CHARACTERIZATION AND SUSTAINABLE RETTING OF RAGWEED FIBERS

Elizabeth N. Alvizo[1], Jitendra S. Tate[1,2*], Serra E. Holthaus[3], and Jennifer A. Irvin[2,3]

Texas State University
San Marcos, TX, 78666
[1]Ingram School of Engineering, Texas State University
[2]Materials Science, Engineering and Commercialization Program, Texas State University
[3]Department of Chemistry and Biochemistry, Texas State University
[*]JT31@txstate.edu; 512-245-1826

ABSTRACT

This work aims to characterize the North American native plant, *Ambrosia trifida,* commonly known as ragweed. The purpose of this research is to build a cost-effective manufacturing process that will produce quality microfibers to be used as a reinforcement in polymer matrix composite (PMC) applications. Chemical retting methods were employed and evaluated based on cellulose content extracted. Hydrogen peroxide (H_2O_2) was used to expedite the retting process as previous experiments have shown it to produce cellulose with less impurities. Water retting was conducted in parallel with H_2O_2. Distilled, tap, and river water were compared based on impurities and time allotted. Sodium hydroxide chemical treatment was used to cleanse the fiber from non-cellulose material. The overall mechanical properties of natural fiber reinforced PMC are highly dependent on morphology, aspect ratio, hydrophilic tendency and dimensional stability of the fibers. Scanning Electron Microscopy (SEM) was used for morphology studies of the fiber. Mechanical properties were identified using MTS Exceed. Tensile strength, tensile modulus, and elongation at break mechanical properties were compared to commercially available natural fibers, such as jute, kenaf, hemp, and flax. After retting, the ragweed fibers were ground up and converted to cellulose acetate through esterification. The soluble cellulose acetate was characterized using Fourier Transform Infrared Spectroscopy (FT-IR) and titrated to determine the degree of esterification. Properties of ragweed based cellulose acetate were compared to commercially sourced cellulose acetate. The resultant cellulose acetate was a soluble polymer that could be electrospun to form a nanofiber.

KEYWORDS: *Fiber-reinforced composites, natural fiber, electrospinning, surface treatments, cellulose, cellulose acetate*

INTRODUCTION

A renewed interest for natural fibers is expected as the global economy strives for sustainable industrial practices. Natural fiber advantages are low specific weight resulting in high specific strength and stiffness; sustainability in that production requires little energy and CO_2 is used while oxygen is given back to the environment; desirable for low-wage countries due to low investment at low cost for materials; friendly processing regarding tool wear; possibility for thermal recycling; and good thermal and acoustic insulating properties. (van Rijswijk, Brouwer & Beukers, 2001) However moderate mechanical properties restrain the fibers from high-tech applications resulting in products restricted to interior and non-structural components.

Cellulose nanocomposites are not only limited to their low-weight, environmentally friendly processing, and flexibility. Cellulose nanocomposites find application in many areas such as packaging, optoelectric, barrier, electronics, biomedical, paper, textiles, military, etc. (Feldman, 2015) Thus, there is a need to improve the compatibility between cellulose nanoparticles and hydrophobic polymer matrices through understanding chemical modifications.

The research of this paper serves to employ Giant ragweed, or *Ambrosia trifida*, as a competitor in the market for natural fiber production. *A. trifida* is native to the U.S. and Canada and is seen as a pest

