Nanocellulose reinforcement for bio-based phenolic thermo-responsive resins

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Introduction

Petroleum reserves are depleting and the push for an efficient low cost alternative has led to extensive research in the area of cellulosic-based biofuels. Waste or non-fuel components of biofuel platforms such as pyrolysis need to find a value-added market to make them economically viable. Methods to separate the phenolic rich fraction (PRF) from pyrolysis bio-oils have been used to develop resins. The PRF is derived primarily from the lignin component of wood. This work evaluated the use of nanocellulose as a reinforcing element to increase the resins mechanical properties. Dispersion is always a concern for nano fibers of all types, by using a low viscosity bio-oil, we can easily incorporate the nanocellulose into the PRF to create a stronger resin

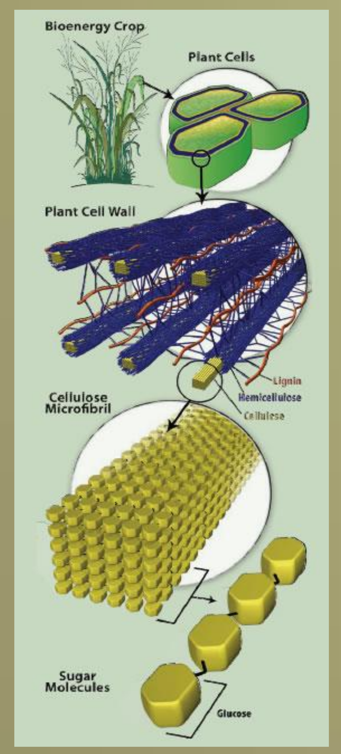
Raw Material (Wood) → Pyrolysis (Bio-Oil) → Fractionation (Isolate Lignin) → PRF (Resin) → Mechanical Properties

Objectives

- Goal: Create a nanocellulose reinforced bio-based phenolic thermo-responsive resins
  - Create miscible blends of phenolic rich fractions (PRF) extracted from the pyrolytic bio-oil, and polycarprolactone (PCL).
    - PCL is used to toughen the PRF
  - Develop a methodology to integrate nanocellulose into the PRF/PCL composition.
  - Perform Dynamic Mechanical Analysis (DMA) on composition to study the rheological response of the materials.

Materials

- Pyrolysis Bio-Oil derived from woody biomass
  - Lignin-based phenolic fraction (PRF) separated from the cellulose-base sugars
- Nanocellulose
  - Cellulose nano crystals obtained through acid hydroysis

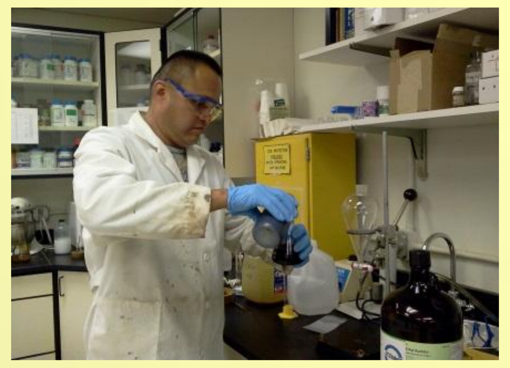


Schematic of plant cell wall utilization of lignin, hemicellulose and cellulose. Adapted from (Sannigrahi et al. 2010).

Pyrolysis

Methodology

- Process to make a PRF resin includes the following steps:
- Pyrolysis of woody biomass
  - Thermal breakdown of Lignocellulose to generate a bio-oil
- Fractionation Process of the Bio-oil
  - Equal amounts of bio-oil and ethyl acetate for extraction of lignin oil.
- PRF Pretreatment
  - Soda wash to reduce acidity
  - Heat treatment to remove existing water, low molecular weight monophenols, and residual ethyl acetate.
- Composite Preparation
  - Disperse nanocellulose into water solution and blend with PRF
  - Melt-blend the nanocellulose PRF with PCL
- Structural analysis
  - Use dynamic mechanical analysis (DMA) to characterize the mechanical properties of the nanocellulose PRF/PCL composite.



1) Addition of ethyl acetate to bio-oil

2) The fractionation and purification process, 4-5 hours

3) Concentration of lignin, ethyl acetate, water and sodium bi-carbonates for purification

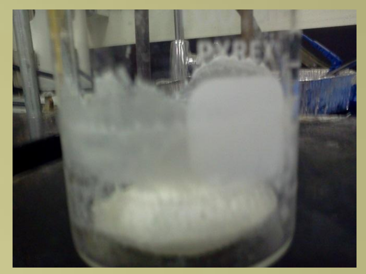
4) Mixture of the PRF and Nanocellulose

Visual state of PRFs without heat pretreatment (a) and after isothermal heat pretreatments of 60C (b) and 100C (c)

