Effect of Single and Double Stage Chemically Treated Kenaf Fibers on Mechanical Properties of Polyvinyl Alcohol Film

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The physico-mechanical properties of lignocellulosic kenaf fiber reinforced polyvinyl alcohol (PVA) biocomposite films were investigated. To improve the properties of the biocomposite, kenaf fibers were chemically treated separately in a single stage (with $Cr_2(SO_4)_3{\cdot}12(H_2O)$) and double stages (with $CrSO_4$ and $NaHCO_3$) to improve the adhesion and compatibility between the kenaf fiber and PVA matrix. PVA was reinforced with various compositions of chemically treated kenaf fiber by using a solution casting technique. Microstructural analyses and mechanical tests were subsequently conducted. Scanning electron microscopic analysis indicated that chemical treatment improved the uniformity distribution of kenaf fiber within the PVA matrix. FTIR and XRD analyses confirmed the presence of chromium on the fiber surface. The tensile strength of PVA reinforced with chemical treated kenaf fiber was found to be higher than those reinforced with untreated kenaf. The Young's modulus, flexural strength, and flexural modulus increased with fiber loading for both untreated and treated kenaf fiber reinforced PVA films. The double stage treated kenaf fiber showed better mechanical properties and lower moisture uptake than the single stage treated kenaf fiber.

Keywords: Kenaf fiber; PVA; Biocomposite film; Chromium treatment; Mechanical properties

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INTRODUCTION

Natural fiber reinforced polymer composites are gaining progressive interest in the composite research community and industry due to their renewability, biodegradability, light weight, low cost, easy processing, fiber surface modification, wide availability, and, more importantly, environmental acceptability (Cao *et al*. 2006; Sgriccia *et al*. 2008). Nowadays, various natural reinforcing fillers are combined with synthetic polymers in order to improve the physico-mechanical properties, which can lead to the development of ecological friendly composites in various applications (Choi *et al*. 2006; Yang *et al*. 2006, 2007; Gu *et al*. 2012; Liu *et al*. 2012; Ishak *et al*. 2013). Recently, a wide range of research has been carried out by using agro-based lignocellulosic fiber residues, including wood residues (saw dust and paper mill discards) and agricultural residues (kenaf, coir, palm, jute, abaca, sisal, corn stover, rice husks, rice straw, wheat straw, sugarcane bagasse, etc.), as a replacement for existing synthetic fibers used for reinforcement in the development of biodegradable composites (Choi *et al*. 2006; Jamil *et al*. 2006; Yang *et al*. 2006, 2007; Hetzer and De Kee 2008; Ochi 2008; Ei-Saied *et al.* 2012). The utilization of these undesirable wastes contributes to the reduction of environmental impacts of waste disposal by incineration (Ei-Saied *et al.* 2012). The advantages of using agro-based lignocellulosic fibers include high specific stiffness and mechanical strength, reduced energy consumption, low hardness, recyclability, biodegradability, and no production of hazardous or toxic by-products (Vink *et al.* 2003; Ching and Ng 2014). A tremendous number of publications over the past two decades have agreed that lignocellulosic fibers such as kenaf fiber (Davoodi 2010), pineapple (Mishra *et al*. 2001), and oil palm empty fruit bunch fibers (Khalil *et al.* 2009) can be used as effective reinforcements in thermoplastics and thermosetting materials.

However, the main drawback of reinforcing synthetic polymers with natural lignocellulosic fibers is the interfacial mismatch between the hydrophilic natural fibers and polymer matrix. In general, the use of natural hydrophilic cellulose-based fiber results in irreversible agglomeration and aggregation in polymer matrices. This might be mainly due to the formation of additional intra-and/or inter-molecular hydrogen bonds between the cellulose molecules. Additionally, due to the presence of hydroxyl groups in the cellulose molecules, lignocellulosic fibers are hygroscopic in nature. The high moisture absorption and dimensional changes of the fibers can result in swelling of the manufactured composites (Lei *et al*. 2007; Mirbagheri *et al*. 2007; Ishak *et al.* 2013). The properties and amounts of the reinforcing fiber, matrix type, and matrix-fiber interaction are the main factors that affect the physico-mechanical properties of natural fiber-based biocomposites (Haque *et al*. 2010; Ching *et al*. 2013). Therefore, better dispersion of the reinforcing fibers in the polymer matrix and enhanced interfacial properties of the resulting composites can be attained by modifying surface properties of the fiber. Generally, raw natural fiber is treated with various chemical methods in order to improve the interfacial adhesion between the natural fiber and polymer matrix. Many studies have been conducted to modify the fiber surface by using a suitable chemical treatments (Yang *et al*. 2006; Liu *et al*. 2007; Haque *et al*. 2010; Mir *et al*. 2013).