prolific crop due to its resilience and pollen production; it is known to be a hardy plant and a discomfort to allergic persons. It does especially well in disturbed soils. Considering many agricultural fields are disturbed an ideal environment is created for *A. trifida* and it becomes a common and prolific competitive weed. More importantly, A. trifida has now become glyphosate (the main ingredient in RoundUp©) tolerant in crop fields and is now a difficult weed to manage (Vink et al. 2012; Westhoven et al. 2009; Powles 2008) Ragweed may grow up to 3.6-m (12-ft) and it is characterized by small, greenish flowers borne on upright terminal spikes and deep-green lobed or dissected leaves. Ragweed is a type of Bast fiber that generally has a wood core surrounded by a stem. Within the stems are fibers bundles, each containing individual fiber cells, or filaments. Figure 1 shows the cross section of different sizes of Ragweed fiber. The layering is noticeably distinct due to age and diameter of the crop. The filaments are the cellulose and hemicellulose that are held together by a pectin and lignin matrix. Retting, or degumming, is a process of removing non-cellulosic material attached to fibers, such as, hemicellulose, lignin, and pectin. The percentage of each non-cellulose material depends on the type of Bast fiber. Table 1 shows the cellulose content in commercially available natural fibers.

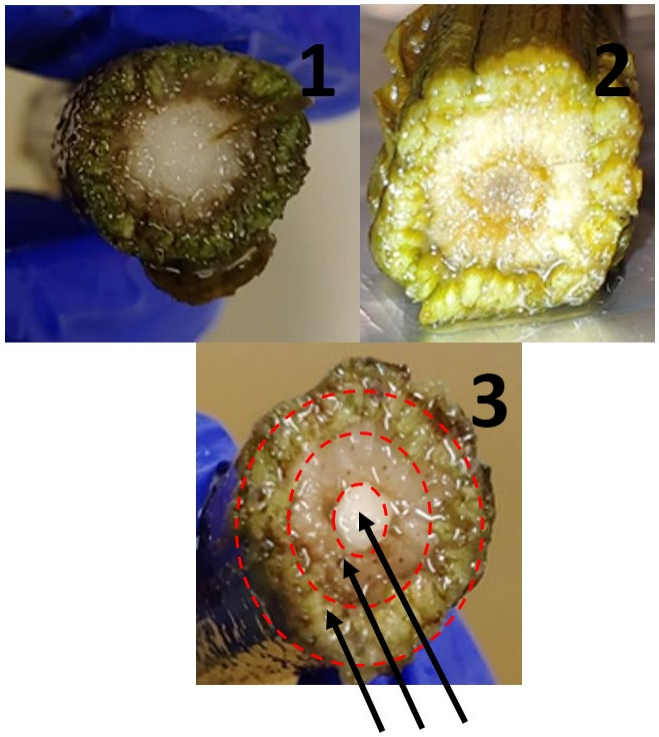

Figure 1. (1) Fiber diameter less than 10-mm (2) Fiber diameter greater than 10-mm (3) Breakdown of layering in fiber

Table 1. Approximate chemical composition (%) of cellulose fibers

Fiber	**Cellulose**	**Hemicellulose**	**Pectin**	**Lignin**	**Fat/wax**
Flax	62 – 71	16 – 18	1.8 - 2.0	2.0 -2.5	1.5
Hemp	67 –75	16 – 18	0.8	2.9 - 3.3	0.7
Jute	59 – 71	12 – 13	0.2 - 4.4	11.8 - 12.9	0.5

Source: Kraessog et al., 1996; Lewin and Pearce, 1998, in Cavaco-Paulo,A. And Gubitz, G.M., Texile

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Traditional retting methods for separating the Bast fiber from the inner core are done by dew or water retting. Both methods may require 14 to 28 days to degrade non-cellulose material. Alternative retting methods such as mechanical decortication, chemical, heat, and enzymatic treatments have been reported with mixed findings. (Tahir et. Al. 2011) Balance of pH for water, temperature and stem thickness are known to play a factor in the quality and efficiency of retting as well. Post-retting alkali (NaOH) solution treatment were employed to aid in binding of fiber and matrix composite material. Literature has shown that concentration and temperature of the solution is vital in exploring improvements in mechanical properties. (Ray et. Al. 2001) Table 2 show properties of natural fibers comparing Flax, Hemp, and Jute without alkali treatment.

