

Kenaf Fibre as Reinforcement in Aliphatic-Aromatic Co-polyester Bio-composites.

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ABSTRACT

Natural/bio-fibres are replacing synthetic reinforcements traditionally used for the preparation of the environmentally friendly composites. Composite materials are also replacing conventional materials in various fields due to their ease of process ability. The main objective of this work has been to study the effect of fibre surface treatment on thermal, mechanical and morphological properties of short kenaf fibre/bio-aliphatic and aromatic co-polyester bio-composites. The composites were manufactured by two-roll mill at 140°C with different fibres loading. The short kenaf fibres were treated with sodium hydroxide with various concentrations (4, 6 and 8%) at room temperature. The test specimens were made by compression moulding. The thermals analysis characterised by DMA and TGA. The UTM machine was used for characterised tensile and flexural properties of the bio-composites. The surface analysis of the fibre was characterised by POM, FT-IR and SEM. The treated bio-composite strength is about 45% better compared to untreated fibre bio-composites. Thermal stability of the treated bio-composite was showed higher than that of the untreated bio-composites. The better understanding between fibre and matrix interface was investigated by Scanning Electron Microscopy. The interfacial adhesion of treated fibre composites shows that adhesion was improved between fibre and matrix.

1. INTROCUCTION

Fiber-reinforced plastic compsites, usually made of glass, carbon and aramid fiber reinforced with epoxy and unsaturated polyester, have played a dominant role during the last several decades in various applications because of their high mechanical strength and modulus. However, usage and disposal of these materials, especially glass-fiber-reinforced plastics (GFRP), have been becoming critical because of their non-biodegradability in light of increasing environmental consciousness and demands of legislative authorities related to their recycling. Recently, completely biodegradable composites reinforced with natural fibers, which are called fully green composites, have attracted much interest to solve these problems.

Natural fbers such as jut, flax, ramie, and sisal [1-10] are usually used as reinforcement in green composites; biodegradable resins made of derivatives from cellulose, starch, lactic acid, etc. are applied as the matrix material. The biodegradable property of both components makes them easily disposed of or composted at the ends of their useful lives. Advantages of natural fibers over other reinforcing materials like glass fiber are their low cost, low density, acceptable specific strength properties, enhanced energy recovery, and biodegradability. Although these green composites are not as strong as the traditional GFRP now, the moderate mechanical properties are suitable for applications in non-durable consumer products and packing materials, etc. Moreover, the hollow tubular structure of natural fibers reduces their bulk density. Therefore, composites made from them are expected to be lightweight. However, the main drawback of natural fibers is that their hydrophilic property lowers compatibility with the hydrophobic polymeric matrix during composite fabrications. As a result, the poor fiber-matrix adhesion engenders low mechanical properties. The other disadvantage is the low processing temperatures that must be used because of the possibility of fiber thermal degradation, which might affect composite properties. It is necessary to improve mechanical and other properties in natural fibers before the fabrication of

composites. In addition, the fact that the high cost of biodegradable resins at present might limit their application for green composites should not be ignored, but those costs are expected to fall in the future. The most important feature of green composites is their full biodegradability. The green composites, at the end of their intended life, these composites can be completely resolved into water and carbon dioxide through degradation by microorganisms after burial in the soil, or incinerated without emissions of toxic gases. Consequently, green composites are a renewable, eco-friendly, and biodegradable materials. A study of the fabrication of green composites was initially reported by Herrmann et al [11]. Composites made from ramie and hemp fibers and a blend of starch and polyvinylalcohol (PVA) resin were prepared and named as a bio-composites. The phrase green composite first appeared in Netravali's paper [7, 12]. They developed a coir-fiber-reinforced polyhydroxybutyrate-co-valerate (PHBV) resin composite and investigated its mechanical properties. In this article, the authors report the preparation of kenaf/aliphatic-aromatic copolymer biocomposites by hot press moulding technique, with an objective of improving the interfacial properties between fiber and matrix by fiber surface treatment.

