BAST NATURAL FIBER REINFORCED SOY-BASED POLYURETHANE BIOCOMPOSITES

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Abstract
A soy-based polyurethane resin was tested as a matrix material with both nonwoven mats and unidirectional natural fiber. The nonwoven mats evaluated were hemp, flax and kenaf while the unidirectional flax fiber was tested with and without a NaOH/Ethanol surface treatment. The hemp mat was found to produce the stiffest, strongest composites under both tensile and flexural loads compared to the other nonwoven mats. The treated unidirectional flax showed an increase in mechanical properties and improved fiber/matrix adhesion.

1 Introduction
Substituting natural fibers for mineral fibers in composite materials can have many advantages, including that natural fibers are renewable and lower density materials [1]. In order to increase the renewable content of a composite further, thermoset matrix polymers can be made in part from plant based oils. One such polymer is soy-based polyurethane (PU), which has been shown to perform similarly in composite materials to a petrochemical-based PU [2].

The current study examines the performance of natural fiber nonwoven mats and unidirectional flax fiber in a soy-based PU matrix. The three different nonwoven natural fiber mats were compared to examine the reinforcing potential of the different fiber types in a soy-based PU matrix. The unidirectional flax fiber in a soy-based PU matrix was studied to determine the effect of a NaOH/Ethanol surface treatment on mechanical properties.

2 Materials and testing methods
2.1 Materials
The soy-based polyurethane used in this study was sold under the trade name SoyMatrix™ and produced by Urethane Soy Systems Company of Volga, SD. It is a non-foaming, rigid polyurethane mixed from a two component system. The A-side is a soy-based polyol and the B-side is isocyanate. The mixing ratio for the system is 100:73.4 (A:B). Approximately 30% of the polyurethane is sourced from renewable feedstock.

Three nonwoven mats consisting of flax, kenaf and hemp were tested. All three mats were air-laid and needle punched, and were provided by the Composites Innovation Centre (CIC) of Winnipeg, Manitoba Canada. All mats had an areal density of approximately 500 gsm.

The unidirectional flax was sourced from China and is uncut and water retted. The surface treatment of the flax fibers was completed by immersing into 10 g/L NaOH/95 % ethanol at 78 °C for 2 hours. The fibers were then washed with distilled water to reduce color from the treated fibers and to attain a pH ≈ 7.0 (checked with pH paper). The treated flax fibers were then dried in an oven for 24 hours at 80 °C.

2.2 Fiber thickness

A sample of the fibers from each nonwoven mat was placed between two glass slides and an image was then recorded using a Nikon Super Coolscan 5000 ED slide scanner. The image is read from the slide scanner using Silverfast® Ai Studio Version 6.5 Professional Scanner Software and is then imported into Adobe® Photoshop®. The image is then loaded into a program called Fibreshape to measure the thickness of the fibers.

2.3 Compression molding

The compression molding of the samples was completed using a hydraulic press and a closed mold approximately 200 mm x 100 mm. To reduce moisture contamination the polyol and fibers were dried at 24 hours at 80 °C. The compression molding was completed at room temperature after the fiber and polyol were allowed to cool. The mold was held under compression for a minimum of 12 hours to allow for full cure.

2.4 Mechanical test methods

The nonwoven composite samples were tested for tensile and flexural properties. The unidirectional composites were tested for tensile, flexural and interlaminar shear stress (ILSS). All testing was completed on an Instron Model 5567 load frame at room temperature. The tensile testing was completed according to ASTM D 3039 [3]. A 30 kN load cell was used in conjunction with a extensometer. Flexural testing was completed according to ASTM D 790 using a 2 kN load cell [4]. The ILSS testing was completed according to ASTM D 2344 using a 2 kN load cell [5].

Since controlling the fiber volume fraction in each composite produced was difficult, all mechanical test results were normalized for fiber volume fraction. This was accomplished using the following equation:

$$\boldsymbol{\sigma_n} = \boldsymbol{\sigma_t} \times \frac{\mathbf{V_f^n}}{\mathbf{V_f^t}} \tag{1}$$

Where $\boldsymbol{\sigma_n}$ is the normalized value, $\boldsymbol{\sigma_t}$ is the measured test value, $\boldsymbol{V_f^n}$ is the chosen normalizing fiber volume fraction, and $\boldsymbol{V_f^t}$ is the measured fiber volume fraction of the test specimen. The nonwoven mat test results were normalized for a 0.35 fiber volume fraction and the unidirectional results were normalized for a 0.45 fiber volume fraction.

