will finish scaling up the reaction to increase the yield of the tetraallylated product, followed by the

epoxidation step using mCPBA to obtain allyl 3,4,5-tris(allyloxy)benzoate. The ratio of tetra-, tri-, di-, and mono-allylated products will again be characterized using GC-MS analysis.

Other Relevant Information

Unforeseen blockers prevented the estimated completion of Task 1 on time. Primarily, the low yield of AGA from the initial synthesis routes prompted additional tests for confirmation before varying the experimental conditions to improve the yield. This variance included more time consulting the literature and cross-examining experimental conditions and results of multiple studies. However, now that the correct conditions have been realized, further progress into the project can proceed. The silver lining here is that the same solutions that were found in Task 1 will also be applied to Task 2 since it uses the same synthesis route. We can therefore say with confidence that Task 2 will take significantly less time than Task 1.

Barring other unforeseen blockers, the potential blocker listed in the proposal submission remains on the horizon: the thermal stability of phytic acid for Task 4. However, the mitigation strategy of using temperatures ranging from 50 to 140°C should prove sufficient as a previous study has reported that the gradual increase in thermal curing temperature, up to 200 °C, does not promote phytic acid instability due to the partial incorporation of phytic acid into the material structure during the curing process. Additionally, the time to test these temperatures is also baked into the project schedule.

Summary

The PI aims to synthesize new thermoset materials in this project, with a focus on applications related to internal can coatings intended for food packaging, using bio-based building blocks extracted from soybean byproducts: Gallic Acid (GA), Phytic Acid (PA), and 1,3-Propanediol (PD). GA can be substituted for the harmful fossil fuel-based aromatic monomers commonly used in food and beverage can coatings, such as Bisphenol A (BPA). PA forms stable complexes by chelating to minerals, making it beneficial for anticorrosion applications; therefore, PA will be used for its anti-corrosive characteristics and as a soybean-derived epoxy hardener. PD will further modify the resin's thermal and mechanical properties by imparting additional flexibility into the crosslinked network. The project objectives encompass five tasks throughout the period of performance. Task 1 was delayed due to low yields of the tetra-allylated gallic acid (AGA) feedstock stemming from the reaction conditions outlined in the literature. These low yields have since been improved, and the AGA used to synthesize the target tetraglycidyl ether gallic (TEGA) with a yield amongst other byproducts of 80%. Further improvements will be made to the yield of AGA, but Task 2 is set to start and take full advantage of the lessons learned in Task 1, significantly reducing the risk of further delays.