Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites

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Natural fibers are currently being developed as a possible substitute for conventional reinforcement materials because they have advantages of low cost, low density, acceptable specific strength properties, ease of separation, carbon dioxide sequestration and biodegradability [1]. Likewise, composites reinforced with natural fibers have also been studied. A current example is elephant grass-based bio-composites being investigated in Europe for automotive applications [2]. Traditionally natural fiber such as kenaf, flax, jute, hemp, and sisal, are used as reinforced for bio-composites; however agricultural by-products such as corn stalk, rice stalk and grass are being investigated as a potential resource for natural fibers since they are quite inexpensive and abundant [3].

Indian grass, belonging to Poaceae family, is a native grass of the USA and grows throughout most of North America. It is a perennial plant, growing during the summer months, and is typically used as livestock feed [4]. However, little attention has been given to Indian grass fiber as a potential reinforcing fiber for bio-composites in the literature.

Alkali treatment is a common method to clean and modify fiber surfaces to lower surface tension and enhance interface adhesion between natural fibers and polymer matrices [5]. Many researchers investigated the effects of alkali treatment on structure and properties of natural fibers [6–8]. However, no studies on the effects of alkali solution treatment on the structure, morphology and properties of Indian grass fiber have been reported prior to this report.

Chopped grass stems (from a Michigan farm) with a length of 20 mm were treated in 5 and 10% sodium hydroxide (J.T. Baker) solution in water. After the appropriate soak time, the fiber was rinsed with distilled water until the PH of the rinse solution stabilized at 7. After storage at room temperature for four days, the alkali treated and raw fibers were dried under vacuum at 80 °C for 16 h. The structure, morphology and thermal properties of raw and alkali treated fibers were studied by using of X-ray photoelectron spectroscopy spectrum (XPS, Physical Electronics 5400 ESCA), Fourier transform infrared spectrum (FTIR, Perkin Elmer system 2000 Spectrometer), environmental scanning electron microscopy (ESEM, Phillips Electroscan 2020) and thermogravimetric analysis (TGA, TA 2950), respectively.

XPS spectra were taken of the grass fibers following each treatment. The inside and outside surface of the fibers were examined separately. Survey scans for each material revealed carbon, oxygen, nitrogen, and calcium. Changes in oxygen:carbon atomic ratio as a function of alkali solution treatment are shown in Table I.

Following a one-hour treatment with a 5% alkali solution, the oxygen:carbon atomic ratio in the outer surface decreased significantly, but the ratio of the inside

TABLE I XPS result of raw and alkali treated Indian grass fibers. Inside refers to inner surface of the grass cylinder. Outside refers to outer surface of grass cylinder

Fiber/treatment	O/C atomic ratio inside	O/C atomic ratio outside
Raw	0.20	0.07
5% Alkali 1 h	0.18	0.37
5% Alkali 2 h	0.33	0.37
10% Alkali 2 h	0.36	0.34
10% Alkali 4 h	0.29	0.44
10% Alkali 8 h	0.33	0.41
10% Alkali 16 h	0.36	0.40

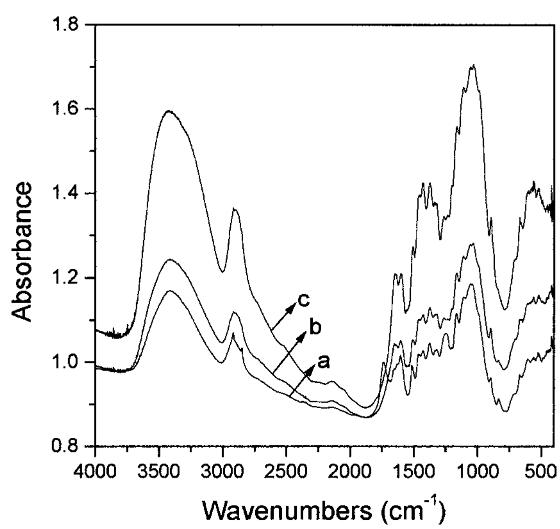

Figure 1 FTIR spectra of (a) raw fiber, (b) grass fibers treated with 5% alkali solution treated for 1 h and (c) grass fibers treated with 10% alkali solution treated for 4 h.