Table 2. Properties of natural fibers

Properties	**Fiber**		
	Flax	Hemp	Jute
Density g/cm3	1.4	1.48	1.46
Tensile strength** 10E6 N/m2	800 -1500	550 - 900	400 - 800
E – modulus Gpa	60 - 80	70	10 - 30
Elongation at failure (%)	1.2 - 1.6	1.6	1.8
Moisture absorption (%)	7	8	12
Price/Kg ($), raw (mat/fabric)	1.3 (1.7/3.8)	0.6 - 1.8 (2/4)	0.35 (.5/0.9 - 2)
**tensile strength depends strongly on type of fiber being in a bundle or a single filament			
Source: http://www.fao.org/3/Y1873E/y1873e0a.htm#bm10			

Electrical charge can be applied to a polymer solution and destabilizes the droplet to form a conical shape known as a Taylor Cone. When Coulombic repulsion exceeds the surface tension, the Taylor cone extends, and the polymer solution travels straight and then bends and loops. During this process, the polymer solution dries and solidifies onto the collector, forming fine nanofibers. Electrospinning has multiple parameters that can affect the quality and properties of the nanofibers, such as the polymer's molecular weight, flow rate, diameter of the needle tip, electric potential, and polymer concentration.

MATERIALS AND METHODS

Ragweed fibers were harvested in June 2019. Hydrogen peroxide retting was conducted in parallel with three different water types. The three different water were tap, distilled and river. River water was collected from the San Marcos river. After the specified retting time, the hydrogen peroxide fibers were rinsed with DI water and then left to dry under a vacuum. Water retted fibers were simply left to dry under the vacuum after removing from retting bin. Fibers were randomly selected to bath in NaOH for 1 hour. The Sodium hydroxide treatment was done using 15% concentration sodium hydroxide. Figure 2 shows a flowchart of ragweed processing. Mechanical testing was done using ASTM C1557 –14 and a 1-kN load cell was used to allow for precise measurements. Table 3 shows how long each fiber was spent retting. The JEOL JSM-6010 PLUS/LA Scanning Electron Microscope (SEM) was used to record SEM images and the Quorum Technologies EMS150T ES was used to prep the samples with a layer of carbon. The samples were nonconductive and were prone to charging under the microscope, so it was important to sputter coat the images for best quality.

The Bruker Tensor II FTIR was equipped with OPUS 7.5 software and a Harrick SplitPea ATR accessory. The instrument was used to acquire FTR-ATR spectra of several types of cellulose (commercially sourced, as well as the outer and inner cores of ragweed-sourced) and of cellulose acetate. The sample was loaded onto the ATR accessory plate and pressed against the crystal. The spectrm was recorded, and the ATR accessory plate was cleaned with DI water so the process could be repeated for the other samples.

Electrospinning was attempted using a Spraybase electrospinning instrument, Gamma high voltage box, New Era Pump Systems, Inc. syringe pump, and Vexta brushless DC motor. Based on the method reported by Konwarh et al., (2013), the cellulose acetate fibers were dissolved in a 24% (w/v) solution of chloroform and dimethylacetamide (1:1 ratio). 5 mL of the solution was loaded into a 10 mL syringe and set on the syringe pump to release at 0.05 mL/min. The voltage was steadily increased until it reached 15 kV.