5) Dynamic Mechanical Analysis

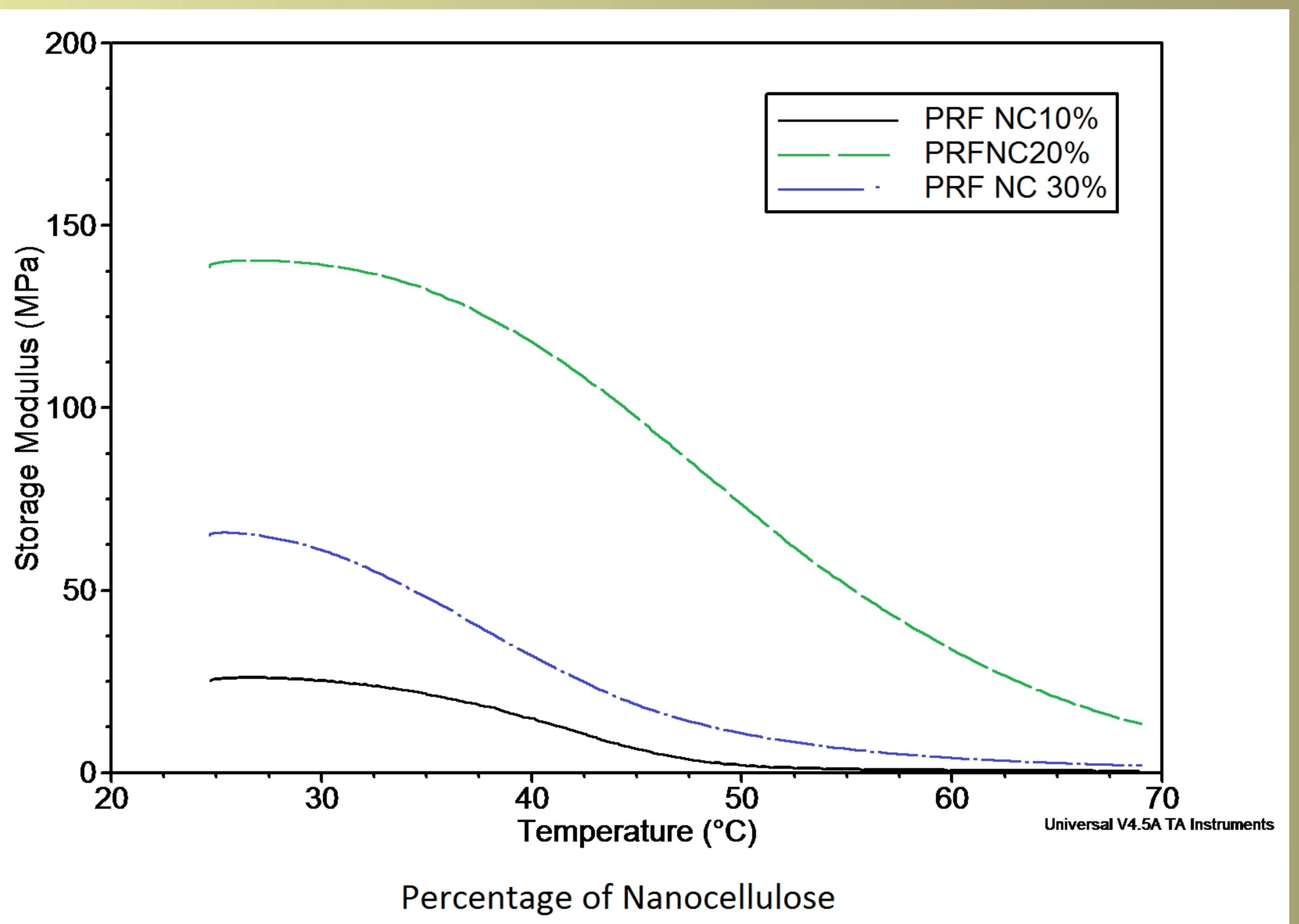
Results

1.) Heat treament at 100 degrees C.



2.) Nanocellulose in grams calculated to per liter

50:50 ml of nanocellulose slurry and water resulted in 3.7mg/liter of nanocellulose. Nanocellulose solution mixed with PRF at 10, 20 and 30% levels.



Dynamic Mechanical Analysis of nanocellulose composites

Conclusions

- Performance of Lignin Base Phenolic Resin
  - Separation of the nanocellulose and PRF was observed. This may likely be in part due to the hydrophilic nature of the nanocellulose.
    - Separation likely meant a lower actual concentration of nanocellulose in the composite.
  - DMA results concluded that a 20% nanocellulose solution had the highest modulus.
    - 30% saw a decrease in modulus which may result from agglomerated nanocellulose.
  - This approach could be a sustainable option for co-products in biofuel production.

Acknowledgements

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