UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

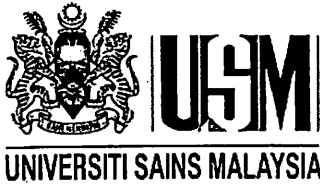# Fabrication & Characterization Of Non-Woven Kenaf Bast Fibre Filled Polyester Composites

By
Assoc. Prof. Dr. Razaina Mat Taib
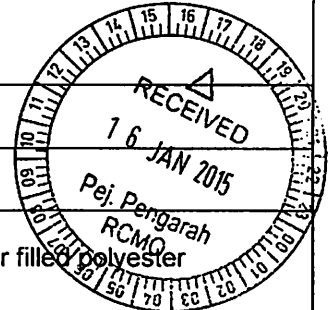Prof. Zainal Ariffin Mohd Ishak
Dr. Tay Guan Seng
Mr. Mohd Zharif Ahmad Thirmizir

2014

UNIVERSITY RESEARCH GRANT
FINAL REPORT
Geran Penyelidikan Universiti
Laporan Akhir

UNIVERSITI SAINS MALAYSIA

A.	**PARTICULARS OF RESEARCH /** *MAKLUMAT PENYELIDIKAN:*
(i)	**Title of Research:** *Tajuk Penyelidikan:* Fabrication & Characterization of non-woven kenaf bast fiber filled polyester composites
(ii)	**Account Number:** 1001/PBAHAN/814134 *Nombor Akaun:*
B.	**PERSONAL PARTICULARS OF RESEARCHER /** *MAKLUMAT PENYELIDIK:*
(i)	**Name of Research Leader:** Assoc. Prof. Dr. Razaina binti Mat Taib *Nama Ketua Penyelidik:*
	1. **Name of Co-Researcher:** Prof. Zainal Ariffin bin Mohd Ishak *Nama Penyelidik Bersama:* Dr. Tay Guan Seng Encik Mohd Zharif bin Ahmad Thirmizir
(ii)	~~School/Institute/Centre/Unit:~~ *Pusat Pengajian /~~Institut/Pusat/Unit~~:* Kejuruteraan Bahan & Sumber Mineral
D.	**Duration of this research:** *Tempoh masa penyelidikan ini:* ***Duration :** 36 months *Tempoh :* **From** : 15/08/2011 **To** : 14/08/2014 *Dari:* *Ke :*

I

E.	**ABSTRACT OF RESEARCH** (An abstract of between 100 and 200 words must be prepared in **Bahasa Malaysia and in English.** This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large) ***Abstrak Penyelidikan*** (Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris.** Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar). Composites of non-woven kenaf fiber mat and unsaturated polyester resin were manufactured via resin transfer molding machine. Non-woven kenaf fiber mats were manufactured by using carding and needle punching techniques. The fiber mats were either treated with alkali at several different concentrations or heat treated at 140 °C for different heating times. The treated fiber mats were characterized via FTIR, SEM, XRD, AFM and tensiometer. The latter characterization was used to determine contact angles and surface surface free energies of the treated fiber mats. The effects of these treatments on the composite properties (tensile, flexural and fracture toughness) were determined and compared. Durability studies were also conducted. Hygrothermal aging at different temperatures were conducted on composites samples and the effects of these exposures on the composites properties were investigated.
F.	**SUMMARY OF RESEARCH FINDINGS** *Ringkasan dapatan Projek Penyelidikan* Alkali treatment changed some properties of kenaf fibers such as surface morphology, crystallinity and surface chemistry. Alkali treated fiber composites showed better mechanical properties than the untreated fiber composites due to improved fiber-matrix adhesion. Alkali treatment reduced the tendency of kenaf fiber-polyester composites to absorb moisture. Absorption of moisture or water adversely affected composite properties. The percent recovery of flexural properties of alkali treated and untreated fiber composites upon redrying process was more than 95% when these composites were exposed to hygrothermal aging at 30°C.

G. **COMPREHENSIVE TECHNICAL REPORT**
Laporan Teknikal Lengkap
Applicants are required to prepare a comprehensive technical report explaining the project.
(This report must be attached separately)
Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Laporan ini mesti dikepilkan]

List the key words that reflect our research:
Senaraikan kata kunci yang mencerminkan penyelidikan anda:

English	Bahasa Malaysia
fibers	gentian
polyester	poliester
alkali treatment	rawatan alkali
mechanical properties	sifat-sifat mekanikal
hygrothermal aging	penuaan higrotermal
resin transfer molding	Pengacuan pemindah resin

H.

a) Results/Benefits of this research
Hasil Penyelidikan

No. *Bil:*	Category/Number: *Kategori/ Bilangan:*	Promised	Achieved
1.	**Research Publications (Specify target journals)** *Penerbitan Penyelidikan (Nyatakan sasaran jurnal)*	12	3
2.	**Human Capital Development**		
	a. **Ph. D Students**	1	1
	b. **Masters Students**		
	c. **Undergraduates (Final Year Project)**		
	d. **Research Officers**		
	e. **Research Assisstants**		
	f. **Other: Please specify**		
3.	**Patents** *Paten*		
4.	**Specific / Potential Applications** *Spesifik/Potensi aplikasin*	1	
5.	**Networking & Linkages** *Jaringan & Jalinan*	2	
6.	**Possible External Research Grants to be Acquired** *Jangkaan Geran Penyelidikan Luar Diperoleh*	1	

- Kindly provide copies/evidence for Category 1 to 6.

b) Equipment used for this research.
Peralatan yang telah digunakan dalam penyelidikan ini.

Items *Perkara*	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment *Peralatan khusus*	Vacuum Assisted Resin Transfer Molding Machine (VARTM)		Science & Engineering Research Center (SERC), Kampus Kejuruteraan, USM
Facility *Kemudahan*			
Infrastructure *Infrastruktur*			

- Please attach appendix if necessary.

4

H.	**COMMENTS OF PTJ'S RESEARCH COMMITTEE**
	KOMEN JAWATANKUASA PENYELIDIKAN PERINGKAT PTJ

General Comments:
Ulasan Umum:

Bilangan penerbitan berfaktor impak - hanya satu. Pencapaian ini agak rendah berbanding dengan bilangan sasaran semasa permohonan ini dilakukan iaitu 12.
Perkara ini sangat penting untuk pertimbangan permohonan masa depan.
Masih terdapat baki sebanyak RM14,666.30 yg tidak dibelanjakan.

Signature and Stamp of Chairperson of PTJ's Evaluation Committee
Tandatangan dan Cop Pengerusi Jawatankuasa Penilaian PTJ

PROFESOR ZAINAL ARIFIN AHMAD
Timbalan Dekan
(Penyelidikan)
P. Peng. Kej. Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia

Date : 12/1/2015
Tarikh :

Signature and Stamp of Dean/ Director of PTJ
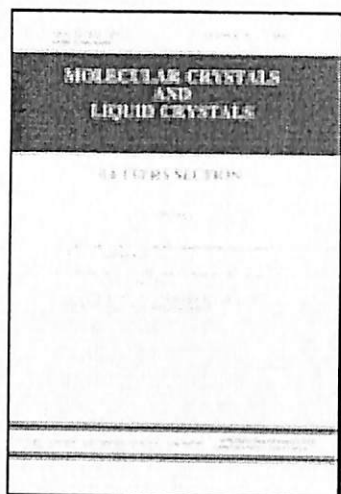*Tandatangan dan Cop Dekan/ Pengarah PTJ*

Date : 12/1/2015
Tarikh :

PROFESOR HANAFI ISMAIL, FASc
Dekan
P. Peng. Kej. Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia

6

Effects of Alkali Treatment on the Properties of Kenaf Fiber-Unsaturated Polyester Composites Prepared by Resin Transfer Molding

Razaina Mat Taib[a], Dody Ariawan[a] & Zainal Arifin Mohd Ishak[a]

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Effects of Alkali Treatment on the Properties of Kenaf Fiber-Unsaturated Polyester Composites Prepared by Resin Transfer Molding

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Composites of untreated and 6% sodium hydroxide (NaOH) treated kenaf fiber mat and unsaturated polyester resin matrix were manufactured via a resin transfer molding (RTM) technique. The treated fibers were characterized with SEM and XRD. Contact angle measurements of the fibers were performed using a tensiometer. Alkali treated fiber-unsaturated polyester composites showed superior flexural properties than the composites with untreated fibers. The water absorption pattern of these composites was found to follow Fickian behavior. The tendency of the composites to absorb water decreased when alkali treated fiber mats were used.

Keywords Kenaf fiber; polyester; alkali treatment; crystallinity; tensile properties; flexural properties

Introduction

Natural fibers have been considered as reinforcements in many polymer matrix composites. In addition to being biodegradable, other advantages of such fibers are: low cost, low specific gravity, renewability, abundance, and high specific strength and stiffness. Currently, a wide variety of natural fibers such as sisal [1], hemp [2], jute [3, 4] and kenaf [5] fibers have been used in the production of thermoplastic and thermoset-based composites. There are, however, some major restrictions for the successful use of natural fibers in these composites. Among them are high susceptibility to moisture absorption and inherent incompatibility of natural fibers with many non-polar polymeric matrices both of which may result in composites with undesirable mechanical properties [2, 4]. Absorption of water by natural fiber can be minimized by modifying the basic chemistry of the fibers with chemicals such as NaOH via alkalization. Alkalization or alkali treatment leads to removal of non-structural materials such as wax and oils from the fiber surface [6] and partial removal of the fiber cell wall polymers, i.e. hemicelluloses and lignin [7, 8]. Such modifications resulted in some changes to the fiber surface morphology as well as chemistry and also the fiber strength

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and stiffness. This eventually may impart some positive improvements on the mechanical properties of natural fiber-polymer composites.

Natural fiber-thermoset composites can be prepared via wet hand lay-up, press-molding, pultrusion, vacuum infusion molding and resin transfer molding techniques. The latter technique is an industrially important process, used to produce composites of various shapes, sizes and degrees of complexity. Studies reported on natural fiber-thermoset composites prepared by this technique are very limited [9].

In this research, composites were prepared from unsaturated polyester and non-woven kenaf fiber mat fiber via a RTM technique. The fiber mat was treated with NaOH solution prior to composite fabrication. The effects of treatment times on the flexural properties and water absorption behavior of these composites were determined and compared.

Experimental

Materials

The polymer matrix used was unsaturated polyester (Reversol P9565) obtained from Synthomer Sdn. Bhd. The initiating system comprised of methyl ethyl ketone peroxide (MEKP, 1.0 wt%) together with cobalt nafthenate (1 wt%). Kenaf fibers were supplied by Kenaf Fiber Industries Sdn. Bhd. Non-woven kenaf fiber mats were prepared using a carding machine followed by needle punching.

Fiber Treatment

Kenaf fiber mats were immersed in 6% solution of NaOH for 1, 2, 3, 4 and 5 hours at room temperature, then neutralized in dilute solution of glacial acetic acid. Finally the fiber mat was rinsed with deionized water and dried at room temperature for 24 h.

Resin Transfer Molding

The RTM machine used was the Innovator Megaject 3250 (8000) equipped with 2 reciprocating pumps. The pumps were filled with hardener and unsaturated polyester resin at a ratio of 1:100. The pump pressure was set at 0.13 MPa while the mold pressure guard was set at 0.06 MPa. Unsaturated polyester resin and hardener mixer was injected into the mold cavity at a constant flow rate. Kenaf fiber mat was placed in the mold cavity prior to filling. After injection was completed, the composite part was cured in the mold. The composite part was post-cured at 80°C (for 6 h) and at 130°C (for 2 h) to ensure a maximum conversion of styrene (the curing agent). Composites parts with fiber volume fraction of 30 wt% were produced via this technique.

Fiber Testing

The treated fiber was observed in a FESEM model Supra 35 VP to characterize the fiber surface morphology. Crystallinity index, CrI, of the fiber was determined using an X-ray diffractometer type D8 Bruker. The equatorial diffraction patterns (2θ) were recorded from 10 to 35° using Cu-Kα radiation at 40 KV and 40 mA. The crystallinity index, CrI, was calculated by using the following equation [10].

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$ (1)

where I_{002} is the counter reading at peak intensity at a 2θ angle close to $22°$ representing the crystalline region and I_{am} is the counter reading at a 2θ angle of around $18''$ representing the amorphous region in the natural fibers. Contact angle measurements were performed using a Dataphysics tensiometer DCAT 21. The capillary rise technique was used and the wetting liquids were deionized water and ethylene glycol. The Washburn equation was used to determine contact angles.

Flexural Testing

Three-point bend tests were performed using an Instron model 5960 in according to ASTM D 790. Samples were tested at a crosshead speed of 2 mm/min. 5 samples for each composite were tested and their average was reported.

Water Absorption Study

Water absorption was conducted according to ASTM D 570. Samples of the composites were immersed in deionized water for 70 days. After removal from the water the samples were surface dried with a towel before measuring the weight. The weights of the samples were measured at regular intervals and the water uptake at any time (W_t) was calculated according to the following equation:

$$W_t(\%) = \frac{W_1 - W_2}{W_2} \times 100 \tag{2}$$

where W_1 and W_2 are the weight after the exposure time t and the dry weight, respectively.

Results and Discussion

Fiber Properties

Scanning Electron Microscopy. Observations of the treated fiber surface (Fig. 1(B)) revealed that the alkali treatment had resulted in the removal of cementing materials, hemicelluloses and lignin, from the interfibrillar regions and impurities such as oils and wax from the fiber surface. Very similar observations have been reported by other researchers
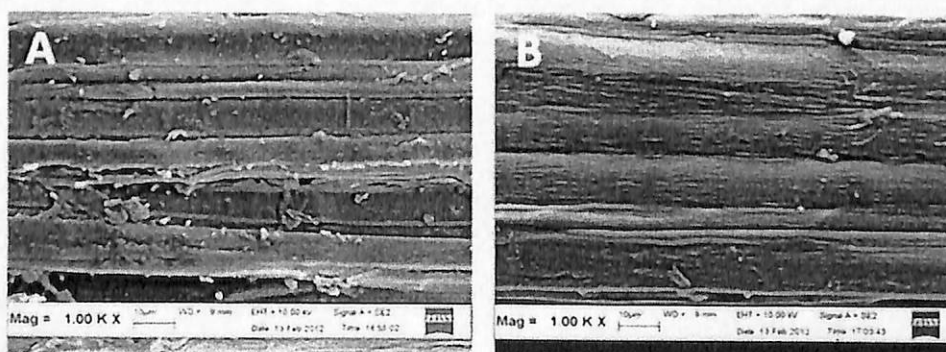

Figure 1. SEM micrographs of surfaces of (A) untreated and (B) 6% alkali treated kenaf fiber (treatment time = 5 hours).
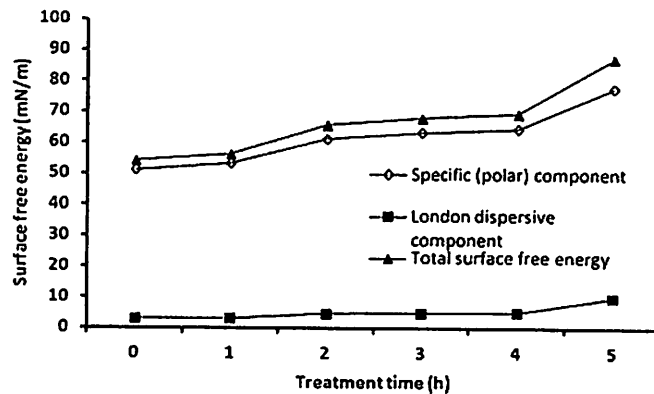
Figure 3. Surface free energies of untreated and alkali treated kenaf fiber.

$$\gamma_S^L = \frac{1}{4} \left[\frac{(1 + \cos\theta_1)\,\gamma_1\,(\gamma_2^L)^{\frac{1}{2}} - (1 + \cos\theta_2)\,\gamma_2\,(\gamma_1^L)^{\frac{1}{2}}}{(\gamma_1^L\gamma_2^{SP})^{\frac{1}{2}} - (\gamma_2^L\gamma_1^{SP})^{\frac{1}{2}}} \right]^2 \tag{5}$$

where the subscripts 1 and 2 in this study represent water and ethylene glycol, respectively.

The results of the surface free energies or surface tensions of the alkali treated kenaf fibers calculated from equations (4) and (5) are shown in Fig. 3. The total surface free energy of the alkali treated kenaf fibers increased, while the London dispersive component remained nearly constant with increasing treatment time. This surface free energy increase can be attributed to the increase in polarity due to the increased cellulose content on the fiber surface, resulting from the removal of impurities as well as cementing materials, hemicelluloses and lignin from the fiber surface following the alkali treatment.

Flexural Properties

Figure 4 shows the flexural modulus and flexural strength of kenaf fiber-unsaturated polyester composites. The flexural strength of the alkali treated kenaf fiber composites was greater than that of the untreated composite (Fig. 4(A)). Such positive improvement was observed when the kenaf fiber mat was treated with alkali for more than 1 h. The highest improvement in the property (+12%) was observed when the fiber mat was alkali treated for 3 h. The increased in the property can be attributed to the enhanced interfacial adhesion between the resin matrix and the kenaf fiber. Alkali treatment may result in fiber fibrillation due to the removal of cementing materials, hemicelluloses and lignin, between the macrofibrils [8]. The exposed interfibrillar regions increased the effective fiber surface area available for wetting by the unsaturated polyester resin during the composite fabrication [11]. In addition, such fiber surface morphology may improve fiber-matrix adhesion by introducing sites of mechanical interlocking [3]. Another factor that can be considered is improved fiber strength due to the increase in cellulose crystallinity following the alkali treatment [10]. Beyond 3 h of alkali treatment the flexural strength of the composites started to decrease but the values were higher than the untreated composite. This observation can be attributed to the decrease in the cellulose crystallinity of the kenaf fiber after prolonged alkali treatment [14].
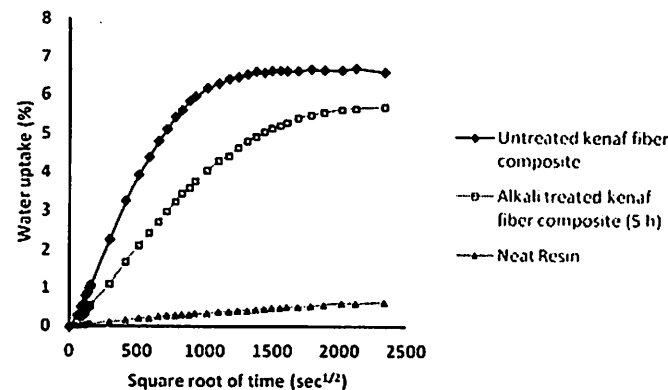
Figure 5. Water uptake curves for untreated and alkali treated kenaf fiber composites (the fiber mat was alkali treated for 5 h).

Conclusions

1. The morphology and structure of the kenaf fibers changed after the alkali treatment. SEM micrographs revealed that the fiber surface became cleaner and smoother after the treatment. The interfibrillar regions were also clearly observed. The crystallinity index as well as surface free energies of the fibers increased following the alkali treatment.

2. Composites with alkali treated kenaf fiber mat showed better both flexural strength and modulus compared to composites with untreated kenaf fiber mat. Maximum improvement in the flexural properties was observed when the kenaf fiber mat was alkali treated for 3 h.

3. Prolonged alkali treatment resulted in a decrease of the flexural properties of the composites due to the negative impact of the treatment on the fiber properties.

4. Composites with alkali treated kenaf fiber mat showed better resistance to water uptake than composites with untreated kenaf fiber mat due to improved fiber wetting by the matrix resin as well as the removal of hygroscopic hemicelluloses from the fiber surface.

