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FUNDAMENTAL STUDY ON THE EFFECT OF ALKALINE TREATMENT ON NATURAL FIBERS STRUCTURES AND BEHAVIORS

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ABSTRACT

In composites, chemical treatment caused better adhesion interface between fibers and polymer. Thus, in this research, alkaline treatment was performed on jute and kenaf fibers in an alkaline solution containing 5wt % sodium hydroxide diluted with distilled water, at room temperature for 30 minutes. The pH levels of the alkaline solution were maintained approximately at pH 11 to pH 12. The untreated and treated fibers were analyzed using Fourier transform infrared (FTIR) spectroscopy in the range of 4000 cm^{-1} to 400 cm^{-1}. It is found out that change in the structure and the removal of outer cell layers, cellulose, hemicellulose, lignin, waxes and other impurities during the alkaline treatment that affected the improvement on the adhesion interface between fibers and polymer.

Keywords: fourier transforms infrared spectroscopy, natural fiber, alkaline treatment, composites.

INTRODUCTION

Increasing environmental awareness regarding on non-biodegradable types of polymer waste has caused the search for renewable and biodegradable resources. The development of biodegradable polymers has become one of the main areas of interest for researchers. It may come from different perspectives such as process-ability, compatibility, durability, and wear-ability. Due to its relatively high cost, natural polymer such as poly-lactic acid (PLA) cannot compete economically with conventional polymers such as polypropylene (PP) [1]. Thus, to reduce the high cost, combining the natural polymer with inexpensive filler such as natural fibers can indirectly produce a cost effective composite.

According to Abdul Razak *et al.* [1], natural fibers are used because it may offer both economic and ecological advantages. Besides that, natural fibers normally used as filler in the composites are because of its non-abrasive behavior during the process, biodegradable, had low density and high specific mechanical properties [2]. Jute and kenaf are widely available in different parts of the world. It is normally used as low-cost reinforcements for composites. The natural fibers mainly consist of carbohydrate components, such as hemicellulose, cellulose and lignin [3]. Some fibers may consist of oil and wax components. Natural fibers are amenable to chemical modification due to the presence of hydroxyl groups. Thus, the adhesion interface between natural fibers and polymer matrices has often been a vital issue in several natural composite materials.

The distinction properties between natural fiber and natural polymer cause poor adhesion interface when both materials were combined, that either because of the natural fibers tend to be hydrophilic or hydrophobic due to chemical treatment. Furthermore, the natural polymer also may tend to be either hydrophilic or hydrophobic depending on the chemical molecular structure behavior it has. Therefore, the surface of the fiber has to be treated in order to promote better adhesion interface. Results from studies using acetylation treatment [4], silane treatment [5,6] and bleaching treatment [1] showed that the treatment on the surface of the fiber can improve the mechanical properties of composites.

A strong understanding of the complex nature of fiber is needed to optimize the modification processes that increased the utility of fiber as part of the component in composites. According to George *et al*. [5], as it is known that the polymers and fibers have different chemical properties that provide strong adhesion at their interfaces for an effective transfer of stress and bond distribution throughout the interface. Thus, several theories were created based on the adhesion phenomena that includes chemical bonding, wetting diffusion, electrostatic and acid/base interaction that act as a driving force for bonding interface. In this study, the effect of alkaline treatment using sodium hydroxide (NaOH) on the fibers properties were investigated using Fourier transform infrared spectroscopy analysis.

METHODLOGY

Materials

Jute (*corchorus capsularis*), and kenaf (*hibiscus cannabinus*) were obtained directly from a local market in Kuching and Kota Samarahan, Sarawak, Malaysia. Caustic soda types of sodium hydroxide with product code 'S/4920/AP1' and Universal Indicator Solution were supplied by Fisher Scientific, UK.

Methods

Fiber preparations

Raw jute and kenaf fibers were chopped into small size varied from 1 mm to 10 mm. After chopped, the natural fibers were sieved to remove the dust. The natural fibers were cleaned and washed using distilled water to

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remove the impurities and dirt at room temperature approximately around 24°C. Later, the fibers were divided into two parts, untreated and treated fibers. For untreated fibers, the cleaned and washed fibers were dried at 60 °C for 2 days in the 'ECOCELL EC55' oven supplied by MMM Group, Germany. The fan of the oven was open to allow forced natural air convection to occur to remove moisture content while drying it. Meanwhile, for the treated fibers, the fibers underwent an alkaline treatment by using sodium hydroxide. The 5wt % sodium hydroxide was dissolved by using distilled water. The dissolve sodium hydroxide with distilled water will create an aqueous solution as referred in chemical reaction (1).