2. EXPERIMENTS

Aliphatic-Aromatic Co-polyester (Ecoflex[®] F) with density 1.25-1.27 g/cm³, melt viscosity 2.5-4.5 ml/10min, melting point 110-120 °C, tensile strength 35-44 N/mm², fracture energy 24 J/mm, were supplied by BASF, South Africa. Kenaf fibre with diameter and length were 40–200 μm (average 100 μm) and 70 mm, were supplied by Fiber & Textile, Port Elizabeth, South Africa. The natural fiber kenaf was treated with various amount (4, 6, 8 wt%) of NaOH at room temperature for 1 hour. These samples were thoroughly washed with distilled water for several times and later dried in an open atmosphere for several days to remove the water. The fiber was further dried in a vacuum oven maintained at 100°C for over night. The dried samples were stored in a vacuum desiccator until they were put to use. Every care was taken to remove water before testing the fibers. The biocomposites were prepared by two roll mill, blended fiber and copolyester composites were loaded stainless mould, the stainless mould was inserted into a hot press kept at 140°C and then the material was pressed to 2 mm in thickness at 10 MPa. After the set heating time, the press was cooled by circulating cold water. The obtained composite board was 150/150/2 mm. The 60wt% fiber weight was kept for all composite sheets. Tensile and flexural specimens were cut from original composite sheets, tests were conducted in accordance with ASTM D 368 for tensile and ASTM D 790 for flexural test on seven samples in order to determine tensile and flexural properties of the biocomposites. The dynamic mechanical properties of the resin and composites were measured using a Mettler Toledo Model DMA 861 under the flexural mode of testing. The dimensions of the specimens were 50 mm x 13 mm x 4 mm. The heating rate was set at 5 °C/min. Perkin-Elmer TGA-7 was used to study the thermal stability of these composites and their constituents. They were heated to 600 °C with a typical rate of 10 °C min⁻¹ under nitrogen flow with at a rate of 20 ml/min⁻¹. The functional group analysis was done using Perkin-Elmer 16 PC FTIR spectrophotometer. Surface morphology of the treated and untreated kenaf fiber was determined by using optical microscope (Olympus, Model Bx50 F4, Japan) with ×50 magnification. The field emission scanning electron microscopy (FESEM) Leo Supra 35VP was used to identify the tensile fracture morphology of the composite samples. The sample surfaces were sputter coated with gold to avoid charging.

3. RESULTS AND DISCUSSION

3.1 FT-IR analysis of kenaf fiber

The Fourier Transform Infrared (FT-IR) spectrum of untreated and treated kenaf fiber (Fig.1) with various alkali treatments are presented in Fig.1. From the Fig.1, shows the presence of hydroxyl, carbonyl, ether groups and absorbed water. The assignment of bands is presented in Table.1. It indicates that the kenaf fiber contains – apart from cellulose-some amount of lignin material. In the case of the FT-IR spectrum of alkali treated fiber, some changes are observed. The peak at 1732 cm^{-1} of kenaf (belonging to the carboxyl group of lignin) has completely disappeared, this tell to us the removal of lignin material. However, the intensity of the peak at 1604 cm^{-1} has lightly increased, indicating the absorption of more water on the surface of the fiber. Moreover, the intensity of the peak around 1032 cm^{-1} , corresponding to C=OH stretching, also increased, the presence of water is still indicated in the spectra. This, in all probability, corresponds to the bound water attached to the cellulose unites, which cannot be removed easily by drying.