Funding

References

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Effect of Heat Treatment on Properties of Kenaf Fiber Mat/Unsaturated Polyester Composite Produced by Resin Transfer Molding

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Abstract. This study investigated the effect of heating time during heat treatment on mechanical and physical properties of the kenaf fiber and its composites. Kenaf bast fibers were modified by heat treatmentat 140°C for 2.5, 5, 7.5, 10 and 12.5 hours. Composites were fabricated by resin transfer molding process with unsaturated polyester as matrix and needle-punched kenaf fiber mat as reinforcement. The fibers were characterized by Fourier Transform-Infra Red (FT-IR) and X-Ray Diffraction (XRD). FT-IR results showed the changes in intensity of hemicelluloce wavelength ($1736\ cm^{-1}$). Besides XRD observation also confirmed the increase of cellulose content in kenaf that described to the increase of crystallinity index of kenaf fiber with heat treatment. The single fiber strength investigation stated that the highest strength and modulus was obtained by kenaf fiber heated for 10 hours in drying oven. SEM observation showed the decreasing numbers of impurities on the fibers surface with fiber treatment compared to untreated kenaf fibers. The flexural properties of composites showed a similar trend to fiber strength, however the fracture toughness has showed contrary results.

Introduction

Kenaf is non-wood lignocelluloses that grow in tropical and sub-tropical areas. The fibers are extracted from the bast and core of the kenaf stem, wherein every stem produces 60 to 75% core fiber and 25 to 40% bast fibers [1]. As lignocelluloses material, kenaf fibers consist of cellulose, hemicellulose, lignin, pectin etc. Cellulose has both crystalline and amorphous regions, whereas lignin and hemicellulose have completely amorphous structure [2]. Kenaf fibers have several advantages such as good mechanical performances, low density, and biodegradability [3]. As lignocellulosic fibers, the kenaf fibers easily absorb moisture and contain a large amount of hydroxyl groups -OH between the macromolecules in the plant fiber cells wall.

For structural application, there are several modifications performed on the kenaf to enhance the properties before mixing it with thermoset or thermoplastic polymer as composites material. The chemical modifications are usually applied as an alternative in order to change the chemical structure of the fiber surface and the cell wall of lignocellulosic fibers. However, chemical modifications have environmental effect such as water pollution. The other modification is heat treatment that can be varied in different temperature and time of heating. The heat treatment method changes the mechanical properties without affecting any changes in the structural and composition of the kenaf fiber [4, 5]. The heat treatment on wood contributes to the thermal degradation of its chemical constituents (ie waxy debris, hemicellulose) and the changing of crystallinity of the cellulose [6]. The modifications of kenaf fiber result in the changes of fiber properties such as surface roughness, elasticity, absorptive capacity, chemical composition, and mechanical properties. To find the influence of treatment, several experiments are needed to determine the fibers property change after heat treatment, such as fiber surface observation, fiber tensile strength, chemical change and crystallinity.

To produce kenaf fibers composites, there are several industrial methods applied, such as resin transfer molding (RTM), vacuum infusion, pultrusion, hand lay-up, spray up, etc. The most popular method is resin transfer molding because this method have several advantages, such satisfactory cycle times, good surface finishing, good dimensional tolerances, good process control, decreasing of material handling, low cost and labor, minimal waste, high fiber loading, and low void content. RTM method exhibits the higher of mechanical properties than hand lay-up method [7] or compression molding method [8].

The addition of kenaf fibers to the unsaturated polyester resin in RTM process result in lower tensile strengths and slightly improved the tensile secant moduli for all fiber volume fractions [9]. The polyester laminates as a matrix gives the highest impact of energy and strength, followed by the vinyl ester and the epoxy laminates [10]. Before applying the composites for structural construction, several experiments for fibers and composites are conducted in this research to investigate the effect of heat treatment on fiber and composites produced by vacuum assisted resin transfer molding.

Experimental methods

Materials. Kenaf fiber were supplied by Kenaf Fiber Industries Sdn. Bhd. Kenaf fiber were subjected to several processes, i.e. bail breaker, wind up machine, carding willow, cross lapping, and needle punching technique to produce fiber mat. The Groz-Beckert conical needles were used in the needle punching process. The machine control was set to 0.2 m/s in speed and 1.5 cm in needle penetration of depth in order to produce uniform thickness of kenaf mat with 1350 g/cm $^{-2}$ in areal density. The needle penetration formed parallel line in same distance and unidirectional to the direction of conveyor.

Matrix used is a mixture of unsaturated polyester (Reversol P9565) supplied by Synthomer Sdn. Bhd., 1% wt. cobalt naphthalene from Sigma Aldrich and 1% methyl ethyl ketone peroxide from Merck. The unsaturated polyester matrix has viscosity of 200-300 cP, density of 1.2 kg/cm^3, volume shrinkage of 8.7% and gel time 18 minutes.

Resin transfer molding. Resin transfer molding machine used in this research was Innovator Megaject 3250 (8000) with 2 reciprocating pumps. The hardener-to-unsaturated polyester ratio was 1:100. The pump and mold pressure were set at 1.3 bar and 0.6 bar respectively. The vacuum pump was set at -0.55 bar.

The cavity of the mold is sized to produce laminates with 30 cm x 60 cm dimension. The composites are kept constant at 30% volume fractions.

Heat treatment. Heat treatments were conducted for 2.5, 5, 7.5, 10 and 12.5 hours at 140°C in heating oven. After treatment, kenaf mat were cooled in room temperature and kept in sealed plastic bag. Prior to RTM process, the mats were dried at 60° for 3 hours.

XRD. The crystallinities of kenaf fibers were analyzed by X-Ray Diffractometer type D8 Bruker settled at 40 KW, 40 mA; radiation was copper Kα ($\lambda = 1.541$ Å). The crystallinity index (CrI) of samples was calculated based on the diffraction intensities of crystalline area and amorphous regions by making use of the following equation:

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \qquad\qquad (1)$$

Where I_{am} is the diffracted intensity of amorphous region at $2\theta = 18.5°$ and I_{002} is the diffracted intensity of crystalline region in 002 plane at $2\theta = 22°$ [11].

FTIR. Fourier transform infrared spectroscopy studies were performed by using a Perkin-Elmer type Spectrum One spectrometer. Sample used a mixture of 2 mg kenaf fiber powder and 98 mg potassium bromide (KBr) that were compacted into thin pellets with a hydraulic press. The measurements wavelengths were taken from 500 to 4000 cm^{-1} at a resolution of 1 cm^{-1}.

Scanning electron microscope (SEM). Micrographs of the composite fracture surface, the composites surface and the cross sections of kenaf fibers were taken using a scanning electron

Hitachi microscope model TM 3000. All sample surfaces were coated with gold by a plasma sputtering apparatus operated at a pressure of 2 mbar for 1 minute before SEM observation.

Single fiber tensile strength test. The tensile strength and the elastic modulus of single fibers under static loading were tested in accordance with ASTM C 1557 standard test method. A single fiber tenacity was tested using a Mesdan-Lab strength tester with the rate of the upper clamp displacement of 3 mm/min and with the load cell of 300 gram. Fiber diameters were measured by a Zeiss SV6 Binocular Stereo Microscope with a digital photographic system.

Flexural properties of composites. The 3-point bending test was carried out in accordance with the ASTM D790 method to determine the flexural strength and modulus of composites. The test was conducted using an Instron 5960 universal testing machine with a crosshead speed of 2 mm/min with 5 kN load cell.

Fracture toughness test. The critical stress intensity factor toughness of the composites were measured by the single edge notch three point bending (SEN-3PB) test according to ASTM D5045 standards. The test was conducted using an Instron 5960 universal testing machine with the crosshead speed of 1 mm/min with 5 kN load cell.

Results and discussion

Fiber characterizations. Fig. 1 shows that the heat thermal treatment did not induce any chemical changes as expected. Hence, the FTIR spectra of both the untreated and heat treated fibers looked almost the same except for the slightly diminished intensity at 1736-1738 cm^{-1} wavelength for the heat treated kenaf fibers. Rong et al [4] stated that the change of intensity at 1736-1738 cm^{-1} might be caused by the removal of some aromatic lignin-like impurities or due to the reduction of OH bonds and O-acetyl group (i.e hemicelluloses or lignin) during heat treatment [12].
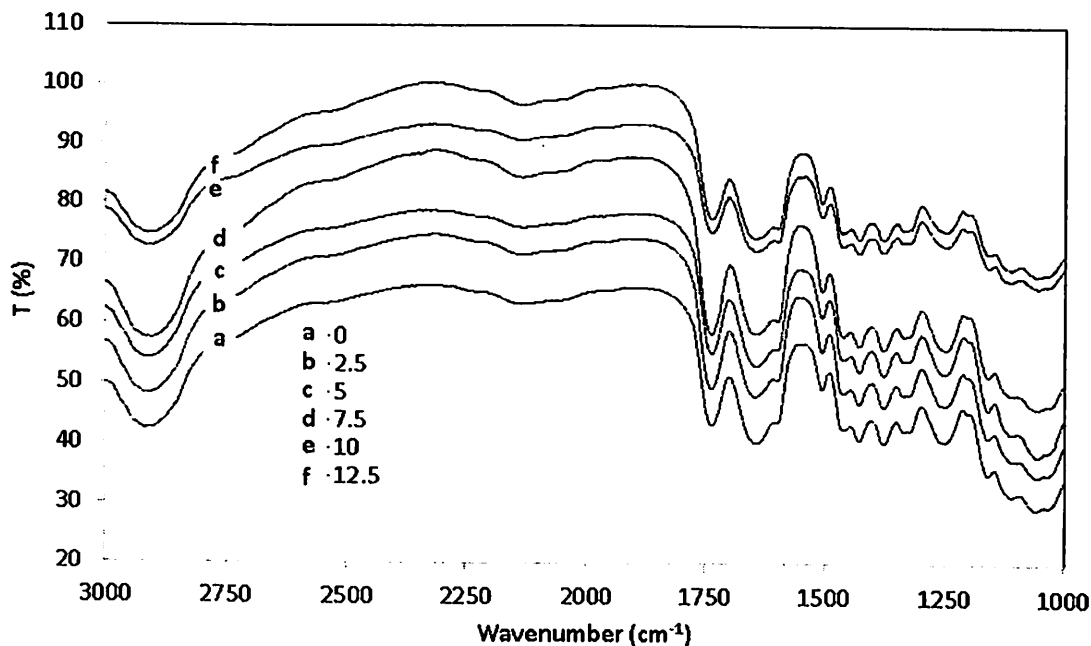

Fig. 1. FTIR observation for heat treated kenaf fiber at different times of heating

The changes in crystallinity index (CrI) values of heat treated kenaf fibers are attributed to the adjustment in the molecular structure at an elevated temperature. The CrI results are consistent with the single fiber tensile result as shown in Table 1. Esteves et al [13] explained that the increase ofcellulose crystallinity after heat treatment is caused by the degradation of amorphous content in fibers (i.e hemicelluloses or lignin) and rearrangement of crystal structures [4].

Table 1 shows the change of tensile strength and modulus of the kenaf fiber after treatment at different points of times during heating. The changes of the kenaf fiber mechanical properties can be attributed to the rearrangement of the molecular structure at high temperature. It can be seen at

the increase of the crystallinity index after the heat treatment and the decrease of the crystallinity index after 12.5 hour of heating. The molecular structural adjustment of heat treated kenaf fibers can increase the tensile strength and the elasticity modulus of the kenaf fiber. However after 12.5 hours heating, the crystallinity index and the mechanical properties of kenaf fibers decreased. The decrease of the crystalinity index may be related tothe damage in the structural molecules of the 12.hours heat treated kenaf fibers.

Fig. 2 (b), and (c) show slightly cleaner surfaces compare to the untreated kenaf fiber (see Fig. 2 (a)) due to removal of impurities such as wax from the surface by heat treatment. These observations indicate that the heat treatments at 140°C partially remove the impurities or the wax on kenaf fiber surface. The removal of impurities on fiber surface influences the properties of its composite [14].

Table 1.Crystallinity index and tensile properties of kenaf fiber

	Time of heating at 140°C (hour)					
	0	2.5	5	7.5	10	12.5
Crystallinity index (CrI)	55.73	56.86	56.5	56.47	56.67	54.80
Tensile strength (MPa)	251.43	268.75	282.82	305.41	320.85	289.61
Elasticity modulus (GPa)	13.38	16.73	17.22	20.88	20.42	19.34

(a)   (b)   (c)
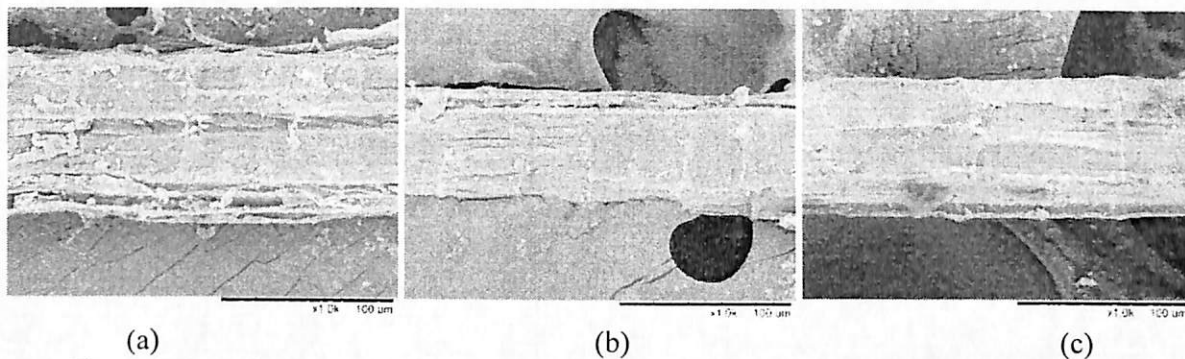
Fig. 2 SEM Micrograph of heat treated kenaf fiber surface for (a) 0 hour, (b) 7.5 hours, and (c) 12.5 hours of heating

Mechanical Properties and Fracture Surface Observation of Composites. From Fig. 3 (a-b), the heat treated kenaf fiber composites show superior flexural properties than that with untreated fiber composites due to the removal of surface impurities and the partial degradation of the amorphous cellulose of the incorporated fiber. Fig. 3 (a) show that the trends of the flexural strength of composites are similar to the trend of tensile strength kenaf fiber. The optimum flexural strength of composite was achieved at 10 hours heating time and further increased in heating time resulted in inferior properties due to severe structural degradation of the 12.5 hours heat treated kenaf fiber composite.

Figure 3 (c) shows that the untreated kenaf composites have better fracture toughness than the treated ones. As already known, resistivity of a material against crack propagation depends significantly upon the energy absorption capability of composites which in turn contribute to the fracture toughness of the composites. If composites components have good interfacial bonding, the fiber rupture will occur instead of debonding and allow lower energy to be absorbed during the crack propagation [15]. The partial removal of impurities and wax on the heat treated kenaf fiber surfaces will produce the high interfacial friction stress between the fiber and the matrix. It induces the decrease of fracture toughness of heat treated kenaf fiber composites.
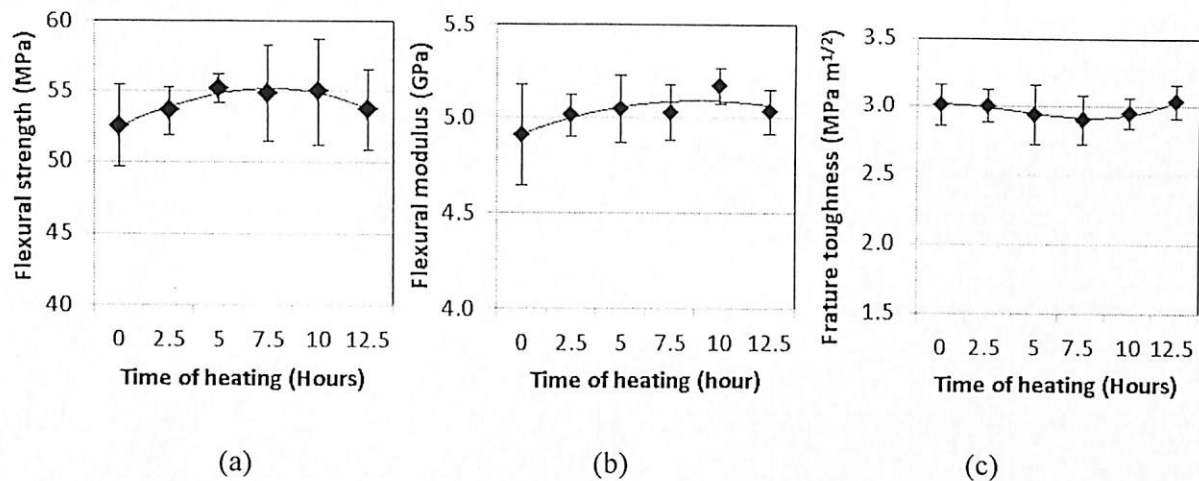
(a)   (b)   (c)

Fig. 3.(a) Flexural strength, (b) flexural modulus and (c) fracture toughness of composites with kenaf after heating at different period of time

hole   waxy surface   pull out   fiber breakage   clean surface

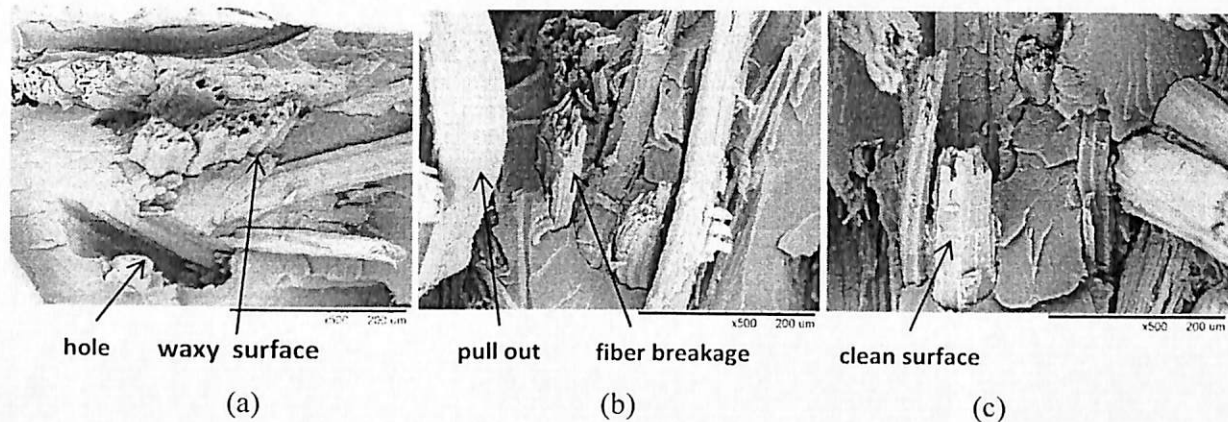(a)   (b)   (c)

Fig.4. SEM micrographs of fracture surfaces at (a) 0 hour, (b) 7.5 hours and (c) 12.5 hours of heat treated kenaf composite

The SEM micrographs of fracture surface as seen in Fig. 4 (a), (b) and (c) show the presence of fiber breakage, pull outs and holes. Furthermore, waxy substances still appear on few areas on the fiber surface (see Fig. 4 (a)) because the heat treatment only diminishing a relatively small amount of the waxy substrates on the fiber surface. The removal of the waxy substances after heat treatment can slightly increase the interfacial adhesion thus enhances the mechanical properties in the composites [14, 16, 17].