$$NaOH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2O(l) \qquad (1)$$

The natural fibers were soaked inside the sodium hydroxide solution for 30 minutes at room temperate approximately around 24 °C. Then, the natural fibers were filtered and rinsed under running distilled water. This helped neutralize the soaked natural fibers into neutral pH 7. Universal Indicator Solution was used under small sample portion of the natural fibers to make sure the fibers under neutral pH. The fiber reacted with a solution of sodium hydroxide will cause a chemical reaction (2). However, the reaction may depend on the character and behavior of the natural fiber itself towards chemical.

$$(Fiber(s) + OH^-(aq)) + Na^+(aq) + OH^-(aq) + H_2O(l) \rightarrow (Fiber(s) + O^-(aq) + Na^+(aq)) + 2H_20(l) \qquad (2)$$

The natural fibers then were dried in the oven at 60 °C for 2 days with forced natural air convection. The chemical compositions of the natural fibers were shown in Table-1 and Table-2.

Table-1. The chemical composition of natural fibers [4,7,8,9].

Natural Fiber	Cellulose (wt %)	Hemicellulose (wt %)	Lignin (wt %)
Jute	61 - 71	14 - 20	12 - 13
Kenaf	72	20.3	9

Table-2. The chemical composition of natural fibers [4,7,8,9].

Natural Fiber	Waxes (wt %)	Ash (wt %)	Pectin (wt %)
Jute	0.5	-	0.2
Kenaf	0.8	1.5	0.9

Fourier transform infrared spectroscopy

Functional groups of natural fibers were obtained using the Fourier transform infrared spectroscopy test under the model name 'IRAffinity-1' supplied by Shimadzu Corporation, Japan. Infrared spectrum was obtained through infrared solution software which presented information in transmittance mode. The results obtained were in the range of 400 cm^{-1} to 4000 cm^{-1} for both untreated and treated natural fibers samples. The test was prepared according to ASTM E168-06 [10] and ASTM E1252-98 [11] standards. Based on the results obtained, the functional groups and behavior of the natural fibers were classified and discussed.

RESULTS AND DISCUSSIONS

The Fourier transforms infrared spectroscopy analyses of the untreated and treated jute are shown in Figure-1 and Figure-2 and untreated and treated kenaf fibers are shown in Figure-3 and Figure-4. In Figure-1, Figure-2 and Figure-3, the region of the broad absorption band at 3600 cm^{-1} to 3000 cm^{-1} for untreated and treated jute fiber and untreated kenaf fiber are characterized with H- bonded and O-H stretching structure that mostly contains major functional groups of phenols, alcohols and waters.

The O-H stretching and H- bonded broad absorption band in the regions is decreased after alkaline treatment for untreated jute and disappeared for untreated kenaf. The decreased or disappeared of the broad absorption band promoted an addition of two small peaks for the treated jute fiber at 3859.56 cm^{-1} and 3237.26 cm^{-1} and three small peaks for the treated kenaf fiber at 3869.20 cm^{-1}, 3711.04 cm^{-1} and 3624..25cm^{-1} that attributed to O-H stretching and free hydroxyl bond structure for functional group of alcohol, waters and phenols. The decrease in the functional group of phenolic and aliphatic hydroxyl in the fiber due to reaction with sodium hydroxide promotes free hydroxyl bond structure.

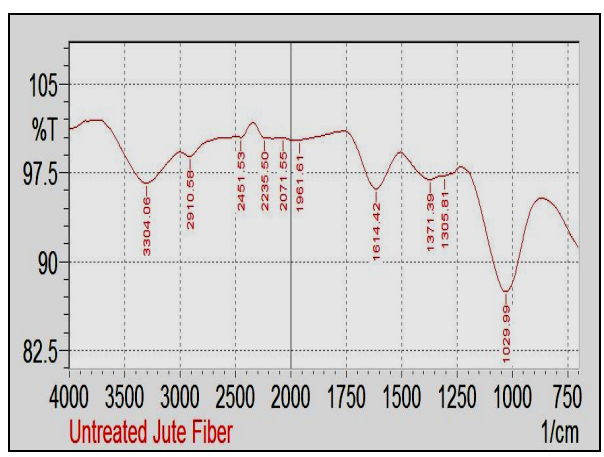

Figure-1. Infrared spectrum results for untreated jute fiber.