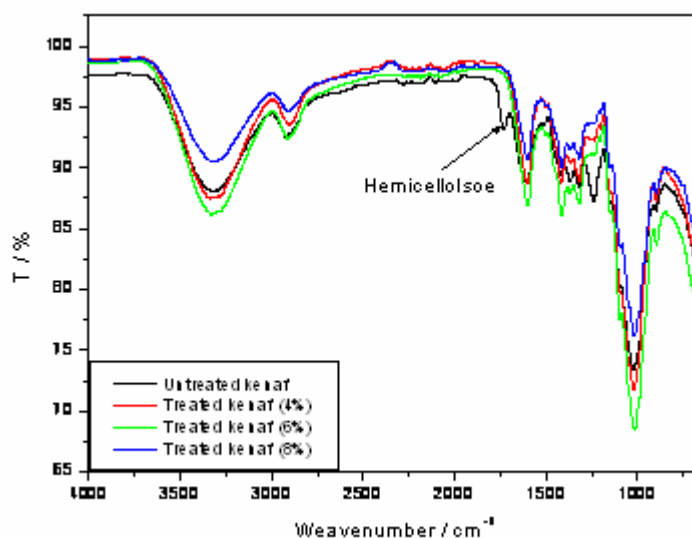


Figure 1: The FT-IR spectrum of untreated and treated kenaf fiber

Table.1 Peak positions and assignments of chemical groups in the treated and untreated kenaf fibers.

Absorption / cm^{-1}	Possible Assignment
3339	O-H stretching
2917	C-H vibration
1732	C=O stretching of Hemicellulose
1604	Absorbed water
1423	CH ₂ symmetric bending
1032	C=OH stretching

3.2 Polarized optical microscopy (POM)

The polarized optical micrograms (POM) of the untreated and treated fiber kenaf is presented in Fig.2. The POM image of the untreated fiber was found to be diffuse (a). This may be a result of the presence of and amorphous hemicellulose layer on the surface of the fiber. However, the microgram images of the alkali treated (with various amount of NaOH) fiber were found to be sharp (b-d). This may be because of the elimination of hemicellulose upon alkali treatment (as shown by the FT-IR spectral analysis at peak 1732 cm^{-1}). The optical micrograms corresponding to 6% and 8% NaOH treatment indicate the formation of microcracks on the surface of the fiber, same observation also SEM micrograms showed.

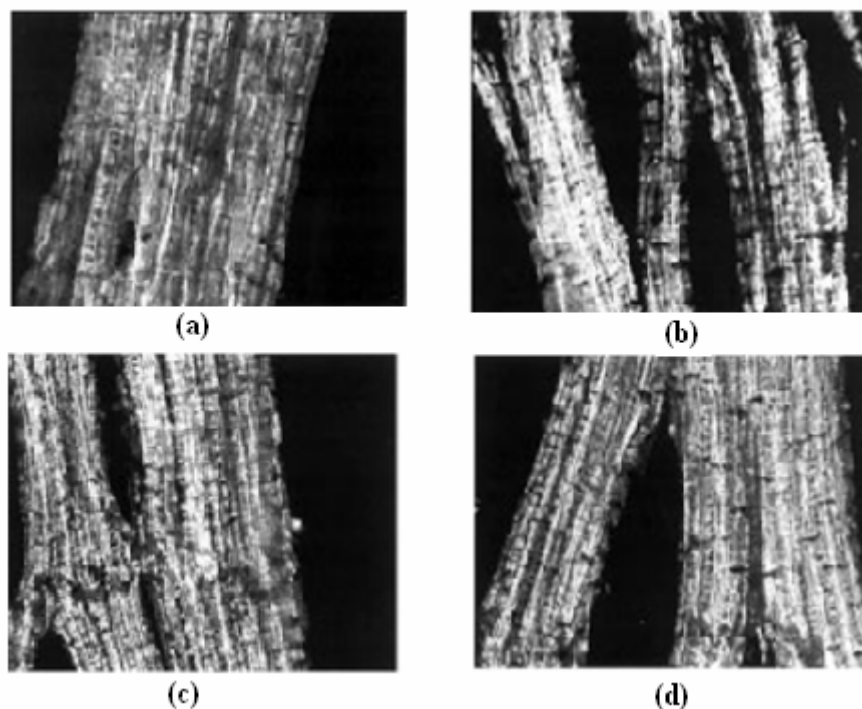


Fig.2. Polarized optical micrograms of kenaf fiber: a) untreated; b) treated 4% NaOH; c) treated 6% NaOH; d) treated 8% NaOH