Conclusions

The heat treatment partially removed impurities and amorphous content in kenaf fiber surfaces, and it is believed allowed the rearrangement of molecules in cellulose thus enhancing the tensile strength and the modulus of the kenaf fibers. The decrease of the amorphous content can be seen from the crystallinity index and are also supported by the peak intensity reduction of FT-IR spectra at the hemicellulose wavelength. The partial removal of impurities on the kenaf fiber surfaces is shown on the SEM observation, wherein it could enhance the interfacial adhesion between fiber and matrix. The highest tensile strength of fiber and flexural strength composites are obtained by 10 hours heat treatment. The 10 hours heat treatment gave the composites the highest properties both in flexural strength and modulus results, but the fracture strength show the opposite result.

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Effect of Heat Treatment on Properties of Kenaf Fiber Mat/Unsaturated Polyester Composite Produced by Resin Transfer Molding

Effect of needle punching direction on nonwoven fiber mat to the mechanical properties of kenaf reinforced epoxy composites produced by vacuum assisted resin transfer molding

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Keywords : needle punching direction, kenaf, resin transfer molding, epoxy

Abstract : This study evaluated the performance of nonwoven kenaf mat reinforced epoxy that was fabricated by vacuum assisted resin transfer molding method. Kenaf mats were formed by carding and needle punching technique at 50 cm^2 sticthing density and 1.5 cm penetration depth. The specimens were prepared from different volume fraction of kenaf mat and epoxy resin, which consist of 18% kenaf mat/ 82% epoxy resin and 27% kenaf mat/ 73% epoxy resin. The tensile and compression properties were studied at 0°, 45° and 90°needle punching direction. Tensile properties increased with the increase of composites volume fraction and were decreased with the increase of needle punching direction degree. On the other hand, the compression properties of composites were reduced with the increase of volume fraction and needle punching direction degree. The composites properties were affected by the orientation and interlocking of fiber caused by needle penetration in direction of depth and movement direction.

Introduction

Kenaf (*Hibiscus cannabinus*, L. family *Malvaceae*) is an herbaceous annual plant that has an excellent strength and renewability. Jawaid et al [1]reported that kenaf fibers have 53.4 % celullose, 33.9 % hemicellulose, 21.2 % lignin, 4.0 % ash content, 1.2 gr/cm^3 density, 295 Mpa tensile strength, 2.7–6.9% elongation.

Vacuum assisted resin transfer molding (RTM) offers several advantages, such as good surface finishing, good dimensional tolerances, good process control, minimal waste, and low void content. Composites produced by RTM method exhibits higher of mechanical properties than hand lay up method[2]. Therefore, it can be applied as automotive interior part, construction material, etc. Rassman [3]concluded that the addition of kenaf fibers into the unsaturated polyester resin in RTM process has resulted in lower tensile strengths and slightly improved the tensile modulusof the composites than the modulus of the unreinforced polyester resin.

Needle punching system is a method to produce non woven mat which usually used for cotton fibers. Needle punching system uses thousands needle to joint and interlock every layer in mat to become a 3 dimensional mat system.It can enhance the strength if the right setting were found. Salim et al [4] has studied the setting parameter such as stitching density and speed to obtain optimum mechanical properties in 1 direction of punching. This research reveals the effect of punching direction on the tensile and compressive properties of non woven kenaf mat composites.

2. Materials and Methods

2.1. Mechanical properties test

Compressive test was conducted at room temperature in accordance to ASTM D695 [5] test method on specimens with 12.7 mm in width and 25.4 mm in length. The crosshead speed was set at 5 mm/minon instron machine type 5960 with 5 KN load cell.

Tensile test on the dumbell shaped rectangularspecimens was carried out using the Biss tensile testingmachine (model Bi-05-172)in accordance with ASTM D3039. Samples were tested at a crosshead speed of 5 mm/min, 200 mm in gauge lengthand 100 KN load cell

2.2. Microscopy Observation

Micrographs of flexural fracture surface were taken using a scanning electron microscope Model TM 3000 Hitachi. Prior to SEM evaluation, the samples were coated with gold by means of a plasma sputtering apparatus operated at a pressure of 2-mbar for 2 minutes.

2.3. Kenaf Fiber Mat

Kenaf bale form were processed by bail breaker, wind up machine, carding willow, cross lapping, and needle punching technique. The Groz- Beckertconical needles were used in the needle punching process. The machine control was set to 0.2m/s in speed and 1.5 cm in needle penetration of depth. It resulted in 50 cm^{-2} ofstitching density for kenaf fiber mat and an uniform thickness. The needle penetration formed a parallel line at the same distance and unidirectional to the direction of conveyor. Kenaf fiber mat cut into 30 cm x 60 cm according to the mold cavity size. Before being placed into mold cavity, kenaf fiber mat was dried in the oven at temperature 60°C for 3 hours [4].
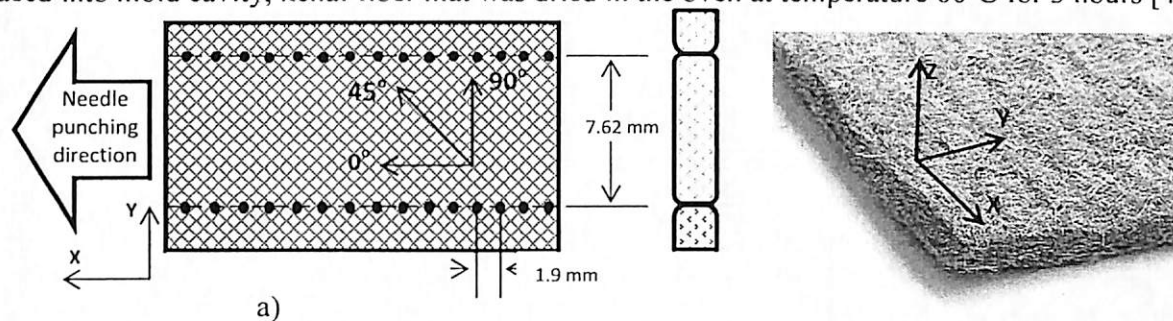

Figure 1. a) Distance/gap between punching in 90° and 0°b) 3 dimensional of axis direction

2.4. Resin Transfer Molding

Resin Transfer Molding machine used in research wasHypaject MKV with 2 reciprocating pumps. The pumps were filled with hardener and epoxy at the ratio of 1 : 2. The mold consists of an upper mold plate and lower mold plate. The cavity of the mold is sized to produce laminates with the dimension of 30cm x 60cm x 0.7 cm.

Laminates were produced with fibre volume fractions of 18% and 27%. Kenaf mat was placed in the cavity and the mold was tightly closed. The vacuum pump was turned on to discharge air in the mold cavity. Then the resin was injected in the mold by compressed air at a 3 Bar.

2.5. Epoxy and Hardener

Epoxy (CP 210DF PART A) and hardener (CP 210DF PART B) Epicote 816 obtained from Hexion TM was used as matrix. The mixture of epoxy-hardener was used as the polymer matrix of the reinforced composite has mixing ratio (weight) of 100 : 50 and gel time of 180 minutes. The mechanical properties of epoxy are 58MPa in tensile strength,1.685 GPa in tensile modulus, 64 MPa in compression strength and 1.977 GPa in compression modulus.

3. Result and Discussion

3.1. Compressive Testing

The microbuckling failure that involved both shear crippling or kinking are the most frequetly occured failure mode in this research and followed by shear failure and transverse tensile rupture (fig. 2). It was in line with the research of Bos et al [5] , wherein the fibrillar structure of the secondary cell wall of the elementary fibers are failed in compression due to kink band formation. Almost all of the compression failure place in x-z plane. Because fiber orientation are mostly distributed in x-y plane. Orientation in z axis are mostly consist of fiber that been pushed or pulled by needle punching process.

Composites with higher volume fraction of kenaf exhibit lower compression strength and compression modulus. It contradict with the value predicted by formula for compressive properties [6], because natural fibers have hollow structure and low density, the other way the synthetic fibers

have solid structure and higher density. Moreover, the higher volume fraction enhance the posibility of transverse stress in y-z plane and z direction when comprossive test was conducted. Thus the compression strength and compression modulus will be decreased if the volume fraction increase.
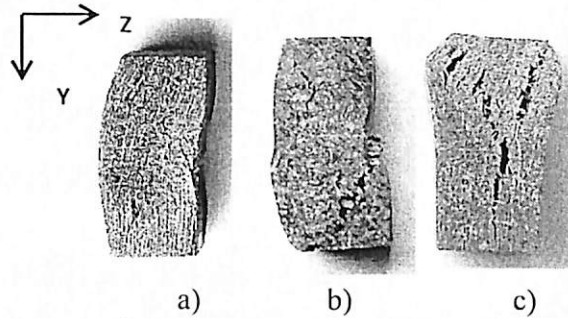

a)   b)   c)

Figure 2. Compressive failure mode in x-z plane (vf = 27%) a) fiber microbuckling, b) tranverse tensile rupture c) shear failure without buckling

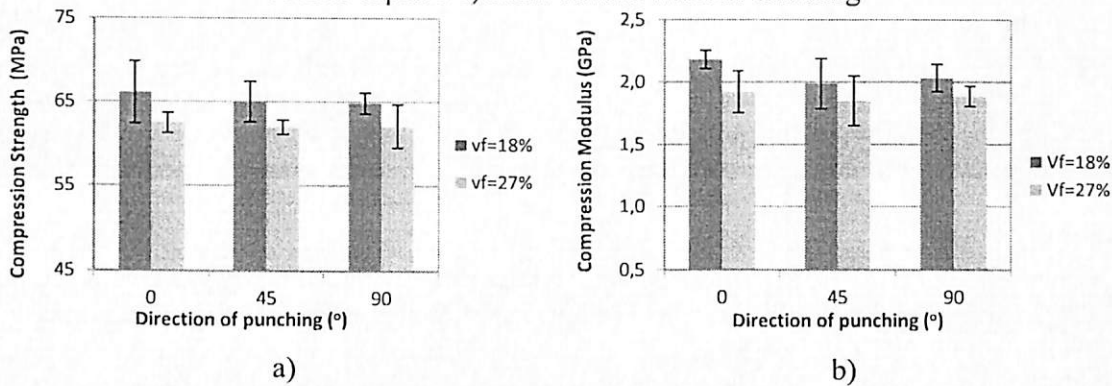
a)   b)
Figure 3. a) Compressive strength   b) Modulus of compressive

3.3. Tensile Testing

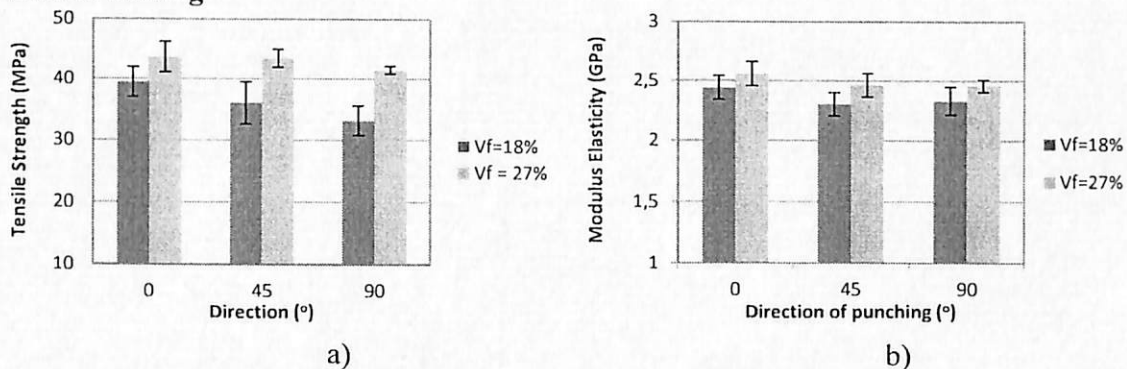a)   b)
Figure 4. a) Tensile strength b) Modulus of compression

At $0°$ needle punching direction, the composites shows higher tensile strength and modulus elasticity, though only slightly differences in modulus elasticity. The orientation of fibers along z axis caused by needle punching may support the composite strength in z axis, because majority of fiber orientation were distributed in x-y plane in fiber mat. The mat kenaf fibers were needle punched at an orientation to z direction at every 1.9 mm in average (see fig.1(a)). The z axis orientation of fiber made several interlocking of fiber that bound the mat to a 3 dimensional fiber orientation. The interlocking system may strengthen the composites/kenaf mat from load in z axis direction, but it can be the first ply failure in composite. The transverse orientation of fiber cannot reinforce the composite if the load is subjected perpendicular to the fiber and this would propagate the fracture to other places. The distance of punching in x axis is closer than y axis, so the fracture propagation or initial crack may be happened easily if the load is subjected in y axis rather than in x axis. Moreover, the tensile properties of the composite at 18 % vol. of fiber was lower than 27 % vol. of fiber. It also occured in different punching direction at each volume fraction. The modulus showed almost the same trend as the tensile strength of composites.
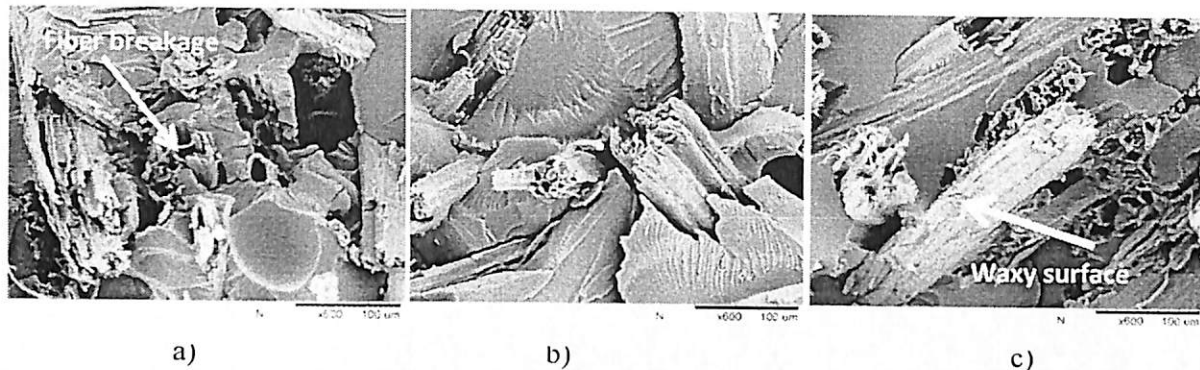
a)   b)   c)

Figure 5. Fracture surface composite at a) $0°$ needle punching direction b)$45°$ needle punching direction c)$90°$ needle punching direction

The SEM micrograph of tensile fracture surface(fig.5 (a), (b), (c)). showed the presence of waxy substances on the untreated fiber surface and fiber debonding at the interfacial area. Waxy substance contributed to ineffective fiber–matrix bonding and poor interfacial adhesion to matrix. The effect of needle punching direction may not be seen on the fracture surface. The SEM figures are only able to give the insight of the interactions between fiber and matrix from fracture surface. It indicate that the fiber mat reinforce matrix has poor interfacial bonding between matrix and fiber.

3. Conclusion

The composites which is fabricated by vaccuum transfer molding technique presented a good mechanical properties. The composites with high volume fractions of kenaf have higher properties both in tensile strength and modulus. Moreover, the composites tested parallel to needle punching direction have the highest properties in tensile and modulus. However, the compressive testing showed a different trend in volume faction. The strength and modulus decreased with increasing volume fraction of kenaf. The properties of composites were slightly decrease at $45°$ and $90°$punching direction. It can be concluded that the direction of punching affects the composites properties, though SEM micrograph can not detected the different of fracture surface among the punching direction.

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Effect of Needle Punching Direction on Nonwoven Fiber Mat to the Mechanical Properties of Kenaf Reinforced Epoxy Composites Produced by Vacuum Assisted Resin Transfer Molding

No.	Category	Thesis Title	Student Name	Status	Supervisor Type
		Data From HCMS			
		- No Record -			
		Data From SMU-P			
1.	PhD	Effect of Additives on Mechanical, Water Absorption and Natural Weathering Properties of Wood Flour Filled Polypropylene Composites	MOHAMAD BASHREE BIN ABU BAKAR	Berijazah	PENYELIA BERSAMA
2.	Master(Research)	Characterization of Kenaf Bast Fibre Filled Poly (Butylene Succinate) Composites: Mechanical, Water Absorption and Weathering Properties	MOHD ZHARIF BIN AHMAD THIRMIZIR	Berijazah	PENYELIA BERSAMA
3.	Master(Research)	Preparation and Properties of Kenaf Bast Fiber Filled (Plasticized) Poly(Lactic Acid) Composites	SUGANTI A/P RAMARAD	Berijazah	PENYELIA UTAMA
4.	Master(Research)	The Effects of Natural and Accelerated Weathering on the Properties of Meranti Wood Flour (WF) Filled Recycled High Density Polyethylene (rHDPE) Composites	NUR SYUHADA BINTI AHMAD ZAUZI	Berijazah	PENYELIA UTAMA
5.	Master(Research)	Preparation and Properties of Low Density Polyethlene (LDPE)/Thermoplastic Sago Starch (TPSS)/Kenaf Composites	ROHANI BINTI ABDUL MAJID	Berijazah	PENYELIA BERSAMA
6.	Master(Research)	Effect of Zinc Borate and Filler Loading on the Properties of Post Biodegradation Meranti Wood Flour Filled Recycled High Density Polyethylene (rHDPE) Composite	NORHAZARIAH BINTI SAMSIR	Berijazah	PENYELIA UTAMA
7.	Master(Research)	Natural Weathering and Hygrothermal Aging Studies of Jute/Glass Fibres Reinforced Unsaturated Polyester Hybrid Composites	TAY HONG KANG	Berijazah	PENYELIA BERSAMA
8.	Master(Research)	Preparation and Properties of Impact Modified Poly(Lactic-Acid)/Kenaf Fiber Composites	ZAID AWS ALI GHALEB	Berijazah	PENYELIA UTAMA
9.	Master(Research)	Preparation, Properties and Durability Studies of HDPE-Kenaf Core Filler Composites	ASHRAF ROHANIZA BINTI ASARI	Berijazah	PENYELIA UTAMA
10.	Master(Research)	Preparation and Properties of Impact Modified Polylactic Acid And Its Composites With Short Kenaf Bast Fiber	HUSNA MADIHAH BINTI HASAN	Berijazah	PENYELIA UTAMA
11.	Master(Research)	Effects of Accelerated Weathering on the Properties of Polylactic Acid Toughened With An Ethylene Copolymer As An Impact Modifier	KOUTH PHOMMACHANH	Berijazah	PENYELIA UTAMA
12.	PhD	Microstructure-properties characterization of kenaf fiber reinforced unsaturated polyester produced by resin transfer molding	DODY ARIAWAN	Aktif	PENYELIA BERSAMA

JABATAN BENDAHARI
UNIVERSITI SAINS MALAYSIA
PENYATA PERBELANJAAN SEHINGGA 30 NOVEMBER 2014

Projek :

No. Akaun : 1001 PBAHAN 814134.

