SURFACE FUNCTIONALIZATION OF KENAF FIBERS WITH LAUROYL CHLORIDE: EFFECTS OF ALKALINE PRETREATMENT METHOD

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Surface functionalization of cellulose fibers is the current focus of research seeking to develop composite materials for various applications. One reason is the low compatibility of natural cellulose-based fibers with thermoplastic matrices for the production of wood-plastic composites. In this research, kenaf fibers (KF) were esterified with lauroyl chloride. Before the esterification reaction, two alkaline pretreatment methods were used: Bain-Marie at low temperature, and at high temperature and pressure in the digester. SEM results showed a smoother surface morphology after esterification. ATR-FTIR results confirmed the substitution of hydroxyl groups of cellulose with lauroylate functional groups. Increasing the carbon content in EDX spectroscopy further supported the successful esterification of kenaf fibers, which is in accordance with ATR-FTIR findings. Based on ATR-FTIR and EDX results, the Bain-Marie pretreatment method was more effective for the esterification reaction. According to the XRD results, the crystallinity index of the fibers slightly increased after esterification reaction. However, the fibers pretreated in the digester had a higher crystallinity index, which was related to efficient removal of amorphous regions due to higher temperature and pressure used in the digester process. This research showed that alkaline pretreatment in Bain-Marie was more effective for the surface functionalization of cellulose fibers than the digester process. These results can be applied in future research works for esterification of cellulose fibers.

Keywords: kenaf fibers, lauroyl chloride, esterification, digester, pretreatment

INTRODUCTION

Wood-plastic composites (WPC) generally comprise a thermoplastic polymer, such as polyethylene, polypropylene, PVC, polylactic acid, etc., as a matrix, and a wood-based filler as reinforcement. Wood flour, mainly of softwood, has been used as a reinforcing agent in WPC. Wood fibers can also be replaced by non-wood ones, such as hemp, jute, sisal, and kenaf fibers.¹ Natural fiber-reinforced thermoplastic composites are one of the common methods for obtaining special composites, with desirable properties, that have attracted the attention of many researchers. Natural fibers offer advantages over synthetic ones, such as low cost, low density, less wear in machines, acceptable process strength, biodegradability, and renewability. Hemp, jute, sisal, and kenaf are the most common natural fibers used in the manufacture of thermoset or thermoplastic composites.²

Kenaf fibers (Hibiscus cannabinus L.) have

attracted the researchers's attention in the past decades.³⁻⁶ Kenaf plants can absorb carbon dioxide at a rate of around 1.5 tons per ton of fiber, which is an environmentally friendly absorption.⁷ Kenaf fibers are considered as good candidates for the reinforcement of biodegradable polymer composites.⁸

It has been established that the fiber-matrix interface plays an important role in determining the physical and mechanical properties of natural fiber reinforced composites.⁹ Most of the natural fibers derived from plant resources are mainly composed of cellulose and hemicelluloses, with a hydrophilic strongly structure, while thermoplastic matrices exhibit hydrophobic chemical structure.¹⁰ Thus, kenaf fibers are largely incompatible with most thermoplastic matrices and cannot make strong fiber-matrix interfaces.^{11,12} In this regard, during the preparation of natural fiber reinforced plastic

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composites, it is very important to adapt the fibers to the polymer matrix, which is mainly hydrophobic. For this purpose, two methods are generally used to improve the mixing of fibers and matrix. One is the use of compatibilizers, and the other is the chemical modification of fibers. Various compatibilizers have been reported in the literature to improve fiber-matrix compatibility, the most important of which is maleic anhydride.^{13,14} Chemical modification is also used to modify the surface of fibers, increase hydrophobicity and improve their miscibility with the matrix.^{15,16} Materials used for surface modification of fibers include caustic soda. potassium permanganate, acetic anhydride, and benzoyl peroxide.¹⁷

One of the substances that can be used for the chemical modification of natural fibers is lauroyl chloride. It has a long alkyl chain (11 carbons) and an acyl group, which can directly react with the cellulose hydroxyl group.¹⁸ In recent years, several studies have focused on modifying cellulose fibers with lauroyl chloride to enhance their properties for different applications.^{19,20} Cellulose nanofiber films were modified with esterifying fatty acids for food packaging applications.²¹ Lauroyl chloride was also used in previous studies to modify lignocellulosic fibers, such as bagasse, and nanocellulose.^{22,23} These studies collectively highlight the potential of modifying cellulose fibers with lauroyl chloride for various applications. To the best of our knowledge, there is no report published on the modification of kenaf fibers with lauroyl chloride so far.