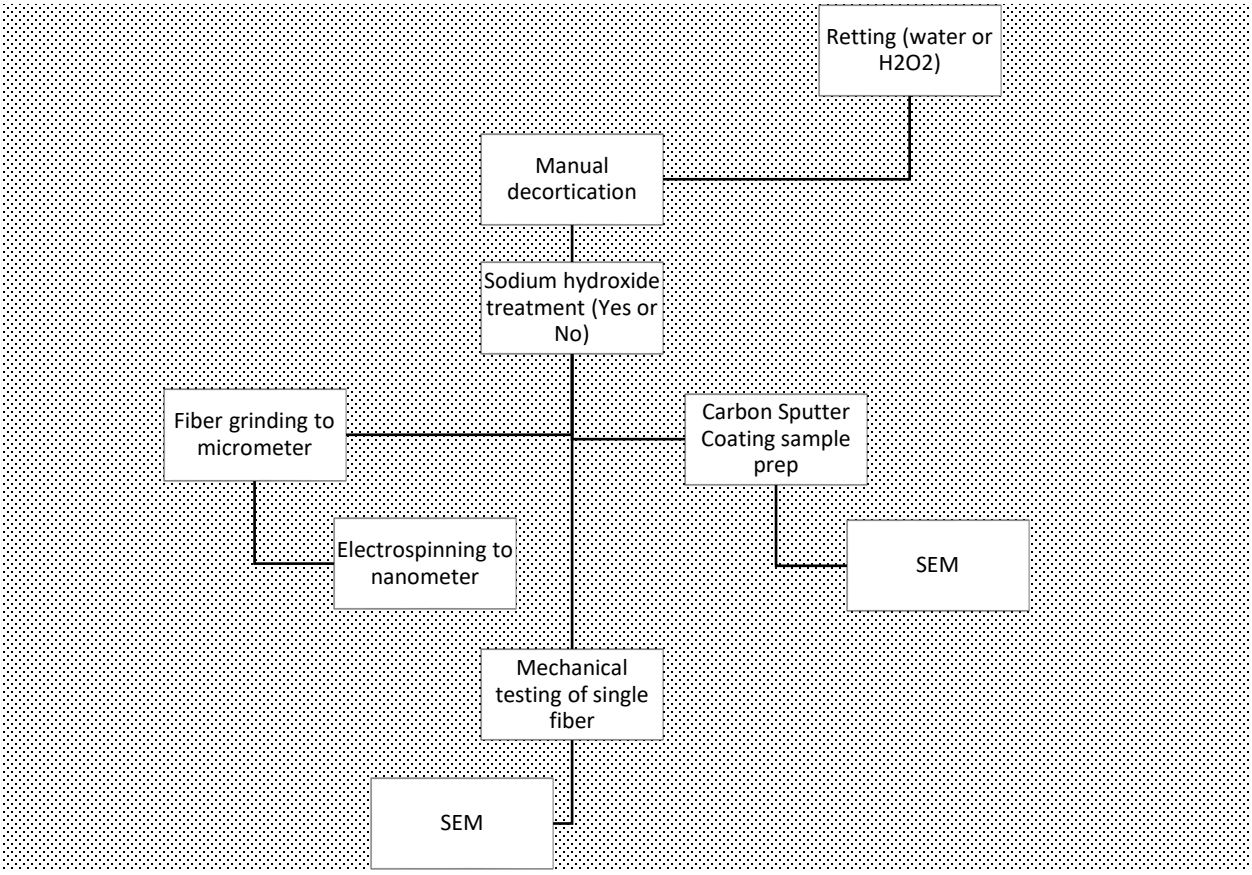


Figure 2. Diagram of ragweed processing outline

Table 3. Retting type and duration inputs and outputs	
Retting methods	Days spent retting
River water sf	14
Distilled water sf	14

Tap water sf	14
Hydrogen peroxide sf	7
Sf =short fiber	

Lab grade cellulose from Ward's science was esterified through the following process, modified from two literature procedures (Rosenthal (1967) and Meng et al., (2017)). Cellulose (0.8g) was suspended in glacial acetic acid (50 mL) at room temperature for 15 minutes. Then, concentrated sulfuric acid (0.14 mL) was added to catalyze the reaction, which was stirred at room temperature for 5 minutes. Finally, acetic anhydride (28 mL) was added, and the reaction was left to stir at 45 °C for 24 hours in air. The resulting cellulose acetate was added dropwise to de-ionized (DI) water that was stirred at 900 rpm. The resultant precipitate was collected by filtration through paper dried under vacuum at room temperature overnight. For further purification, the cellulose acetate was dissolved in chloroform and added dropwise into rapidly stirring methanol, filtered, and vacuum dried under the same conditions.