3.3 Scanning electron microscopy analyses (SEM)

The SEM images of untreated and treated kenaf fiber are presented in Fig.2. From Fig.2(a), untreated fiber at low magnification does not show any hemicellulose or lignin materials, it can be seen at high magnification (Fig.2 (b)), the fiber surface covered all the lignin and other non-cellulosic materials bonded between the fibers. The 8% treated fiber was found at low magnification (Fig.2(e)), it is clearly showed, that the fibers are folded each and other compared to 4 and 6% treated fibers (Fig.2(c-d)). The SEM of alkali treated kenaf fiber at high magnification is shown in Fig. 2 (f). From the figure, it is clearly evident that the fibers has a rough cellular structure. This type of structure might have been formed because of the removal of the lignin. The SEM micrograms corresponding to 8% alkali treatment indicate the formation of microcracks on the surface of the fibers. This observation indicate the total removal of hemicellulose of the fibers at 8% alkali content. The loss of hemicellulose resulted in the loss of polar groups such as COOH or the conversion of polar groups such as COOH and OH, possibly to COO Na and O Na, there by repelling the fibers from each other in the fiber [13]. However, the surface of the alkali-treated fiber was found to be

rough when compared to that of the untreated fiber. This suggests that better bonding between the alkali-treated fiber and the matrix.

