CHARACTERIZATION OF NATURAL FIBER SURFACES

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Abstract

Experiments have been performed to further the development of natural fiber reinforced composites as a replacement for glass fiber composites. Untreated and treated surfaces of natural fibers were characterized using FTIR and ESEM. Changes in the peaks in the FTIR spectrum at 1730, 1625 and 1239 cm^{-1} indicated that the alkali treatment removes hemicellulose and lignin from natural fiber surfaces. ESEM indicated the presence of silane on treated hemp and kenaf. Water absorption experiments were also conducted to determine saturation mass gain. Alkali treated fiber composites absorbed more water than silane treated or untreated composites. The natural fiber composites absorbed more water than the glass fiber composites.

1 Introduction

Lignocellulosic natural fibers such as sisal, coir, jute, ramie, pineapple leaf (PALF), and kenaf have the potential to be used as a replacement for glass or other traditional reinforcement materials in composites. These fibers have many properties which make them an attractive alternative to traditional materials They have high specific properties such as stiffness [1], impact resistance [2], flexibility [3], and modulus [4]. In addition, they are available in large amounts [5], and are renewable and biodegradable. Other desirable properties include low cost, low density, less equipment abrasion [3, 6], less skin and respiratory irritation [7], vibration damping[1, 2], and enhanced energy recovery[7, 8]. The hydrophilicity of natural fibers results in moisture absorption and weak adhesion to hydrophobic matrices. The natural fibers can be chemically treated to improve the adhesion to matrix materials. Additionally, most natural fibers have low degradation temperatures (~200 ºC), which make them incompatible with thermosets that have high curing temperatures. This also restricts natural fiber composites to relatively low temperature applications. There are several other challenges presented by natural fibers such as large variability of mechanical properties [2, 4], lower ultimate strength [6], lower elongation [6], problems with nozzle flow in injection molding machines [6], bubbles in the product [6], and poor resistance to weathering [9]. Natural fibers can be grouped into three categories; bast, seed and leaf. In this study, three types of bast fibers (kenaf, flax and industrial hemp) and one kind of leaf fiber (henequen) were used. These fibers were chosen because they are all grown in the United States. U.S. auto makers are interested in these fibers because they can avoid the cost of transporting them from overseas. Fiber treatments such as silane and alkali are required to increase the adhesion between the hydrophilic natural fibers and the hydrophobic epoxy matrix.

Mwaikambo and Ansell et al used FTIR to confirm that hemicellulose was removed by the alkali treatment [10]. FTIR was used to confirm fiber/matrix bonding by Mohanty et al. [11]. Water absorption experiments are important for natural fiber composites studies. Caulfield et al. found that maleic anhydride decreased the amount of water absorbed in hemp and sisal polypropylene composites [12]. Dash et al. studied jute/polyester composites in outdoor weathering conditions and found that bleached fiber composites absorbed less water than the untreated fiber composites [13].

Experiments were conducted to characterize the surfaces of treated and untreated fibers and to investigate the absorption of water in natural fiber composites. FTIR was used to determine the chemical composition of the fiber surfaces. ESEM images were taken to show the effect of the silane. Water absorption tests were used to determine the saturation point of natural fiber composites.

2 Experimental

The natural fibers (kenaf, flax, industrial hemp supplied by Flax Craft Inc. and henequen supplied by Dr. Pedro Herrera Franco from Mexico) were soaked in hot distilled water for 1 h, dried for 48 h in air at room temperature, and dried in the oven at 373.15 K for 3 h. The ¼ in. epoxy compatible chopped glass fibers were supplied by Johns Manville (JM) Company and were used as such.

Diglycidyl ether of bisphenol-A (DGEBA), supplied by Adtech Corp., cured with diaminodiphenyl sulfone (DDS), supplied by TCI, was used to produce the epoxy. The DGEBA was mixed with the DDS in the ratio of 2.79:1. Next 15% wt of fibers were mixed into the epoxy. The mixture was degassed in a 373.15 K vacuum oven for 20 min. The composites were cured in a convection oven. The composites in these experiments had 15 wt% fiber loading. Several grams of composite were placed in a silicone rubber mold. The composites were cured in a 418.15 K oven for 2 h.

Fibers were treated using five percent solution of sodium hydroxide. The fibers were submerged in the sodium hydroxide solution for one hour at room temperature, rinsed with tap water, and then neutralized in a 2% glacial acetic acid and tap water solution. The fibers were then rinsed with deionized water and dried at room temperature for 24 h.

Fibers were also treated using a one percent solution of 3-glycidoxypropyltrimethoxysilane (Z-6040 from DOW Corning) in deionized water and ethanol in a 1:1 ratio. The pH of this solution was adjusted to 4 using 2% glacial acetic acid. The solution was stirred for two hours before the fibers were added. The fibers were washed with deionized water after the silane treatment. The fibers were then dried for 12 hours in air and then cured in a convection oven for five h.

The samples were observed in Philips ElectroScan 2020 ESEM. The sample chamber pressure was reduced to approximately 586.6 Pa. The working distance ranged from 6 – 9 mm. ESEM is used to examine the morphology of the fibers and the composites.

