

EFFECT OF ALKALI TREATMENT ON THE PERFORMANCE OF FLAX FIBER REINFORCED POLYESTER COMPOSITES

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ABSTRACT

Environmental concerns and depleting petroleum resources have forced researchers to find suitable alternatives to conventional polymer based synthetic fiber composites. Natural fibers provide good alternatives to synthetic fibers like glass fibers in providing composites with comparable properties. They are available in large quantity across the world, biodegradable and renewable. However, they have poor wettability and absorb moisture which can be overcome by surface treatment. In this study, alkali treatment was used to treat flax fibers at two different temperatures and their composites were prepared with polyester resins. Results of the study show that fiber treatment enhances the properties of composites while reducing moisture absorption.

Keywords: Flax Fibers, Alkali Treatment, X-ray Diffraction, Moisture Absorption, Mechanical Properties.

1. INTRODUCTION

Growing global environmental and societal concern, high rate of depletion of petroleum resources and new environmental regulations have forced the research to new composites from green materials. Broadly defined, biocomposites are composites made of natural fibers and petroleum based biodegradable polymers. These fiber reinforced composites are used in many applications from sporting goods to automotive industry. Major industrial application of these composites is in automotive sector. Production of natural fiber composites is quite similar to that of glass composites with an exception that processing temperature must not exceed 200° C and exposure time to high temperature should not be long to avoid damage to the fiber which restricts the choice of matrix material [1, 2]. Natural fibers are more effective than conventional reinforcing fibers due to their low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to processing equipment), enhanced energy recovery, CO₂ neutral when burned and biodegradable. Natural fibers are also known for good acoustic and thermal insulation in automobile applications due to their hollow tubular structure which further reduce the bulk density [16, 31]. Major drawback of natural fibers is high moisture absorption leading to swelling and increase in void content at fiber matrix interface, which results in poor mechanical properties and dimensional stability. This hydrophilic nature of cellulose fibers when compounded to non-polar thermoset or thermoplastic matrix leads to non-uniform dispersion of fibers in the matrix resulting in low efficiency of the composite. To overcome some of

the disadvantages, researchers have worked on surface treatment of natural fibers [3-5]. Alkali treatment is the most commonly used method as it removes natural and artificial impurities leading to fibrillation of fiber bundles into separate fibers. In other words, alkali treatment increases the surface topography (surface roughness) and expose cellulose content on the surface, resulting in better mechanical interlocking between fiber and matrix. Effect of concentration of alkali treatment has been studied by many researchers. The concentration limited to 2-10% at shorter treatment time showed better mechanical properties. These parameters change according to fibers and their retting process. However, it should be noted that higher alkali concentration results in degradation of fibers. Shrinkage of fiber is also observed which eventually damages the properties of natural fiber. Some group of authors has studied how temperatures and time of alkali treatment affect the speed and the rate of degradation of lignin component of fiber [6, 7]. Typically at high treatment temperatures non-cellulose components will be removed at faster rate. However, very high treatment temperature may lead to degradation of fiber cellulosic components resulting in low strength and stiffness.

Islam et.al [8] studied industrial hemp fiber reinforced polylactic acid (PLA) composites by compression molding. Alkali treatment was performed to improve bonding of fibers with PLA. Interfacial shear strength (IFSS) results demonstrated that interfacial bonding was increased by alkali treatment of fiber which also leads to improved composite mechanical properties. Assarar et.al [9] studied the influence of water ageing on

mechanical properties and damage events of two reinforced composite materials i.e. flax fibers and glass fibers. Results show that flax fibers absorb 12 folds more water than glass fibers but the tensile modulus and the failure strain of flax fiber composites are hardly affected by water ageing whereas only the tensile stress is reduced in comparison with the glass fiber composites. Rosa et al. [10] studied the effect of fiber treatment on tensile and thermal properties of coir biocomposites and showed that alkaline treatment increased the tensile strength of composite up to 53% compared to untreated composites. Cordeiro et al. [11] have investigated the surface properties of physico-chemically modified natural fibers using inverse gas chromatography. In this study, the treatments used were 4% NaOH and 2% Zein which affected the chemical composition, crystallinity and morphology of fibers, thus these treatments decrease the dispersive surface energy and the specific free energy of adsorption.

