Study of the effect of surface treatment of kenaf fiber on chemical structure and water absorption of kenaf filled unsaturated polyester composite

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Abstract. In this research, unsaturated polyester/kenaf fiber (UP/KF) composites was prepared by using hand lay-up process. The effect of surface treatment of kenaf fiber on mechanical properties of kenaf filled unsaturated polyester composites were studied. Different concentrations of stearic acid (SA) were applied, i.e. 0, 0.4, and 0.8 wt%. The Fourier transform infrared (FT-IR) spectra of kenaf fiber shows high intensity of the peak around 3300-3400 cm⁻¹, which is attributed to the hydrogen bonded O-H stretching. However, the treated kenaf fiber with stearic acid shows the elimination of O-H group and this peak is vanished. This is due to the reaction of (-COOH) group of stearic with (-OH) group of kenaf fiber. The results of water absorption study revealed that increasing the loading of KF in the composite will result is increasing the tendency to absorb water. However, the absorption was significantly decreased after treatment with stearic acid as well as the time to reach to the equilibrium state.

1. Introduction
Recently, there is a drastic growing attention in utilization of natural fibers materials as reinforcing component in thermoplastics as well as thermosets. Natural fibers seem to be a superior material which has emerged as an abundant and sustainable replacement for the nonrenewable and expensive synthetic fibers. The advantages of natural fibres overtraditional reinforcing materials such as lower density, less abrasive, acceptable specific strength and stiffness, greater deformability and less irritation to skin and respiratory [1]. Several natural fibers have been used as a reinforcement in composites materials for advanced applications such as banana, sisal, oil palm, jute, kenaf and coir. Among different types of fibers, kenaf fiber has been widely explored over the past several years [2]. Kenaf (Hibiscus cannabinus, family MalvaceaeL.) is a perennial plant herb. Kenaf is a plant heat-season annual lane and can be used for several industrial applications. Kenaf fiber has several The
attractive features over other traditional reinforcement materials, as such it has gained research interest as a natural filler in polymer composites. The availability of kenaf fiber in Asia is more and it is abundantly available, environmental friendly, renewable, and cheap. Moreover, it has advantages the absence of silica content, which is critical in the reduction of abrasiveness to processing equipment. The biodegradability of kenaf fiber has a great contribution to a healthy ecosystem while their low cost and high performance satisfies the economic concern of manufacturers [3,4].

The greatest challenge in working with natural fiber reinforced plastic composites is their large variation in properties and characteristics with respect to different condition [2]. Bio composite’s properties are influenced by a number of variables, including the fiber type, environmental conditions (where the plant fibers are sourced), processing methods, and any modification of the fiber. Recently there has been a surge of interest in the industrial applications of composites containing biofibers reinforced with biopolymers [5]. Another problem is incompatibility to hydrophilic thermoplastic and thermoset matrix weak interfacial strength between natural fiber surfaces and a polymer matrix. This is due to the chemical structure of natural fibers (such as kenaf) which is mainly has hydrophilic moiety (mainly OH), which will cause high polar characteristic. Therefore, it is important to enhance compatibility between the fiber and the polymer matrix in order to obtain a uniform composites with good properties. Several chemical treatments can be done to natural fibers in order to obtain better compatibility [6,7].

Therefore, a number of chemical and physical surface modification studies on a variety of natural fibers have been devoted to understand and improve the interfacial strength between natural fibers and the polymer matrix. Various methods such as corona treatment [8], plasma treatment [9], mercerization [10], heat treatment [11], graft copolymerization [12,13] and silane treatment [10,14] have been reported to investigate the compatibility of natural fiber in polymeric composites, in most cases the results were positive [15-17]. However, these treatments have many disadvantages such as the use of expensive equipment or the use of expensive chemicals. A very attractive treatment is to modify the surface of natural fibers with fatty acids such as stearic acid [18-22]. The principle of this treatment is the carboxyl group of stearic acid reacts with the hydroxyl groups of the fiber through an esterification reaction and, thus, reduces the hydroxyl groups number available to bond with water molecules. One more advantage of treatment with stearic acid is that it is not sensitive to oxidation during the processing temperatures of natural fiber/polymer composites [22-26].

Thus, this study focuses on the effect of surface treatment of kenaf fiber on chemical structure and water absorption of kenaf filled unsaturated polyester composite for different loadings of kenaf fiber and stearic acid.

2. Experimental

2.1. Materials

Kenaf fiber was obtained from Rahamatullah Sdn. Bhd, Malaysia. The kenaf in this study were used in the form of mat. Unsaturated polyesters resin was supplied by Castmesch Technologies Sdn. Bhd. MEKP (solution in dimethyl phthalate) was from Kaumjung Akzo Nobel peroxide Ltd. Stearic acid was purchased from Acidchem International Sdn. Bhd, Malaysia.