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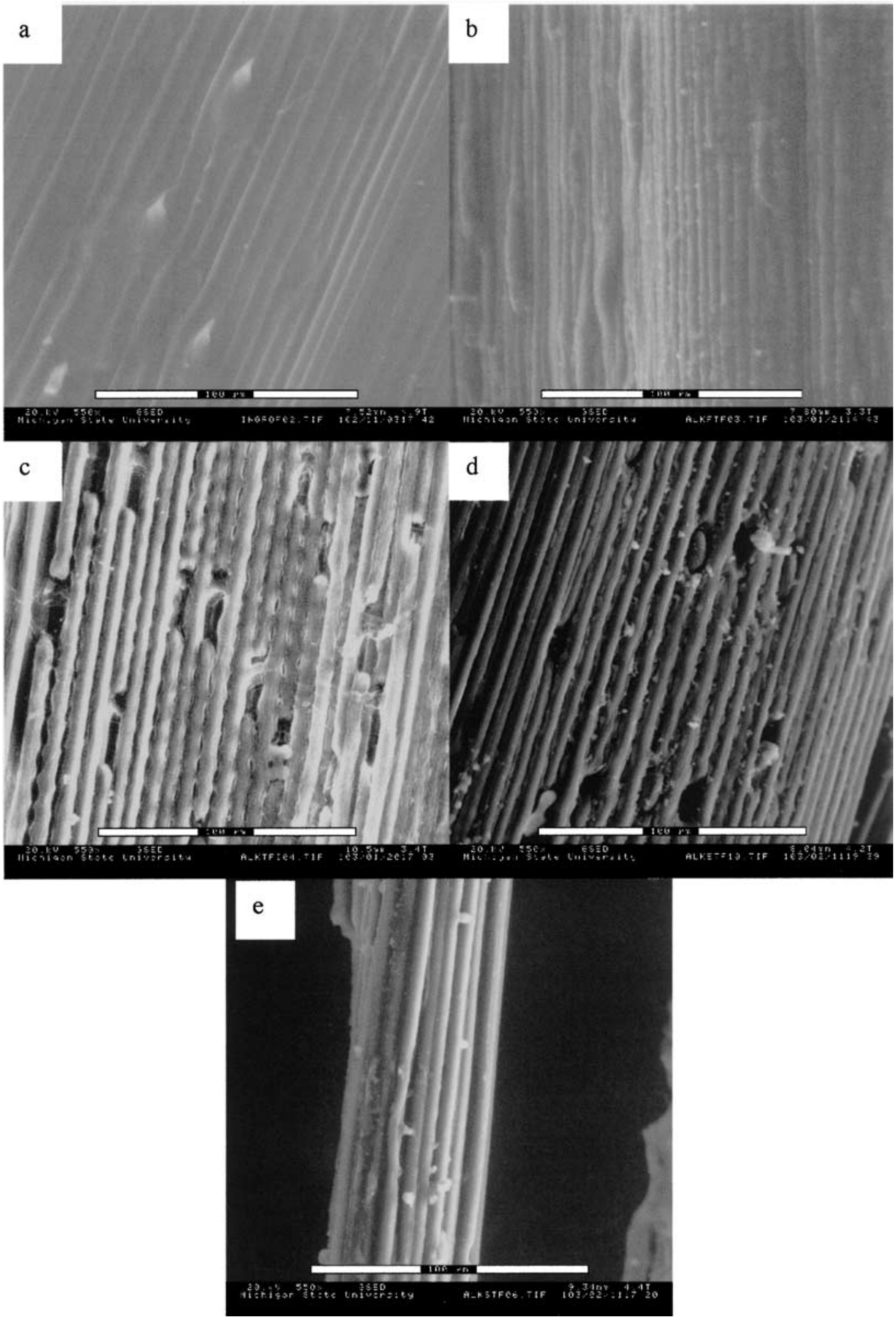

Figure 2 ESEM images of raw and alkali treated fiber with a magnification of 550× and scale bar of 100 μm for (a) raw fiber, (b) grass fiber treated with 5% alkali solution for 2 h, (c) grass fiber treated with 10% alkali solution for 4 h, (d) grass fiber treated with 10% alkali solution for 8 h, and (e) grass fiber treated with 10% alkali solution for 16 h.

surface did not change. When treated with 5 or 10% alkali solution for two or more hours, not only does the outside surface but also the inside surface of the fiber exhibit a significant decrease in the oxygen:carbon atomic ratio.

It is well known that natural fiber mainly consists of cellulose, hemi-cellulose and lignin [9]. Hemicellulose, is composed of a mixture of different sugars and other various substituents which are water or base soluble. Lignin has low oxygen to carbon ratio and the structure of lignin is similar to a highly unsaturated or aromatic polymer. Part of lignin is soluble in alkali solution. Therefore, it is likely that a part of hemicellulose and lignin was dissolved during alkali solution treatment so that the content of hemicellulose and lignin on the surface of fiber decreased, leading to an increase in oxygen:carbon atomic ratio.

Changes in the grass fibers as a function of alkali treatment were followed by FTIR and are shown in Fig. 1. Careful examination of the spectra revealed that several changes did occur. First, the vibration peak at 1737 cm^{-1}, assigned to a C=O stretching vibration of carboxylic acid or ester, disappeared due to the removal of hemicellulose. Second, the vibration peak at 1515 cm^{-1}, assigned to the benzene ring vibration of lignin, reduced as it was removed. Third, the vibration peak at 1254 cm^{-1}, which belongs to a C—O stretching vibration of the acetyl group in lignin component, was reduced. Additionally, a vibration peak at 2918 cm^{-1}, belonging to the C—H stretching vibration in cellulose and hemicellulose, decreased after alkali solution treatment indicating that part of the hemicellulose was removed. These results all indicate that alkali treatment leads to the partial removal of lignin and hemicellulose. This correlates with the changes in O:C ratios observed by XPS.