The purpose of this research has been to pretreat and modify kenaf fibers with lauroyl chloride to increase the interactions between the fibers and the matrix. It is expected that pretreatment can remove hemicelluloses, lignin or other impurities from the surface of the fibers, resulting in a rougher surface, which can enhance the reaction of lauroyl chloride with the hydroxyl groups of cellulose. For this purpose, the fibers were pretreated with alkali and then reacted with lauroyl chloride, and the formation of hydrophobic groups on their surface was investigated by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), elemental analysis and energy dispersive X-ray scattering (EDX) techniques. Also, the effect of alkaline pretreatment on the morphology and crystallinity of kenaf fibers was evaluated by scanning electron microscopy (SEM) and X-ray

diffraction (XRD) analyses.

EXPERIMENTAL Materials

Ethanol was provided by Taghtir Khorasan Production Company (Mashhad, Iran). Acetone, nitric acid, acetic acid, sodium chloride and toluene were purchased from Dr. Mojallali Company (Dr. Mojallali Industrial Chemical Complex Co., Tehran, Iran). Lauroyl chloride and pyridine were provided by Merck (Germany).

Preparation, biometrical properties and moisture content of kenaf fibers

Kenaf sacks made from natural kenaf fibers were obtained from KHB Fibres Ltd., Dhaka, Bangladesh – the leading exporter and supplier of natural fiber products in Bangladesh. A hammer shredder was used to convert kenaf sacks into fibers (Fig. 1). The crushed fibers were then passed through a sieve with a pore size of 6 mm to obtain short fibers.

The method proposed by Franklin (Franklin, 1954)²⁴ was used to separate the fibers. At least 50 fibers were separated and their dimensions, including average fiber length and diameter, were measured from the images acquired by a light microscope, equipped with an Olympus microscope camera (Japan).

The moisture content of kenaf fibers was determined according to TAPPI standard T4120m-9, using Equation 1:

$$M_{\sigma}(\%) = \frac{M_{h} - M_{0}}{M_{0}} \times 100 \tag{1}$$

where M_c is the moisture content, M_o and M_h are the dry and wet weights of the samples.

Lignocellulosic content of kenaf fibers

The oven-dried kenaf fibers were ground and screened by mesh 200, then subjected to a Soxhlet extractor to extract both water-soluble and ethanol-soluble components for 24 h. The extractives and lignin contents were measured according to T204-cm-07 and T222-om-06 TAPPI standards, respectively. The holocellulose and cellulose contents were determined according to T264-cm-7 and T264-om-88 standards, respectively. The extractive-free component of kenaf was prepared according to T264cm-7 standard.

Alkaline pretreatments and chemical modification of kenaf fibers

Alkaline delignification of kenaf fibers was performed to provide more reactive sites on the surface of kenaf fibers in the esterification reaction. The fibers were extensively washed with tap water, passed through a sieve with 20 and 200 mesh screens, washed with distilled water and finally, dried in an oven. Alkaline pretreatment was performed by two different methods: in a digester (A), and in a Bain Marie water bath (B), as described below, under the conditions provided in Table 1: (A) In this method, a digester apparatus (Ghoms Wood Machinery Design and Production Company) was used for alkaline pretreatment. About 50 g of dried ground kenaf fibers were pretreated by NaOH (8% w/w) at a liquid:solid ratio of 5:1 in the pulp digester at 110 °C for 5 min;