The fibers were tested with FTIR using a Perkin Elmer Instruments Spectrum One with the Attenuated Total Reflectance (ATR) technique.

Composites with dimensions 25.4 mm x 38.1 mm x 3 mm were immersed in distilled water. Before taking weight measurements, the composite surfaces were blotted with paper towels to remove surface water. Measurements were taken at 6, 24, 48, 72, and 144 h for untreated samples. The weight was then measured weekly until the composites were saturated. The treated samples were weighed at 5, 24, 48, 120, and 168 h and thereafter weighed weekly until saturated.

3 Results and discussion

Kenaf and hemp fibers were prepared with three different fiber treatments; alkali, silane, and alkali and silane. The untreated and treated fibers were analyzed using ESEM and FTIR. Water absorption experiments were also performed on untreated and treated fiber composites. Only hemp and kenaf were selected to be treated with alkali and silane based on previous experiments on natural fiber composites [14]. Hemp and kenaf showed improved curing times with microwaves. Also hemp reached a greater extent of cure with microwave curing than with convection oven curing and had a relatively high degradation temperature compared to the other natural fibers. Kenaf was more compatible with the epoxy matrix materials.

The FTIR peaks are baseline corrected to 3323 cm^{-1} (see Fig. 1 and Fig. 2). The CO stretch at 2900 cm^{-1} is present in all fibers. The carbonyl peak at 1730 cm^{-1} can be seen in all the fibers not treated with alkali. The lignin peak (1500 cm^{-1}) is present in kenaf fibers but not present in any hemp fibers. COOH bending peaks (664 cm^{-1}) are present in all fibers. CH$_2$ symmetric bending peaks at 1432 cm^{-1} are also present. The peak at 1625 cm^{-1} in hemp is present in the non-alkalized fibers only. In the kenaf, and silane treated kenaf fibers the peak at 1239 cm^{-1} is much larger than the peak in the alkali treated samples.

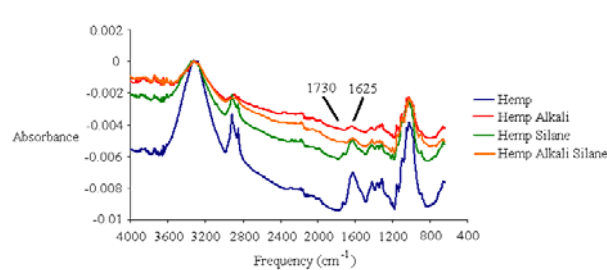Fig. 1: Spectrum of treated and untreated hemp fibers.

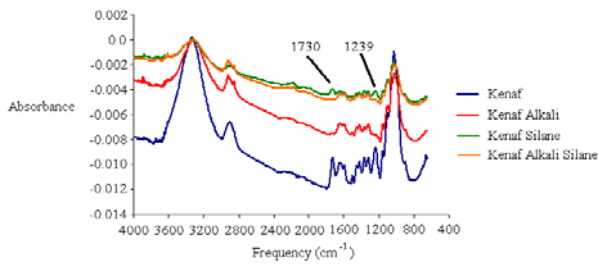Fig. 2: Spectrum of treated and untreated kenaf fibers.

Fig. 4: Left: kenaf. Right: silane treated kenaf. Magnification 500x, scale bar 100 μm.

The effects of fiber treatment on the natural fiber surfaces were also studied using FTIR. The peak 1730 cm^{-1} is attributed to the C=O stretching of the acetyl groups of hemicellulose [15, 16]. This peak is not present in the alkali treated samples. The removal of hemicellulose from the fiber surfaces causes this peak to disappear [16]. The peak at 1239 cm^{-1} in the kenaf fibers is much smaller for alkali treated samples. This peak is a C-O stretch of the acetyl group of lignin and is reduced because lignin is partially removed from the fiber surface [16]. The peak at 1625 cm^{-1} is reduced in hemp alkali treated fibers and removed in kenaf alkali treated fibers. This peak represents the C=O bonds on hemicellulose and is further evidence that hemicellulose is removed from fiber surfaces by the alkali treatment [10]. FTIR does not show the presence of silane on the fibers. Peaks should be present at 766 cm^{-1} and 847 cm^{-1} [21]. It is possible that the concentration of silane on the fiber surfaces is too small to detect by FTIR. The ESEM images show the presence of silane on the hemp and kenaf fibers (see Fig. 3 and Fig. 4). This demonstrates that the silane treatment was effective for coating the fibers in order to make the treated fiber composites.
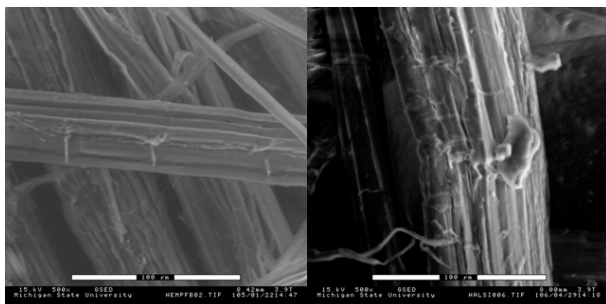
Untreated henequen composites absorbed the most water (see Fig. 5 and 6). Glass composites absorbed the least amount of water. Henequen composites absorbed water most quickly followed by kenaf, hemp and flax, and glass composites in the short run. Long term, flax, kenaf and hemp have the same absorption rate. Henequen, flax, kenaf, and hemp composites reached saturation at 816 h while glass composites reached saturation at 648 h.
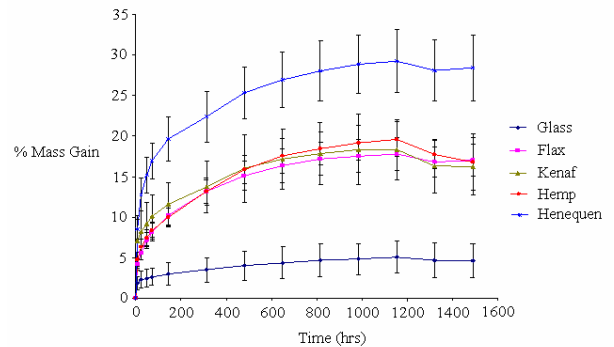