The aim of the current research was to develop biodegradable lignocellulose fiber reinforced polymer composite films with improved mechanical and barrier properties that can be used for different applications such as membrane, food packaging, agricultural, medical, electronic packaging, *etc*. In this study, kenaf fiber was selected as the reinforcing material due to its biodegradable properties, natural abundance, and minimal effects on the environment. The lignocellulosic base fibers mainly consist of cellulose, hemicellulose, and lignin. Cellulose is a straight chain polymer composed of a linear homopolysaccharide with β-1-4-linkages (Brännvall 2007). Lignin consists of a variety of functional groups, such as aliphatic and phenolic hydroxyl groups, carboxyl and methoxyl groups, and carbonyl groups (Demirbas 2008; Nurfatimah *et al*. 2014, 2015). Hemicellulose is comprised of different monosaccharide units bonded in branched, short chains of around 200 units. Polyvinyl alcohol (PVA), which is a biodegradable, semi-crystalline, and non-toxic water-soluble synthetic polymer, was used as a matrix in this research. In addition to the alkali treatment, the chromium (III) ion was used to modify the fiber surface in order to achieve better interfacial adhesion between the fiber and matrix. In general, chromium is a hazardous heavy metal. However, the chromium (III) salt and complexes are non-hazardous and do not have dramatic effect on the human health (Miretzky and Cirelli 2010). Trivalent Cr(III) salt is about 300 times less toxic than Cr(VI). Moreover, Cr(III) is essential to animals and plants and it plays an important role in sugar and fat metabolism.

The use of Cr(III) is only harmful if it is used in excess since the high dosage of this chemical will cause allergic skin reactions and cancer (Miretzky and Cirelli 2010).

Up to now, there has been a lack of information on the effect of different chemical treatment stages on mechanical properties, moisture absorption, morphology, and crystallinity properties of the modified natural fibre/biopolymer composite. Besides, a lack of comparative analysis also was found in research papers that show the effect of chemical treated kenaf fibers on the mechanical properties, crystallinity, and moisture absorption of the kenaf-reinforced PVA composite film.

In this study, kenaf fiber were treated with alkali, single stage, and double stages treatment before used as reinforment filler to fabricate PVA/kenaf biocomposite films. The properties of biopolymer films reinforced with kenaf fiber treated with various stages of chemical treatments were compared with those reinforced with raw kenaf fiber. The objective of this project was to investigate the effect of different chemical treated kenaf fiber on the mechanical properties, crystallinity, morphology, and moisture absorption of PVA film, which will be useful for packaging materials and membrane applications.

MATERIALS AND METHODS

Materials

Polyvinyl alcohol (PVA) (Kuraray PVA-220S, 87 to 89% partially hydrolyzed) was supplied from Kuraray Co., Ltd. (Singapore). The specific gravity of PVA-220S is 1.27 to 1.31 with a crystallinity of 82%. Kenaf fiber (*Hibiscus cannabinus*) obtained from the Agriculture Department of Malaysia was used as the reinforcing agent. The diameter of the kenaf fiber was 150 µm. Raw kenaf is comprised of 63.5% cellulose, 17.6% hemicellulose, 12.7% lignin, 2.2% ash, and 4% extractives. The chemicals used for the surface treatment of kenaf fibers were hydrochloric acid (HCl) (Labchem Sdn. Bhd.), sodium hydroxide (NaOH) (Chemo Lab, Malaysia), potassium chromium (III) sulfate ($KCr(SO_4)_2$) (Chemo Lab, Malaysia), and sodium bicarbonate ($NaHCO_3$) (J. Kollin Chemical, Malaysia).

Chemical Treatment of Kenaf Fiber

The kenaf fibers were initially collected, cleaned, and naturally dried. Three types of chemical treatments were performed on the kenaf fibers: alkali treatment, single stage treatment (SST), and double stage treatment (DST). First, the kenaf fibers were treated with alkali by immersing the fibers in a 2% NaOH solution at 70 °C for about 2 h. The fibers were then washed and dried to remove excess NaOH.

During single stage treatment (SST), a 4% solution of chromium (III) salt was prepared with an initial pH of 2.5-3 by adding 2 to 3 drops of HCl. The pH became 8 to 9 during the reaction. The kenaf fibers were continuously shaken at 100 rpm inside the prepared solution for 3 hours. The treated fibers were then properly washed by using distilled water, indicating the completion of the SST process.

The double stage treatment (DST) was performed using the same procedure as the SST, with an additional 2-h treatment in a solution of 4% chromium (III) salt solution, plus an additional dosage of $NaHCO_3$ to maintain a final pH of 10. Then the solution, along with the 3-h treated kenaf fibers, was shaken for another 2 h. After the completion of the DST, the fibers were washed properly with distilled water and dried.

Preparation of Kenaf Fiber-PVA Composites

PVA/kenaf fiber composites of various fiber loadings were prepared using a solution casting technique. In order to obtain a final fiber content of 0, 2, 5, 10, 15, and 20% (w/w), the required amounts of untreated and treated kenaf fibers were added to prepared aqueous PVA solutions. The resulting suspensions were vigorously stirred with a magnetic bar at 80 °C for 20 min. The matrix and fiber were mixed carefully in order to prevent water bubbles and voids. The uniformly mixed fiber and PVA were then cast in the petri dish and allowed to dry slowly at room temperature. Once completely dried, the specimen was carefully discharged from the mould and cut into various specimen sizes for testing.

Characterization

Fourier transform infrared spectroscopy

The Fourier transform infrared spectra of both treated and untreated kenaf fiber were recorded on a Nicolet 380 Spectrophotometer. This work was done with co-addition of 200 scans at a resolution of 4 cm^{-1} in order to characterize the chemical change of the fiber upon treatment with NaOH and chromium (III) salt.