From these studies it is clear that chemical treatments of natural fibers affect properties of biocomposites. Increase in the properties may be attributed improved interfacial bonding between fiber and the matrix, decrease in moisture absorption, increase in fiber crystallinity due to variation in treatment time and temperature. However, there has not been much published work discussing how the chemical, structural and physical properties vary with the alkali treatment temperature. Obtaining an optimal treatment temperature is important, because it is possible to damage the natural fibers if treated at high temperatures or at higher concentration. Hence, in this study effect of temperature and alkali treatment on the performance of flax fiber reinforced polyester resins was investigated.

2. EXPERIMENTAL

2.1 Materials

Flax fibers used as reinforcement in composites were obtained from Alvin Ulrich Company in Canada. Sodium Hydroxide was obtained from Fisher Scientific. The resins used were as follows: thermoset resins, AOC atryl resin TCA.

2.2 Surface Modifications

2.2.1 Concentration treatment

Alkali treatment was done by treating flax fibers with 2.5, 5, and 7% solutions of NaOH concentration for one hour. Fibers were then dried in an oven for 24 hours at 80° C.

2.2.2 Temperature treatment

Fiber surface treatment was carried out at room temperature, 35° C and 45° C with NaOH concentration of 2.5 wt. % for an hour, followed by washing of fibers in distilled water until a neutral pH value was obtained. The fibers were then dried in an oven at 80° C for 24 hours.

2.3 Spectral and Thermal Analysis

Techniques used to determine morphology of the fibers include X-ray diffraction (XRD), Fourier Transfer Infra-Red Spectroscopy (FTIR), scanning electron microscopy (SEM) and Optical microscopy. These

experiments were done to determine the effect of alkali treatment on fibers. Thermal properties were determined through differential scanning calorimetry studies.

2.4 Fabrication of composites

Fibers mats were prepared by immersing the fibers in water and oven drying them for 24 hours at 80° C. Preparation of bio-composites was done by soaking fiber mats in resin bath and hot pressing the mats using compression molding method for 2 hours at 110° C. Polyester and ENVIREZ 1807 resin systems were used as the matrix to differentiate between the synthetic and biopolymer. Composites were prepared with 3 types of mats (untreated, 2.5wt. %, and temperature treated) and 3 weight percentages (40%, 50%, and 60%) of fibers.

2.5 Characterization

The flexural properties of the bio-composites were determined by means of three-point bend test using an INSTRON testing machine as per ASTM standard D3039-08. At least seven samples of each type were tested. To determine the viscoelastic properties, dynamic mechanical analysis test was carried out using double cantilever mode at a frequency of 1 Hz with amplitude of 15 μm. The test temperature was increased from room temperature to 200° C at a rate of 10°/C. Through this test, storage modulus and glass transition temperature (Tg) were determined. Water absorption rate of the composites was determined through ASTM D570-98(2010) test. In this test, composite specimens were soaked in distilled water for a week at room temperature. Samples were weighed each day. Amount of water absorbed by composites was calculated as following:

$$\text{water absorption} = \frac{\text{wet wt} - \text{dry wt}}{\text{dry wt}} \times 100$$

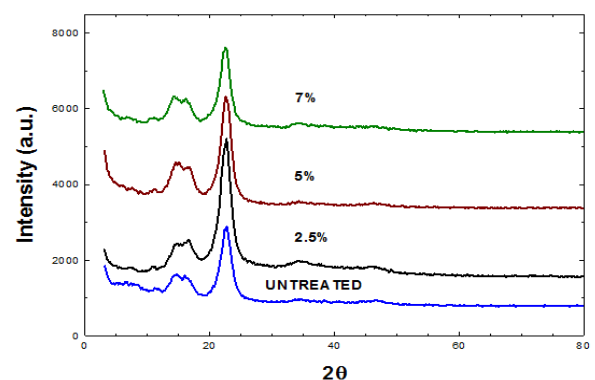


Fig 1. XRD of concentration treated fibers.