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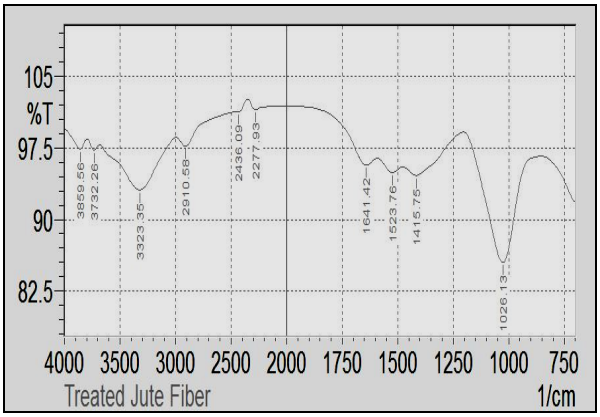

Figure-2. Infrared spectrum results for treated jute fiber.

According to Sreekala *et al.* [12], the alkaline treatment caused the globular pultrusions present in the untreated fiber disappeared that leading to the formation of a larger number of voids. These voids may promote mechanical interlocking between fiber and matrix. The loss of cuticle by the rupture due to alkaline sensitive bonds leads to the rough surface. A small peak at 2910.94 cm^{-1} for the untreated and treated jute fiber and 2900.94 cm^{-1} for untreated kenaf fiber were attributed to the C-H stretching and O-H stretching bond structure for functional group of alkanes (cellulose and lignin) and carboxylic acids [13].

The small peak in the region of the C-H stretching bond structure includes the functional group of methyl (CH_3), methylene (CH_2) and aliphatic saturated (CH) (cellulose and lignin) [14, 15]. The four small peak band at 2451.53 cm^{-1}, 2235.50 cm^{-1}, 2071.55 cm^{-1} and 1961.61 cm^{-1} for the untreated jute fiber were reduced to two small peak at 2436.09 cm^{-1} and 2277.93 cm^{-1} for the treated jute fiber are characterized as C≡C stretching and C≡N stretching bond structure of the functional group of nitriles and alkynes. However, for kenaf fiber, the small peak at 2411.02 cm^{-1} for the untreated kenaf fiber were broken into two small peaks at 2445.74 cm^{-1} and 2266.36 cm^{-1} for the treated kenaf fiber. This showed that not all fibers tend to have the same behavior and reaction due to alkaline treatment.

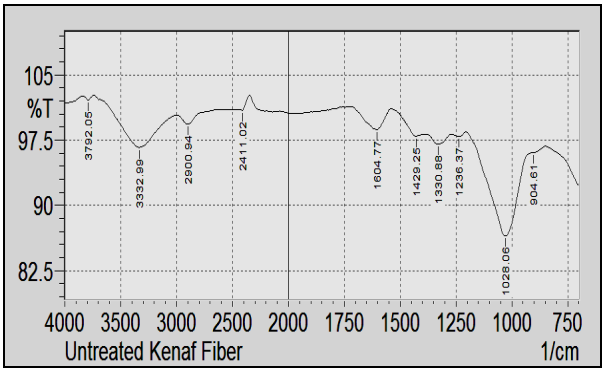

Figure-3. Infrared spectrum results for untreated kenaf fiber.

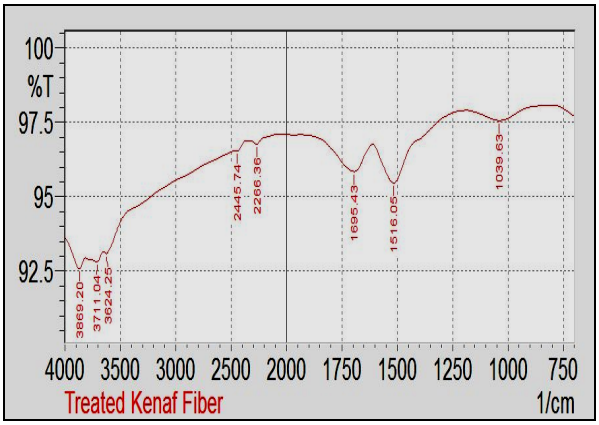

Figure-4. Infrared spectrum results for treated kenaf fiber.

The peak at 1614.42 cm^{-1} for the untreated jute fiber, 1641.42 cm^{-1} for the treated jute fiber, 1604.77 cm^{-1} for the untreated kenaf fiber, and 1695.43 cm^{-1} for the treated kenaf fiber are characterized as the C=C stretching bond structure of the functional group of alkenes. The decreased in the absorption in the peak were due to removal of lignin. The small peak at 1371.39 cm^{-1} and 1305.81 cm^{-1} for the untreated jute fiber, 1523.76 cm^{-1} and 1415.75 cm^{-1} for the treated jute fiber, 1429.25 cm^{-1}, 1330.88 cm^{-1} and 1236.37 cm^{-1} for the untreated kenaf fiber and 1516.05 cm^{-1} for the treated kenaf fiber are characterized as the C-H bending bond structure of the functional group of alkanes. The decreased in the absorption in the peak were due to removal of cellulose, hemicellulose and lignin.