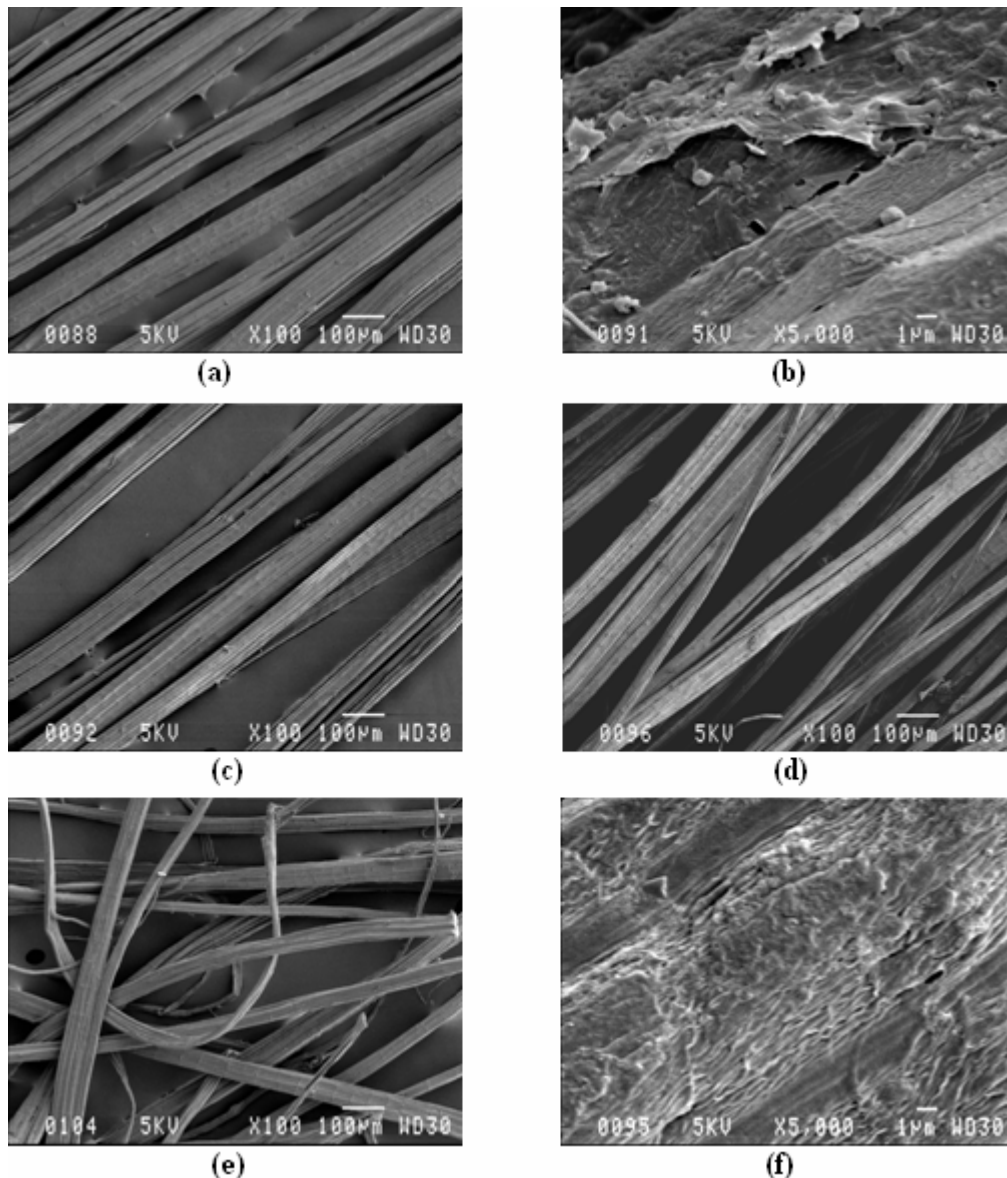


Fig.3 Scanning electron microscopy (SEM) of untreated and treated kenaf fiber at low and high magnifications: a) untreated at low magnification; b) untreated at high magnification; c) 4% alkali treated at low magnification; d) 6% alkali treated at low magnification; e) 8% alkali treated at low magnification and f) 8% alkali treated at high magnification.

3.4 Mechanical properties of the biocomposites

The tensile strength and modulus with and without alkali treated biocomposites of kenaf / copolyester are presented in Fig.4 (a and d). It was found that the tensile strength and modulus of the composites improved after fiber alkali treatment. Compared to that of the untreated composites, the strength and modulus of alkali treated fiber should be increased [14]. This is because the content of hemicellulose and lignin decreased in this system after alkali treatment and thereby increase the effectiveness of orientated cellulose fibre. The 4% alkali treated composites showed maximum tensile strength and modulus. The flexural strength and modulus of the

kenaf / copolyester composites with and without alkali treatment are presented in Fig.4 (c and d). It was found that strength and modulus of the composites increased with increasing alkali treatment up to 4% content than it is decreases. When kenaf fiber was treated with 4% alkali, the bending properties improved. This indicates that flexural properties of kenaf / copolyester biocomposites has the same trends as the tensile properties of the composites.