3. RESULTS AND DISCUSSION

3.1 Surface modifications

3.1.1 XRD analysis

Figure 1 shows XRD spectrum of fibers tested before and after the alkali treatment indicating the change in crystallinity of fibers. Broader XRD peaks with lower intensities suggest lower crystalline material. A lower crystallinity index in case of 5, 7% flax fiber means poor order of cellulose crystals in the fiber.

Cellulose crystals were not oriented along the fiber axis. For the fibers that were treated with 2.5% alkali solution, the XRD results show better alignment of cellulose crystals are better oriented in along the fiber axis. Figure 2 shows the effect of temperature treatment on flax fibers. The increase in temperature results in the removal of natural polymer from the surface of the fiber bundles. The crystallinity of fibers increases with increase in temperature and decreases at higher temperature. The fibers at 35°C show higher crystallinity compared to 45°C.

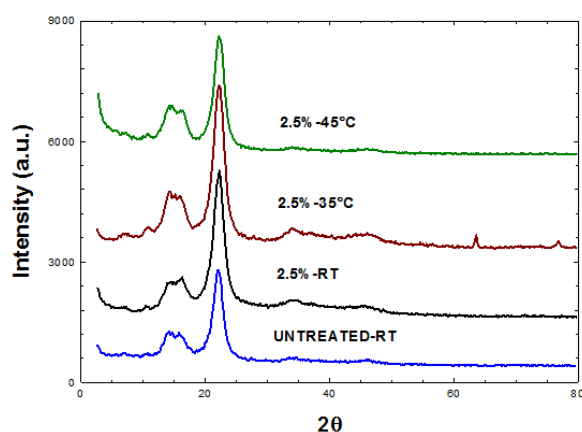


Fig 2. XRD of temperature treated fibers.

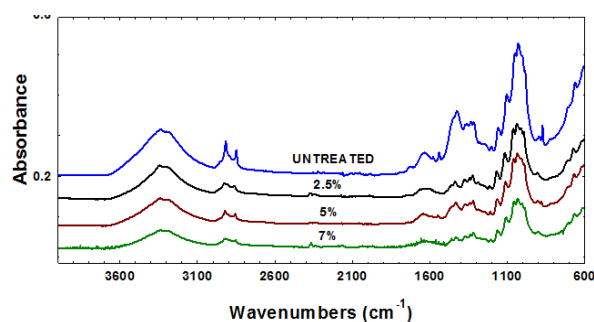


Fig 3. Effect of concentration treatment on fibers.

3.1.2 FTIR analysis

Figure 3 shows FTIR spectra to illustrate the effect of concentration treatment on fibers whereas the spectra in figure 4 give the results on the effect of temperature treatment on flax fibers. At the range of 700 to 1000 cm^{-1} , the peaks represent the tertiary alkyl groups which are decreasing in treated fibers as alkali treatment dissolves the amorphous cellulose content without modifying the crystalline type of cellulose. Peaks in the range of 1125-1000 cm^{-1} are attributed to typical xylems of plant fiber. Strong peak located at a wavelength of 1040 cm^{-1} shows decrease in intensity as treatment concentration increases. This is attributed to the decrease in absorption of C-O, C-C or C-OH stretching in hemicelluloses. The shoulder at 1254 cm^{-1} belongs to C-O stretching vibration of acetyl groups in lignin component and the peak at 1525 cm^{-1} is due to benzene vibrations of lignin which are seen missing in treated fibers due to effect of mercerization. Absorption bands at 3300, 3175 cm^{-1} are typical of the -OH stretching intramolecular hydrogen bonds present in the crystalline cellulose II. From the spectra, the peak for hydroxyl group was highest for as

received fibers and this was due to presence of lignin and hemicelluloses absorbing more water. On the other hand, the intensity of -OH groups in hemicelluloses eventually decreased as alkali concentration increased. It was assumed that when alkali concentration increases the rate of degradation of non-cellulose components would increase.