RESULTS

The table below shows tensile test results from previous experiments using the specified fiber types. Side view of the fiber show microscopic differences in the fibers but how that affects mechanical properties is not fully understood. More tests need to be done in order to form a reputable assumption of the mechanical properties. Mechanical testing was tricky in that fibers were very sensitive when securing in the grips. Attempts were made to test the most recent fibers however the data was not ideal considering issues with failing at the grips of the test specimen. Mechanical testing shows that fibers are nowhere near superior compared to hemp, flax, and jute fibers however when fibers were bathed in NaOH it shows that properties were significantly improved. This supports previous literature in that alkali treatments are important to understand and implement.

Table 4. Tensile Mechanical Properties of Ragweed Fibers

Fiber Type Tested	Number of Tests	Average Peak Load (N)	Average Area (mm2)	Average Peak Stress (MPa)	Average Strain at Break (mm/mm)	Modulus (Total Secant, MPa)	Average Strain at Yield (mm/mm)
H2O 7Days 20mm	3	10.93909	0.357578	30.59217849	0.0166	1842.902319	0.00906
H2O 7Days 40mm	3	5.877736667	0.357578	16.43763505	0.0161	1020.971121	0.0116
NaOH 20mm	3	26.57434667	0.36312	73.18337372	0.0244	2999.318595	0.0244
NaOH 40mm	3	25.15211333	0.36312	69.26667034	0.016	4329.166896	0.0159

DISCUSSION AND CONCLUSIONS

Fibers that appeared to produce more mucous were easier to decorticate and it was important to decorticate right after retting. Allowing the fiber to dry made it more difficult to remove the inner core and allowed increased risk of possible damage to the fiber. It appears that 100% removal of core was impossible considering that small fragments would remain on some fibers, especially with larger fiber diameters. All water retted fibers had a strong unpleasant odor, especially the river retted water. Hydrogen peroxide fibers had less mucous but finer fibers as the result. Photographs of retted fibers can be seen in Figure 3.

Figure 3. (top) Water retting fibers showing mucous after retting (bottom) hydrogen peroxide fibers with less mucous

SEM imaging of the fibers (Figures 4 and 5) showed the fibers to be around 300 micrometers in diameter. NaOH fibers produced concentrated areas of unknown white dots. Hydrogen peroxide interestingly did

not produce a clean even fiber. However, on a macroscopic scale the hydrogen peroxide retted fibers appeared to be finer in nature.