Vot	Nama Vot	Peruntukan Projek	Perbelanjaan Terkumpul Sehingga Thn Lalu	Baki Peruntukan Tahun Lalu	Peruntukan Thn Semasa	Jumlah Peruntukan Thn Semasa	Tanggungan Semasa	Bayaran Thn Semasa	Jum Belanja Thn Semasa	Baki Projek
111	GAJI	60,000.00	0.00	60,000.00	0.00	60,000.00	0.00	0.00	0.00	60,000.00
221	PERJALANAN DAN SARA HIDUP	-8,403.07	0.00	-8,403.07	0.00	-8,403.07	0.00	997.50	997.50	-9,400.57
224	SEWAAN	4,000.00	0.00	4,000.00	0.00	4,000.00	0.00	0.00	0.00	4,000.00
227	BEKALAN DAN BAHAN LAIN	4,470.86	0.00	4,470.86	0.00	4,470.86	0.00	34,446.15	34,446.15	-29,975.29
228	PENYELENGGARAAN & PEMBAIKAN KECIL	2,250.00	0.00	2,250.00	0.00	2,250.00	0.00	9,950.00	9,950.00	-7,700.00
229	PERKHIDMATAN IKTISAS & HOSPITALITI	6,927.16	0.00	6,927.16	0.00	6,927.16	260.00	6,925.00	7,185.00	-257.84
335	HARTA MODAL	-2,000.00	0.00	-2,000.00	0.00	-2,000.00	0.00	0.00	0.00	-2,000.00
	Jum lah	67,244.95	0.00	67,244.95	0.00	67,244.95	260.00	52,318.65	52,578.65	14,666.30

Fabrication & Characterization of non-woven kenaf bast fiber filled polyester composites

By

Razaina Mat Taib

Table of Contents

Abstract

Kenaf fibers were immersed in 6% solution of sodium hydroxide (NaOH) for 1, 2, 3, 4 and 5 hours. The treated fibers were characterized with various methods such as scanning electron microscopt (SEM), atomic force microscopy (AFM), X-ray photoelectron microscopy (XPS) and X-ray diffraction (XRD). Contact angle measurements of the fibers were performed using a tensiometer. The morphology and structure of kenaf fibers changed after the alkali treatment. SEM micrographs revealed that the fiber surface became cleaner and smoother after the treatment. Removal of hemicelluloses and lignin from the fiber surfce following the treatment was evident from the fourier transform infrared (FTIR) spectroscopt and XPS results. Crystallinity index of kenaf fibers increased with the alkali treatment which account for the positive effect on the tensile strength and modulus of the treated fibers. The maximum improvement in both properties was observed when the fibers were immersed in NaOH solution for 2 hours. Beyond 4 hours of treatment, the tensile strength and modulus of the treated fibers started to decrease due to excess depolymerization of cellulose chains which resulted in a decrease in the crystallinity index. Composites of untreated and alkali treated kenaf fiber mat and unsaturated polyester resin matrix were manufactured via a resin transfer molding (RTM) technique. Alkali treated kenaf fiber-unsaturated polyester composites showed superior tensile and flexural properties than the composites with untreated fibers probably due to better interaction primarily via mechanical interlocking between the treated fiber and the polyester matrix as reflected in the results of interlaminar shear strength (ILSS). Maximum improvement in tensile strength and modulus of the treated fiber composites was observed when kenaf fibers alkali treated for 3 hour were used. The water absorption pattern of these composites at 30 °C was found to follow Fickian behavior but at 60 and 90 °C, the composites showed non-Fickian

5

behavior of water absorption. The tendency of the composites to absorb water decreased when alkali treated fibers were used. The results of flexural properties indicated that the properties deteriorated following water absorption or hygrothermal aging. Composites immersed at 30 °C recovered more than 95% for both the flexural strength and modulus upon redrying process. The percent of recovery of both properties, however, was less than 75% when the composites were exposed to hygrothermal aging at 60 and 90 °C due to some permanent damages introduced in the composites.

Chapter 1- Introduction

1.1 Problem statement

The utilization of lightweight, low cost natural fibers like kenaf, hemp, flax, jute and sisal offers the potential to replace a large segment of the glass and mineral fillers in numerous different applications [1]. In automotive applications for example, natural fiber-composites are being used to manufacture door panels, seat backs, headliners, package trays and dashboards. Other than lightweight and low cost, natural fibers also offer other benefits such as reductions in CO_2, recyclability, no potential health hazards, good specific mechanical properties, non-abrasive behavior during processing and biodegradability [1].

The application of natural fibers as reinforcements in composite materials requires a strong adhesion between the fiber and the polymer matrix [2]. Natural fibers are polar materials due to the presence of abundant of hydroxyls groups in the fiber cell walls while most of polymer matrices are non-polar materials. Both materials therefore are not compatible and may result in unsatisfactory final composite properties due to poor fiber-matrix interaction or adhesion. The poor fiber-matrix interaction can be improved via physical and chemical treatments of the fiber surface. Examples of chemical treatments of natural fibers are dewaxing, alkali treatment, cyanoethylation, vinyl grafting and treatment with various coupling agents [3]. The presence of hydroxyl groups in the fiber cell wall also responsible for the high absorption of water by the composites that adversely affect the composite properties and reduce their utility in many applications [3]. The absorption of water by natural fiber composites can be minimized by modifying the fiber properties making them more hydrophobic and ensuring sufficient fiber-matrix interaction so as to restrict penetration of water molecules inside the composite structures.

The manufacture of natural fiber composites includes the use of either a thermoset or thermoplastic polymer matrix combines with natural fibers. Thermoset composites are more desirable than thermoplastics, because of their superior mechanical properties. The primarily thermoset resins used in natural fiber composites for particularly automotive applications are polyester, vinylester and epoxy resins [4]. Resin transfer molding (RTM) is an industrially important process, used to produce thermosetting resin based reinforced composites of all shapes, sizes and degrees of complexity. It's a flexible net-shape technique that involves a pre-catalyzed resin injected under pressure into a pre-formed reinforcement, in a closed die mould. [4].

In this study composites of kenaf fibers and unsaturated polyester resin were manufactured via a resin transfer molding technique. The fibers were in the form of non-woven fiber mats. The fibers were alkali treated and characterized using various techniques such as scanning elecron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron specroscopy (XPS) so as to ascertain the changes in fiber properties that contribute to the improvement in the composite properties. The interlaminar shear strength (ILSS) of the composites was measured using the short beam method. In many engineering applications a key point for a successful use of a composite is the knowledge of how a given property changes with selected environmental variables. For this purpose, the impact of hygrothermal aging on the mechanical properties of the natural fiber composites was investigated.

1.2 Research objectives

The objectives of this study were: 1) to properly examine the changes in the kenaf fiber properties as a result of alkali treatment; 2) to investigate the effect of alkali treatment on the

mechanical properties of kenaf fiber-unsaturated polyester composites and 3) to study the effect of hygothermal aging on the mechanical properties of the composites.

Chapter 2 – Literature review

2.1 Natural fiber

Conventional and traditional composites are usually made of glass, carbon, or aramid fibers reinforced with epoxy, unsaturated polyester resins, polyurethanes, or phenolics. These composites have been used for structural and non-structural applications such as those used in consumer products for casing and packaging. Since both the fiber and the matrix are non-degradable materials, such composites do not degrade under normal environmental conditions resulting in various forms of environmental pollution. With increasing environmental consciousness and demands of legislative authorities, manufacturers are forced to use environmentally friendly materials in their products.

Natural fibers have been evaluated to replace traditional reinforcement materials such as glass fibers in composites. In addition to being biodegradable, other advantages of natural fibers are low cost, low density, high toughness, acceptable specific strength and modulus, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery, and biodegradability [3]. Table 2.1 lists the mechanical properties of some natural and traditional reinforcing fibers.

Cellulose is a semicrystalline polysaccharide made up of D-anhydroglucose units linked together by b-(1-4)-glucosidic bonds [Fig. 2.2]. The repeat unit in cellulose is the anhydrocellulobiose. Each repeat unit contains six hydroxyl groups, which responsible for hydrophilic properties of natural fibers [6]. Natural fibers, therefore, when used to reinforce hydrophobic polymer matrices such as polypropylene results in a very poor fiber-matrix interface and the composites formed showed poor resistance to water absorption [5]. The degree of polymerization (DP) of cellulose is between 8000 and 10000. The mechanical properties of a natural fiber depend significantly on the DP [6]. Cellulose is highly crystalline and may contain as much as 80% crystalline regions. Cellulose macromolecules exist in tightly packed, slender rod-like crystalline structure called microfibrils. The remaining portion that has a lower packing density is referred to as amorphous cellulose [6].
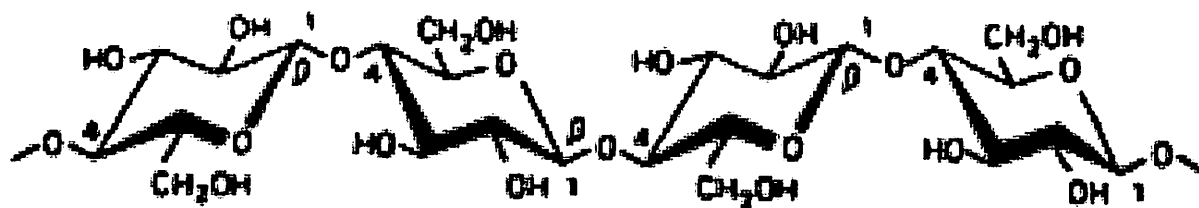

Fig. 2.2 Structure of cellulose [7]

Hemicellulosic polymers are branched, fully amorphous and have a significantly lower molecular weight than cellulose. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is partly soluble in water and hygroscopic. Hemicellulose is strongly bound to cellulose fibrils presumably by hydrogen bonds. Lignins are amorphous, highly complex, mainly aromatic, polymers of phenylpropane units but have the least water sorption of the natural fiber components [5]. Lignin is generally resistant to microbial

stiffness, whereas a strong interface produces high strength and stiffness. In order to obtain useful composites, fiber-matrix interface has to be optimized and this can be achieved via surface chemical modifications of natural fibers. Chemical modifications provide an effective means to add functional groups to enable better interaction with the polymer matrix. Examples of such chemical modifications include alkali treatment, silane treatment, acetylation, benzoylation, use of maleated coupling agents, peroxide treatment, permanganate treatment, and isocyanate treatment. Amongst the various methods presented, alkali and silane treatments have been widely reported.

2.2.1 Alkali treatment

Alkaline treatment or mercerization is one of the most used chemical treatment of natural fibers when used to reinforce polymer matrices either thermoplastics or thermosets [5]. In alkali treatment, fibers are immersed in sodium hydroxide (NaOH) solution for a given period of time. As a result of alkali treatment, the following reaction [Eq. (1)] takes place:

$$\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O-Na} + \text{H}_2\text{O} \tag{1}$$
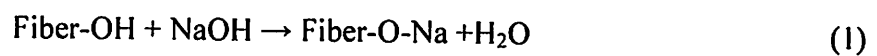
Alkali treatment removes some amount of hemicelluloses, lignin and non-cellulosic materials such as wax and oils from the fiber surface. It is reported that alkaline treatment has two effects on the fiber: (1) it increases surface roughness resulting in better mechanical interlocking; and (2) it increases the amount of cellulose exposed on the fiber surface, thus increasing the number of possible reaction sites with the matrix material or coupling agent [5]. Consequently, alkaline treatment has a lasting effect on the mechanical behavior of flax fibers,

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especially on fiber strength and stiffness [5]. When the hemicelluloses are removed, the interfibrillar region is likely to be less dense and less rigid, and thereby makes the fibrils more capable of rearranging themselves along the direction of tensile deformation. Such rearrangements among the fibrils would result in better load sharing by them, hence higher stress development in the fiber. Increases in fiber thermal stability and fibre crystallinity index have also been shown to result from alkali fibre treatments [9]. The increase in the percentage of crystallinity index of alkali-treated fibers occurs because of the removal on the cementing materials, hemicelluloses and lignin, which leads to a better packing of cellulose chains.

2.3 Thermoset resins

Thermosets are resins, which readily crosslink during curing. This process involves the application of heat and/or the addition of a component known as curing agent as hardener. Thermosets are usually brittle at room temperature and have low fracture toughness values. Because of the crosslinked structure, thermosets cannot be re-melted or dissolved. Compared to thermoplastics, thermosets can be used at higher temperatures, since they have higher glass transition temperatures and better creep properties. They are also more resistant to chemical attacks than most thermoplastics [10]. Examples of thermoset resins are epoxy, phenolic, vinyl and unsaturated polyester resins.

2.3.1 Unsaturated polyester resin

Unsaturated polyester resins are commercially available polymeric materials with numerous applications. They are used in the manufacturing of a broad range of products, such as structural parts of automobiles, building materials and coating materials.

The starting material to produce a thermoset polyester matrix is an unsaturated polyester resin containing a number of C=C bonds. It is usually prepared by the reaction of maleic anhydride and a glycol (ethylene or propylene glycol). Saturated acids, such as isophthalic or orthophthalic acid, are also added to modify the chemical structure between the crosslink sites. The resulting polymer is dissolved in a reactive diluent, such as styrene, which reduces its viscosity and makes it easier to handle. The diluents also contains C=C bonds and bridges adjacent polyester molecules at their unsaturation points. Curing is accomplished by the addition of suitable initiators, usually organic peroxides or hydroperoxides, capable of producing free radicals under appropriate conditions. These initiate the copolymerization of styrene with the unsaturated polyester. Other initiators such as azonitriles or photo-initiators can also be used. Polyester resins can be tailored to suit a very wide variety of structural applications by carefully selecting the adequate raw materials. Advantages of polyesters are low viscosity, fast curing time and low cost [11]. Fig. 2.4 shows the chemical reactions that form the unsaturated polyester resin. Unfortunately, unsaturated polyester resins contain ester groups in their chains, especially maleate and phthalate groups that are characterized by a relatively high sensitivity to hydrolysis with respect to vinyl esters. Additionally, acidic and alcoholic chain ends of the resins are also chemically sensitive. Consequently, an embrittlement of fiber-reinforced unsaturated polyester composites exposed to wet media occurs [12]
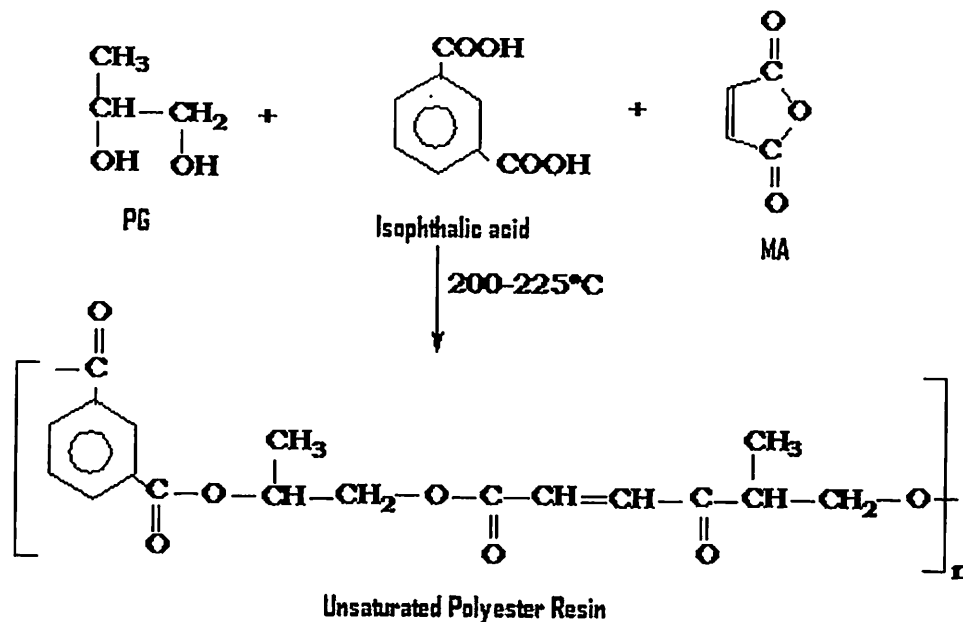
Fig. 2.4 Chemical reactions to produce unsaturated polyester resin [13].

2.4 Natural fiber-thermoset composites

Several studies have been reported on the properties of natural fiber-thermoset composites. Some of these studies are described in this section. Das and Chakraborty (14) treated bamboo fibers in the form of strips and dust with various concentrations of NaOH (10, 15 and 20%). These treated and untreated samples were then subjected to FTIR and XRD studies. Results from XRD showed that during alkali treatment a lattice transformation from cellulose-I to cellulose-II took place in the fibers and the conversion is maximum in between 15 and 20% of alkali treatment as indicated by the value of IR index. Degree of crystallinity and crystallinity index for bamboo strips increases with increasing treatment concentration of alkali and falls off after 15% alkali concentration. This is also supported by d-spacing value. Orientation factor f_x was calculated from the FWHM and it was found that f_x value has been increased from 0.9879 to 0.9915 for 15% alkali treated and again lowered to 0.8522 for 50% alkali treated samples. Same

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observation of X-ray study was obtained for dust samples but at an earlier concentration. Morphological study of bamboo dust with scanning electron microscope indicates fibrillation at higher alkali concentration [14].

Aziz and Ansell [15] used 0.06 M NaOH solution to chemically modify the surface of hemp and kenaf fibers. A general trend was observed whereby alkalized and long fiber composites gave higher flexural modulus and flexural strength compared with composites made from untreated fiber. Alkali treated kenaf fiber–polyester composites possessed superior mechanical properties to alkali treated hemp fiber–polyester composites. Scanning electron microscopy micrographs of the treated hemp and kenaf fibres showed the absence of surface impurities which were present on the untreated fibers. Apparent density measurements on hemp and kenaf fibers did not show a significant change after alkali treatment with 0.06 M NaOH. Dynamic mechanical thermal analysis carried out on the polyester matrix composites showed that the alkali treated fiber composites have higher E values corresponding to higher flexural moduli indicating greater interfacial bond strength and adhesion between the matrix resin and the fiber [15].

Sreekumar and co-workers [16] subjected sisal fibers to various chemical and physical modifications such as mercerization, heating at 100 °C, permanganate treatment, benzoylation and silanization to improve the interfacial bonding with matrix. Composites were prepared by these fibers as reinforcement, using resin transfer molding (RTM). The mechanical properties such as tensile, flexural and impact strength were examined. Mercerized fiber-reinforced composites showed 36% of increase in tensile strength and 53% in Young's modulus while the permanganate treated fiber-reinforced composites performed 25% increase in flexural strength. However, in the case of impact strength, the treatment has been found to cause a reduction. The

water absorption study of these composites at different temperature revealed that it is less for the treated fiber-reinforced composites at all temperatures compared to the untreated one. SEM studies have been used to complement the results emanated from the evaluation of mechanical properties [16].

Dhakal and co-workers [17] manufactured hemp fiber reinforced unsaturated polyester composites (HFRUPE) and subjected them to water immersion tests in order to study the effects of water absorption on the mechanical properties. HFRUPE composites specimens containing 0, 0.10, 0.15, 0.21 and 0.26 fiber volume fraction were prepared. Water absorption tests were conducted by immersing specimens in a de-ionised water bath at 25 °C and 100 °C for different time durations. The tensile and flexural properties of water immersed specimens subjected to both aging conditions were evaluated and compared alongside dry composite specimens. The percentage of moisture uptake increased as the fiber volume fraction increased due to increased voids and cellulose content. The tensile and flexural properties of HFRUPE specimens were found to decrease with increase in percentage moisture uptake. Moisture induced degradation of composite samples was significant at elevated temperature. The water absorption pattern of these composites at room temperature was found to follow Fickian behaviour, whereas at elevated temperatures it exhibited non-Fickian [17]

2.5 Composite fabrication

Natural fiber reinforced thermosets are processed by relatively simple processing techniques, such as hand lay-up and spraying, and liquid composite molding (LMC). Other processing techniques are filament winding, pultrusion, reinforced reaction injection molding, rptational molding and vacuum forming. LMC techniques cover a wide range of composite

manufacturing processes, such as resin transfer molding (RTM), resin infusion and injection compression molding. In general all LMC processes involve placement of a fibrous reinforcing material within some form of closed mold. The fibrous material or perform, is then compacted before being impregnated with a thermoset resin. The perform offers resistance to flow, which has a great influence on the time required to fill a mold. Once the mold is filled, curing of the thermoset polymer is initiated and the part is removed from the mold [18].

