Characterization and Modification of Asphalt With Epoxy Resins Synthesized From Pyrolysis Oil, a Derivative of Lignocellulosic Biomass

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Introduction

Asphalt is an important commodity that has a vital purpose in civic infrastructure, both in urban and rural communities alike. Polymer-modified asphalt has become a popular topic of interest due to the advantageous property modifications provided by its polymer components. Such alterations include increased moisture resistance, higher tensility, better resistance to long-lasting deformation, greater elasticity, and lower temperature susceptibility. In this study, asphalt was modified with an epoxy resin synthesized from pyrolysis oil (a derivative of lignocellulosic biomass). Typically, in commercial and industrial settings, epoxy resins are formed by treating bisphenol-A with chloromethyloxirane (epichlorohydrin). Lignocellulosic biomass, namely lignin, houses similar hydroxyl environments like those found in bisphenol-A, and thus can be used as a substitute.

Overall Process Flowchart

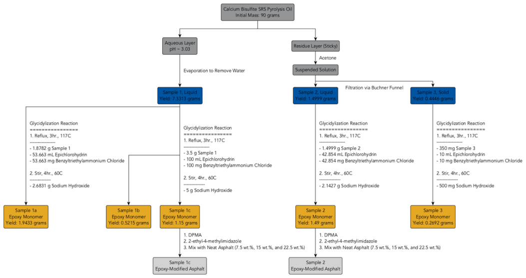

Figure 1. Flowchart delineating the overall process of asphalt modification via pyrolysis oil.

Reaction Scheme

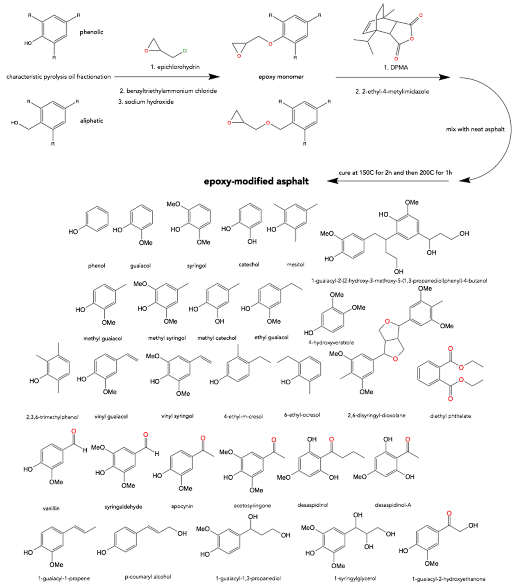

Figure 2-3. Reaction scheme and an extensive list of pyrolysis fractionations.

Experimental Methods

Three separate samples were obtained from extraction and separation processes performed on the starting pyrolysis oil solution. The phenolic and hydroxymethyl functional groups belonging to the pyrolysis oil fractionations in these samples were reacted with epichlorohydrin as follows: 350 mg of sample, 10 mL of epichlorohydrin, and 10 mg of benzyltriethylammonium chloride were combined and set to reflux for 4 hours at 117°C. The mixture was then cooled to 60°C, 500 mg of sodium hydroxide was added, and stirring occurred for 3 hours. The remaining epichlorohydrin was evaporated, leaving the desired epoxy monomer. The epoxy monomer was then mixed with the Diels-Alder adduct produced from the reaction between dipentene and maleic anhydride (DPMA) using 1wt.% 2-ethyl-4-methylimidazole as a catalyst. The mixture was then combined with neat asphalt at different concentrations: 7.5 wt.%, 15 wt.%, and 22.5 wt.%, respectively. The epoxy-modified asphalt was then cured at 150°C for 2 hours and then 200°C for 1 hour. **Note**: The glycidylization reaction was performed on all of the samples in the same numerical ratios as described.

Analytical Methods and Results

Gas Chromatography & Mass Spectroscopy

A ThermoScientific Focus GC was used in concordance with a ThermoScientific ITQ 1100 to estimate the highest probable fractionations in the pyrolysis oil samples.

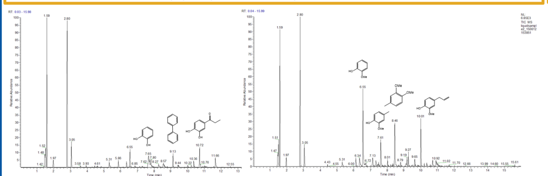

Figure 4-5. GC-MS peaks indicating the most probable pyrolysis oil fractionations.

Differential Scanning Calorimeter

A non-isothermal TA Instruments 2920 Modulated DSC was used under a nitrogen atmosphere to test if the epoxy monomers could be successfully cured.

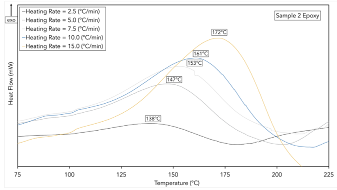

Figure 10. DSC curves for Sample 2 at 5 different heating rates.

Thermal Gravimetric Analysis

A TA Instruments SDT Q600 was used to evaluate the thermal stability and degradation behavior of the pyrolysis oil samples.

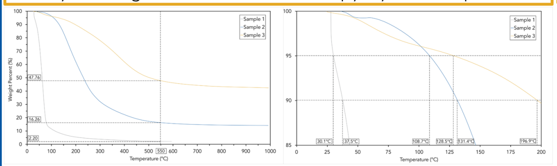

Figure 6-7. TGA graphs showing thermal stability and degradation. Char yield is indicated in Fig. 6 and $T_{5\%}$ and $T_{10\%}$ are indicated in Fig. 7.

Fourier Transform Infrared Spectroscopy

A ThermoScientific Nicolet Nexus 670 FT-IR was employed to test samples before and after epoxidization in order to determine if the glycidylization reaction was successful.

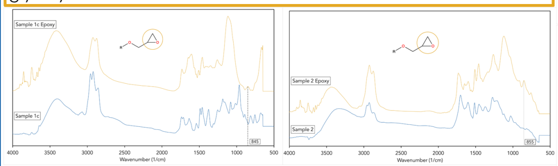

Figure 8-9. FT-IR peaks for before and after glycidylization. Both figures are marked to show peak changes that show epoxide ring formation.

Rheology

A TA Instruments Discovery HR-2 Hybrid Rheometer was used to test the viscoelastic properties of the epoxy-modified asphalt.

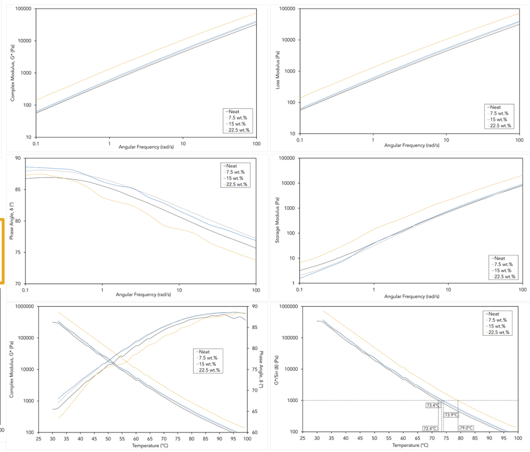

Figure 11-16. Rheology test results for both angular frequency and temperature.

References

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Conclusions

According to the rheology test results, the epoxy-modified asphalt exhibits greater viscoelastic properties, specifically the asphalt containing 22.5 wt.% of the epoxy/DPMA mixture.

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