(B) In this method for alkaline pretreatment, an Erlenmeyer flask, containing ~50 g of the dried ground

kenaf fibers and NaOH (6% w/w), at a liquid:solid ratio of 5:1, was placed in a Bain Marie water bath, operating at 110 °C for 3 h. The Erlenmeyer flask content was passed through vacuum filtration and then extensively washed with distilled water until the pH of the exit water became completely neutralized.²⁵



Figure 1: Kenaf sack texture before (a) and after (b) crushing, and optical microscopic images of kenaf fibers with 10x magnification (c, d)

Table 1
Pretreatment type and condition for the samples prepared

Sample	Pretreatment	Pretreatment temperature (°C)/	Chemical
	method	Time	modification
KF	-	-	-
A-KF	Digester (A)	110, 5 min	-
B-KF	Bain Marie (B)	110, 3h	-
MKF	-	-	Lauroyl chloride
A-MKF	Digester (A)	110, 5 min	Lauroyl chloride
B-MKF	Bain Marie (B)	110, 3 h	Lauroyl chloride

The pretreatment method and the conditions applied for the samples prepared in this study are listed in Table 1. Unmodified kenaf fibers are abbreviated as KF, the pretreatment method as A or B, and modified fibers are abbreviated as MKF.

For the chemical modification with lauroyl chloride, 18 mL of toluene, 1 mL of lauroyl chloride and 1 mL pyridine per gram of dry fibers were added in a three-necked round bottom flask placed in an oil bath, and the reaction was carried out for 2 h at 95 °C under reflux. The flask contents were then vacuum filtered and the fibers left on the funnel were washed

several times with ethanol to remove the unreacted lauroyl chloride. Finally, the modified fibers were dried in an oven at 50 $^{\circ}$ C.^{23,26,27}

Characterization of modified fibers ATR-FTIR spectroscopy

The FTIR spectra of the samples were recorded on a Perkin Elmer spectrometer (Frontier, Germany), in the range 4000-600 cm⁻¹, with a resolution of 4 cm⁻¹.

XRD analysis

The structure of the modified and unmodified kenaf

fibers was assessed by an X'Pert diffractometer (PW-1730 Philips). XRD patterns were recorded between 2 θ angles of 10-80° under Co-K α lamp at the wavelength of 1.7889 Å, a current of 30 mA, and an electrical potential difference of 40 kV. Samples were firstly cast on a silicon substrate and then subjected to X-ray. The crystallinity index (CI) was estimated using Segal's method,²⁸ using the following formula:

$$CI(\%) = \frac{\mathbf{I}_{200} - \mathbf{I}_{am}}{\mathbf{I}_{200}}$$
(2)

where I_{200} is the intensity of the 200 peak (at about 22.6°) and I_{am} represents the intensity of the minimum between the two crystalline peaks (110 and 200), which in this work was around 18.6°.

SEM/EDX analysis

The morphology of the unmodified and modified kenaf fibers was investigated by an SU3500 SEM (Hitachi, Tokyo, Japan), equipped with an EDX system. Before imaging, the samples were coated with a thin layer of Au. EDX was used to monitor the atomic distribution (carbon and oxygen) before and after modification of kenaf fibers.

Elemental analysis

The amount of carbon and oxygen atoms and their ratio after alkalization and esterification was measured using a CHNS elemental analyzer (Elementar, Germany).

Statistical analysis

Experimental data were plotted using MATLAB 2016 software. Statistical analysis of data was performed using Minitab 21.1.0 software and a P-value less than 0.05 was considered as significant difference in the case of mean comparison between groups.

RESULTS AND DISCUSSION

Lignocellulosic composition and moisture content of kenaf fibers

The lignocellulosic composition of the neat kenaf fibers is presented in Table 2. As can be seen, cellulose and holocellulose are the main components of the fibers. However, 15% lignin is also present, which is responsible for the brown color of the fibers. The results are in accordance with those reported in other studies.^{29,30} Slight differences in the cellulose and lignin contents may arise from the source of kenaf fibers, genetic variation, environmental growing conditions or harvesting and processing methods.