2.6 Hygrothermal aging

Hygrothermal aging refers to the process in which the deterioration of the mechanical performance and integrity of composite materials results from the combined action of moisture and temperature. This issue is of concern since, in service, composite materials are frequently exposed to an environment in which the temperature and moisture content vary in a prescribed manner [19]. Moisture diffusion in polymeric composites has shown to be governed by three different mechanisms. The first involves of diffusion of water molecules inside the micro gaps between polymer chains. The second involves capillary transport into the gaps and flaws at the interfaces between fibre and the matrix. This is a result of poor wetting and impregnation during the initial manufacturing stage. The third involves transport of microcracks in the matrix arising from the swelling of fibres (particularly in the case of natural fibre composites). Generally, based on these mechanisms, diffusion behaviour of polymeric composites can further be classified according to the relative mobility of the penetrant and of the polymer segments, which is related to either Fickian, non-Fickian or anomalous, and an intermediate behaviour between Fickian and non-Fickian. In general moisture diffusion in a composite depends on factors such as volume fraction of fibre, voids, viscosity of matrix, humidity and temperature [17].

Moisture absorption may induce irreversible changes to polymers and composites, such as chemical degradation, cracking and debonding [20] resulting in more detrimental effects on the mechanical properties of the materials. Natural fibers are hydrophilic and can absorp water. As natural fbers absorb water, they swell, which in turn can affect the surrounding matrix by initiating cracks or weakening the fiber-matrix interaction .

Chapter 3 – Experimental

3.1 Materials

The polymer matrix used was unsaturated polyester (Reversol P9565) obtained from Syhthomer Sdn. Bhd. The initiating system comprised of methyl ethyl ketone peroxide (MEKP, 1.0 wt%) together with cobalt nafthenate (1 wt%). Kenaf fibers were supplied by Kenaf Fiber Industries Sdn. Bhd. The mechanical and physical properties of the polyester used in this study are presented in Table 3.1.

Table 3.1 Properties of unsaturated polyester resin

Viscosity (cps)	200 – 300
Density (g cm^{-3})	1.2
Volume shrinkage (%)	8.7
Gel time at 25°C (minutes)	12 - 15
Elongation at break (%)	2.5 – 3.1
Tensile strength (MPa)	63.9 - 72
Elastic modulus (GPa)	3.4 – 3.6

Non-woven kenaf fiber mats were prepared using a carding machine followed by needle punching. Fig. 3.1 shows the manufacturing process for making the fiber mats. Sodium hydroxide and acetic acid were purchased from Merck and Sigma Aldrich, respectively.
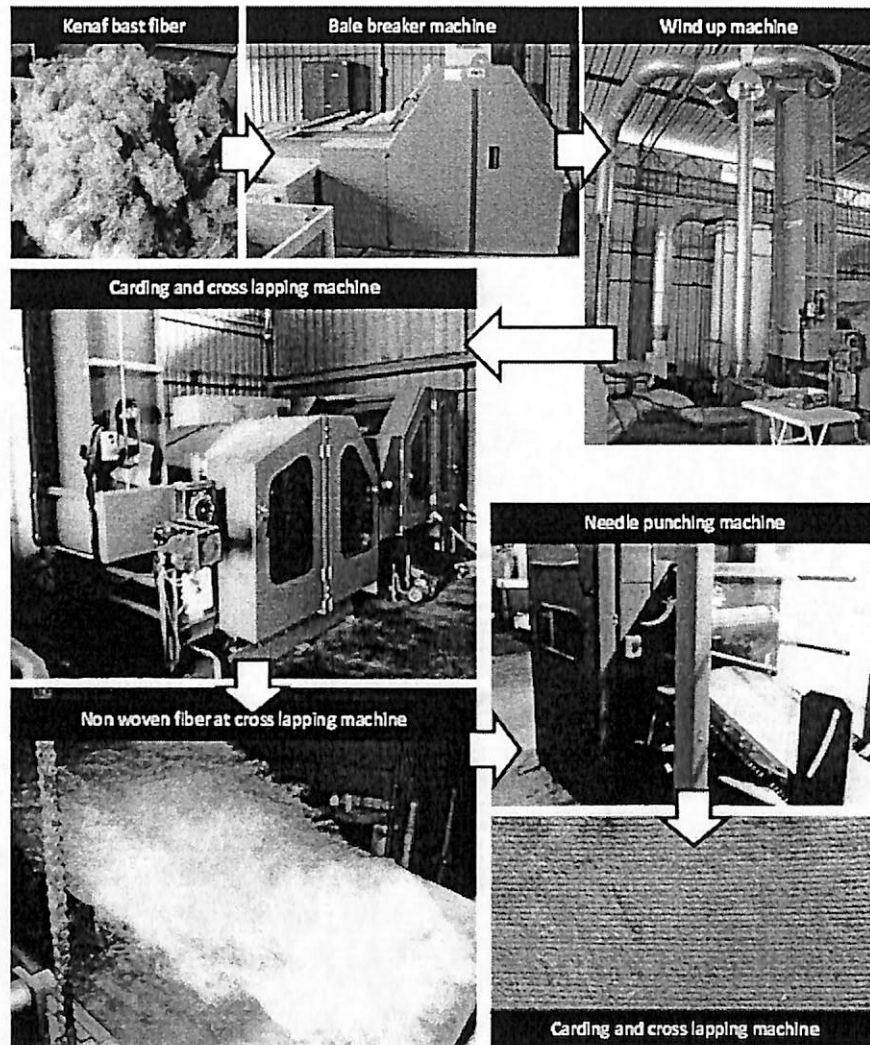

Fig. 3.1 Manufacturing process for making non-woven kenaf fiber mats via carding and needle punching machines.

3.2 Alkali treatment

Kenaf fibers were submerged in 6% solution of sodium hydroxide (NaOH) for 1, 2, 3, 4 and 5 hours of immersion at room temperature. A solution to fiber ratio of 20:1 (mL/g) was maintained for all experiments. The resulting fibers were thoroughly rinsed several times with distilled water to remove any alkali solution sticking to the fibers surface, neutralized with dilute acetic acid and finally rinsed again with distilled water. A final pH of 7 was maintained. The fibers were then dried at room temperature for 48 h followed by oven drying at 100°C 6 h.

3.3 Composite preparation

The resin transfer molding (RTM) machine used was the Innovator Megaject 3250 (8000) equipped with 2 reciprocating pumps. The pumps were filled with hardener and unsaturated polyester resin at a ratio of 1:100. The pump pressure was set at 0.13 MPa while the mold pressure guard was set at 0.06 MPa. Unsaturated polyester resin and hardener mixture was injected into the mold cavity at a constant flow rate. Kenaf fiber mat was placed in the mold cavity prior to filling. After injection was completed, the composite part was cured in the mold. The composite part was post-cured at 80°C (for 6 h) and at 130°C (for 2 h) in a convection oven to ensure complete and homogeneous curing of the polyester matrix. Composites parts with fiber volume fraction of 10, 20 and 30 wt% were produced via this technique.

3.4 Scanning electron microscopy (SEM)

The surface morphology of kenaf fiber before and after alkali treatment, as well as the fracture surfaces of the composites after failure under flexural test were examined by a Supra 35 VP field emission scanning electron microscopes operated at 10 kV. Samples were mounted with

double sided tape on aluminum stubs and then sputter coated with gold to avoid electrical charging during SEM examination.

3.5 Atomic force microscopy (AFM)

Atomic force microscope (AFM, nanonaviSPA-300HM) was used to determine surface roughness of untreated and treated fibers. The roughness was analyzed based on images obtained over a 2 μm x 2 μm area.

3.6 X-ray photoelectron spectroscopy (XPS)

The XPS wide and narrow scan spectra were acquired using AXIS Ultra DLD, Kratos, equipped with a Al Kα X-ray source (1486.6 eV) at 10mA, 15kV, analyzing a 300μmm X 700 μmm area under 7.6 X 10^{-9} torr ultra vacuum environment inside sample analyze chamber. Analyzed were performed in the hybrid lens mode with the slot aperture and the pass energy of the hemispherical analyzer was set at 160eV for the wide scan and 20eV for narrow scans. The spectra were analyzed using vision software which included with vision manager and vision processing. The linear method was used for background subtraction and curve fitting.

3.7 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the fibers before and after treatment were obtained using an FTIR spectrometer (Perkin Elmer, Spectrum ONE). Kenaf fibers were mixed with dry potassium bromide (KBr) in a ratio of 98:2 mg (KBr:kenaf fiber) and pressed to form pellets. All the FTIR spectra were recorded in transmittance units within the wavenumber range of 4000 to 500 cm^{-1}, with a resolution of 1 cm^{-1}. There were 32 scans for each spectrum.

3.8 X-ray diffraction (XRD)

Untreated and treated kenaf fibers were analyzed by XRD. The fiber samples were scanned on X-ray diffractometer type D8 Bruker equipped with a sealed tube Cu-Kα source, diffracted-beam graphite monochromator, and scintillation detector. The equatorial diffraction patterns (2θ) were recorded from 10 to $30°$ using Cu-Kα radiation at 40 KV and 40 mA. The crystallinity index, CrI, was calculated by using the following equation [Eq. (2)] [21].

$$CrI = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

(2)

where I_{002} is the counter reading at peak intensity at a 2θ angle close to $22°$, and I_{am} is the amorphous counter reading at a 2θ angle of around $18°$. The scattered intensity is in arbitrary units and not normalized to sample mass, so ratios of peak heights, rather than absolute intensities, are used for the comparison between different samples.

3.9 Thermogravimetric analysis (TGA)

TGA of the kenaf fiber was carried out using a Perkin Elmer TG Analyzer TGA7 under air atmosphere. The temperature profile was from 30 to $600°C$ at a heating rate of $10°C/min$. The amount of sample used was approximately 6 mg.

3.10 Contact angle measurements

Contact-angle measurements of the treated fibers were performed with a dynamic contact angle and tensiometer (DCAT 21, DataPhysics Instrument GmbH, Filderstadt, Germany). The treated fibers of 2 h were packed into the apparatus and then mounted indirectly to the measuring

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arm of the microbalance. The wetting liquids used for the contact-angle measurements were n-hexane, deionized water and ethylene glycol. The surface free energy (or surface tension) and other characteristics for the wetting liquids are listed in Table 3.2.

Table 3.2 Characteristics of wetting liquids used in this work

Wetting liquid	$\gamma_L^{l,a}$ (mJ/m²)	$\gamma_L^{sp,b}$ (mJ/m²)	γ_L^c (mJ/m²)	η^d (mPa s)	ρ^e (g/cm³)
n-Hexane	18.4	0	18.4	0.33	0.661
Water	21.8	51	72.8	1	0.998
Ethylene glycol	31.0	16.7	47.7	17.3	1.100

[a] γ_L^l : London dispersive component of surface free energy.

[b] γ_L^{sp} : specific component of surface free energy.

[c] γ_L : total surface free energy.

[d] η : viscosity

[e] ρ : density.

3.11 Fiber tensile test

Tensile test of single kenaf fibers were performed according to the standard method ASTM D 3379. The fibers were mounted on a rectangular card and glued with cyanocrylate adhesive / glued on special cardboard frames of gauge lengths 3.5 and 8 mm. The samples were tested using a micro-tensometer with a maximum load cell of 1.0 N. The crosshead speed was

2.5 mm/min. The fiber diameter was measured prior to testing with the help of an optical microscope. The tensile strength of 35 specimens of single fibers was measured for each condition.

3.12 Tensile test

Tensile tests were carried out using the Biss tensile testing machine (model Bi-05-172) manufactured by Testresources in accordance with ASTM D 3039 for composite samples and ASTM D638 for resin samples. Samples were tested at a crosshead speed of 2 mm/ min, 200 mm in gauge length and 100 kN load cell at room temperature.

3.13 Flexural test

Three-point bend tests were performed according to ASTM D 790. The tests were conducted using an Instron model 5960 with a 5 kN load cell. Samples were tested at a crosshead speed of 2 mm/min. At least five replicates were tested for each composite and their average was reported.

3.14 Fracture toughness test

Single edge notch three point bending (SEN-3PB) test is conducted to get the critical stress intensity factor toughness composites according to ASTM D5045 standard. Sample has 8 mm thickness, 16 mm width, 74 mm length and 3 mm notch in centre of sample (Fig 3.2). Crosshead speed was set at 1 mm/min with 5 kN load cell and 60 mm in span length. The load–displacement curves were recorded and the maximum loads upon fracture were used to determine the K_{IC} value, which is defined by the following equation (Eq. (3)] [22]:

$$K_{IC} = Y \frac{3PS\sqrt{a}}{2BW^2}$$

(3)

Where Y is shape factor, P is the maximum load, S is the length of the span, B is the specimen thickness, W is the specimen width, and a is the total notch length (produced by saw and fresh razor blade). For specific specimen geometry, the shape factor be determined by the equation as follows [Eq. (4)] [22]:

$$Y = 1,93 - 3,07\left(\frac{a}{W}\right) + 14,53\left(\frac{a}{W}\right)^2 - 25,11\left(\frac{a}{W}\right)^3 + 25,8\left(\frac{a}{W}\right)^4$$

(4)
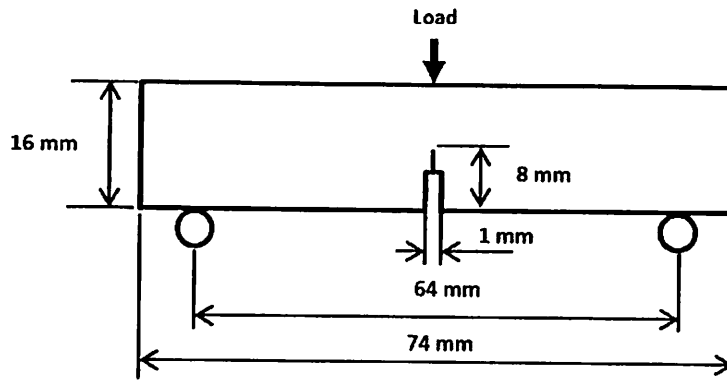
Fig. 3.2 SEN-3PB specimen geometry used for the fracture toughness

3.15 Interlaminar shear strength (ILSS)

Short beam shear (8 x 16 x 48 mm) tests were done according to ASTM D-2344 to estimate the apparent inter-laminar shear strength (ILSS). The ILSS was determined using a loading flexure fixture. It was performed at with a crosshead speed of 2 mm/min, 5 kN load cell

and 40 mm in span length. Interlaminar shear strength test was conducted at universal testing machine model Instron machine type 5960.

3.16 Hygrothermal aging test

Rectangular specimens for flexural samples (thickness 8 mm, width 18 mm, span length 130 mm and overall 160 length mm) were used to measure the weight change in water absorption studies. Prior to aging, the specimens were dried in an oven at 60°C for 24 hours, and cooled at room temperature in a desiccator until a constant weight was achieved, before weighing. The conditioned specimens were weighed for the first time and fully dipped in water. The specimens were kept at different temperatures of room temperature, 60°, and 90°C. Weight gains were recorded by periodic removal of the specimen from water bath and weighing on a balance (Mettler Toledo AL 204) with a precision of 0.1 mg.The samples were then wiped with a clean dry cloth paper to remove surface water, and weighed with an analytical balance until the weight of water content reached equilibrium.

The specimens were dried in a circulating oven at 60°C for 24 hours and weighed. The weighing was repeated until the specimen's mass was constant. The water absorption graph was calculated using the weight differences. The percentage water uptake of the samples was measured at different time intervals and the moisture content versus the square root of time was plotted. The water uptake was evaluated using the following equation [Eq. (5)]:

$$M(\%) = \left[\frac{M_1 - M_0}{M_0}\right] \times 100 \qquad (5)$$

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Where, $M(\%)$ is the water uptake as a percentage, M_t is the weight of the wet sample at a given time, and M_0 is the initial weight of the sample. Diffusion coefficient (D) was calculated from the slope of moisture content versus the square root of the time by the following equation [Eq. (6)]:

$$D = \pi \left(\frac{h}{4M_m}\right)^2 \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \tag{6}$$

Where, M_1 and M_2 are the water content (percent weight) at times t_1 and t_2, respectively, M_m is the maximum weight gain (%), and h is the thickness of composites (mm).

Chapter 4 – Results and discussion

FIBER CHARACTERIZATION

4.1 Scanning electron microscopy (SEM)

Surface morphologies of untreated, alkali treated and heat treated kenaf fibers as determined via SEM are shown in Fig. 4.1. SEM micrograph of the untreated kenaf fiber showed uneven surface suggesting the presence of a natural protective layer which is among others consists of lignin, pectin, waxy substances and natural oils. Some impurities were also observed on the fiber surface. Observation of the alkali treated kenaf fiber on the other hand showed different surface morphology. The alkali treated fiber had smoother and clearner surface without obvious impurities. Alkali treatment cleans fiber surface by removing impurities, waxy substances and natural oils. Kenaf fiber is made up of single fibers or macrofibrils cemented together by lignin and hemicelluloses. In addition to the protective layer, the alkali treatment also removed the cementing materials to some extent exposing the interfibrillar regions between the

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macrofibrils resulting in a rough fiber surface. Striations along the fiber length can be seen on the surface of the alkali treated fiber as evident in Fig. 4.1(b). The exposed interfibrillar regions increased the effective fiber surface area available for wetting by the polymer matrix during composite fabrication [23]. Such surface morphology also may improve fiber-matrix adhesion by introducing additional sites of mechanical interlocking [24]. Liu and co-workers [25] investigated the effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers. They observed that the interfibrillar region became more pronounced with increasing alkali concentration and treatment time due to the removal of more hemicelluloses and lignin. The effect of alkali treatment on the surface morphology of kenaf fiber [8, 15] and other natural fibers such as hemp [3], jute [26], grass [25], and sisal [27] has been reported by many researchers. The results observed are in line with those reported by these researchers. As seen in Fig.4.1 no evidence of fiber cell wall damaged was observed after the alkali treatment. The possible reaction mechanism during the alkali treatment of kenaf fiber is as shown in Scheme 1.
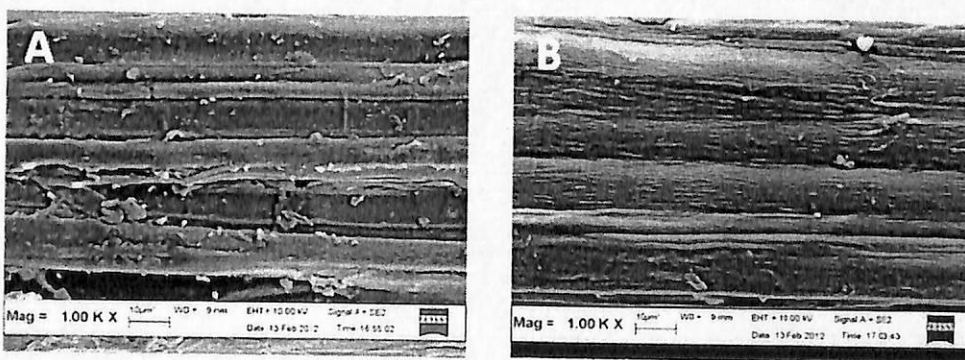

Fig. 4.1 SEM micrographs of surfaces of (A) untreated and (B) 6 % alkali treated (treatment time = 5 hours) kenaf fibers.

$$\text{Fibre-OH} + \text{NaOH} \longrightarrow \text{Fiber-O}^-\text{Na}^+ + \text{H}_2\text{O}$$

Scheme 1. Possible reaction mechanism during the alkali treatment of kenaf fiber [5].