2.2. Treatment with stearic acid

In this study, treatment of kenaf fiber by using stearic acid was carried out. Prior to treatment, kenaf fiber mat was cut to 20 cm x 20 cm dimensions. Different concentrations of stearic acid were applied, i.e. 0, 0.4, and 0.8 wt%. Stearic acid was added to water and warm up at 75 °C to form a suspension. Kenaf fiber was immersed in the suspensions containing stearic acid and stirred for 60 min at 70 °C. The treated kenaf fibers were then washed with distilled water until pH=7 by using pH meter. The treated kenaf fiber layers were placed in a conventional oven to dry at 80°C overnight.
2.3. Composite preparation
Initially kenaf mat was cut to 20 cm×20 cm dimensions and treated with different concentrations of stearic acid, this followed by compressing the untreated and treated kenaf fibers with stearic acid using compress machine at 90 °C. The composites formulation is presented in Table 1. Then prior putting to the mold and hand lay-up resin to bottom of the kenaf, then the kenaf was put inside the mold. Resin impregnated into untreated and treated kenaf via hand lay-up method and 2% of MEKP was added as a hardener for all the samples. This followed by separating it from mold using hack saw. The prepared composite was measured and cut to 2.5×20 cm about 13 samples were obtained.

Table 1. Composites formulation table.

| No. | Kenaf mats % | SA % | UP % |
|-----|--------------|------|------|
| UP  | 0            | 0    | 100  |
| KF1 | 10           | 0    | 90   |
| KF2 | 20           | 0    | 80   |
| KF3 | 30           | 0    | 70   |
| KF4 | 40           | 0    | 60   |
| KF1-SA0.4 | 10 | 0.4 | 90 |
| KF2-SA0.4 | 20 | 0.4 | 80 |
| KF3-SA0.4 | 30 | 0.4 | 70 |
| KF4-SA0.4 | 40 | 0.4 | 60 |
| KF1-SA0.8 | 10 | 0.8 | 90 |
| KF2-SA0.8 | 20 | 0.8 | 80 |
| KF3-SA0.8 | 30 | 0.8 | 70 |
| KF4-SA0.8 | 40 | 0.8 | 60 |

2.4. Fourier Transform Infrared Spectroscopy (FT-IR)
Infrared spectra were recorded using a Perkin-Elmer Spectrum 65 Infrared Spectrometer with 10 scans at 4 cm⁻¹ resolutions. Kenaf fiber without treatment, with 0.4% treatment with stearic acid and 0.8% treatment with stearic acid were analyzed directly using an ATR technique within the wave number range of 4000-650 cm⁻¹.

2.5. Water absorption test
Water uptake was determined by soaking the sample in water and measuring the weight periodically. The samples were cut into 25 mm length, 12.7 mm width and 7 mm thickness in accordance to ASTM D5229. The samples were dried until consistent weight was obtained prior to water absorption test. The samples were then immersed in distilled water at room temperature and the weight change monitored as a function of time. All the experiments were done in triplicates. The absorption behavior weighed were studied at every 24 hours and up to 648 hours (27 days) within 5 min of removing from distilled water. The formula used to calculate the water absorbency is shown in Equation 1.

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\text{Percentage of water absorbency} = \frac{(W_f-W_o)}{W_o} \times 100 \%
\]  (1)

Where \( W_o \) = Initial weight of the sample before immersion inside water and \( W_f \) = Weight of wet sample.

3. Results and discussion
FTIR analysis was carried out to study the characteristics of the kenaf fibers, before and after treatment with SA. FT-IR spectrum of untreated KF is shown in Figure 1. The broad peak at 3373 cm⁻¹ is attributed to the hydrogen bonded O-H stretching, whereas the peak at 2923 cm⁻¹ was attributed to the characteristic of C-H asymmetric and symmetric stretching. This is related to the
aliphatic groups in cellulose and hemicellulose. Another peak at 1739 cm$^{-1}$ corresponds to ester carbonyl vibrations from the acetyl, feruloyl and p-coumaryl groups in lignin. A stretching peak detected at 1633 cm$^{-1}$ is attributed to the carbonyl group of the acetyl ester in hemicellulose and the carbonyl aldehyde in lignin. The broad peak at 1252 cm$^{-1}$ that corresponds to C–O vibration [16].

Figure 1. FT-IR spectrum of untreated KF.

The Fourier transform infrared (FT-IR) spectrums of treated KF with 0.4% and 0.8% of SA are shown in Figure 2 and 3, respectively. As can be seen, the intensity of the peak around 3300-3400 cm$^{-1}$, which is attributed to the hydrogen bonded O-H stretching, is vanished after treatment of KF with SA.