2.5 Chemical Analysis

Fiber composition was determined through a number of tests conducted by the Animal Sciences department at North Dakota State University. These included dry matter testing, neutral detergent solution and acid detergent solution characterization, and starch spectrophotometry. These allowed for the collection of percentage dry matter, as well as percentage cellulose, hemicellulose, lignin, starch, and ash. Dry matter determination was done according to AOAC standard 930.15, in samples were massed at room temperature, heated at 100 °C for 24 hours, cooled in a desiccator, and then massed a second time. Neutral detergent fiber, acid detergent fiber, and acid detergent lignin analysis were performed using

an ANKOM200/220 Fiber Analyzer according to methods spelled out in USDA Agricultural Handbook No. 379 [6]. Determination of starch was performed after an acid and enzymatic isolation using a micro-titre reading with a SPECTRAmax 340 Microplate Reader, as specified in literature [7].

3 Results and Discussion

3.1 Nonwoven mat test results

The results of the fiber thickness testing are shown in Table 1. The thickness of the kenaf fiber was found to be nearly three times that of the flax fiber. The hemp was found to be slightly less than that of the kenaf fiber.

Fiber	Thickness [µm]
Flax	21.78
Kenaf	61.87
Hemp	50.19

Table 1. Average fiber thickness for nonwoven mats.

The normalized tensile elastic modulus results are shown in Figure 1. It was found that the hemp composite was the stiffest, followed by the flax and then kenaf composites. All fiber reinforced composites were found to be stiffer than the neat polymer. Figure 2 shows the normalized results for the tensile strength of the composite compared to the neat PU. All composites had similar tensile strengths, and were greater than that for the neat polymer.

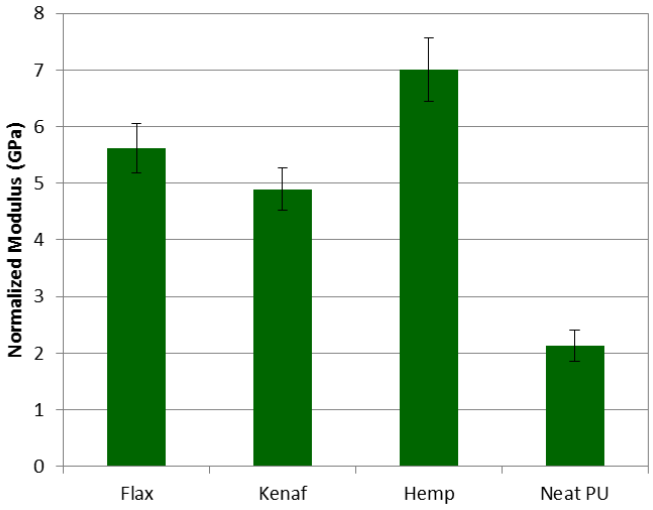

Figure 1. Normalized tensile modulus results of neat PU and nonwoven mats in a PU matrix.

The normalized flexural modulus results are shown in Figure 3. The hemp composite was again the stiffest, and the flax and kenaf were less stiff and very similar. Figure 4 shows the normalized results of the flexural strength, and again the hemp composite has the superior performance. The coarser fibers performed better in the flexural testing, but this trend was not observed in the tensile testing.

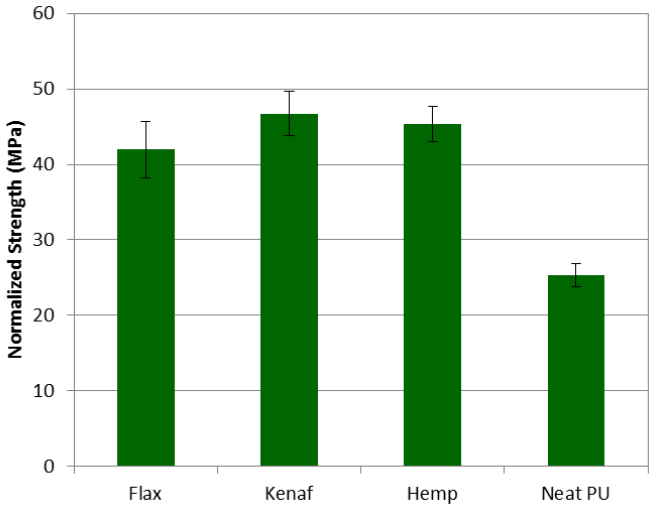

Figure 2. Normalized tensile strength results of neat PU and nonwoven mats in a PU matrix.