Fig. 5: Water absorption of natural and glass fiber composites (untreated).

Fig. 3: Left: hemp. Right silane treated hemp. Magnification 500x, scale bar 100 μm.
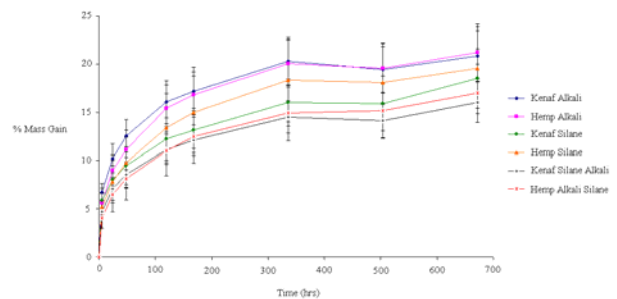

Fig. 6: Water absorption of natural and glass fiber composites (treated).

The alkali treated kenaf and hemp composites absorb more water than the silane only or alkali and silane treated samples. The alkali and silane treated samples absorbed the least amount of

water. Kenaf composites absorbed less water overall than their hemp counterparts.

Alkali treated kenaf composites absorbed more water than untreated, silane treated, or alkali and silane treated composites. The silane treated, alkali and silane treated, and untreated composites had similar water absorption profiles. For hemp composites, the alkali and silane treated composites absorbed more water than the untreated or silane/alkali treated composites.

Water absorption experiments were conducted because the absorption of water can cause changes in the shape, debonding, or loss of strength in products regularly exposed to moisture [17]. These experiments show that the untreated and treated natural fiber composites absorb significantly more water than the glass fiber composites. This was expected as natural fiber composites absorb water in the fibers and matrix and water also exists in the voids of the composite. While in glass fiber composites, water is not absorbed into the fibers. Olmos et al. conducted experiments on silane treated glass fiber composites (25wt%) and obtained a saturation mass gain of 4.21 – 5.22% depending on the treatment [18]. The untreated fibers in our experiments had 4.6% mass gain. The rate of water absorption in our samples is consistent with those in the treated fiber experiments. Williams and Wool tested composites made using plant oil based resins and flax fibers (30wt%) [19]. The saturation weight for these composites ranged from 10.4 to 12.4%. Tserki et al. made 30wt% flax and polyester composites with a saturation mass gain of approximately 6.5% [17]. Our flax fiber and epoxy composites had a saturation mass gain of 17.2%. Tserki et al. made 30wt% hemp polyester composites with a saturation mass gain of ~6% [17]. The hemp epoxy samples in our experiments reached 18.4% mass gain. Tajvidi et al. conducted experiments on 25wt% kenaf polypropylene composites which had a saturation mass gain of around 2%. [20]. The kenaf epoxy samples in our experiments reached 17.8% mass gain at saturation. Differences between our results and literature results can be attributed to different fiber loading and matrix composition and possibly due to voids present in our composite samples. In Fig. 5 and Fig.6, it can be seen that the alkali treated composites absorb more water than the untreated or silane treated composites. Fibers are treated with NaOH to remove lignin, pectin, waxy substances, and natural oils covering the surface of the fiber cell wall. This makes the surface of the fiber rough by revealing the fibrils [10]. This roughening of the fiber surface may create more voids for water to absorb into.

4 Conclusions

Experiments were conducted to characterize the surfaces of chemically treated and untreated fibers and to investigate water absorption in natural fiber composites. Natural fiber composites absorb more water than glass fiber composites. Alkali treatment removes lignin and hemicellulose from the surface of natural fibers. The silane treatment is visible on the natural fibers using ESEM. The treatment will be used in future experiments to improve the adhesion between the natural fibers and the epoxy matrix.

5 Acknowledgements

6 References

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