The KF treated with SA have a hydrophobic chain of stearic acid molecules which imparts water resistance to the composite. Absorption peak appeared at 2925 and 2853 cm$^{-1}$ are attributed to C-H asymmetric and symmetric of methylene group. The peak at 1715 cm$^{-1}$ is the characteristic band for carbonyl (C=O) stretching. The peak at 1461 cm$^{-1}$ is attributed to C-H bending frequency of hemicellulose. The peak at 1102 cm$^{-1}$ is attributed to C-O-C stretching vibration of cellulose [17].

Figure 2. FT-IR spectrum of treated KF with 0.4% of SA.  
Figure 3. FT-IR spectrum of treated KF with 0.8% of SA.

The treatment of KF with SA undergoes the reaction which is presented in Figure 4. The principle of this treatment is that the carboxyl group (–COOH) in SA reacts with the hydroxyl groups of the
fiber through an esterification reaction and, thus, this treatment reduces the number of hydroxyl groups available for bonding with water molecules. Furthermore, the long hydrocarbon chain of stearic acid (18 carbon atoms) provides an extra protection from water since it is itself quite hydrophobic.

Figure 4. Schematic Illustration of the Reactions SA with KF during treatment.

When composites specimens were immersed into water, the water molecules penetrate and inducing the weight gain. The weight gain was recorded every one day (24 hours) in order to have a better understanding of water absorbency mechanism.

The water absorption of untreated UP/KF composites, UP/KF composites treated with 0.4 wt% of SA and UP/KF composites treated with 0.8 wt% of SA are depicted in Figures 5, 6 and 7, respectively.

Figure 5. Water absorption kinetic study of untreated UP/KF composites.

Figure 6. Water absorption kinetic study of UP/KF composites treated with 0.4% of SA.

It can be seen from the figures that all the composites show similar pattern of water absorption, which is at the beginning of the curve (within 10 days for untreated UP/KF composites, 5 days for UP/KF composites treated with 0.4 wt% of SA and 4 days for UP/KF composites treated with 0.8 wt% of SA) the weight increased sharply indicating the rapid water penetration into the composite.
materials. Then, the water abruption slows down to reach equilibrium stage, i.e. the composite was unable to absorb additional water. This can be due to the presence of KF, which is hydrophilic, which allow the composite to absorb water. However, the effect of SA treatment is clearly obvious from the figures. The reduction in water absorption after treatment with SA can be attributed to the improvement in interfacial adhesion due to reducing of hydroxyl moiety of cellulose in the surface of KF, which has been confirmed by FT-IR results. This would avoid an easy access of water molecule into the treated KF composites.

**Figure 7.** Water absorption kinetic study of UP/KF composites treated with 0.8% of SA.

The water absorbency equilibrium study of UP/KF composites are depicted in Figure 8. It was found that water absorption % of UP was only 1.5% after one day and it remains constant. This can be due to the fact that UP is hydrophobic in nature. The results reveal that increasing the loading of KF in the composite will result is increasing the tendency to absorb water, and 40 wt% loading of untreated KF showed the highest water absorption % which is 14.9 %. This is due to the nature of KF which is hydrophilic that lead to formation of hydrogen bonding between water molecule and hydroxyl moiety of cellulose, hemicellulose and lignin in the cell wall of KF. Thus, as KF loading increases in the composite, the number of hydrogen bonds between the organic molecules and water molecule increase and absorb higher amount of water. water absorption % increased with time and it reached to equilibrium state after 27, 17, and 11 days of conducting the experiment for untreated UP/KF composites, UP/KF composites treated with 0.4 wt% of SA and UP/KF composites treated with 0.8 wt% of SA, respectively. The difference in equilibrium time and water absorption % can be attributed to the effect of treatment of KF with SA as the tendency to absorb water is significantly lower in comparison to that of untreated fibers as the concentration of SA increased. This phenomenon is complementary match with FT-IR results.

It can be seen from the figure that increasing the loading of KF in the composite will result is increasing the tendency to absorb water, and the highest water absorption % is for 40 wt% of KF loading was 14.9%. When composites specimens were immersed inside water, the water molecules penetrate and inducing the weight gain. For all the composites, at the beginning of the curve, the water absorption % increased sharply indicating the rapid water penetration into the composite materials. However, after 10-12 days, the water absorption % was slow indicating that the tendency is less to absorb water as it was reaching the equilibrium state.
4. Conclusion
The major challenge for natural fiber matrix is its affinity to water, it has high absorption to moisture which have serious consequences to its properties. FT-IR analysis shows the elimination of OH group from kenaf fiber after treatment with stearic acid. The water absorption decreased with increasing of stearic acid concentration because stearic acid has modified kenaf fiber into hydrophobic material.

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