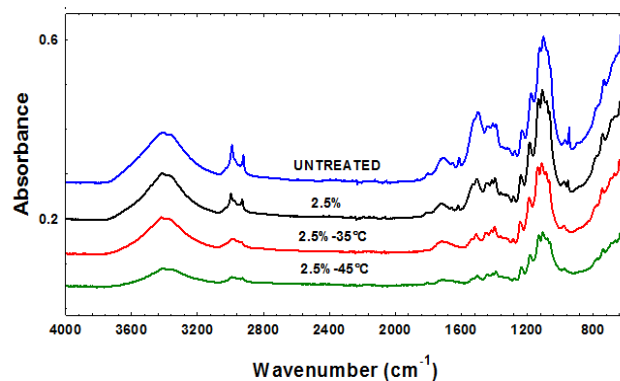


Fig 4. Effect of temperature treatment on fibers.

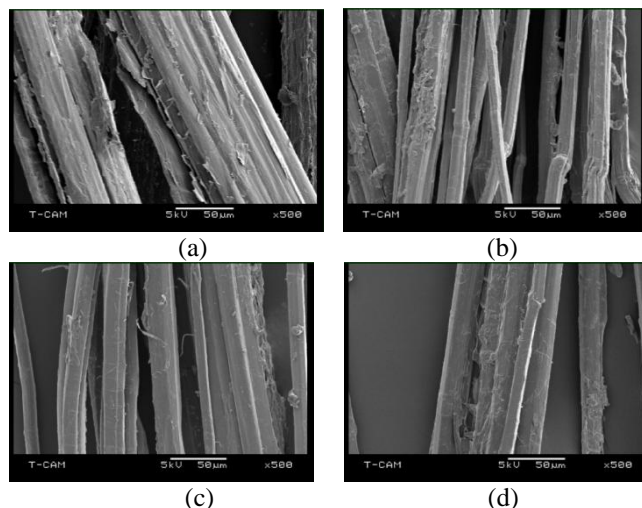


Fig 5. SEM micrograph of a) untreated b) 2.5% c) 5%, and d) 7% treated fibers.

Figure 5a shows the micrographs of the untreated flax fiber bundle. The untreated fibers clearly show the binding of individual fibers with each other with the help of natural polymer (lignin). When subjected to alkali treatment, the bonding between individual fibers is seen to decrease (Fig. 5b-d). At 2.5% it appeared that alkali treatment was successful in removing most of the binding from the surface of fiber. As the concentration of alkali increases, fibers were separated. It was believed that due to the deterioration and removal of lignin, the fibers got separated leading to the exposure of reactive sites on the surface of fiber. However, at higher concentration, it was believed that the cellulosic content was degraded along with hemicellulose and lignin. Fig. 5(d) shows fiber bundles with cracks and breakage resulting from excess alkali treatment. When the fibers were treated with 2.5 wt.% NaOH solution at 35° C, separation of fiber bundles was seen with some content

of hemicelluloses or lignin but when treated with the same concentration of alkali at 45° C, degradation of fiber microstructure was observed with minor cracks visible on the surface as shown in the Fig. 6b.