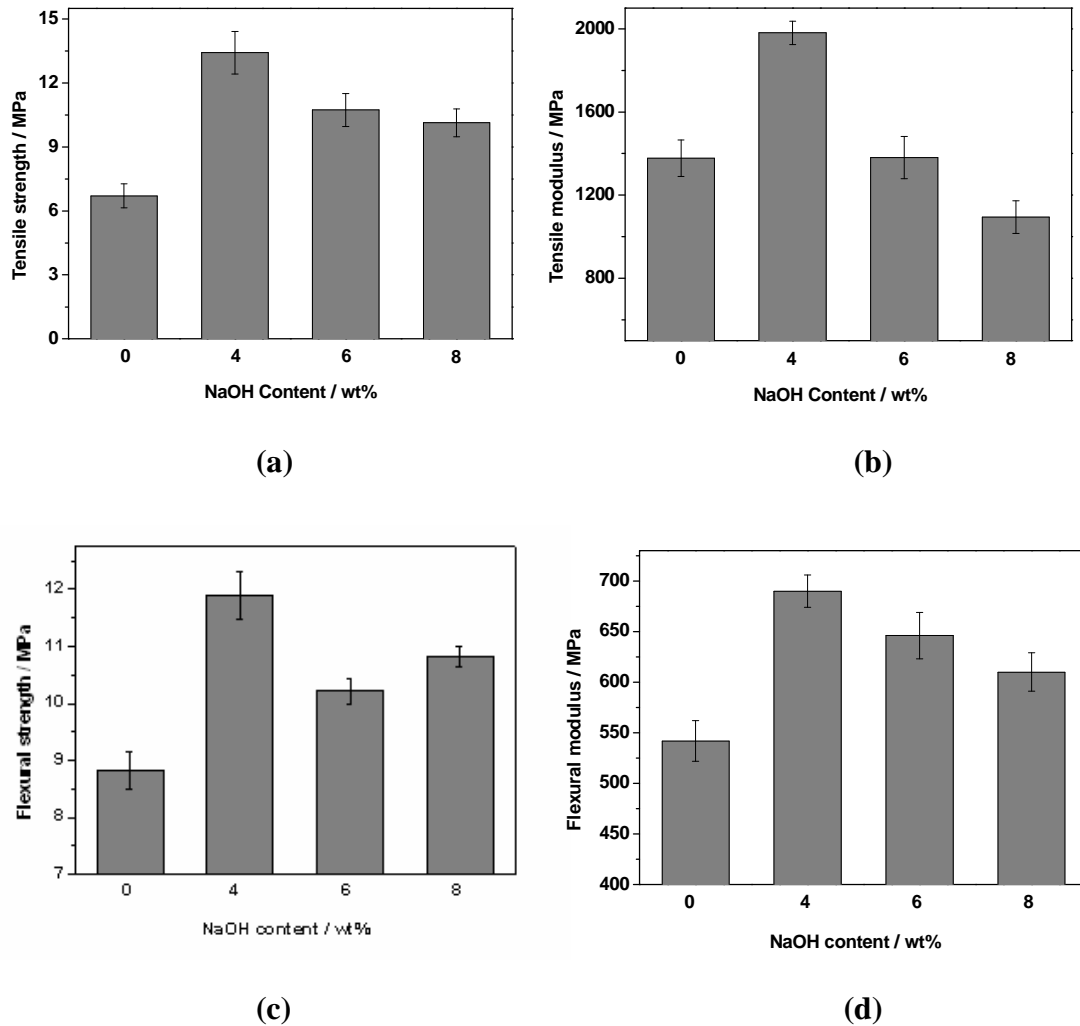


Fig.4 Tensile and flexural properties of kenaf / copolyester biocomposites: a) tensile strength; b) tensile modulus; c) flexural strength and d) flexural modulus

3.5 Dynamic mechanical analysis (DMA)

DMA measures the deformation of materials in response to vibrational forces. The storage modulus, E' indicates stiffness of a material and $\tan \delta$ gives the amount of energy dissipated as heat during the deformation [15]. The investigation of dynamic storage modulus and internal friction over a wide range of temperatures and frequencies has proven to be very useful in studying the structure of polymers and the variations of properties in relation to end-use performance [16]. Fig.5 showed the storage modulus of kenaf/copolyester composites with 4, 6 and 8% alkali treatment. DMA curves indicates that the storage modulus, E' increased abruptly around onset glass transition (T_g) temperature of untreated fiber composites. Addition of NaOH content decreased the storage modulus of the biocomposites. This is clearly shown in Fig.5. The

biocomposites with 8% alkali treatment showed low storage modulus compared to 4% alkali treated composites. This is resulting from the amount of NaOH that over-packed the untreated fiber composites and gave out poor mechanical properties. This result supported the tensile and flexural properties, which was discussed earlier. Value of T_g depend on the chemical structure. Flexibility of the molecular chain, steric hindrance and bulkiness of the side groups attached to the backbone chain affect the value of T_g . The onset, loss modulus and $\tan \delta$ obtained from DMA is shown in Fig.5. In the glassy region, thermal energy is sufficient to surmount the potential barriers from translational and rotational motions of segments of the polymer molecules. Delta (δ) in $\tan \delta$ sometimes referred to as internal friction or damping such as vibration or sound damping. It is the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle. Fig.6 delineated the variation of $\tan \delta$ of biocomposites. An improvement in interfacial bonding between matrix and fiber adhesion was observed with lowering of $\tan \delta$ values [17]. The higher damping at the interfaces was, the poorer the interface adhesion would be. The molecular motions at the interfacial region generally were contributed to the damping of the material apart from those of the constituents [15].