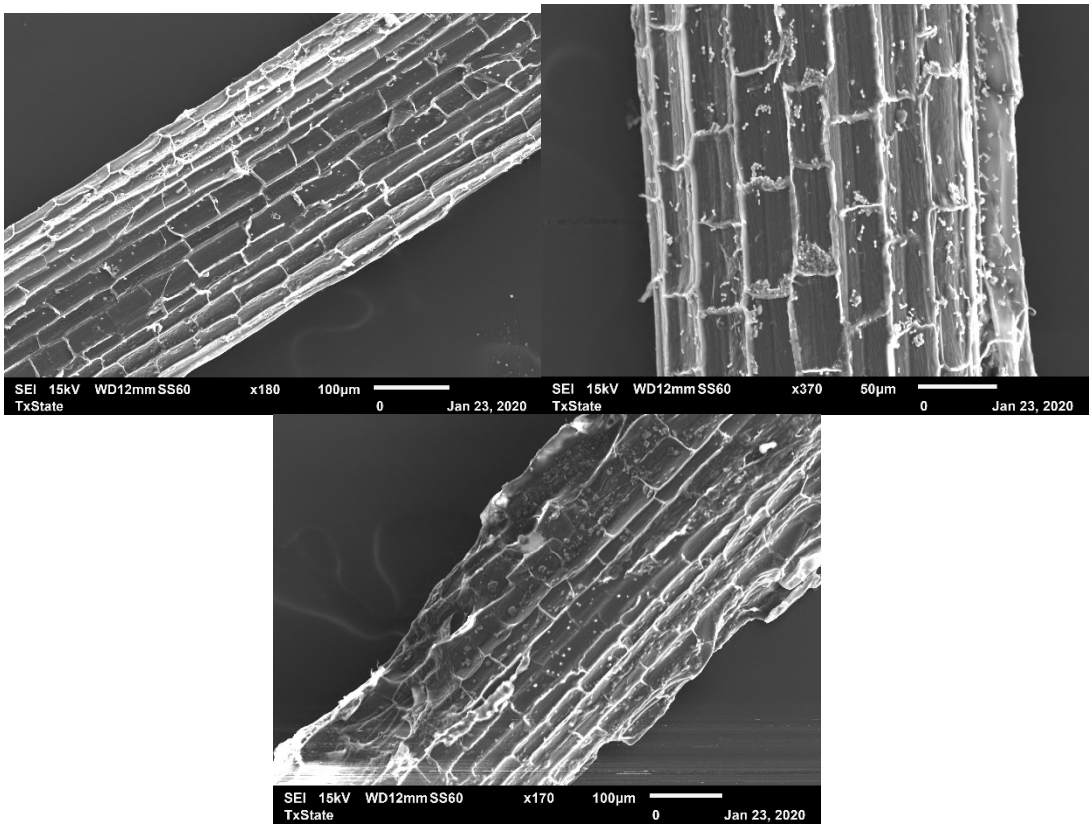


Figure 4. (top left) Regular tap water fiber retting (top right) Fiber after NaOH bath (bottom) Hydrogen peroxide fiber retting

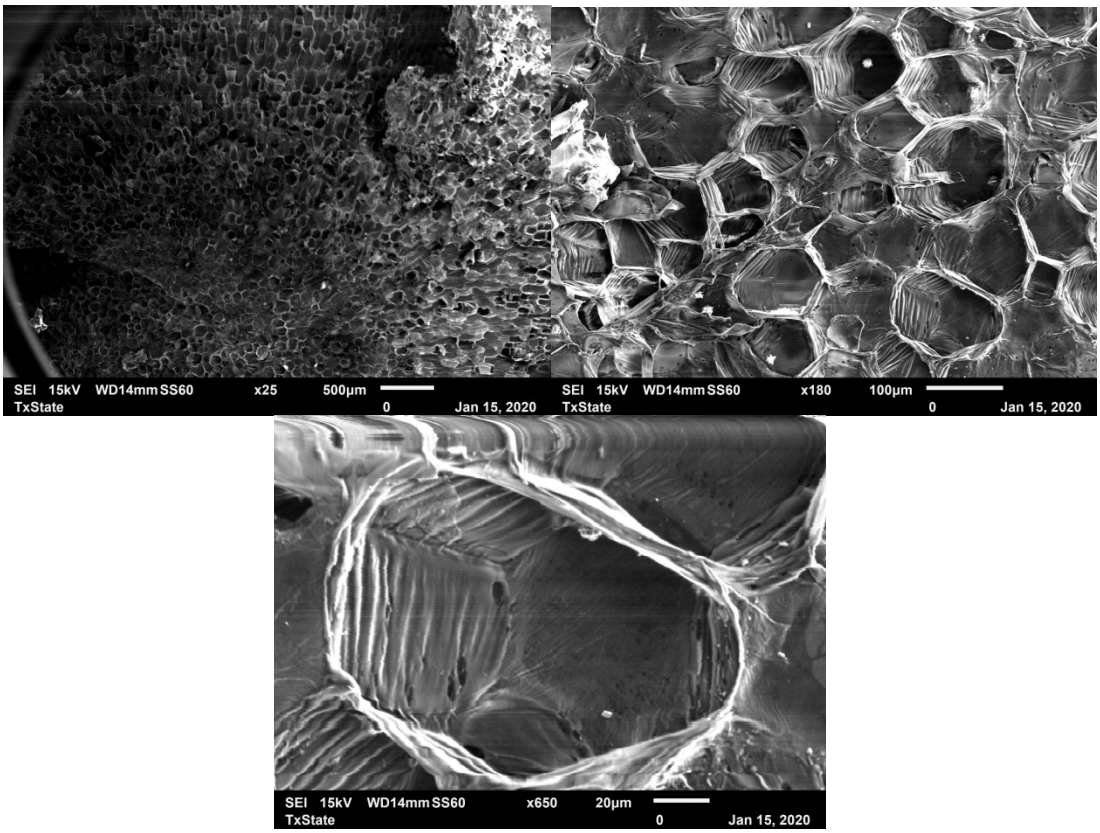
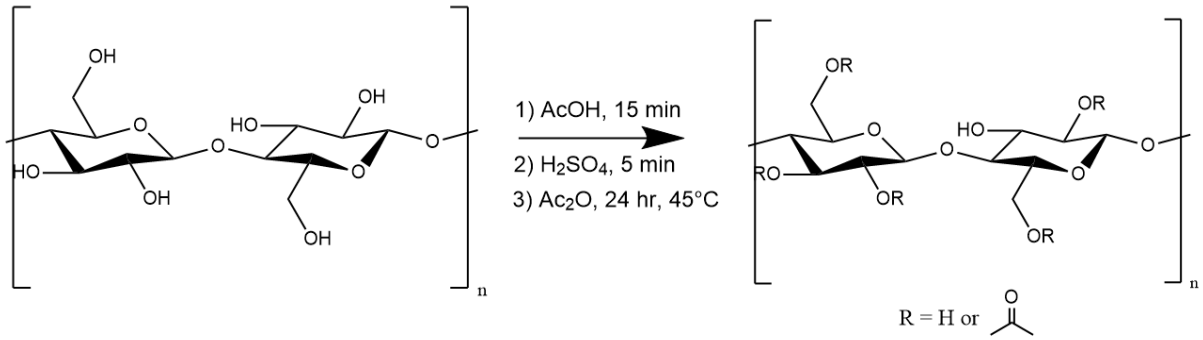