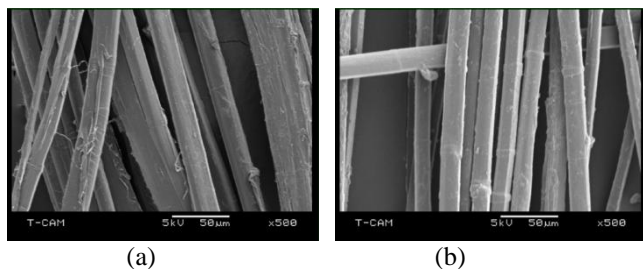


Fig 6. SEM micrograph of a)2.5%-35°C b)2.5%-45°C

3.2 Characterization of Biocomposites

3.2.1 Water absorption

Figures 7 show the amount of water absorbed by the biocomposites with polyester for different weight content of fibers. It is seen that composites with untreated fibers absorbed most water. As hemicelluloses and lignin are the water absorbing components, higher weight gain is seen in composites with untreated fibers compared to those with treated fibers. When alkali treated these components of the fiber are removed and hence there is a drastic reduction in the amount of water intake. When treated fibers were compared, composites with room temperature treated fibers had higher water absorption relative to those with temperature treated fibers. Moisture absorption was the least for 50% fiber weight content in polyester resin system. Composites with untreated fibers and polyester resins with 60 wt. % fibers had the highest absorption rate. This could be attributed to improper wetting of fibers at that high fiber wt. %.

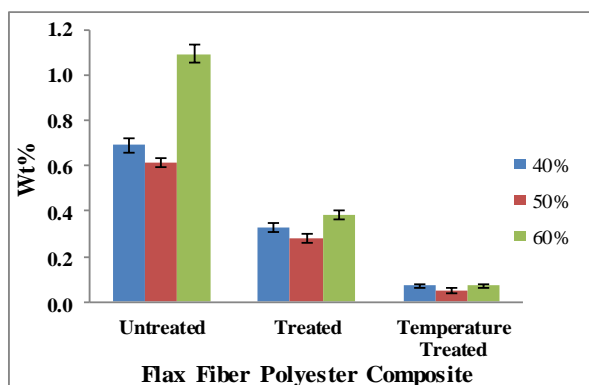


Fig 7. Water absorption rate of polyester composite

3.2.2 Mechanical Properties

Flexural behavior of biocomposites was studied to determine if alkali treatment improved the mechanical properties. Figures 8 shows the flexural strength of flax fibers/polyester composites prepared with different fiber-matrix ratio. It is observed that the treated composites show higher strength compared to untreated fibers due to better fiber wetting which enhanced the mechanical interlocking between fiber and matrix. The

amount of fiber content also changed the properties of composite. As the fiber content increased, increase in strength was observed for both untreated resin composites but decreases for treated and temperature treated at 60%. This can be again due to insufficient matrix to completely wet the fibers. Unless, there is good fiber wetting, the composite properties will not improve. A decrease in flexural strength is normally indicative of lower fiber-matrix bonding.

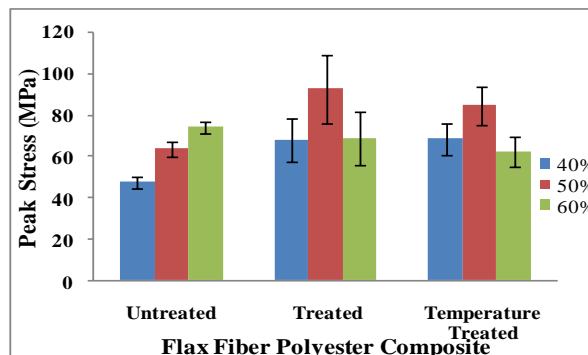


Fig 8. Flexural strength of polyester composites.

As seen in Figure 9, storage modulus. E' of the neat polyester resin increased after the untreated flax fibers were added. However, the storage modulus of the commercial polyester composites were observed to increase when fiber used to make biocomposites were alkali treated at elevated temperature. These results were in agreement with the findings for the flexure data. It was observed that the E' was higher in the treated polyester composites, because of an increase in the fiber-matrix adhesion. When flax was treated, the fiber-matrix interaction increased. As the fiber ratio increased the storage modulus increased. However, for the alkali treated fiber reinforced polyester biocomposites, the storage modulus increased initially with fiber weight content from 40 to 50% but decreased at 60 wt. %. These trends are consistent with those observed during the testing of biocomposites under flexural loading. On the other hand loss modulus, which represents the damping response of composites showed decreasing trend for the composites with untreated fibers and was seen to have the lowest value at 50% when alkali treated fibers were used.