X-ray diffraction analysis

X-ray diffraction (XRD) analysis was conducted to identify the crystalline phases of the raw and chemically treated kenaf fiber samples. Experiments were conducted using an X-ray diffractometer (Siemens D5000). A voltage of 40 kV and an anode current of 40 mA were applied. Cu Kα radiation (λ = 0.15405 nm) was used in a continuous scanning mode with a 0.02 step size and a 0.5 second set time for collecting the data in a 2θ scan range of 4° to 80°. The crystal size of cellulose substances was measured using the half-height width of the I_{002} reflection (at ~2θ =22° to 24°). The relative amount of crystalline material in the substance is called the crystallinity index (*CI*), and it can be calculated according to the Segal empirical method as shown in Eq. 1 (Segal *et al*. 1959).

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \tag{1}$$

In Eq. 1, *CI* is the crystallinity index, I_{002} is the maximum intensity of the crystalline fraction, and I_{am} is the low intensity peak of the amorphous region.

Mechanical testing

Different mechanical testing methods were used to characterise the mechanical properties of treated and untreated PVA/kenaf fiber composites. Tensile tests were carried out at a crosshead speed of 10 mm/min using a Shimadzu Universal Tensile Machine (UTM). The dimensions of the specimens used were 100 mm × 16 mm × 1 mm. For each test and each type of composite, five samples were tested. The average and standard deviation values were reported. Static flexural tests were carried out using the same crosshead speed and UTM machine mentioned above following ASTM D790M-93. The dimension of the specimen used was 100 mm × 16 mm × 1 mm.

Scanning electron microscopy

The morphology of both the untreated and treated fiber/PVA composites was examined under an AURIGA Scanning Electron Microscope (SEM). The surface properties and fiber distribution of the biocomposite films prepared under different treatment methods were investigated. The SEM was operated with an accelerating voltage of 15 kV and a working distance of 20 mm. All samples were sputter-coated (50 nm thickness) with gold to provide enhanced conductivity, since the kenaf and the composites were not conductive. The thin gold coating resulted in electron interaction with the inner atomic shells of the samples.

Moisture uptake test

Moisture uptake tests were performed under 75% RH (relative humidity) at 22 °C (Gassan and Bledzki 1997). All specimens for moisture uptake test were preprared with dimensions of 40 mm x 10 mm. Before the absorption experiments, the specimens were thoroughly washed and then vacuum dried until a constant weight was attained. The specimens were taken out from the chamber at predetermine intervals for measurement of weight % changes using an analytical balance.

RESULTS AND DISCUSSION

FTIR Spectroscopic Analysis

Figure 1 shows the FTIR spectra of kenaf fiber before and after various chemical treatment stages. Figure 1(a) shows a broad peak around 3400 cm^{-1}, which can be attributed to the O–H group of raw kenaf fiber. The peak observed at 2920 cm^{-1} corresponds to the C–H group stretching vibration. The regions between 2000 and 1000 cm^{-1} are assigned to the carbonyl group stretching (C=O, 1735 cm^{-1}), C=C stretching of the aromatic ring vibration (1590 cm^{-1}), and the strong C-O band (1050 cm^{-1}) due to the C-O-CH$_3$ group; these bands confirm the presence of lignin structure in the kenaf fiber (Khan *et al*. 2004).

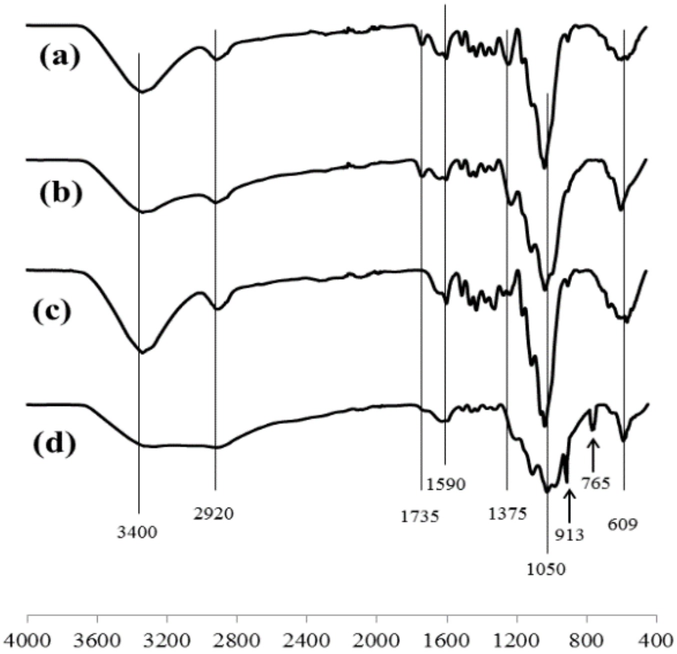


Fig. 1. FTIR spectra of kenaf fiber (a) raw, (b) with NaOH treated, (c) after single stage treatment (SST) and (d) after double stage treatments (DST)

The peak observed in all of the spectra at 1050 cm^{-1} also can be related to C-O-C of glucopyranose ring skeletal vibration (Elanthikkal *et al*. 2010). The peak at 3400 cm^{-1} decreased after alkali treatment (Fig. 1 (b)) as compared to the raw kenaf fiber (Fig. 1 (a)). Chromium (III) treatment diminished the peak intensity of the carbonyl group (Figs. 1 (c) and (d)). The peak intensity of the hydroxyl group was also greatly decreased after single stage and double stage treatment due to bond formation of chromium (III) with –OH groups. Thus, the carbonyl and hydroxyl groups from the cellulose and lignin in kenaf fiber were involved in chromium adsorption mechanisms on the fiber surface. The additional peak at 609 cm^{-1} was due to the bending modes of aromatic compounds of cellulose (Garg *et al*. 2007). The peak involving the carbonyl (1735 cm^{-1}) group disappeared, indicating that the carbonyl and methoxyl groups may be involved in the mechanism of chromium (III) adsorption on kenaf fiber (Suksabye *et al*. 2007). After double stage treatment, the band observed at 913 cm^{-1} may be due to both Cr=O and beta glucosidic linkage, while the peak at 765 cm^{-1} was related to Cr-O (Fig. 1 (d)) (Singh *et al*. 2008). So, this FTIR spectra result demonstrated that the chromium ion had been introduced onto the kenaf fibers after treatment.