Figure 5. Bast fiber cross section

Commercial cellulose was used to evaluate esterification (Scheme 1) protocols. Spectroscopic evidence for successful esterification of commercial cellulose and successful isolation of cellulose from the inner core of ragweed can be seen in Figure 6. Samples of inner core cellulose (gray line in Figure 6) and commercial cellulose (blue) both reveal similar FTIR spectra that are consistent with values found in the literature (Shoba et al., 2018). The spectrum of outer core cellulose (orange) is somewhat similar to that of commercial cellulose and inner core cellulose, although outer core cellulose exhibits an additional peak at 1652 cm^{-1} that is characteristic of carbonyl groups. This may be residual organic species such as chlorophyll that were not decomposed under the retting conditions used for that sample (DI water only, no NaOH or H_2O_2). Characteristic cellulose absorptions include C-O-C (1057 and 1108 cm^{-1}), CH_2/CH_3 (2900 cm^{-1}), and O-H (3344 cm^{-1}). Additional peaks consistent with cellulose acetate (green) include ester C-O-C (1239 cm^{-1}) and C=O (1749 cm^{-1}). Differences in peak intensities between samples are due to sample-to-sample inconsistencies on the ATR crystal compounded by differences in sample morphologies.The absorption an 2359 cm^{-1} in all samples is an artifact from background atmospheric gases. Next steps include esterification of ragweed-sourced cellulose and gel permeation chromatography to determine molecular weight of cellulose acetate.



Scheme 1. Esterification of cellulose to produce cellulose acetate.