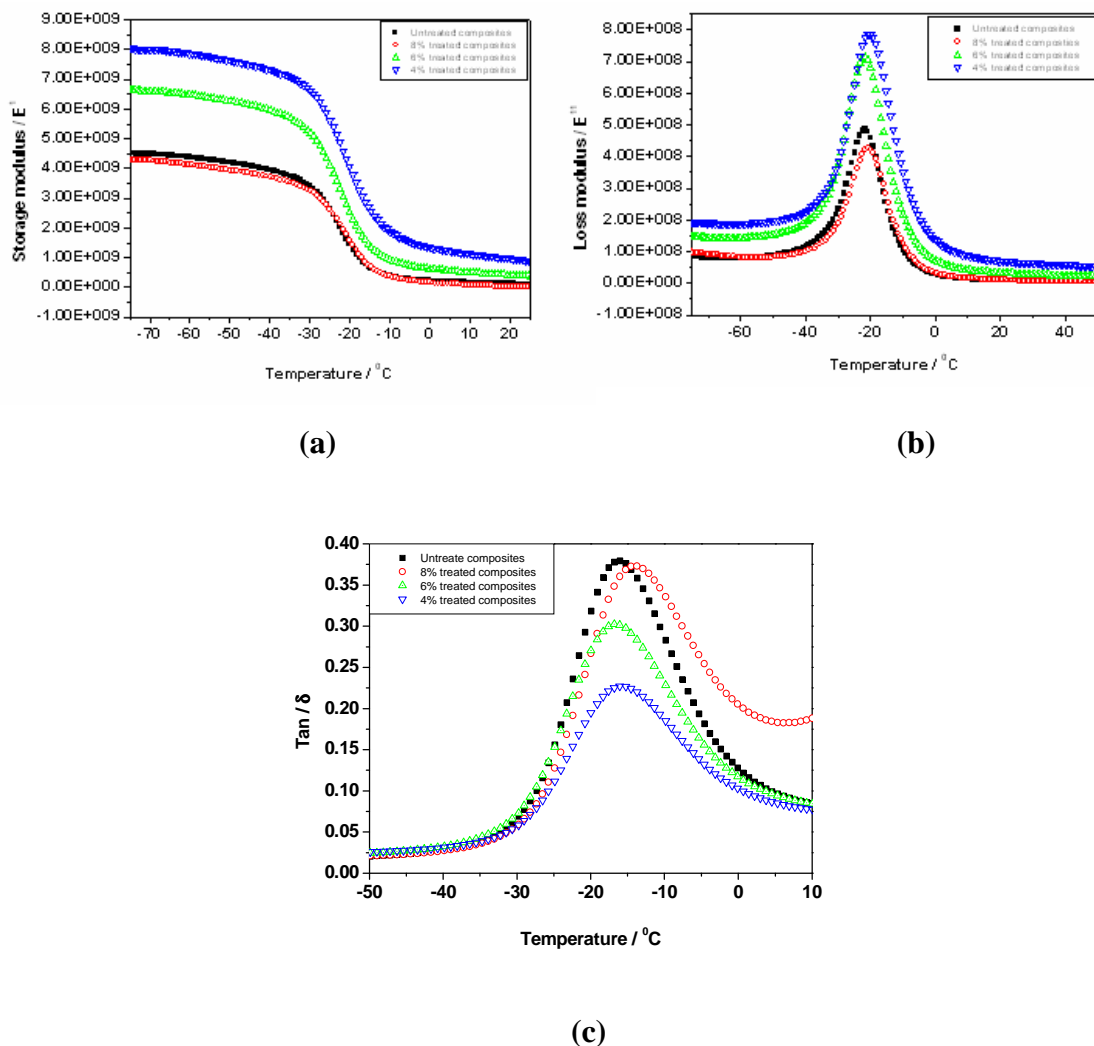


Fig.5 The DMA spectrums of kenaf / copolyester composites: a) storage modulus; b) loss modulus and c) $\tan \delta$

