Chemical Modification of Cellulose Nanofibrils by Graft Polymerization
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Introduction
Achieving homogeneous dispersion and good interfacial adhesion between cellulose nanofibrils (CNF) and polymer matrices is important for obtaining optimal nanocomposite properties. Surface modification of CNF by graft polymerization using maleated styrene block copolymer (SEBS-g-MA) would alterate CNF surface hydrophilicity:
- Improved dispersibility
- Better compatibility with apolar polymer

Cellulose Nanofibrils (CNF)
- Merits: biodegradable, high stress transfer ability, low density, low abrasiveness, and low cost
- Demerit: strong self-association tendency by hydrogen bonds of cellulose on surface:
  - Agglomeration
  - Poor water resistance
  - Poor compatibility with apolar polymer

Maleated Styrene Block Copolymer (SEBS-g-MA)
Consists of a reactive anhydride group as coupling agent and elastomeric segments composed of a hard segment, poly(styrene) (PS), and a soft elastic segment, poly(ethylene-co-but-1-ene) (PEB). Merits: balanced elasticity, good thermal stability and compatibility with other polymer.

Chemical Modification: Concept
Grafting onto approach: anhydride group reacts with cellulose hydroxyl groups to form ester linkages.

Chemical Modification: Synthesis
1. Disperse CNF and SEBS-g-MA in tetrahydrofuran (THF)
2. Air-dried sample was cured at 100-120°C and excess homopolymer was washed
3. Film preparation by solvent casting

Chemical Modification: Results
- Graft Efficiency ($G_e$)
  $G_e$ up to 62% was measured by UV-spectroscopy at 260 nm from PS absorbance of supernatant for case of graft polymerization with limiting amount of polymer.
- Surface Morphology: Optical images and Surface hydrophobicity
  Untreated CNF film shows strongly entangled fiber.
  Modified CNF film displays more porous network due to:
  - Limited hydrogen bond interaction
  - Steric repulsion of grafted polymer

Materials
- Poor compatibility with apolar polymer
- Limited hydrogen bond interaction
- Better compatibility with apolar polymer

Dispersions Quality in Nanocomposites
Better compatibility with apolar polymer matrices
Aggregates at microscale are still visible for higher CNF filler nanocomposites

Mechanical Properties of Nanocomposites
- Effects of CNF filler:
  - Increase in tensile strength
  - Increase in elongation
  - Overall increase in stiffness

Summary and Future Work
- Chemical modification by styrene block copolymer graft polymerization can alter the hydrophilic surface of CNF into hydrophobic
- Modified CNF can reduce agglomeration affinity, increase water resistance, and improve compatibility with apolar polymer
- Modified CNF as nanocomposites reinforcement filler can enhance the mechanical properties and maintain good thermal stability
- More effective graft polymerization method is important to achieve high dispersion level for higher CNF filler content
- Preparation of controlled surface modification without intensive solvent exchange is needed for larger scale quantity

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