XRD Analysis

Figure 2 shows the X-ray diffraction patterns of (a) raw, (b) NaOH-treated, (c) SST, and (d) DST kenaf fiber. As cellulosic natural fibers contain both crystalline (ordered) and amorphous regions (disordered). Thus, the existence of dual features in the fiber is consistent with the presence of ordered and disordered regions (Sharma *et al.* 2013). In the present research, raw and treated kenaf fiber exhibited two main peaks at $2\theta = 14.81°$ and 22.60°, which can be assigned to the (110) and (200) planes of amorphous and crystalline cellulose, respectively (Sharma *et al*. 2013). New, sharp peaks were observed only for DST kenaf fiber at 2θ values of 32°, 34°, 36°, 38°, 40°,41°, and 45°, which correspond to the CrO_2(110), Cr_2O_3(104), Cr_2O_3 (110), Cr_2O_3 (006), Cr_2O_3 (312), CrO_2 (111), and Cr_2O_3 (024) treatments, respectively (Kumar *et al*. 2011; Lin *et al*. 1997; Sousa *et al*. 2005). These peaks are attributed to the adsorption of chromium on kenaf fiber (Fig. 2 (d)), indicating the crystalline nature of DST kenaf fiber. This phenomenon was previously reported in the literature (Kumar *et al*. 2011).

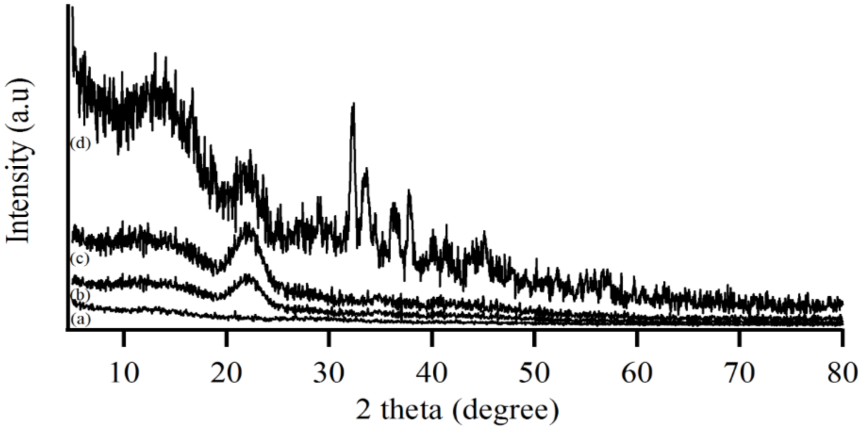


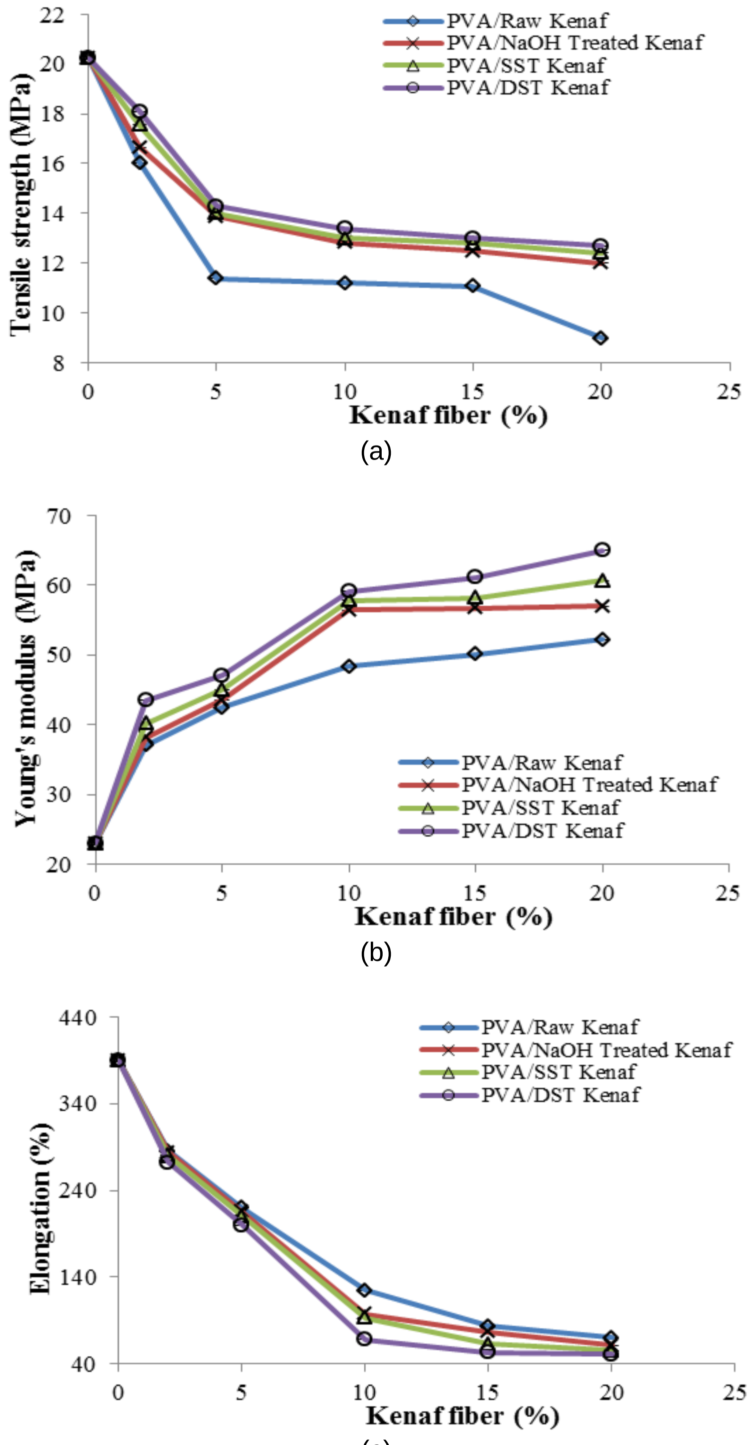
Fig. 2. Effect of chemical treatments on XRD patterns of a) raw fiber; b) NaOH treated fiber; c) single stage treated (SST) fiber and d) double stage treated (DST) fiber