Lastly, the peak at 1029.99 cm^{-1} for the untreated jute fiber, 1026.13 cm^{-1} for the treated jute fiber, 1028.06 cm^{-1} for the untreated kenaf fiber and 1039.63 cm^{-1} for the treated kenaf fiber are characterized as the C-O stretching bond structure of the functional group of alcohols. It can be seen that in the untreated jute fiber, the peak was brought deeper for the treated jute fiber and for the untreated kenaf fiber the peak was almost diminished in the treated kenaf fiber. The different behaviors of the fibers tend to remove cellulose, hemicellulose and lignin and change in bending or stretching structure. A small peak at 904.61 cm^{-1} for the untreated kenaf fiber is characterized as C-H "oop" bond structure of the functional group for aromatic. The peak was totally disappeared that showed alkaline treatment removed the aromatic smell and the lignin structure of kenaf fiber.

Alkaline treatment in general caused reduction of cement materials inside the fiber structure that followed by the removal of unstable materials with rupture bonds [5]. Furthermore, crystalline structures of fibers were obtained due to chemical treatment [16]. The alkaline treatment caused the change in the color of natural fiber. Change in the color of natural fiber was due to removal of natural dye inside the natural fiber materials. Besides that, due to change in the structure and surface roughness of the fiber, the natural frequency it can absorb for vibration and sound were different than the untreated fiber. Addition and

removal of certain molecule such as hydrogen and oxygen were also caused changes in the vibration and sound absorption. The addition in the fiber caused swelling in the fibers. Moreover, the fiber may either be more damping or less damping (more stiffness or less stiffness) depending on the behavior of fiber reaction to alkaline treatment. Other than that, due to changes in the molecular bond structure of O- or H- bond either by stretching or bending, the fiber may be more brittle or ductile as it reacted with alkaline based. The stretching and bending also caused tortuosity inside the fiber structure. Table-3 and Table-4 show the characterization of jute and kenaf using infrared spectral analysis

Table-3. The characterization of jute using infrared spectral analysis.

Bond - Functional Group	Untreated jute fibre (Wavenumber, cm^{-1})	Treated jute fibre (Wavenumber, cm^{-1})
O-H stretching , Free hydroxyl - Alcohol, Water, Phenols	-	3859.56, 3732.26
O-H stretching , H-bonded, - Alcohol, Water, Phenols	3304.06	3323.35
C-H stretching, O-H stretching - Alkanes (CH; CH_2; CH_3), carboxylic acids	2910.58	2910.58
C≡C stretching, C≡N stretching – Nitriles, Alkynes	2451.53, 2235.50, 2071.55, 1961.61	2436.09, 2277.93
C=C stretching - Alkenes (lignin)	1614.42	1641.42
C-H bending - Alkanes (cellulose; hemi-cellulose; lignin)	1371.39, 1305.81	1523.76, 1415.75
C-O stretching - Alcohol (cellulose; hemi-cellulose; lignin), Carboxylic acids, Esters, Ethers.	1029.99	1026.13

Table-4. The characterization of kenaf using infrared spectral analysis.

Bond - Functional Group	Untreated kenaf fibre (Wavenumber, cm^{-1})	Treated kenaf fibre (Wavenumber, cm^{-1})
O-H stretching , Free hydroxyl - Alcohol, Water, Phenols	3792.05	3869.20, 3711.04, 3624.25
O-H stretching , H-bonded, - Alcohol, Water, Phenols	3332.99	-
C-H stretching, O-H stretching - Alkanes (CH; CH_2; CH_3), carboxylic acids	2900.94	-
C≡C stretching, C≡N stretching – Nitriles, Alkynes	2411.02	2445.74, 2266.36
C=C stretching - Alkenes (lignin)	1604.77	1695.43
C-H bending - Alkanes (cellulose; hemi-cellulose; lignin)	1429.25,1330.88,1236.37	1516.05
C-O stretching - Alcohol (cellulose; hemi-cellulose; lignin), Carboxylic acids, Esters, Ethers.	1028.08	1039.63
C-H "oop" – Aromatic ring	904.61	-

CONCLUSIONS

In the nutshell, change in the structure and the removal of outer cell layers, cellulose, hemicellulose, lignin, waxes and other impurities during the alkaline treatment affected the improvement on the adhesion interface of fibers. It creates rough, void and tortuous structure of the fibers that create different natural frequencies that allowed different vibration and sound absorption. The rough surfaces caused better adhesion between fiber and polymers.

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