4.2 Atomic force microscopy (AFM)

AFM images of untreated and alkali treated kenaf fibers are shown in Fig. 4.2. These images illustrated some reduction of the surface roughness of kenaf fiber due to alkali treatment. Untreated fiber exhibited a root mean square (RMS) roughness value of 21.6 nm, whereas the alkali treated fiber exhibited 11.21 nm of RMS roughness. The decrease in the fiber surface roughness following the alkali treatment was probably due to the removal surface impurities and some materials such as lignin and waxy substances from the fiber surface.
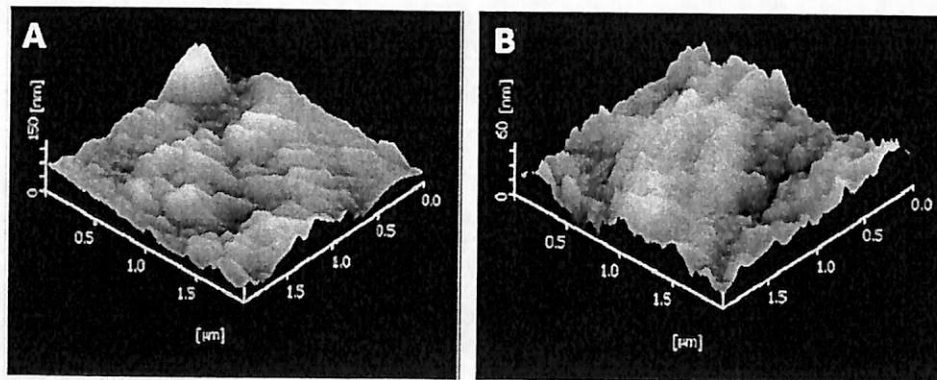

Fig. 4.2 Three-dimensional presentation of AFM contact mode images for (A) untreated and (B) 6% alkali treated (treatment time = 5 hours) fibers.

4.3 X-ray photoelectron spectroscopy (XPS)

Samples of untreated and treated kenaf fibers were examined using XPS. The XPS spectra with the resolved peaks, as a function of binding energy, are plotted in Fig. 4.3. Relative amount of atoms at the fiber surface, oxygen to carbon ratios and carbon peak area ratios for untreated, alkali and heat treated kenaf fibers are given in Table 4.1. The major elements comprising natural fibers, consisting of celulose, hemicellulose, lignin, and wax, are carbon, oxygen and hydrogen. Therefore, it is not surprising that high electron intensity of carbon and oxygen are detected in all fibers. The untreated fibers had an O/C value of 0.37 which agrees with the value of 0.39 for *Pinus silvestris L.* [28] and the value of 0.41 for *Pinus radiata* [29]. The observed alkali treated kenaf fibers O/C ratio of 0.59 was greater than the untreated fibers suggesting that the surface of the treated fibers was rich in oxygen. This was expected and can be attributed to the removal of extractives, waxes, surface lignin during the treatment with alkali solution exposing to some extent the underlying cellulose component.

(A)   (B)
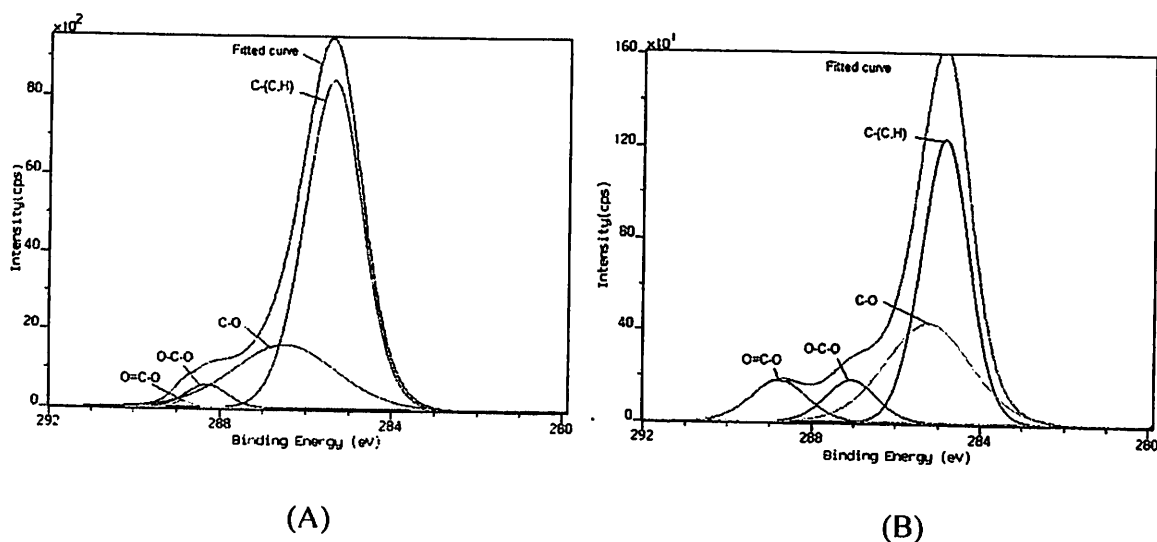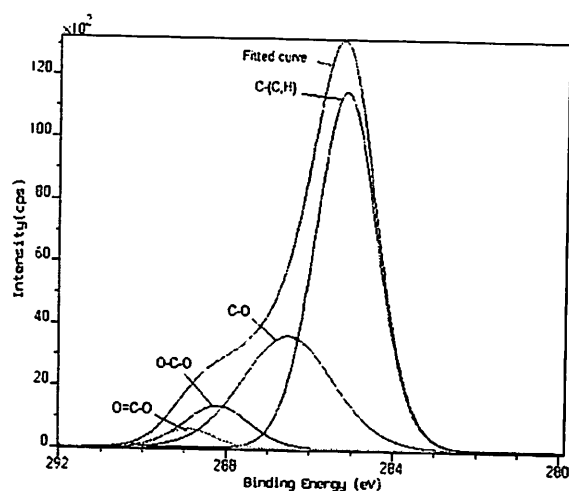
<p style="text-align:center">(C)</p>

Fig. 4.3. High resolution C(1s) XPS spectra of (A) untreated (B) alkali and (C) heat treated kenaf fibers.

Table 4.1 Relative amount of atoms at the fiber surface, oxygen to carbon ratios and carbon peak area ratios for untreated, alkali and heat treated kenaf fibers.

Sample	Elements			O/C	Peak areas				Peak area ratios		
	C (%)	O (%)	N (%)		C_1	C_2	C_3	C_4	C_2/C_1	C_3/C_1	C_4/C_1
Untreated	69.96	26.00	1.14	0.37	71.1	24.9	3.6	0.4	0.35	0.05	0.006
Alkali treated fiber	61.91	36.83	0.73	0.59	51.0	32.2	8.1	8.8	0.63	0.16	0.172

4.4 Fourier transform infrared (FTIR) spectroscopy

Examination of Fig. 4.4 (a) revealed several changes on the FTIR spectra of the kenaf bast fibers after the alkali treatment. The absorption peak at 1737 cm^{-1}, assigned to a C=O

<p style="text-align:center">35</p>

stretching vibration of carboxylic acid or ester, was found to disappear following the alkali treatment due to the removal of hemicelluloses from the fiber surface [25]. Other significant changes are reduction in the intensity of the absorption peaks at 1515 and 1254 cm^{-1} which are assigned to the benzene ring vibration of lignin and a C-O stretching vibration of the acetyl group in lignin component, respectively. Reductions in these absorption peaks indicate removal of surface lignin from the fiber after the alkali treatment [25].
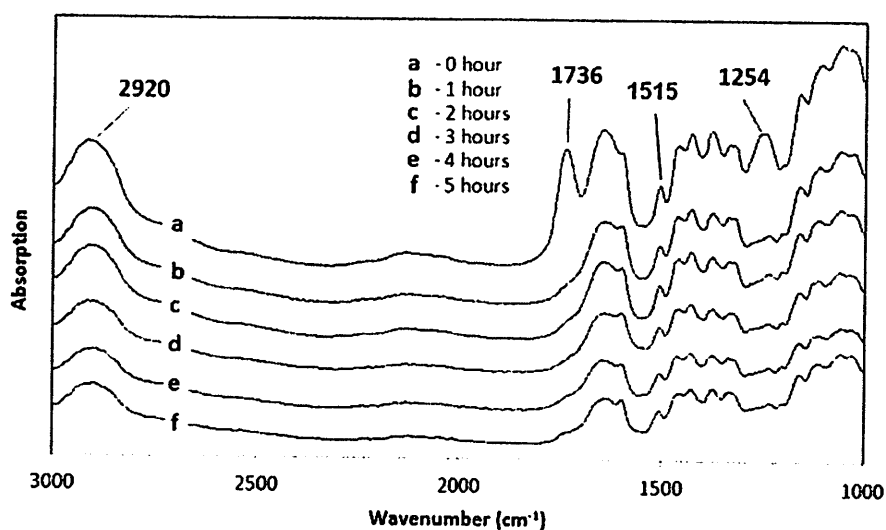
Fig. 4.4 FTIR spectra of alkali treated kenaf fiber at different treatment times.

4.5 Crystallinity index

Cellulose is a semicrystalline polymer. The crystal structure of native cellulose is cellulose I. Cellulose I structure is made of parallel chains characterized by an intermolecular hydrogen bond network extending from O_2-H hydroxyl to the O_6 ring oxygen of the next unit. Another crystal structure of cellulose is cellulose II. Cellulose II structure is most often obtained from cellulose I via either of two processes: regeneration and mercerization or alkali treatment.

In the crystal structure of cellulose II, chains with opposite polarity are staked to form corrugated sheets. Hydrogen bonding exists within the sheets as well as between them.

Fig. 4.5 shows the diffraction patterns of untreated and alkali treated kenaf fibers. The diffraction patterns of these fibers showed two characteristic peaks of cellulose I crystal structure at $2\theta = 22.4°$ (200) and $2\theta = 16.3°$. Cellulose II crystal structure exhibits a couple of weak peaks (a doublet) at $\sim 20°$ and $21°$ and a peak at $\sim 12°$. The results of XRD therefore indicated that alkali treatment did not lead to transformation of the cellulose crystal structure of kenaf fibers from cellulose I to cellulose II.
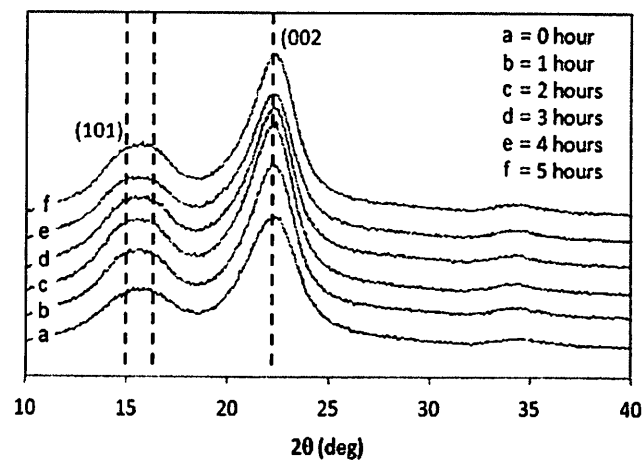
Fig. 4.5 XRD patterns of alkali treated kenaf fibers at different treatment times.

The crystallinity index values of untreated and alkali treated kenaf fibers are given in Table 4.2. Crystallinity index of kenaf fibers improved with alkali treatment after 1, 2, 3, 4 and 5 hours of treatment. The maximum improvement was observed after 2 hour of treatment (+ 11%). Beyond that the crystallinity index of the treated fibers reduced but the values were higher than that of the untreated fiber. Changes in crystallinity through alkali treatment for natural fibers have been reported by many researchers [21, 26]. The improved crystallinity of natural fiber after

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the treatment has been attributed to the removal of the cementing materials, hemicelluloses and lignin, which probably leads to better packing of cellulose chains [26] and thickening of the fiber cell wall [21]. Removal of these materials releases the initial strain between the cellulose chains. This allows the formation of new hydrogen-bonds leading to a closer packing of cellulose chains. In addition to the removal of the cementing materials, alkali treatment also partially depolymerizes cellulose chains [5]. After 4 and 5 h of treatment, excess depolymerization of cellulose chains might have occurred damaging the fiber cell wall i.e. the cellulose chains rearrangement leading to an overall decrease in the crystallinity index of the treated fiber. In addition the firmly bound three-dimensional network of cellulose chains arrangement may be partially destroyed upon prolonged alkali treatment.

Table 4.2 Crystallinity index of alkali treated and heat treated kenaf fiber.

| Material	Treatment time (h)	Crystallinity index
Untreated fiber	0	55.73
Alkali treated fiber	1	61.62
	2	61.65
	3	61.40
	4	60.10
	5	59.95

4.6 Thermogravimetric analysis (TGA)

Natural fibers including kenaf fiber consist of 3 main components, cellulose, hemicelluloses, and lignin. These chemical components degrade at different temperatures. Cellulose is highly crystalline and therefore is thermally stable. Both hemicelluloses and lignin are amorphous and they start to degrade before cellulose. Hemicelluloses are the least thermally stable wood components due to the presence of acetyl groups. Hemicelluloses degradation occurs at 200-260 °C and cellulose degradation at about 240-350 °C. Lignin degrades partly over a wide temperature range, starting at relatively low temperatures. Lignin degradation occurs at 280-500 °C. Natural fibers also contain small amount extractives which include: phenolic compounds, non-structural sugars, organic acids, waxes, fatty acids, and other minor components. Extractives have much lower thermal stability than hemicelluloses.

Thermogravimetric (TGA) and derivative (DTG) curves for untreated, alkali treated and heat treated kenaf fibers are shown in Fig. 4.6. Table 4.3 lists the temperature corresponding to 2 % weight loss ($T_{2\ wt\ \%}$, °C) and the maximum thermal degradation temperature (T_{max}, °C) for all untreated and treated fibers. Untreated and treated fibers showed rapid thermal decomposition between 275 and 375°C. The DTG curves of the untreated and treated fibers did not show an initial peak associated with loss of moisture suggesting that the fibers were relatively dried prior to the analysis. The DTG curve of the untreated kenaf fiber showed two decompositions steps, a shoulder at 295°C and a strong peak at 360°C (the maximum thermal degradation temperature) that can be attributed to hemicelluloses and cellulose decomposition, respectively. The DTG curve of alkali treated fiber, however, showed one decomposition step associated to α-cellulose decomposition at 355°C. The step of hemicelluloses decomposition was not detected. This was expected due the removal of hemicelluloses to some extent during the alkali treatment, in

39
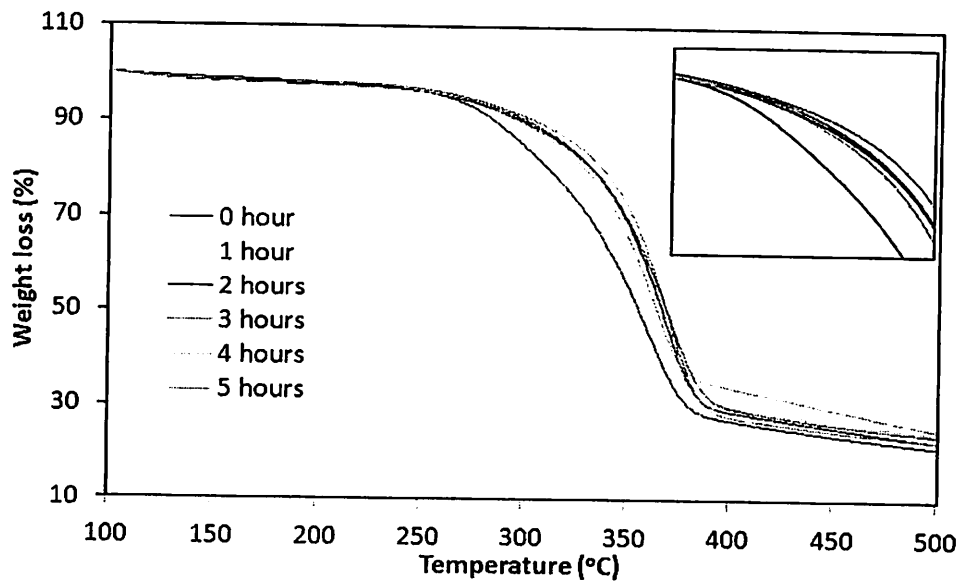
(A)
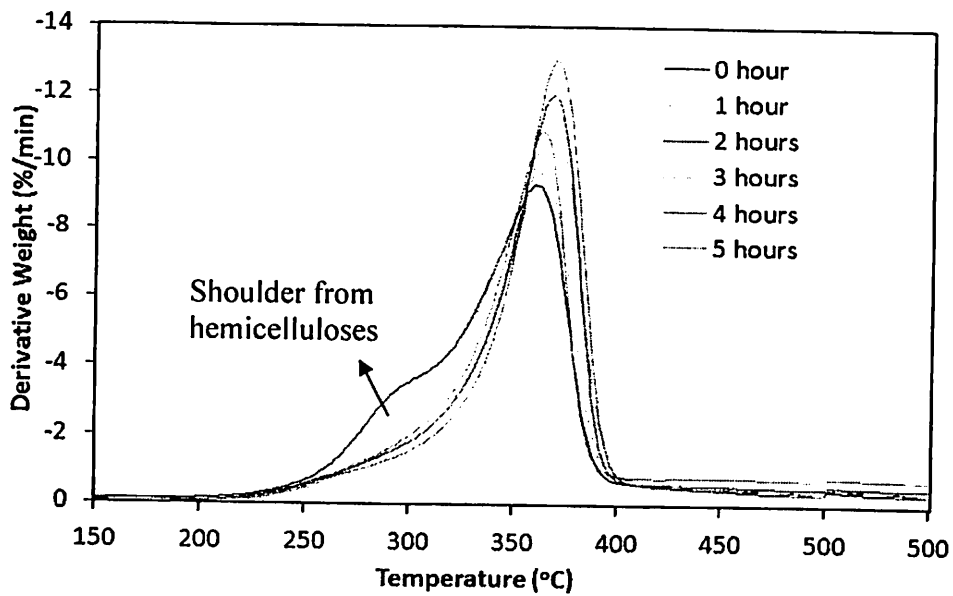
(B)

Fig. 4.6 (A) TGA and (B) DTGA thermograms for alkali treated kenaf fiber.

accordance with FTIR analysis. The peak corresponding to α-cellulose decomposition increased from 363 to 373°C, which indicates that the alkali leads to an enhancement in the thermal

stability of kenaf fibers, as has been noted by other researchers on different natural fibers [3, 27, 30]. The maximum decomposition rate temperature of the treated fibers was slightly shifted to a higher temperature with increasing treatment time. Therefore, the thermal stability of alkali treated kenaf fibers was dependent on the treatment time.

Table 4.3 Thermogravimetric results of untreated and treated kenaf fibers

	T_2 (°C)[a]	Max. degradation temperature (C)
Untreated fiber	263	360
Alkali treated fiber		
1 hr of treatment	269	369
2 hr of treatment	267	368
3 hr of treatment	269	362
4 hr of treatment	273	369
5 hr of treatment	267	363

[a] Temperature corresponding to 2 % weight loss.