The percentage of crystallinity was calculated using Eq. 1 for both untreated and treated fibers, and the values were found to be 35.5%, 36.3%, 46.6% and 49.2% for raw , alkali treated, SST, and DST kenaf fiber, respectively. The increase in the crystallinity index is attributed to two effects: (a) the removal of some of the amorphous materials and (b) the rearrangement of the crystalline regions into a more ordered structure after all treatments (Li *et al*. 2010). According to Zhang *et al* (2013), the chemical treatments would remove the amorphous region such as lignin and hemicellulose, thus leading to larger spaces between microfibers, rearrangement of microfibers to more ordered structure and formation of new hydrogen bonds between microfibers. Consequently, the crystallinity of the fiber increased with the increasing of treatment stages as confirmed by XRD spectra in Fig. 2.

Tensile Properties

Figure 3(a) shows the variation in tensile strength of raw and chemical treated kenaf fiber reinforced PVA biocomposite films as fiber loadings ranging from 0 to 20 wt%. The tensile strength of the raw kenaf reinforced PVA biocomposites decreased with fiber loading (Thwe and Liao 2002). This indicates that the weak interfacial area between the kenaf and PVA matrix increased with the increase in fiber loading. The poor interfacial adhesion between the kenaf fiber and PVA matrix resulted in decreased tensile strength. The same trend was observed in the tensile strength of treated kenaf reinforced PVA composite films. Generally, there was a change in the structure of the cellulose unit of kenaf due to the chemical treatment that influenced the overall tensile strength. The coupling with basic chromium sulfate salt, sodium bi-carbonate and sodium hydroxide reduced the hydroxyl groups of the cellulose in kenaf. However, PVA reinforced with chemically treated kenaf fibers showed higher tensile strength than the PVA composite with raw kenaf fiber. PVA/kenaf composite films that were reinforced with double stage treated kenaf fiber exhibited the highest tensile strength, followed by composites reinforced with single stage treated kenaf and raw kenaf, respectively. This might be due to the removal of hemicellulose and lignin in the course of chemical treatement, which likely causes the interfibrillar region to be less dense and less rigid, thus allowing the fibrils to rearrange themselves along the loading direction.These arrangements among the fibrils appear to contribute to better load sharing and higher tensile strength in the composite (Joseph *et al*. 2003). Similar result has been observed in the study of chemical treated sisal fibre reinforced polypropylene composites (Joseph *et al.* 2003) and alkali-treated jute fiber reinforced PLA composites (Gunti and Alturi 2014).

The Young's moduli of PVA/kenaf fiber composite films reinforced with treated and raw kenaf fiber at different levels of fiber loading are shown in Fig. 3(b). The Young's moduli increased with an increase of fiber loading (Lewin and Pearce 1985; Joseph *et al*. 2002). Stress propagation between the fiber and the matrix was obstructed due to the creation of partially separated micro-spaces during tensile loading. The degree of obstruction increased with fiber loading, resulting in higher stiffness. Both the alkali and chromium treatments improved the bonding between PVA and treated fiber, thus resulting in an improvement in mechanical properties of the final composite. PVA film reinforced with double stage treated kenaf fiber showed the highest Young's modulus, followed by the composite reinforced with single stage treated fiber and the composite with alkali treated fiber. The biocomposite films with raw kenaf fiber showed the lowest Young's modulus, which is attributed to the poor adhesion between the fiber filler and PVA matrix.



(a)

(b)

(c)

Fig. 3. Effect of various stages of chemical treatments on mechanical properties of PVA/kenaf composite films a) tensile strength; b) Young's modulus; c) elongation at break

Figure 3(c) shows the variation of elongation at break for various PVA/kenaf biocomposite films. The elongation decreased with fiber loading (Novák *et al.* 2002). Raw kenaf reinforced PVA composite films showed the highest elongation values, followed by composite films reinforced with sodium hydroxide treated kenaf, single stage treated kenaf, and double stage treated kenaf, respectively. The reduction of the elongation at break after chemical treatment was due to the increase of stiffness as observed in Fig. 3(b). The decrease of elongation at break after chemical treatment was also observed in previous research (Gunti and Alturi 2014).

