Improving Polymer-Modified Asphalt by Changing the Characteristics of SBS Using Click Chemistry

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The United States has more than 2.7 million miles of paved roads and highways, and 94 percent of those are surfaced with asphalt\(^1\). Asphalt is made of aggregates (e.g., crushed rock and sand) and mixed with a binder called bitumen, a derivative of crude oil. However, high-volume traffic has resulted in a shorter lifespan for asphalt roads and the permanent strain on asphalt, including rutting and cracking, can make driving rough and dangerous\(^2\). Increased cost of maintenance is also directly correlated with high traffic volume and strained asphalt. The need for polymer-modified asphalt is now at the forefront with its increased durability and improved viscoelastic properties. Polymer-modified asphalt has stronger heat and cracking resistance than traditional asphalt. Even so, drawbacks such as separation of polymer-asphalt mixture and poor solubility prevent polymer-modified asphalt from replacing traditional asphalt.

This project is aimed at investigating a polystyrene-block-polybutadiene-block-polystyrene-triblock copolymer (SBS), a thermoplastic elastomer, to improve polymer-modified asphalt so that it can be a possible replacement for traditional asphalt. Thermoplastic elastomers have both rubber and plastic properties that can improve the elasticity of asphalt when added. When SBS and asphalt are mixed together, there is sufficient swelling and uniform dispersion. Both of these are necessary for application. However, the difference in polarity results in unsatisfactory storage stability and incompatibility. SBS is a nonpolar copolymer, while asphalt has polar components mixed in such as sulfur, nitrogen and oxygen\(^3\). Therefore, polymer-modified asphalt, the SBS and asphalt mixture, must be produced on demand, which increases costs dramatically.

Modification of SBS has the potential to overcome these negative characteristics\(^3\). In order to modify SBS, functional groups were added to the 1,2 double bonds. In my project, 2,2-azobisobutyronitrile (AIBN) was used as a free radical initiator. It was added in excess due to inhibitors present in sodium 3-mercaptor-1-propanesulfonate (NaMP), the modifying agent, and tetrahydrofuran (THF), the main solvent. Inhibitors were used to prevent compounds from reacting with themselves during storage. The reaction occurred in a nitrogen-filled reaction flask at temperatures above 65 °C to prevent AIBN from reacting with oxygen and to determine the temperature with the most effective conversion ratio. The flask was placed in a silicon oil bath to create a constant temperature environment. The two-neck reaction flask was connected to a condenser in order to prevent THF vapor buildup and increase the surface area for both vapor-liquid contact and heat exchange, as shown in Figure 1. The reacted product was dried in the vacuum oven and characterized with nuclear magnetic resonance (NMR).

Modification of SBS has the potential to overcome these negative characteristics\(^3\). In order to modify SBS, functional groups were added to the 1,2 double bonds. The goal was to improve the stability and miscibility of polymer-asphalt mixtures. Click chemistry is a stereospecific, free radical reaction that will selectively add functional groups to the 1,2 double bonds. In my project, 2,2-azobisobutyronitrile (AIBN) was used as a free radical initiator. It was added in excess due to inhibitors present in sodium 3-mercaptor-1-propanesulfonate (NaMP), the modifying agent, and tetrahydrofuran (THF), the main solvent. Inhibitors were used to prevent compounds from reacting with themselves during storage. The reaction occurred in a nitrogen-filled reaction flask at temperatures above 65 °C to prevent AIBN from reacting with oxygen and to determine the temperature with the most effective conversion ratio. The flask was placed in a silicon oil bath to create a constant temperature environment. The two-neck reaction flask was connected to a condenser in order to prevent THF vapor buildup and increase the surface area for both vapor-liquid contact and heat exchange, as shown in Figure 1. The reacted product was dried in the vacuum oven and characterized with nuclear magnetic resonance (NMR).

**Figure 1:** Reaction setup for thiolene click chemistry with SBS using a two-neck flask with a condenser and oil bath.
In the future, trials will be run with cleaned THF (free of water and oxygen) and a higher percentage of excess AIBN to significantly improve the conversion of double bond to function group. Additionally, other modifying agents will be tested to provide a diverse set of modified SBS block copolymers. Once the desired products are obtained, they will be characterized with NMR, differential scanning calorimetry, and gel permeation chromatography. The mechanical properties will be tested and mixed with asphalt binder at The National Center of Asphalt Technology to examine their potential for field application in Alabama roadways.

**Statement of Research Advisor**

Tina has made good progress as she attempts to produce modified SBS triblock copolymers for use in asphalt pavements. She has developed synthetic methods for performing her target chemistry and we are looking forward to testing the fruit of her efforts with asphalt binders to investigate their potential.

– **Bryan B. Beckingham, Chemical Engineering**

**References**

