



Modification of the cellulosic component of hemp fibers using sulfonic acid derivatives: Surface and thermal characterization



Michael George, Paolo G. Mussone, David C. Bressler*

Biorefining Conversions and Fermentation Laboratory, Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, Canada

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ABSTRACT

The aim of this study was to characterize the surface, morphological, and thermal properties of hemp fibers treated with two commercially available, inexpensive, and water soluble sulfonic acid derivatives. Specifically, the cellulosic component of the fibers were targeted, because cellulose is not easily removed during chemical treatment. These acids have the potential to selectively transform the surfaces of natural fibers for composite applications. The proposed method proceeds in the absence of conventional organic solvents and high reaction temperatures. Surface chemical composition and signature were measured using gravimetric analysis, X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red spectroscopy (FTIR). XPS data from the treated hemp fibers were characterized by measuring the reduction in O/C ratio and an increase in abundance of the C–O signature. FTIR confirmed the reaction with the emergence of peaks characteristic of disubstituted benzene and amino groups. Grafting of the sulfonic derivatives resulted in lower surface polarity. Thermogravimetric analysis revealed that treated fibers were characterized by lower percent degradation between 200 and 300 °C, and a higher initial degradation temperature.

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1. Introduction

The uncertainty surrounding oils prices, its dwindling reserves, along with increased environmental concerns have resulted in renewed attention to the development of new eco-friendly products and materials. The use of lignocellulosic natural fibers as fillers for matrices offers an opportunity to transition from glass fiber reinforced composites. Natural fibers are advantageous due to their biodegradability, low density, low abrasion processing equipment and comparable specific mechanical properties to glass fiber reinforced composites (George, Mussone, & Bressler, 2014). Despite these properties, incompatibility with non-polar matrices, moisture absorption, and vulnerability to thermal degradation are the main bottlenecks for the use of natural fibers in composites. The incompatibility and moisture absorption defects results from the highly polar surface of the fibers. This in turn leads to poor composite properties because of poor stress transfer and swelling of composite macrostructure. The modification of natural fibers to circumvent enabling the utilization of these abundant and biodegradable feedstocks.

The properties of composites are influenced by the fiber architecture (aspect ratio and orientation of fibers), fibre-matrix interface, fiber modification, and the processing technique used (Kalia, Kaith, & Kaur, 2009; Mulinari, Cioffi, & Voorwald, 2010). Lei, Zhang, & Liu (2012). [4] using a 3D tension–shear chain illustrated that aside from the volume fraction, shape, and orientation of the reinforcements, the distribution of fibers also played a significant role in the mechanical properties of unidirectional composites. It was their opinion that the stair wise model (fiber assembly in nature) is more applicable for composites formulation compared to random staggering. Their work may provide useful guidelines and insights for the design of high performance short fiber reinforced composites in the near future. The effect of the fiber matrix interface is of utmost importance because it facilitates the transfer of stress evenly within the composite. This allows the structure of the composites to withstand the effect of the load without failing. In order to induce better compatibility, researchers have focused on modifying natural fibers to render them less hydrophilic by using physical (Mukhopadhyay & Fanguero, 2009), chemical (Li, Tabil, & Panigrahi, 2007), or biological methods (Brumer, Zhou, Baumann, Carlsson, & Teeri, 2004). The processing techniques used to combine the fibers with matrices depend on the nature of the polymer (thermoplastic or thermoset), the end application of the composites, and the desired relative volume of fiber to be used. Resin transfer

* Corresponding author. Fax: +1 780 492 8914.

E-mail address: david.bressler@ualberta.ca (D.C. Bressler).

molding (Sreekumar, Joseph, Unnikrishnan, & Thomas, 2007; Rouison, Sain, & Couturier, 2006) and injection molding (Peltola, Madsen, & Nattinen, 2011) are the popular methods for processing thermosets and thermoplastics respectively. With those thoughts in mind, one can appreciate the intricacies associated with improving the properties of natural fiber composites.

The chemical composition and structural assembly of natural fibers dictates the extent of their potential modification. Plant fibers are composed mainly of cellulose, hemicellulose and lignin. Minor components such as waxes and pectin are regarded as surface impurities. The chemical composition, including moisture content, can help to determine properties and end uses of the fibers. For instant, higher cellulose content correlates to high strength and stiffness and is ideal for polymer reinforcement. Cellulose is considered the most important component of plant fibers with relevance to the composite world (Roy, Semsarilar, Guthrie, & Perrier, 2009; Mwaikambo & Ansell, 2002). The chemical structure of cellulose contains three hydroxyl groups, which in the macromolecular cellulose network forms hydrogen bonds. Two of these hydroxyl groups form intermolecular bonds, while the third forms intramolecular hydrogen bonds (Bodig & Jayne, 1982, chap. 10). The ultimate aim is to modify these hydroxyl groups so as to reduce the surface polarity without affecting the strength of the fiber network.