4.7 Contact angle and surface free energy

Contact angles of untreated and treated fibers are shown in Fig. 4.7. Alkali treatment improved the wettability of kenaf fibers. The contact angles of water on alkali treated kenaf fibers were less than 90°, suggesting that the fibers were hydrophilic in nature. The contact angles of the treated fibers were less than the contact angle of the untreated fibers. This signified that water can wet the treated fibers better than the untreated fibers. In other words,

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hydrophilicity of the fibers was significantly increased by alkali treatment. This was probably due to the removal of low molecular weight materials, waxes and extractives, as well as the cementing materials from the fiber surface exposing more of the underlying cellulose component which is rich in hydroxyl groups.
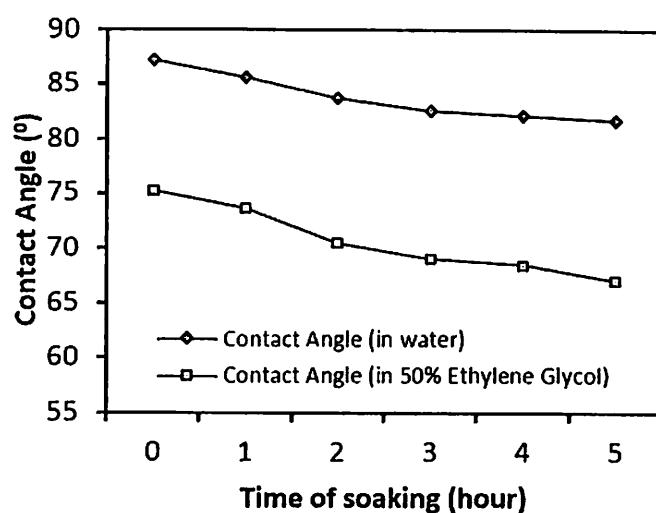

Fig. 4.7 Contact angles of untreated and alkali treated kenaf fibers at different treatment times.

The specific (SP) and London (L) dispersive components of the surface free energy of the untreated and alkali treated kenaf fiber were determined by measuring the contact angles of two test liquids with their known specific and London dispersive components and analyzing the results in accordance with the method proposed by Owens and Wendt [31] and Kaelble [32] using the geometric mean.

$$\gamma_L(1+\cos\theta) = 2\left(\gamma_L^l\gamma_S^l\right)^{\frac{1}{2}} + 2\left(\gamma_L^{sp}\gamma_S^{sp}\right)^{\frac{1}{2}} \tag{7}$$

where the subscripts L and S represent the liquid and solid states, respectively. Using the two wetting liquids the specific and London dispersive components of the fibers were calculated by the following equations.

$$\gamma_S^{SP} = \frac{1}{4}\left[\frac{(1+\cos\theta_2)\gamma_2(\gamma_1^L)^{\frac{1}{2}} - (1+\cos\theta_1)\gamma_1(\gamma_2^L)^{\frac{1}{2}}}{(\gamma_1^L\gamma_2^{SP})^{\frac{1}{2}} - (\gamma_2^L\gamma_1^{SP})^{\frac{1}{2}}}\right]^2 \tag{8}$$

$$\gamma_S^L = \frac{1}{4}\left[\frac{(1+\cos\theta_1)\gamma_1(\gamma_2^L)^{\frac{1}{2}} - (1+\cos\theta_2)\gamma_2(\gamma_1^L)^{\frac{1}{2}}}{(\gamma_1^L\gamma_2^{SP})^{\frac{1}{2}} - (\gamma_2^L\gamma_1^{SP})^{\frac{1}{2}}}\right]^2 \tag{9}$$

where the subscripts 1 and 2 in this study represent water and ethylene glycol, respectively.

The results of the surface free energies or surface tensions of alkali treated kenaf fibers calculated from equations (3) and (4) are shown in Fig. 4.8. The total surface free energy of alkali treated kenaf fibers increased, while the London dispersive component remained nearly constant with increasing treatment time. An small increase in the dispersive component was observed when the fibers were treated for 5 h. The increase in surface free energy can be attributed to the increase in polarity due to the increased cellulose content on the fiber surface, resulting from the removal of impurities as well as cementing materials, hemicelluloses and lignin from the fiber surface following the alkali treatment.
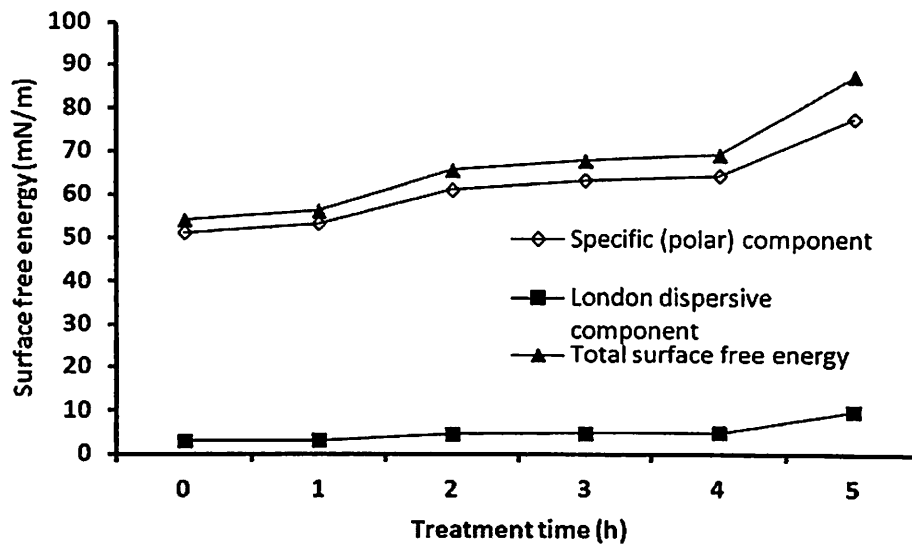
Fig.4.8. Surface free energies of untreated and alkali treated kenaf fibers.
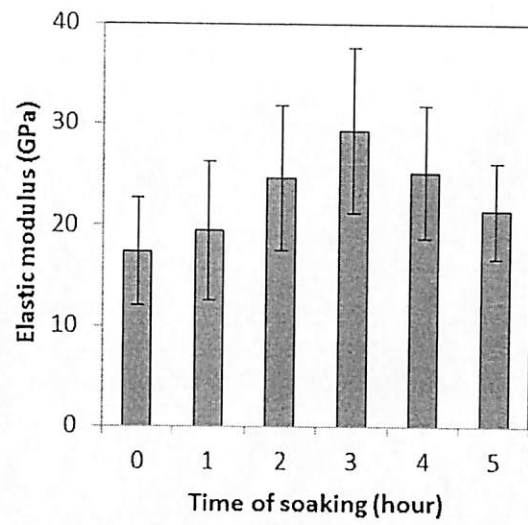
4.8 Tensile strength

The effect of alkali treatment on the properties of natural fibers depend on the type and concentration of the alkali solution as well as the temperature and time of treatment [2]. It is clear from Fig. 4.9 (a) that alkali treatment had an effect on the tensile strength of the treated fibers. All alkali treated fibers at different treatment times were stronger than the untreated fiber. The increase in the fiber strength can be attributed to an increase in packing density and molecular orientation of cellulose chains due to the removal of the cementing materials, lignin and hemicelluloses [32]. On removal of hemicelluloses, the internal constraint is removed and the fibrils become more capable of rearranging themselves in a compact manner leading to a closer packing of cellulose chains. Crystallinity of the fibers is thus increased, causing improvement in the fiber strength properties. Removal of hemicelluloses also makes the interfibrillar region less densed less rigid which facilitate the microfibrils to rearrange themselves in the direction of tensile deformation. Applied load, therefore, are shared more efficiently

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among the microfibrils resulting in higher stress development in the fiber [32]. Maximum improvement in the fiber strength was observed when the fibers were alkali treated for 2 and 3 h. Beyond these treatment times the fiber strength began to decrease to values still higher than that of untreated fiber. Such observation was probably due to partial depolymerization of crystalline cellulose chains at longer treatment times leading to a decrease in the crystallinity index as seen in Table 4.2. Crystallinity index is one of main factors contribute to the strength and stiffness of natural fibers.

Fig. 4.9 (b) shows the effect of alkali treatment on the elastic modulus of alkali treated kenaf fibers. The fibers showed greater elastic modulus than the untreated fibers after the alkali treatment. The overall variations in the elastic modulus with treatment time were similar to the tensile strength. Maximum improvement in the property was observed for kenaf fibers after 3 h of treatment after which the elastic modulus started to decrease with increasing treatment time. The increase in the elastic modulus was due to the improvement in the crystallinity index of alkali treated fibers. Prolonged treatment in alkali treament might have resulted in an excess removal of cementing materials, hemicelluloses and lignin. Removal of lignin to some extent might have adversely affect the stiffness of the fibers since lignin is the rigid component of natural fibers. Another factor was a decrease in the crystallinity index of the alkali treated fibers after 4 and 5 h of treatment. Strain at break of alkali treated fibers steadily decreased with increasing treatment time (Fig. 4.9 (c)). The results showed that alkali treated fibers were stronger, stiffer but brittle than the untreated fibers.
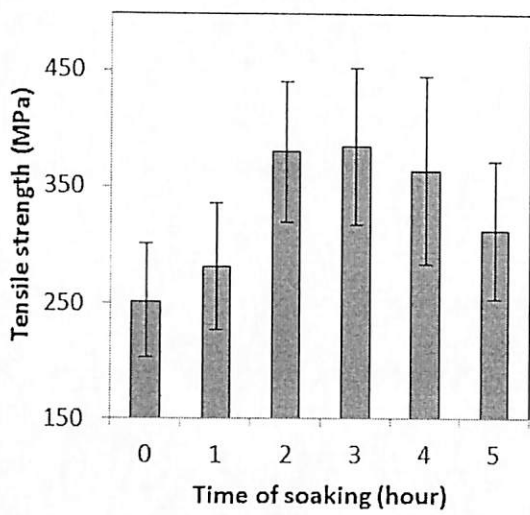
(A)

(B)
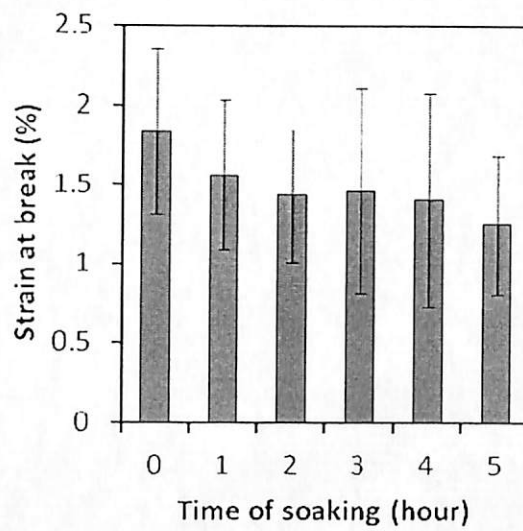
(C)

Fig. 4.9 Tensile properties of alkali treated fibers (A) tensile strength (B) tensile modulus and (C) strain at break.

COMPOSITE CHRACTERIZATION

4.9 Tensile properties

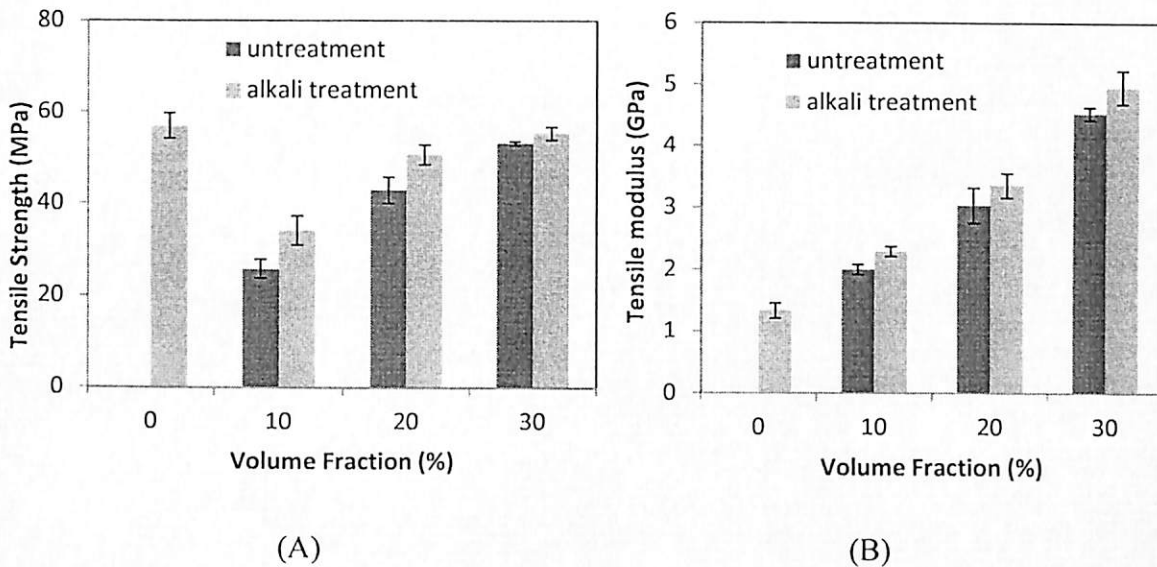(A)   (B)

Fig. 4.10 (A) Tensile strength and (B) tensile modulus of untreated and alkali treated kenaf fiber composites (treatment time = 5 h) as a function of fiber volume fraction.

With untreated fibers, the composites showed an increasing trend in the tensile strength and tensile modulus with fiber volume fraction (Fig. 4.10). The same tend was observed for alkali treated kenaf fiber composites. Properties of fiber-reinforced composites are strongly dependent on the quality of the fiber-matrix interfacial adhesion. Alkali treated kenaf fiber composites showed better tensile strength than untreated fiber composites and this was observed irrespect of different fiber volume fractions. Improvement in the tensile strength can be attributed to the enhanced interfacial adhesion between the resin matrix and the kenaf fiber. Alkali treatment as observed in Fig. 4.1 resulted in the removal of cementing materials, hemicelluloses and lignin, exposing the interfibrillar regions between the macrofibrils. The exposed interfibrillar

regions increased the effective fiber surface area available for wetting by the unsaturated polyester resin during the composite fabrication [23]. In addition, such fiber surface morphology may promote fiber-matrix mechanical interlocking resulting in better fiber-matrix interfacial adhesion. With sufficient fiber-matrix adhesion, the interface formed can effectively transmit the applied stress from the matrix to the fiber, resulting in enhanced composite strength. Other factors that may account for the improvement in the tensile strength is improved fiber strength due the increase in cellulose crystallinity (Table 4.2) and better wettability of the alkali treated fiber by the matrix resin as the alkali treatment increased the surface free energy of the fiber (Fig. 4.8). The improvement in the tensile modulus of all composites with increasing fiber volume fraction can be attributed to the higher inherent stiffness of the kenaf fibers as compared to the polyester matrix. Alkali treated kenaf fiber composites showed greater tensile modulus than the untreated composites. The enhanced fiber-matrix interfacial adhesion resulted in a greater restrictions to the molecular mobility of polymer chains at the interface increasing the overall stiffness of the treated fiber composites.

4.10 Flexural properties

Fig. 4.11 shows flexural strength and flexural modulus of untreated and alkali treated kenaf fiber composites as a function of fiber volume fraction. Untreated and treated fiber composites showed an increase in the flexural strength and flexural modulus with increasing fiber volume fraction. With increasing fiber volume fraction, applied load are shared more efficiently among the fibers resulting in higher stress development in the composites. The improvement in the flexural modulus of all composites with increasing fiber volume fraction can

be attributed to the higher inherent stiffness of the kenaf fibers as compared to the polyester matrix.

(A)   (B)
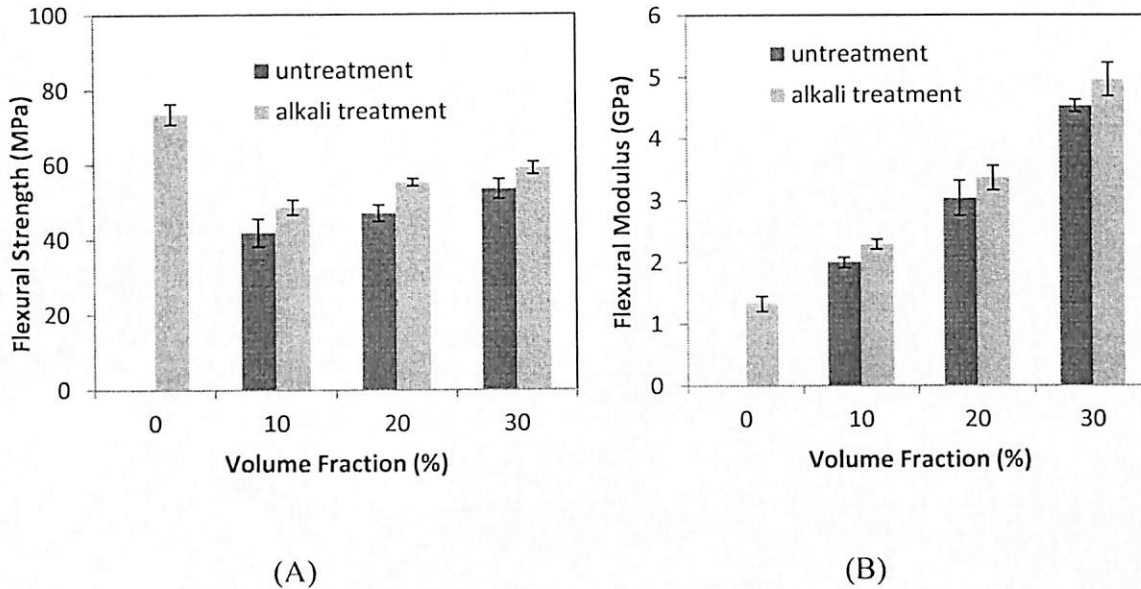
Fig. 4.11 (A) Flexural strength and (B) flexural modulus of untreated and alkali treated kenaf fiber composites (treatment time = 5 h) as a function of fiber volume fraction.

The flexural strength of alkali treated kenaf fiber composites was greater than that of the untreated composite (Fig. 4.12 (A)). The highest improvement in the property (+ 12%) was observed when the fibers were alkali treated for 3 h. The increased in the property can be attributed to the enhanced interfacial adhesion between the resin matrix and the kenaf fibers. Beyond 3 h of alkali treatment the flexural strength of the composites started to decrease but the values were higher than the untreated composites. This observation can be attributed to the decrease in the cellulose crystallinity of the kenaf fiber after prolonged alkali treatment. The flexural modulus of alkali treated kenaf fiber composites also exhibited similar trends. After 5 h of alkali treatment, however, the flexural modulus of the composites decreased (- 9%) to a value

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much lower than that of the untreated composite (Fig. 4.12 (B)). Prolonged treatment in alkali treament might have resulted in an excess removal of cementing materials, hemicelluloses and lignin. Removal of lignin to some extent might have adversely affect the stiffness of the fibers (Fig. 4.9 (B)) since lignin is the rigid component of natural fibers. Another factor was a decrease in the crystallinity index of the alkali treated fibers as observed in Table 4.2.
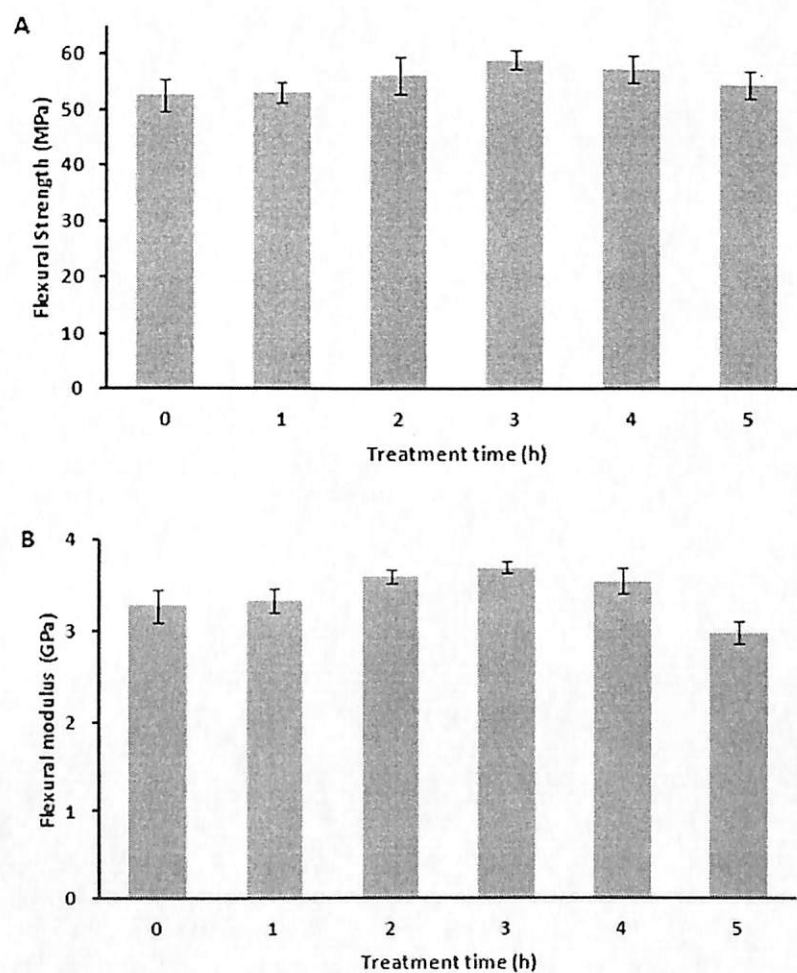

Fig. 4.12 (A) Flexural strength and (B) flexural modulus of untreated and alkali treated kenaf fiber composites at different treatment times (fiber volume fraction = 0.3).
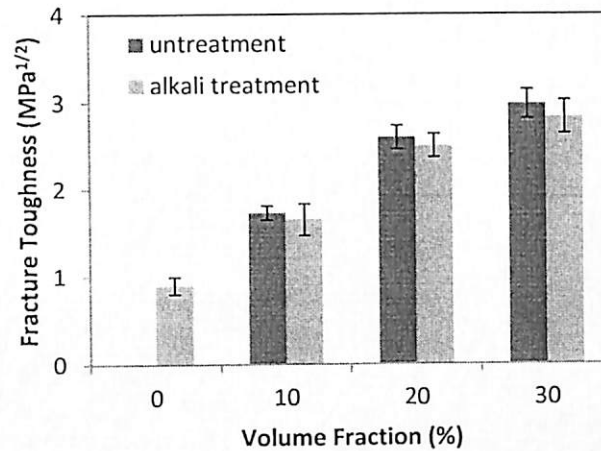
4.11 Fracture toughness

Fig. 4.13 Fracture toughness of untreated and alkali treated kenaf fiber composites (treatment time = 5 h) as a function of fiber volume fraction.