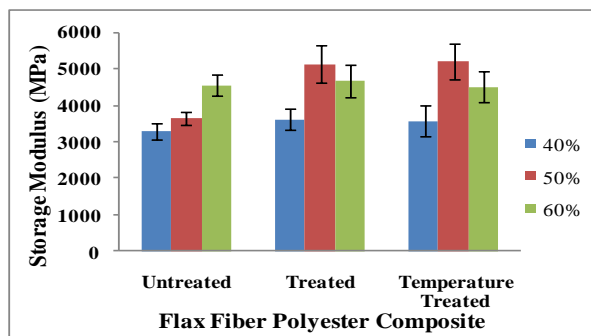


Fig 9. Storage modulus of polyester composites.

The decrease in the loss modulus intensity (Fig. 10) was the result of increased stiffness and a decrease in chain mobility from enhanced fiber-matrix bonding. When treated flax was used, the loss modulus intensity was observed to be lower than the loss modulus intensity of the untreated polyester composite. This was because the fiber-matrix interaction was higher for treated flax polyester composites compared to the interaction with the untreated composites.

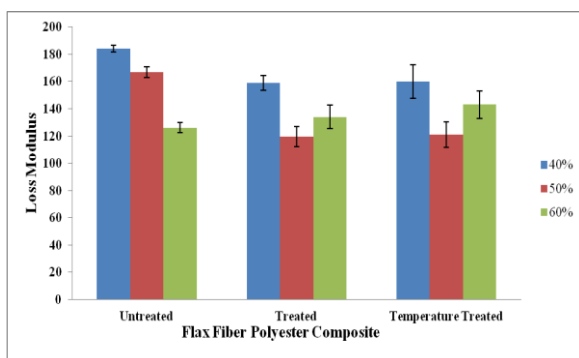


Fig 10. Loss modulus of polyester composites.

It was also observed that the loss modulus peak shifted towards higher temperatures for the untreated and treated commercial unsaturated polyester composites, compared to the neat commercial polyester resin. Normally, when a shift in the $\tan \delta$ (ratio of loss to storage modulus) peak intensity occurs, it is an indication of increased or decreased chain mobility as a result of cross linking. If increased stiffness is observed, the increased stiffness ultimately lowers the vibrational damping. Because the shift for loss factor peaks for the composites decreased compared to the neat UPE, it was believed that decrease in internal friction occurred. Although it was observed that alkali treatment increased the storage modulus for treated and temperature treated samples, no decrease or change in the $\tan \delta$ peak was observed for composites with treated fibers when compared to composites with untreated flax fibers.

4. CONCLUSION

Treatment of flax fibers by alkali solution of 2.5 wt. % and temperature of 35° C was carried out. Three types of flax fiber mats were prepared which were designated as untreated, treated and temperature treated fibers. For the most part, temperature treated composites had a negative impact on flexure and thermo-mechanical properties. Comparing the properties of temperature treated composites with untreated possess positive results but comparing with concentration treated fiber composites possess negative results. Flax fiber polyester composite with 40 wt. % showed less strength and modulus in all categories. Overall, 50% flax fiber composites showed proper wetting of fibers and good fiber matrix adhesion compared to 60 wt. % composites. The DMA results showed that flax fibers had a greater reinforcing effect on dynamic properties with three different types of fiber mats and with different fiber wt. %. Storage modulus of 50 wt. % flax fiber polyester composites was the greatest in the all flax fiber polyester

composites. The flexural strength was highest for 50% treated flax polyester composites with a peak stress of 97MPa when compared to with neat unsaturated polyester resin was 54.5 MPa. The glass transition temperature increased in all composites by approximately 18.5%.

5. ACKNOWLEDGEMENTS

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