The moisture content of the kenaf fibers was found to be $8.5\pm0.5\%$. This result is in accordance with the previously reported values for kenaf fibers.³¹ The value obtained for the moisture content indicates the hydrophilicity of the fibers, unfavorable which is for mixing and thermoplastic reinforcement of matrix composites.

Fiber morphology

The average length and diameter of neat kenaf fibers were measured from the optical microscopic images. The average length and diameter were 7.7 ± 2.5 and 0.6 ± 0.2 mm, respectively.

SEM micrographs of the kenaf fibers (KF), lauroylated kenaf fibers (MKF) and lauroylated alkaline pretreated kenaf fibers (A-MKF and B-MKF) are shown in Figure 2. It can be seen that the surface morphology of the kenaf fibers without pretreatment did not significantly change after chemical modification with lauroyl chloride (Fig. 2 a, b), but the surface morphology of the lauroylated kenaf fibers was smoother after alkali pretreatment (Fig. 2 c, d). Indeed, the lauroylated alkali-treated fibers were more regular than untreated fibers. This may be attributed to the partial dissolution of the amorphous parts (waxes, hemicelluloses, pectins, and lignin) of kenaf fibers after alkali treatment.³² These findings proved the proper surface coverage of the alkaline-treated fibers with ester groups of the lauroyl chain.

	Table	2		
Chemical com	position of	of neat	kenaf	fibers

Component	Content (%)
Holocellulose	81.5
Cellulose	63
Hemicelluloses	18.5
Lignin	15
Extractives	2.8
Ash	0.7



Figure 2: SEM images of KF (a), MKF (b), A-MKF (c) and B-MKF (d)

EDX analysis

The EDX spectra of the samples, together with the percentage of carbon and oxygen, before and after esterification, are presented in Figure 3 and Table 3, respectively. The results show that the C/O ratio increased after esterification. However, alkali-pretreatment of kenaf fibers prior to lauroylation (A-MKF and B-MKF) increased the C/O atomic ratio to higher values compared to the sample without pretreatment (MKF). The Bain Marie bath caused a significant increase in the C/O ratio, compared to the digester method. The visible increase in the carbon content of B-MKF proved the efficient esterification of alkaline pretreated fibers in the Bain Marie bath. It was reported that increasing the carbon content of cellulose after the esterification reaction arises

from the replacement of hydroxyl groups by ester groups.³³ The results of our work are consistent with those of other studies. Alkaline treatment increases the amount of cellulose exposed on the fiber surface, which results in increasing the number of possible reaction sites.³⁴ These findings were further supported by FTIR and XRD analyses.

ATR-FTIR results

ATR-FTIR spectroscopy was applied to investigate the effect of lauroylation on the structure of kenaf fibers. ATR-FTIR spectra of pristine kenaf fibers (KF), chemically modified kenaf fiber (MKF), and modified alkali pretreated kenaf fibers (A-MKF and B-MKF) were presented in Figure 4.

Samula		E	Clement (wt%)
Sample	Carbon	Oxygen	Carbon to oxygen (C/O) ratio
KF	51.78	48.22	1.07
MKF	52.36	47.19	1.11
A-MKF	54	45.95	1.18
B-MKF	63.60	36.4	1.75

 Table 3

 EDX elemental analysis of unmodified and modified kenaf fibers



Figure 3: EDX spectra of KF (a), MKF (b), A-MKF (c) and B-MKF (d)



Figure 4: ATR-FTIR spectra of modified and unmodified kenaf fibers

The presence of bands at 3200-3500 cm⁻¹ in all the samples is attributed to the –OH stretching vibration. Pristine kenaf fibers presented an absorption band at 2922 cm⁻¹, belonging to the C– H stretching vibration of methyl and methylene groups. The characteristic bands at 1726, 1605 and 1032 cm⁻¹ are ascribed to C=O, C=C (in the aromatic ring) and C–O stretching vibrations, respectively. These characteristic bands are related to the presence of lignin and hemicelluloses in the structure of kenaf.^{12,35}

In order to check the effect of pretreatment on the chemical structure of kenaf fibers, the ATR-FTIR spectrum for the alkaline pretreated kenaf fibers (A-KF and B-KF) was also collected. Results showed that the bands mentioned, which indicate the presence of lignin and hemicelluloses, disappeared after alkaline pretreatment. This result is in accordance with the SEM micrographs, which show a smoother surface for the pretreated modified kenaf fibers.