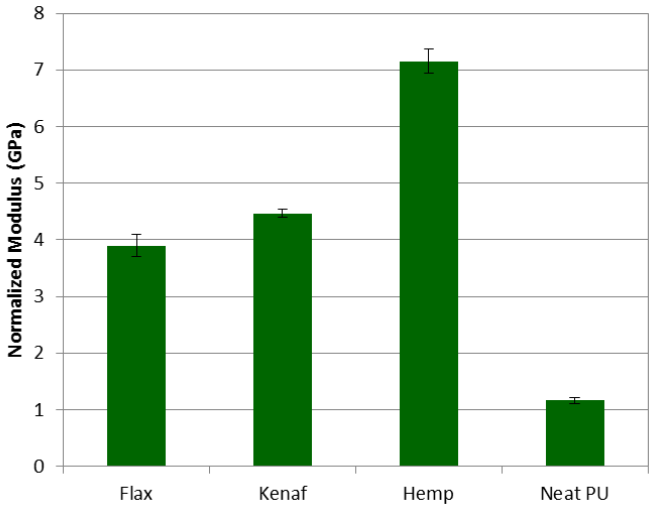

Figure 3. Normalized flexural modulus results of neat PU and nonwoven mats in a PU matrix.

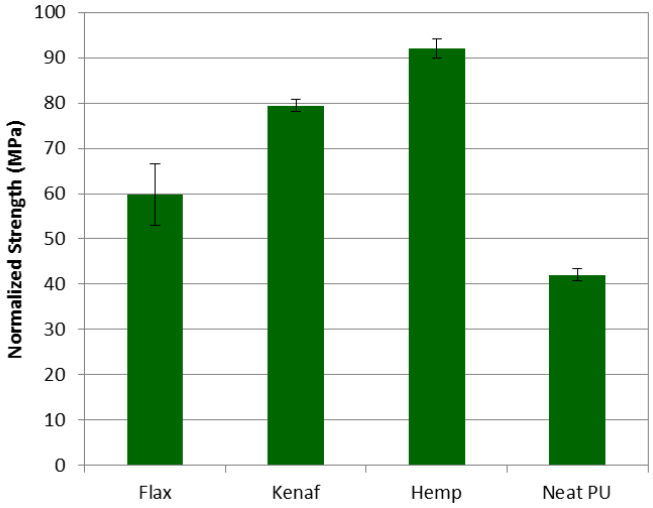

Figure 4. Normalized flexural strength results of neat PU and nonwoven mats in a PU matrix.

3.2 Unidirectional flax mat test results

Table 2 shows the results of the chemical analysis of the untreated and treated flax fiber. The surface treatment increased the cellulose content from 72% to 89%, while reducing all other major constituents. The surface treatment can clean the fiber surface and remove the non-cellulosic chemicals, which can leads to better interfacial bonding and good load transfer between flax fiber and PU matrix.

Sample	Dry Matter %	Ash %	Crude Protein %	Cellulose %	Hemi--Cellulose %	Lignin %	Crude Fat %
Untreated Flax	94.21	1.93	5.33	72.00	8.15	6.52	1.04
NaOH/Ethanol Treated Flax	96.63	1.17	1.27	89.22	4.93	2.94	0.37

Table 2. Chemical analysis of untreated and treated flax fiber.

The normalized tensile modulus is shown in Figure 5. The stiffness of both composites was significantly greater than that of the neat polymer. The tensile performance of flax/PU composites is dominated by the properties of flax fiber. Thus, the tensile moduli of both flax/PU composites showed higher values than neat PU. On the other hand, surface treatment on flax removed partial of non-cellulosic chemicals, which leads to better interfacial bonding and better load transfer. Therefore, the average treated flax/PU was found to be stiffer than that of untreated flax/PU. However, NaOH/Ethanol treatment did not show significant effects on the elastic modulus of flax fiber. Thus, the elastic moduli of both untreated and treated flax are close to each other. The difference of the tensile modulus between untreated and treated flax/PU are fairly small. Figure 6 shows the normalized tensile strength results for the treated and untreated flax, as well as the neat PU. The trend is similar to the results of tensile modulus. The treated flax had a higher tensile strength than the untreated flax, with both composites showing a similar amount of variation. The interface between treated flax and PU has a better load transfer than untreated flax and PU.