Flexural Properties

Figures 4(a) and 4(b) show comparative flexural strength and flexural modulus, respectively, for both raw and treated kenaf fiber reinforced PVA biocomposite films. The flexural strength increased with an increase of fiber loading (Fig. 4(a)). The same trend was observed by other researchers in their works (Joseph *et al*. 2002; Rana *et al*. 2003). Additionally, the flexural strength increased with an increase in chemical treated kenaf fiber content. This result was attributed to the better adhesion between the chemically treated fibre and matrix, as previously discussed. Double stage treated kenaf reinforced PVA films showed the highest flexural strength, while the composites with single stage treated kenaf showed better flexural properties compared to composites reinforced with sodium hydroxide treated kenaf and raw kenaf fiber.

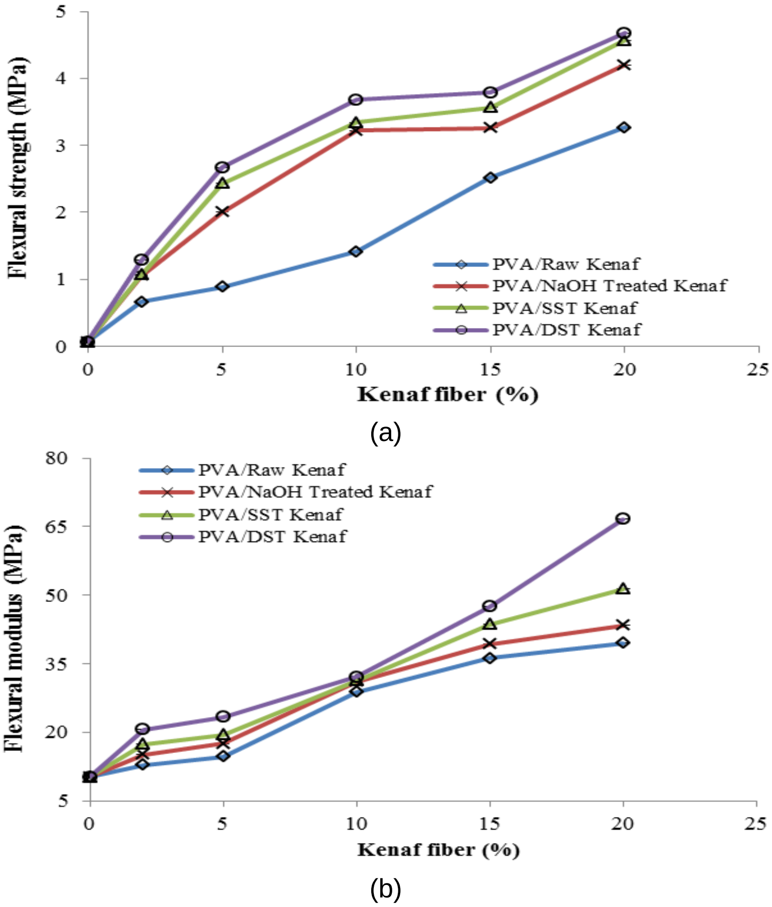


Fig. 4. Effect of various stages of chemical treatments on flexural properties of PVA/kenaf composite films a) flexural strength and b) flexural modulus

The flexural modulus of all the raw kenaf and chemical treated kenaf reinforced PVA composite films increased with an increase in fiber loading, as shown in Fig. 4(b). The flexural modulus of PVA reinforced with 20 wt% double stage treated kenaf fiber was approximately 80% higher than the PVA reinforced with the same amount of raw kenaf fiber. The higher modulus of DST kenaf fiber reinforced composites compared to the raw, alkali treated, and SST kenaf fiber reinforced composites provides evidence of homogeneous distribution of the fiber particles into the matrix and better fiber-matrix interaction.

Mechanism of Chemical Treatments of Kenaf Fibers

The tensile properties indicated that the alkali treatment improved the filler/matrix interaction by removing the hemicellulose and lignin from raw kenaf fiber. Alkali treatment also leads to fibrillation, breaking of the untreated fiber bundle down into smaller fibers through the dissolution of the hemicellulose (Cao *et al*. 2006). This fibrillation increases the effectiveness of the surface area of fibers to contact the matrix (Bisanda and Ansell 1991). Thus, fibrillation resulted in better fiber-matrix interfacial adhesion and improvements in mechanical properties (Joseph *et al*. 2002; Ray *et al*. 2001, 2002). Alkali treatments produce the following reaction:

$$\text{Kenaf-OH} + \text{NaOH} \longrightarrow \text{Kenaf-O- Na+} + H_2O \qquad (6)$$

In the case of treatment of kenaf fibers with chromium (III) salt, Cr^{3+} ions cross-linked with -OH groups from fiber cellulose; the Cr^{3+} ion has the affinity to form a coordination bond with electronegative atoms such as oxygen. In the cellulose anhydroglucose unit, one primary hydroxyl group at C_6 and two secondary hydroxyl groups at C_2 and C_3 are present (Jonoobi *et al*. 2009; Kaewkuk *et al*. 2013). The chromium (III) salt broke the -OH group of carbon 6 and carbon 2 during the reaction, although the primary hydroxyl group is more reactive than the secondary groups. During the chromium single stage treatment, the chromium (III) salts reacted with the cellulose hydroxyl groups. However, the hydroxyl groups were completely shared by chromium atoms during the double stage treatment with basic chromium (III) salt and $NaHCO_3$. This process transformed the hydroxyl groups into a chrome complex, as shown in Fig. 5. Kenaf fibers mainly consist of cellulose and lignin. However, there were no free hydroxyl groups in lignin to react with the chromium salt. Lignin components were dissolved in $NaHCO_3$ during the double stage treatment, increasing the percentage of cellulose in kenaf (Mir *et al*. 2013).