Researchers in the past have focused on grafting different chemicals onto the surface of plant fibers. The main aim was to reduce surface polarity by chemically modifying the hydroxyl groups. Bledzki, Mamun, Lucka-Gabor, and Gutowski (2008) studied acetylation of flax fibers and its polypropylene composites. It was found that there were improvements in the water absorption properties along with the tensile and flexural strength of the composites. In another study, the effect of acetylation and propionylation on the surface properties of hemp and flax were studied (Tserki, Panayiotou, & Zafeiropoulos, 2005). Acetic and propionic anhydride were used to esterify the surface of the fibers. Their findings included a reduction in moisture absorption of the fibers, a smoother surface, and importantly, they found that the amount of hemicellulose relative to lignin dictated the extent of esterification. These studies served to show that chemical modifications have been successful in the past in addressing the key limitations of fibers for composite applications.

The key objective of this communication was to investigate whether sulfonic acid derivatives can be used to modify hemp fibers at low temperatures and in the absence of organic solvents. This objective was deemed important because of the high energy and waste scenario associated with most chemical methods in the literature. The derivative sulfonic acids (aniline-2-sulfonic acid-A2S and 4-aminotoulene-3-sulfonic acid-AT3S) were modeled using the reaction conditions outlined in the communication cited in the previous paragraphs. In this communication, we specifically enhanced the surface and thermal properties of hemp fibers using a system that requires little or zero organic solvent. Also, one key objective was to get the system to work at low temperatures, instead of higher temperatures required for esterification reactions in the literature (Tserki et al., 2005; Lei et al., 2012). The derivative sulfonic acids were firstly converted to their corresponding acid chlorides because of the superior reactivity of acid chlorides when compared to hydroxyl groups. The second stage involved reacting the acid chlorides with the hemp fibers under aqueous conditions.

2. Materials and methods

2.1. Materials

Hemp fibers were obtained from Alberta Innovates Technology Futures, Alberta, Canada. The properties of these fibers were

within Canadian Hemp Association guidelines. Aniline-2-sulfonic acid [A2S] (173.19 g/mol, 99%) and 4-aminotoulene-3-sulfonic acid [AT3S] (187.22 g/mol, 99%) were sourced from Sigma (Minneapolis, U.S.A). Acetone (58.08 g/mol, 99.9%), anhydrous ethanol (mol. wt. 46.07 g/mol) and sulfuric acid (98.08 g/mol, 99.99%) used were obtained from Sigma (Minneapolis, U.S.A). Hydrochloric acid (36.46 g/mol, 37%), anhydrous sodium hydroxide pellets (40.00 g/mol, 98%) and phenolphthalein solution (2% in ethanol, 318.32 g/mol) were purchased from Sigma (Minneapolis, U.S.A). Distilled water was used for experiments.

2.2. Methods

2.2.1. Treatment of hemp fibers

Prior to all analyzes, samples were pre-conditioned at 80 °C for 5 h to maintain constant moisture content for all treated and untreated samples. All analyzes were done in triplicate.

2.2.2. Preparation of acid chlorides

An established and proven procedure outlined by Freire, Silvestre, Neto, Belgacem, and Gandini (2006) was used to convert the sulfonic acids into the corresponding acyl chlorides. The main modification to the method was substituting phosphorus pentachloride with thionyl chloride. Approximately 4.2 g (0.035 mol) of thionyl chloride was added to each reaction flask gradually over a 30 min period.

2.2.3. Chemical treatment

A 250 mL round bottom flask was used for all the reactions. Approximately 1.0 g of hemp fibers (detergent washed and oven dried) was placed in a flask and 100 mL of the maximum sulfonic acid soluble in water (0.01 M) was added to the flask slowly. A few drops of pyridine were added during the course of the reaction. The flask was heated to the desired temperature and the reaction maintained for 90 min. Reaction temperatures of 30, 40, and 50 °C were studied.

In preliminary reactions, the treated fibers were soxhlet extracted with ethanol for 2 h to remove un-reacted reagents. Fibers were also washed with the solvents and the results indicated little or no difference between soxhlet extracted and solvent rinsed fibers. Hence, fibers were washed instead of soxhlet extracted onwards. The samples were washed sequentially with 25 mL ethanol and 25 mL acetone to remove excess reagents. The fibers were oven dried at 80 °C for 5 h and stored for future analysis. Apart from the washing step, organic solvents were avoided as the main aim is to utilize the system in an aqueous medium.

2.2.4. Chemical composition of hemp fibers

The chemical composition of the fibers were characterized before and after treatment. A control consisting of everything, except the sulfonic acid reagents was also tested. The procedure outlined by George et al. (2014) [1] was used to estimate the cellulose, hemicellulose, lignin, protein, and ash content of the fibers. The CHNS content of the fiber samples were estimated using Carlo Erba CHNS-O EA1108 elemental analyzer. Finally, the changes in mass of the fiber as a result of treatment were measured after each treatment.

$$\text{Change in mass} = \frac{m_f - m_i}{m_i} \times 100\%$$

The equation above was used to monitor the changes in the mass of each sample as a result of treatment. m_f and m_i are final and initial mass of samples, respectively.

2.2.5. Characterization of hemp fibers

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