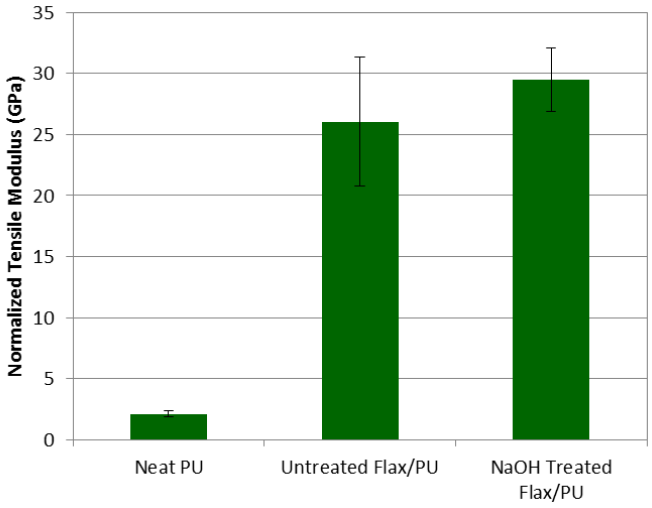

Figure 5. Normalized tensile modulus results for treated and untreated unidirectional flax in a PU matrix and neat PU.

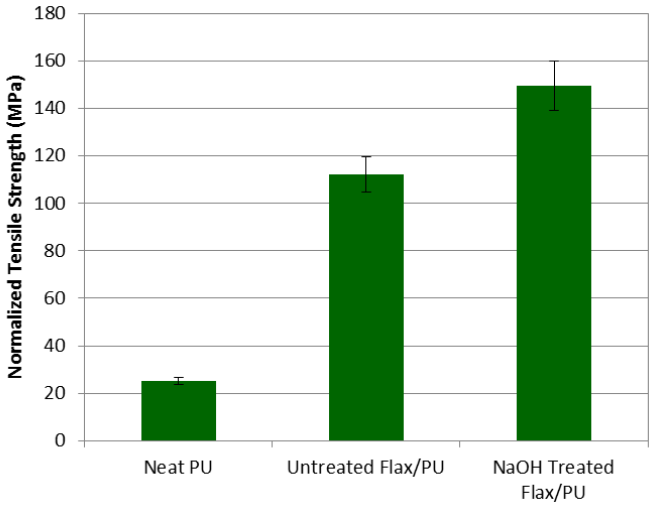

Figure 6. Normalized tensile strength results for treated and untreated unidirectional flax in a PU matrix and neat PU.

Figure 7 shows the normalized flexural modulus results. The treated flax composite was found to be stiffer than the untreated flax. The results of the normalized flexural strength for the untreated and treated flax fiber composites are shown in Figure 8. The NaOH treated fiber had a higher flexural strength than that of the untreated fiber. Both composites performed better than the neat PU. The trends of flexural results are similar to the results of tensile tests. The flexural properties of the composites are also related to the properties of flax fiber and the efficiency of load transfer. Thus, treated flax/PU performed better than others in flexural properties.

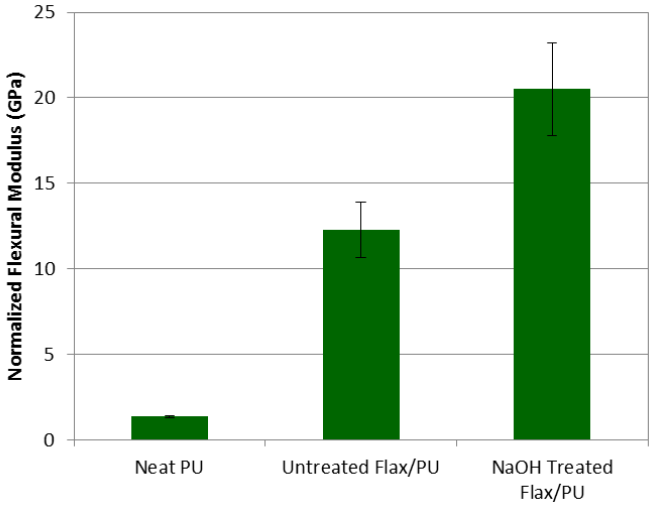

Figure 7. Normalized flexural modulus results for treated and untreated unidirectional flax in a PU matrix and neat PU.