The affinity of chromium for –OH groups in cellulose is moderate at low pH, allowing for the penetration of chrome onto the fiber. The pH value was increased after complete penetration of Cr^{3+} into fiber. The increase of pH value resulted in reactions between chromium (III) salts and kenaf fibers. This phenomenon involved several simultaneous competing reactions. The following reactions occurred between the Cr^{3+} ion of the chrome complexes and the carboxyl -OH groups of the fiber cellulose during the single stage and double stage treatment processes (Hossain *et al*. 2013).

(i) In acidic solution (pH around 2), the Cr^{3+} ion held/adhered to the first OH group of the fiber filler.

(ii) As the pH of the solution was increased, the chromium (III) salt became dissociated at the hydroxyl groups and the second -OH group started to react with chromium. During these reactions, the acidic nature of the solution was decreased while the pH was increased.

(iii) When the pH reached 8 to 9, the reaction was completed by sharing most of the hydroxyl groups with chromium.

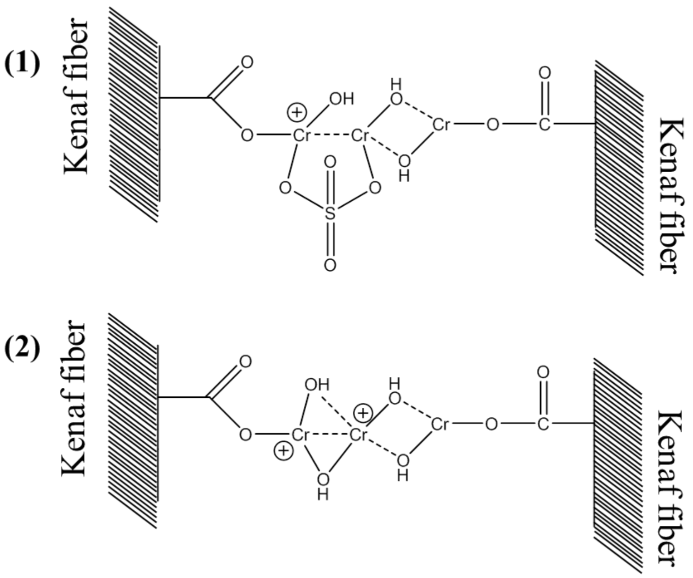


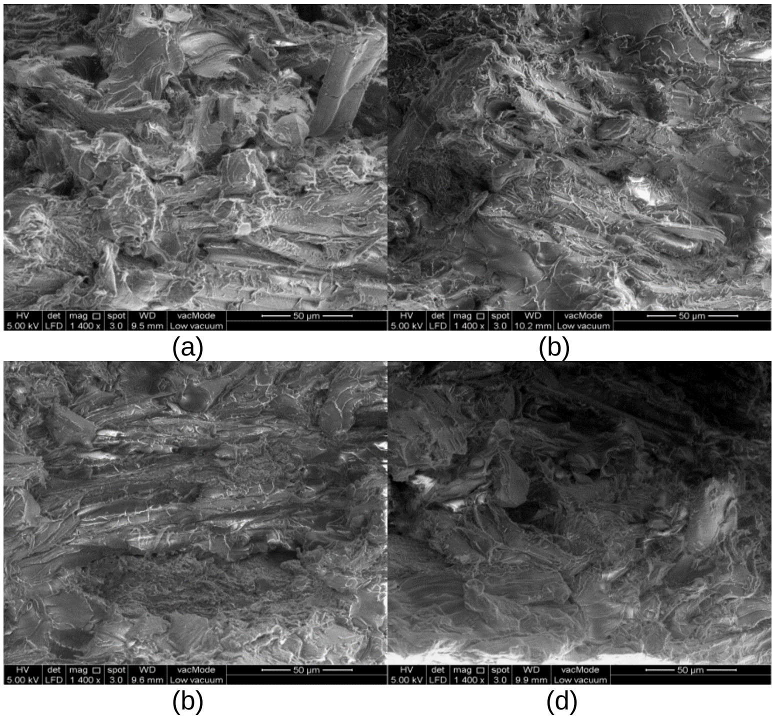
Fig. 5. Chemical reaction between cellulose of kenaf fiber and chromium (III) salt

At the beginning of the single stage treatment of kenaf fiber, the pH of the medium was maintained at around 2 to 2.5. A thin coating was formed on the fiber surface due to chemical reactions between the chromium (III) salts and filler –OH groups. However, the reaction was still incomplete after single stage treatment. During double stage treatment, the addition of $NaHCO_3$ increased the pH to 10, the chromium became fully occupied in reducing hydroxyl groups, and the reaction was thus completed. In this case, an even thicker coating was formed on the fiber surface due to the chemical reactions between the chromium (III) salts, $NaHCO_3$, and the fiber cellulose (Hossain *et al*. 2013).