3.6 Thermogravimetric analyses (TGA)

The thermal stability of kenaf fiber / copolyester composites was investigated in terms of weight loss as a function of temperature by thermogravimetric analysis carried out in nitrogen. TGA curves are presented in Fig.6, with and without alkali treatment. It can be observed that the treated composites increased thermal stability to compared untreated composites. Fig.6 shows the TGA thermographs of the samples. Initial degradation of untreated composites was started around 300°C while treated fiber composites started around 310°C

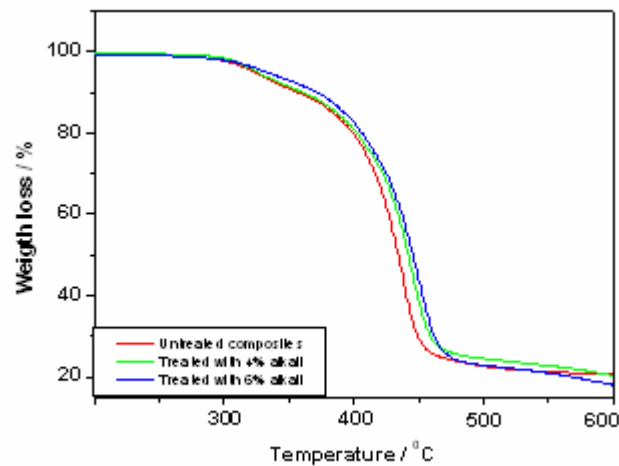


Fig.6 Thermogravimetric analyses of kenaf fiber / copolyester composites

3.7 Scanning electron microscopy (SEM)

The morphology of the fractured samples of the kenaf / copolyester biocomposites are shown in Fig.7. Untreated fiber composite is not well bonded, the fiber bunched together, with almost no matrix attached to the fiber surface. Alkali treated fiber composites shows a large amount of matrix adhering to the fiber surface, indicative of good adhesion with matrix. The reason for better adhesion between fiber and matrix is that the relative content of hydroxyl group on the surface of fiber increased after alkali treatment because of the removal of hemicellulose and lignin.

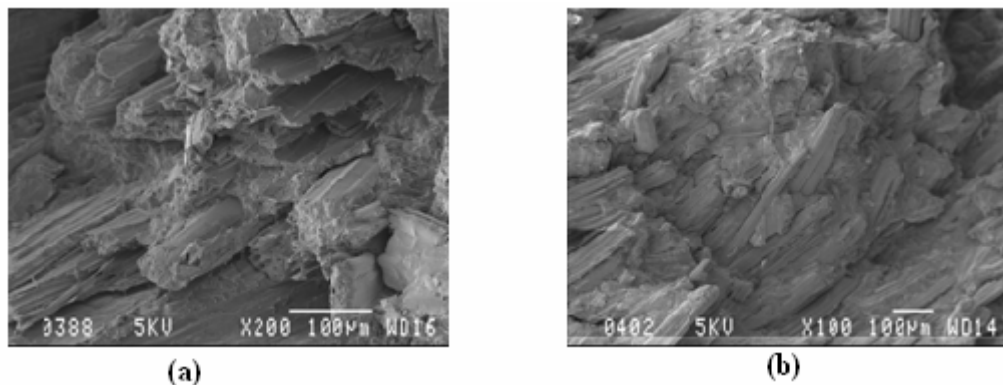


Fig.7 The scanning electron micrograph of kenaf fiber/copolyester composites
a) untreated composites and b) treated composites

4. Conclusions

Alkali treatment of kenaf fiber removes hemicellulose and lignin and allows the separation of the fiber into finer micro-fibers. This results in better adhesion of kenaf fiber and matrix. The adhesion of kenaf fiber in matrix improved with alkali treatment. The tensile and flexural properties of the composites were improved at 4% alkali treatment. The FT-IT, SEM and POM morphological properties showed removed of the hemicellulose and lignin for all the NaOH content treatment. The DMA and TGA analysis also showed increased thermal stability and storage modulus of the composites, when NaOH was used. The SEM analysis of the composites was found good interracial strength between treated fiber and matrix.

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