Replacement of Petroleum-based Rubber with "Bio-rubber" from Vegetable Oils

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Background

• The rubber industry has been dominated by petroleum based synthetic rubbers, especially those made from styrene-butadiene rubber (SBR).

• As awareness of the environmental effects and costs of petroleum have increased so has the need to find suitable replacements.
Biopolymer

• A biopolymer
  • a polymer that is derived from a natural source, and is renewable.
  • Our research set out to find a suitable replacement to petroleum based products.

• Soybean Oil
  • We found that block copolymers of styrene-soybean oil produced similar properties as those of SBR type rubbers.
Method

- Soybean Oil
  - Triglyceride
  - About 4.6 double bonds
- Modification
  - Soybean oil was modified in order to improve reactivity and polymerization
  - Epoxidation and Acrylation
- Polymerization
  - Two methods used: ATRP and RAFT
Epoxidation and Acrylation

- Epoxidation performed through addition of formic acid, hydrogen peroxide.
- Acrylation performed through addition of acrylic acid.

\[ \text{(II)} \]

\[
\begin{align*}
\text{Acrylated epoxidized Soybean Oil (AESO)}
\end{align*}
\]
ATRP

- Atom Transfer Radical Polymerization
  - Controlled polymerization

- Reagents required
  - benzyl chloride as initiator
  - Copper 1 chloride as catalyst
  - Copper 2 chloride as counter catalyst
  - N,N,N',N,N Pentamethyl-diethylenetriamine (PMDETA) as ligand

- Varied temperatures of reaction, initiator concentration, solvent ratios, catalysts, and monomer concentration.

\[
RX + M^nX + L \rightleftharpoons RX-M^nXL \quad \text{dormant species}
\]

\[
M + R^* + M^{n+1}X_2L \quad \text{active species}
\]
RAFT

- Reversible addition-fragmentation chain-transfer polymerization
- Controlled polymerization

- Reagents used
  - AESO monomer
  - AIBN as initiator
  - Solvent
  - RAFT Chain Transfer Agent
    - Varied

\[ i \text{ Initiation} \]
Initiator \[ \rightarrow \] I^*
\[ I^* + M \rightarrow P_{n+1}^* \]

\[ ii \text{ Initial equilibrium} \]
\[ P_{m+1}^* + S \rightarrow P_{m+1} \rightarrow P_{n+2} + S \]

\[ iii \text{ Reinitiation} \]
R^* + M \[ \xrightarrow{k_{\text{init}}} \] P_i^* \[ \xrightarrow{k_p} \] P_{n+1}^*

\[ iv \text{ Main equilibrium} \]
\[ P_{n+1}^* + S \rightarrow P_{n+2} \rightarrow P_{n+3} + P_{m+1}^* \]

\[ v \text{ Termination} \]
\[ P_{n+1}^* + P_i^* \xrightarrow{k_{\text{term}}} \]
\[ P_{n+1}^* + P_i \]
\[ P_{n+2}^* + P_{m+1}^* \]
Triblock copolymer

• Both ATRP and RAFT were used to make triblock copolomers from styrene and AESO monomers
• These polymers were SAS style in that they were Styrene-AESO-Styrene
Products

• Varied:
  • Temperature, monomer/initiator concentration, solvent ratio, catalysts
  • Found rubbery viscoelastic properties

• We characterized our products using:
  • GPC, NMR, DSC, TEM

• GPC
HNMR

Styrene peak
Results

• Molecular weight
  • Molecular weights ranged from 10kDa to 1MDa

• Polydispersity
  • Measures range of Mw within a sample of polymer
  • PDI’s were generally low, <2.0

• Viscoelastic properties
  • Similar to SBR type rubber
  • Properties suggest success in use as asphalt
Future Work

• Our results showed the effectiveness of controlled polymerization on a multifunctional monomer into a thermoplastic elastomer.

• Also showed promise as use as a rubber, and especially for use as an asphalt modifier.

• Our next goal will be scaling up of synthesis of this polymer, and involving companies in our work.
Works Cited

• http://en.wikipedia.org/wiki/File:Iowa_State_Cyclones_logo.svg
• Nacu Hernandez: ACS Presentation
• http://powerlisting.wikia.com/wiki/Rubber_Manipulation
• http://www.nature.com/nchem/journal/v2/n10/full/nchem.853.html
• http://www.eastman.com/Markets/Tackifier_Center/Pages/Block_Copolymer.aspx
• http://www.biobusinessaccelerator.com/pilot-plant/