ESEM micrographs detailing the morphology of raw and alkali solution treated Indian grass fiber are shown in Fig. 2. From these pictures, it was found that grass fibers consist of aligned fibrils with materials cementing the fibers together. After treatment with alkali solution, the materials in the interfibrillar region were obviously etched away. Based on the results of FTIR and XPS and the structure of natural fiber, the cementing materials would be expected to be hemicellulose or lignin. It is well known that hemicellulose is a branched amorphous polymer with a lower degree of polymerization, which always is associated with lignin through covalent bonds and interacts with cellulose by hydrogen bonding [10]. Therefore, grass fibers should be thought of as a composite material with fibrous reinforcement and a mixture of hemicellulose and lignin as matrix. This interpretation is reinforced by close examination of the ESEM images. For raw Indian grass as shown in Fig. 2a, it clearly indicates that a grass fiber is a composite, composed of orientated fibrils and hemicellulose and lignin in the interfibrillar region.

The grass composite is sensitive to alkali because of its structure. With increasing alkali concentration and treatment time, the fibrous region becomes more pronounced as the interfibrillar region is removed (shown in Fig. 2b, c and d). This result shows that with increasing alkali concentration and treatment time, more hemicellulose and lignin was etched. Following treatment with 10% alkali solution for 16 h (shown in Fig. 2e), the fiber surface was clean and only a small amount of material remained in the interfibrillar region. After removal of hemicellulose, the interaction between fibers is reduced, which made the fibers easier to separate. The ESEM images further support the FTIR and XPS results to verify the removal of hemicelullose and lignin.

TGA and differential thermal gravimetric analysis (DTGA) curves of raw and alkali treated Indian grass fibers are shown in Fig. 3. After treatment with the alkali solution, the temperature at the maximum rate of decomposition of the grass fiber increased, indicating that the alkali solution treatment improved the thermal stability of the grass fiber. This is due to the fact that the relative content of lignin and hemicellulose in the grass fiber decreased after alkali solution treatment. The changes of the maximum decomposition rate temperature with treatment condition were shown in Table II. The maximum decomposition rate temperature of the grass fiber was slightly shifted to a higher temperature with increasing treatment time, with a greater shift to higher temperature with increasing concentration of the alkali solution. Therefore, the thermal stability of grass fibers treated with alkali solution was dependent on the concentration of alkali solution and treatment time.

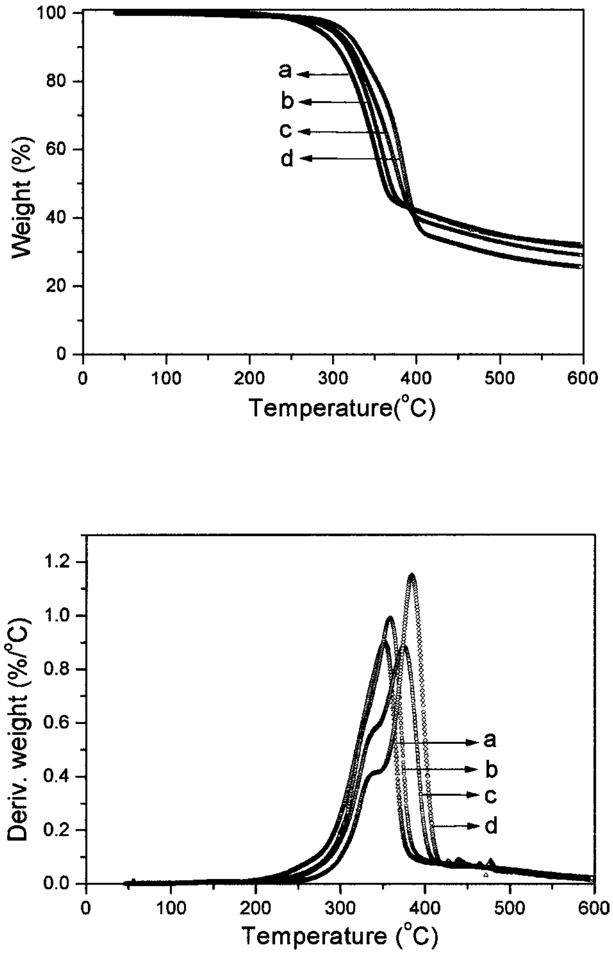

Figure 3 TGA and DTGA curves of (a) raw grass fiber, (b) grass fiber treated with 5% alkali solution for 2 h, (c) grass fiber treated with 10% alkali solution for 2 h, and (d) grass fiber treated with 10% alkali solution for 16 h.

TABLE II TGA result of raw and alkali treated Indian grass fibers

Fiber	Maximum thermal decomposition rate temperature (°C)
Raw	352
5% Alkali 1 h	357
5% Alkali 2 h	359
10% Alkali 2 h	374
10% Alkali 4 h	381
10% Alkali 8 h	383
10% Alkali 16 h	384

The present study revealed for the first time the influences of alkali treatment on structure, morphology and thermal properties of grass fiber, which are consistent with that of others cellulose fibers [6–8].

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