The band appearing in the range 2910-2860 cm⁻¹, for esterified fibers, originated from the stretching vibration of the methylene group (– CH_2 –) in the structure of lauroyl chloride.¹² The

absorption band at 1750 cm⁻¹ in the esterified samples is related to the stretching vibration of the carbonyl group belonging to the ester groups of lauroyl chloride substituted on the surface of the kenaf fibers.³⁵ For lauroylated kenaf fibers, the intensity of the absorption band for the hydroxyl group (~3300 cm⁻¹) significantly decreased, indicating the successful substitution of lauroyl groups on the surface of kenaf fibers.³⁵ Of the two methods used for pretreatment, B-MKF exhibited a lower intensity of the hydroxyl group. This finding is in accordance with the EDX results and indicates that the pretreatment with the Bain Marie water bath was more effective for the esterification of kenaf fibers.

XRD results

XRD patterns of the untreated and treated kenaf fibers are presented in Figure 5. Two visible peaks appearing at 2θ around 18.6° and 22.6° in all the samples were attributed to the (110) and (200) planes of the cellulose I structure, respectively.^{36,37}



Figure 5: XRD results of unmodified and modified kenaf fibers

Sample	Crystallinity index, CrI(%)
KF	79.7
MKF	81.1
A-MKF	82.9
B-MKF	81.5

 Table 4

 Crystallinity indices (CrI) of unmodified and modified kenaf fibers

XRD patterns of unmodified (KF) and modified kenaf fibers (MKF, A-MKF and B-MKF) do not show significant changes in the patterns.

This indicates that the esterification reaction does not affect the crystalline structure of cellulose. Thus, it can be concluded that the esterification reaction mainly occurs in the amorphous areas of the cellulosic fibers of kenaf and indicates that crystalline regions are less accessible for reacting with lauroyl chloride.

The crystallinity indices of cellulose fibers (CrI) calculated using Segal's method for KF, MKF, A-MKF and B-MKF are presented in Table Results showed that alkalization 4. and esterification did not influence the crystalline nature of the kenaf fibers. Esterified kenaf fibers showed only a slightly higher crystallinity index in comparison with pristine kenaf fibers. This result may be related to the hydrophobic interaction between the long hydrocarbon chains of the grafted lauroylate functional groups, as well as the method used for pretreatment.³⁸ Among the samples, A-MKF showed the highest crystallinity index (82.9%). This may be explained by the method used for the alkaline pretreatment. The digester apparatus, which was used for pretreatment of A-MKF, worked at higher temperature and pressure. These harsh conditions removed lignins and disrupted the amorphous phases of the cellulosic materials of kenaf fibers. Thus, the remaining cellulosic content after alkaline pretreatment in the digester may contain higher crystalline areas, compared to the sample treated by the Bain-Marie method, which used lower temperature and pressure.

CONCLUSION

This research deals with the lauroyl chloride esterification of kenaf fibers. Two alkaline pretreatment methods were used and the results showed that the Bain-Marie method is more effective for the esterification reaction. ATR-FTIR results confirmed the substitution of hydroxyl groups of cellulose with lauroylate functional groups. The surface morphology of the fibers was smoother after esterification. XRD results showed that the esterification reaction slightly increased the crystallinity index of the fibers, but fibers pretreated in a digester had a higher crystallinity index, which was related to the higher temperature and pressure used in this process. The results of this work show that alkaline pretreatment can be used as an effective method to increase the efficiency of the esterification reaction of cellulose fibers. This research also showed that alkaline pretreatment in Bain-Marie at low temperature is more effective than in the digester at high temperature and pressure. These results can be applied in future research works on the esterification of cellulose fibers to develop natural fiber reinforced plastic composites.

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