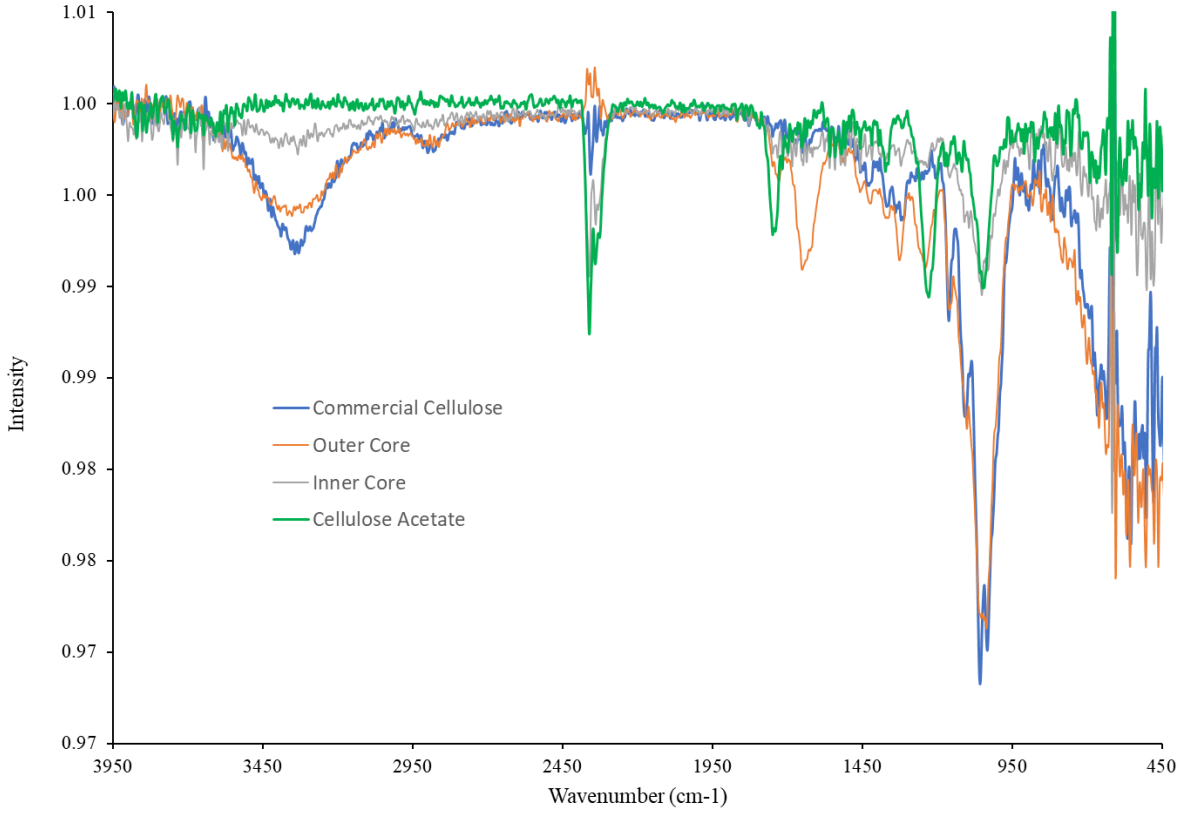


Figure 6. FTIR spectra of commercial cellulose (blue), outer core of ragweed-sourced cellulose (orange), inner core of ragweed-sourced cellulose (gray), and cellulose acetate prepared by esterification of commercial cellulose (green).

Multiple attempts to prepare electrospun nanofibers of cellulose acetate were unsuccessful, producing powders rather than nanofibers. Powders are often formed when viscosity and/or concentration are too low, but the sample preparation and electrospinning parameters used duplicated those reported by Konwarh et al. (2013). We suspect that the molecular weight of our cellulose might be lower than that used by Konwarh. Furthermore, while electrospinning, the polymer would start to precipitate on the needle before it could reach the collector, presumably because the acetone was evaporating. Next steps

include molecular weight determination, determination of degree of esterification, and electrospinning in alternative solvent systems as well as with esterified ragweed-sourced cellulose.

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