SEM Morphology

SEM micrographs of tensile fracture surfaces on the PVA/kenaf fiber biocomposite films reinforced with raw and treated kenaf fibers are shown in Fig. 6. In Figure 6(a), scanning electron micrographs of a PVA/kenaf fiber composite with raw kenaf fiber showed a rough surface. Kenaf fibers are easily differentiable due to poor adhesion between untreated kenaf fibers and the PVA matrix. Agglomeration of fibers, micro-voids and fiber pull out traces were found in raw kenaf reinforced PVA film due to strong fiber–fiber interaction. Figures 6(b)-(d) illustrate that the fracture surface of a composite reinforced with treated kenaf fiber was clean and smooth. The pull out traces and micro-voids were found to be substantially decreased in treated composites, indicating that better interfacial bonding between the PVA/kenaf fiber occurred upon chemical treatment of kenaf fiber. The dispersion of kenaf fiber in the PVA was improved after alkali treatment, basic single stage and double stage chromium treatment, as shown in Figs. 6(b), 6(c) and 6(d), respectively.

For composites reinforced with kenaf after two-stage treatment with $CrSO_4$ and $NaHCO_3$, the fibers were found to be well dispersed within the reinforced matrix, and the kenaf fiber was not easily differentiable due to the good adhesion between the kenaf fiber and PVA matrix (Fig. 6(d)). In this study, the chromium (III) ions form complexes with cellulose hydroxyl groups which would decrease the relative abundance of hydroxyl groups for the formation of inter and/or intra molecular hydrogen bonds within the cellulose molecules of kenaf fiber. As a result, the agglomeration of fibers will be reduced and the fiber dispersion in the composite was improved after SST and DST.



(a) (b)

(b) (d)

Fig. 6. SEM micrographs of tensile fracture surfaces of PVA/kenaf fiber biocomposite films with varies types of kenaf fiber: (a) raw, (b) alkali treated, (c) single stage treated (SST) and (d) double stage treated (DST)

Table 1. Moisture Uptake of Various PVA-Kenaf Biocomposite Films

Sample type	Fiber (wt%)	Number of days					
		2	4	6	10	14	18
		Moisture Uptake (%)					
PVA-raw kenaf film	5	2.8	4.8	6.8	9.8	12.8	15.8
	10	2.2	4.5	6.5	9.5	12.5	15.5
	15	2.0	4.2	6.3	9.3	12.2	15.2
	20	1.8	3.9	5.9	9.0	12.0	15.0
PVA-NaOH treated kenaf film	5	2.2	4.2	6.2	9.2	12.3	15.4
	10	2.0	4.0	6.0	8.9	11.9	15.0
	15	1.8	3.8	5.8	8.7	11.7	14.7
	20	1.6	3.5	5.6	8.5	11.4	14.4
PVA-SST Kenaf film	5	1.9	4.0	5.9	8.6	11.9	14.9
	10	1.7	3.7	5.7	8.3	11.5	14.6
	15	1.5	3.5	5.5	8.3	11.2	14.3
	20	1.3	3.3	5.3	8.1	11.0	14.0
PVA-DST Kenaf film	5	1.7	3.8	5.6	8.6	11.6	14.6
	10	1.5	3.5	5.4	8.3	11.3	14.3
	15	1.3	3.2	5.2	8.1	11.0	13.9
	20	1.1	2.9	4.9	7.9	10.7	13.6

Moisture Uptake Properties

The moisture uptake characteristics of various PVA-kenaf biocomposite films are tabluated in Table 1. The moisture uptake (%) increased with the increase of fiber content and duration of exposure days for all the treated and untreated kenaf fiber reinforced PVA composte. PVA/kenaf composite films that were reinforced with double stage treated (DST) kenaf fiber exhibited the lowest moisture uptake properties, followed by composites reinforced with single stage treated kenaf (SST), alkali-treated and raw kenaf (Table 1). The decrease of moisture uptake of the treated samples may be due to the decrease of the hydroxyl groups as well as the the micro-voids in the composites responsible for moisture absorption (Ishak *et al*. 2013; Mir *et al.* 2013). During SST and DST, the chromium (III) ions formed complexes with cellulose hydroxyl groups, which would decrease the relative abundance of free hydroxyl groups for the formation of inter and/or intra molecular hydrogen bonds in the cellulose molecules of kenaf fiber. This resulted in a decrease of fiber agglomeration and improved of fiber dispersion within the PVA matrix, which reduced microvoids (Laxmeshwar *et al.* 2012).

CONCLUSIONS

1. In the present study, raw and chemically treated kenaf fiber-reinforced PVA composite films at various fiber loadings were prepared using a casting technique.
2. FTIR and XRD analyses confirmed the presence of chromium on the kenaf fiber surfaces and the effect of chromium and alkali treatment to increase fiber crystallinity.
3. The chemical treatment on kenaf fiber improved the interfacial bonding between the kenaf fiber and PVA matrix
4. Mechanical properties of the composite films reinforced with double stage chemical treated kenaf improved compared to composites with kenaf treated with alkali and the single-stage treatment.
5. The chemical treated kenaf fiber successfully reduced the overall moisture uptake properties of the PVA/kenaf fiber composite.
6. The introduction of the double stage chemical treatment successfully modified the surface of the kenaf fiber and improved the fiber/matrix adhesion of the final composite for better performance in food packaging and membram applications.

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