The results for the interlaminar shear stress are shown in Figure 9. The treated fiber had a higher interlaminar shear stress, showing the higher cellulose content improved the fiber/matrix adhesion, which provides the evidence that alkaline treatment increase the interfacial bonding between flax and PU. It explained why treated flax/PU showed better tensile and flexural performance than untreated flax/PU.

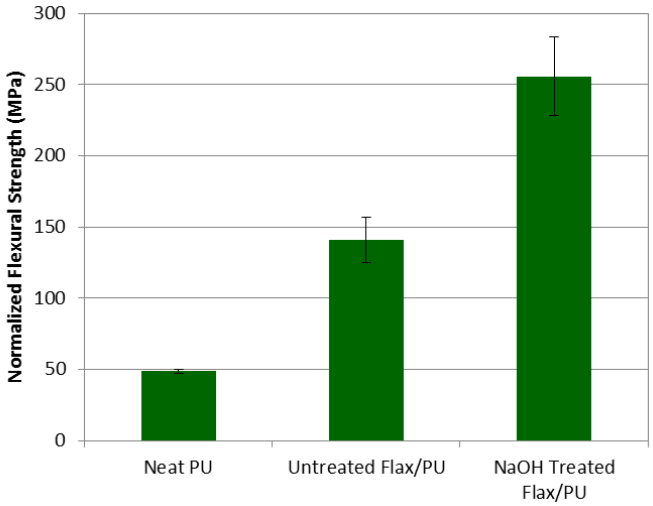

Figure 8. Normalized flexural strength results for treated and untreated unidirectional flax in a PU matrix and neat PU.

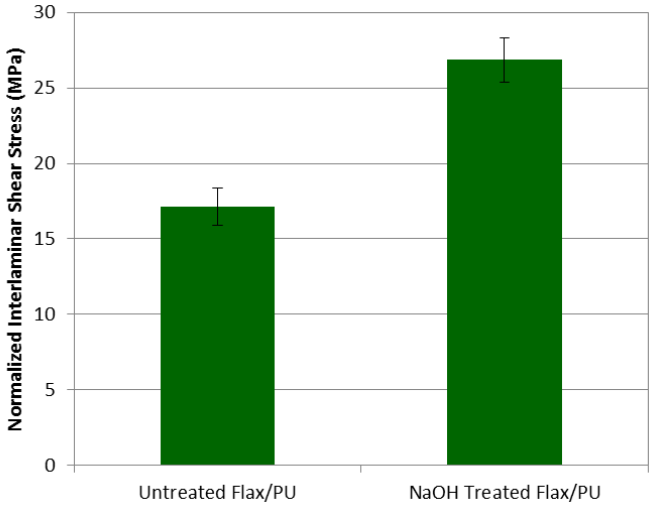

Figure 9. Normalized interlaminar shear stress results for treated and untreated unidirectional flax in a PU matrix.

4 Conclusions

Of the soy-based polyurethane composites reinforced with nonwoven mats, the hemp/PU samples performed equal to or better than the flax/PU and kenaf/PU in tensile and flexural testing. Hemp/PU had the highest tensile elastic modulus, and all mats performed similarly for tensile strength. Under flexural loading, hemp/PU was also stiffer and had a higher flexural strength than the other mats. The coarser fibers performed better under flexural loading.

The NaOH/ethanol surface treatment increased the cellulose content of the fiber from 72% to 89%. This resulted in improved interfacial bonding and load transfer. This treatment also resulted in a slight improvement in tensile elastic modulus and an increase in tensile strength. Under flexural loading, the treated flax/PU showed an improved flexural modulus and flexural strength. Additionally, the higher interlaminar shear stress of the treated flax/PU composite verified the higher cellulose content improved fiber/matrix adhesion and explained the improvement in tensile and flexural properties.

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