The fracture toughness results of the composites are shown in Fig. 4.13. Fracture toughness of untreated and alkali treated kenaf fiber composites was found to increase with increasing fiber volume fraction. The matrix toughness is attributed to the energy dissipation mechanism by plastic deformation. With fibers addition this mechanism is hindered and other toughnening mechanisms related to the fibers, such as pull-out of fibers from the matrix and fiber-bridging mechanism begin to act, which result in more superficial area and consequently larger fracture energy of fracture toughness [34]. The alkali treatment was found to slightly reduce the fracture toughness of kenaf fiber composites. This can be attributed to the strong fiber-matrix interaction that hinders the development of energy absorption mechanisms, such as debonding and fiber pull-out [34].

4.12 Fractured surface morphology

Fig. 4.14 illustrates the fracture surface characteristics of untreated and alkali treated kenaf fiber composites. Both long and short exposed fibers were observed from the micrographs. The long exposed fibers indicated fiber pullout while the short exposed fibers indicated fiber fracture near the failure zone (as indicated by the circles in Fig. 4.14). Holes due to the pulled-out of fibers were also observed on these micrographs. The obvious difference between both fracture surfaces was the gaps between the fibers and the surrounding matrix. Clear gaps were observed from the micrographs of untreated kenaf fiber composite while relatively smaller or near to absence of gaps were observed for the micrograph of the alkali treated kenaf fiber composite. The latter morphology observed indicates better fiber-matrix interaction in the composite and this is probably due to better wetting of the fiber by the matrix and the formation of mechanical interlocking of the fiber and the matrix at the interface.
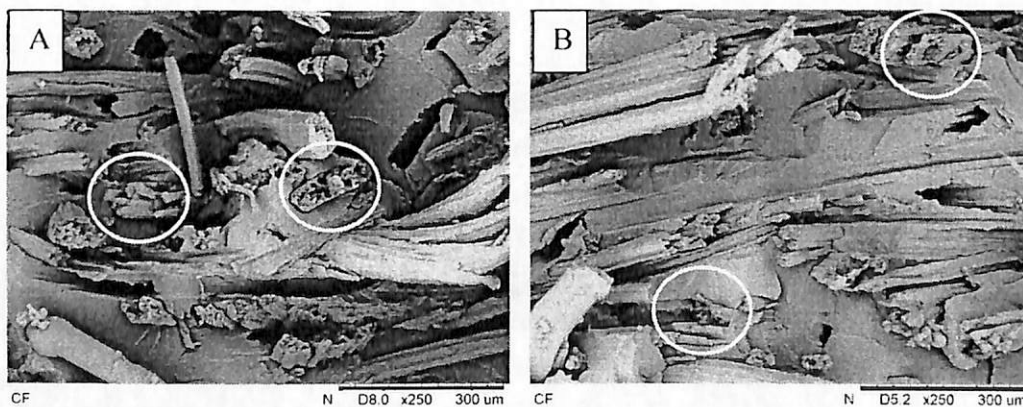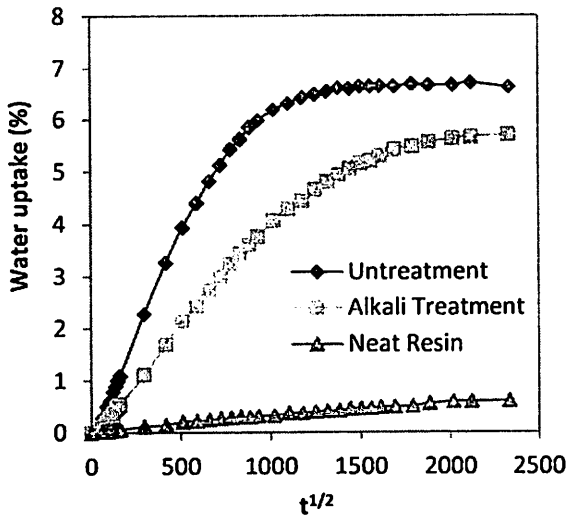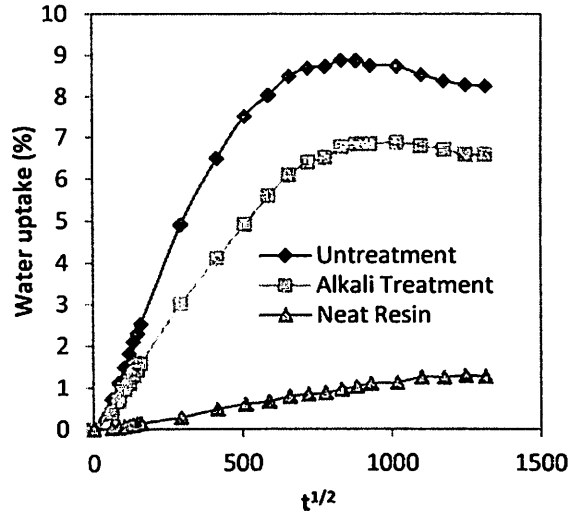

Fig. 4.14 SEM micrographs of fracture surfaces of (A) untreated and (B) alkali treated composites for 3 h of treatment (fiber volume fraction = 0.3).
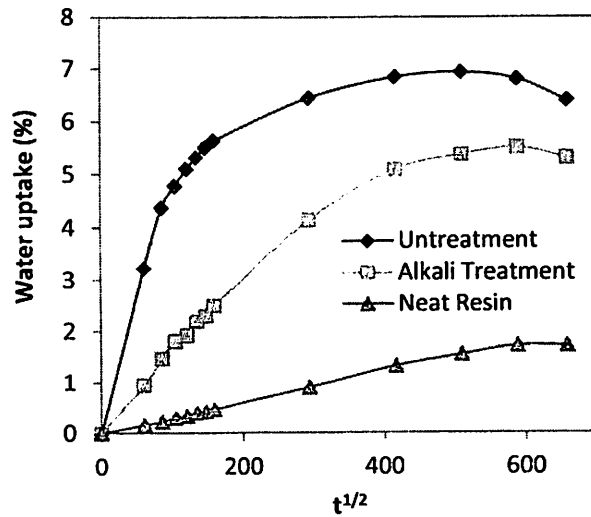
during composite fabrication. The water uptake of neat resin and both untreated and alkali treated kenaf fiber composites increased steadily with $t^{1/2}$ in the initial stage, and then

(A)

(B)

(C)

Fig. 4.16 Water uptake curves of untreated and alkali treated kenaf fiber composites at (A) 30 °C, (B) 60 °C and (C) 90 °C (fiber volume fraction = 0.3).

began to level-off following complete saturation suggesting Fickian behaviour of water absoption. This was observed when the samples were immersed at 30 °C. Samples immersed at 60 and 90 °C showed different trend of water uptake after the initial stage, which was non-Fickian behaviour. After reaching the maximum water uptake, the water uptake of these samples began to decrease with $t^{1/2}$ probably among others due to leaching out of surface fibers and low molecular-weight materials from the composites. The uptake of water by neat resin, untreated and alkali treated fiber composites increased with increasing immersion temperature. Like other natural fibers, kenaf fibers, absorption of water may lead to fiber swelling resulting in the formation of microcracks in the composites. The ester groups in polyester resin may undergo hydrolysis resulted in the formation of microvoids. Both of above among others may account for the uptake of more water by the samples at high immersion temperatures. Alkali treated kenaf fiber composites absorbed less water than the untreated fiber composites. This can be attributed to the removal of hemicelluloses to some extent from the fiber cell wall due to alkali treatment. Another factor was due to the enhanced fiber-matrix interaction which restricted mobility of water molecules to penetrate via capillary action inside the composite structures. Maximum water uptake by neat resin, untreated and alkali treated kenaf fiber composites are showed in Table 4.4. The reasons may explain for the variations of maximum water uptake by the samples at different immersion temperatures. It is clear from Table 4.4 that the D values for all samples increased with immersion temperature probably due the formation of more defects such as microcracks and microvoids, which enhanced the driving for water molecules to penetrate inside the samples.

Table 4.4 Values of saturation moisture uptake, initial slope of plot, diffusion, sorption and permeability coefficient for treated kenaf/polyester composites at different temperatures.

| Material	Temperature Aging (^{0}C)	Maximum water uptake (%)	Difussion Coefficient, D, $\times 10^{-12}$ m^2/s
Neat resin	30	1.71	4.46
Untreated fiber composites	30	6.80	17.77
Alkali treated fiber composites	30	5.70	8.14
Resin	60	1.13	7.75
Untreated fiber composites	60	8.74	56.64
Alkali treated fiber composites	60	6.88	39.15
Resin	90	0.61	26.99
Untreated fiber composites	90	6.63	655.10
Alkali treated fiber composites	90	5.50	235.71

4.14.2 Flexural properties

From Fig. 4.17, it can be seen that hygrothermal aging has resulted in a dramatic reduction in the flexural strength of neat resin, untreated and alkali treated kenaf fiber composites. The interaction of water molecules with polyester resin might have resulted in permanent damage to the material. The water molecules may hydrolyze the ester groups resulting in the formation of microvoids in polyester resin. Microvoids are stress concentrators and may decrease the strength of polyester resin. The decreased in the flexural strength may also be attributed to the plasticization effect of water molecules on polyester resin. In addition to the formation of microvoids, the poor flexural strength of untreated and alkali treated kenaf fiber composites can be attributed to 1) the formation of microcracks in the composite structures resulted from fiber swelling; 2) the relatively poor fiber properties and 3) degradation of fiber-matrix interaction. The adverse effect of water on the flexural strength of neat resin and composites was more severe at higher immersion temperatures due to the formation of more composite defects. Alkali treated kenaf fiber composites showed better flexural strength after water absorption at 30 and 60 °C. This can be attributed to better fiber-matrix interaction which limited the adverse effect of water absorption such the formation on microcracks, on the composites. At immersion temperature of 90 °C, however, both the untreated and treated fiber composites showed comparable flexural strength suggesting severe degradation of fiber-matrix interaction in alkali treated fiber composites at this immersion temperature. Both untreated and alkali treated fiber composites recovered more than 95% of the flexural strength after the redrying process following the water immersion at 30 °C suggesting that plasticization effect of water molecules on the composites was the main mechanism that responsible for the decrease in the property after the water absorption. Such effect is a reversible physical process and may
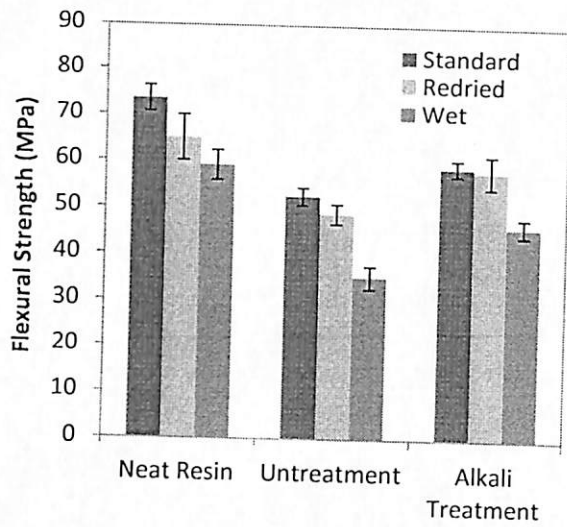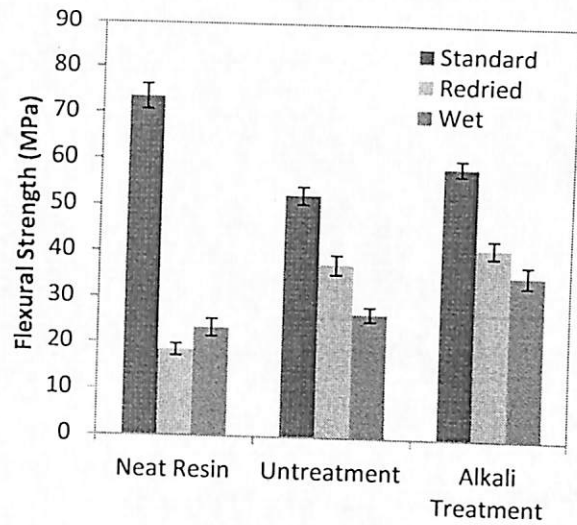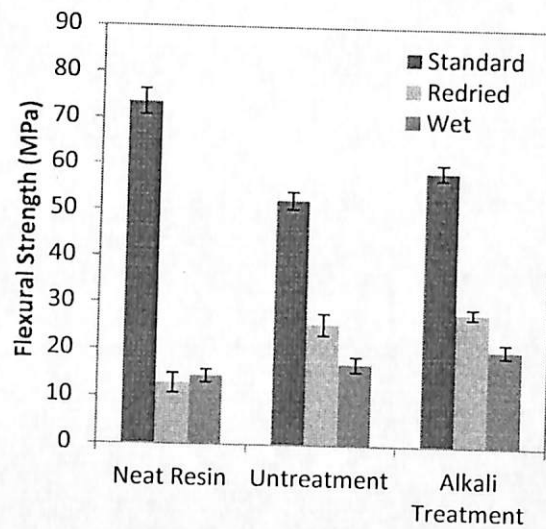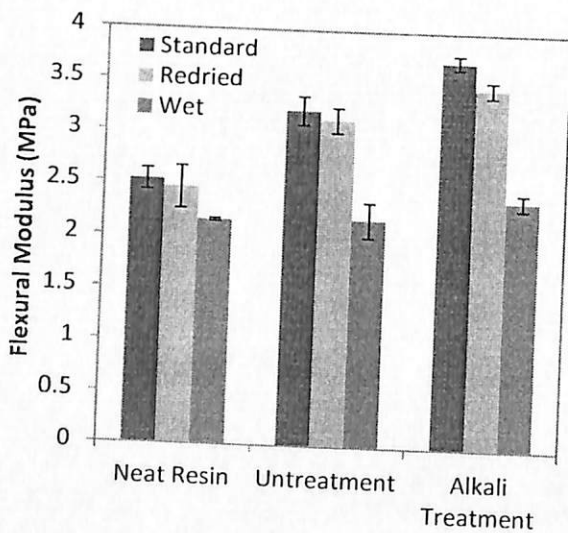
Fig. 4.17 Flexural strength of neat resin and composites after hygrothermal aging at (A) 30 °C, (B) 60 °C and (C) 90 °C (fiber volume fraction = 0.3).

explain the high percent recovery of the composites. The percent recovery of the flexural strength decreased to less than 75% and 50% when these composites were immersed at 60 and

90 °C, respectively suggesting irrevesible effects of water absorption on the composites. The water molecules might have penetrated deep in the composites. The interaction of water molecules with kenaf fibers may result in fiber swelling and thus inferior fiber properties. Fiber swelling may also lead to microcracking of the surrounding polyester matrix. Such damages are irreversible and could not be restored upon redrying. As a result, the composites showed recovery of the flexural strength after the redrying process.

The similar trend was observed for the flexural modulus of neat resin, untreated and alkali treated kenaf fiber composites after hygrothermal aging at 30, 60 and 90 °C (Fig. 4.18). Unlike the flexural strength, both untreated and alkali treated fiber composites showed greater than 70% recovery of the flexural modulus after the redrying process following the hygrothermal aging at 60 and 90 °C.

(A)
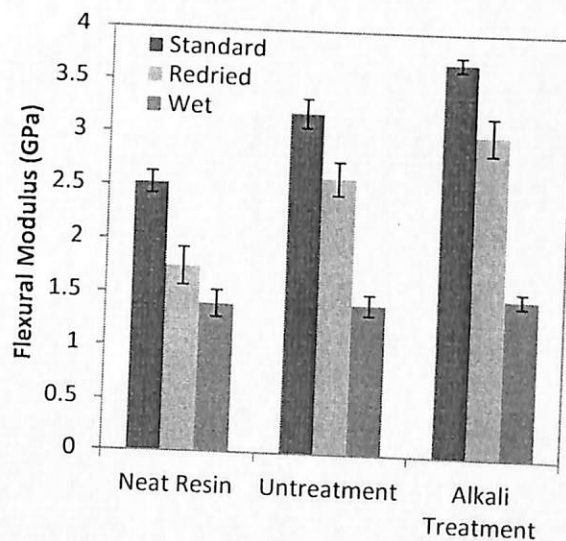
(B)
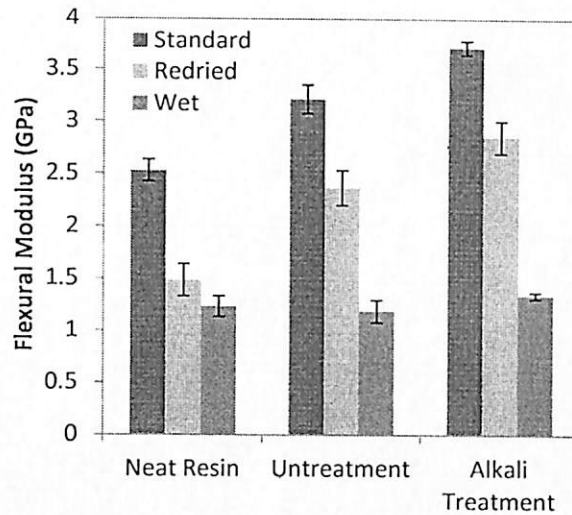
(C)

Fig. 4.18 Flexural modulus of neat resin and composites after hygrothermal aging at (A) 30 °C, (B) 60 °C and (C) 90 °C (fiber volume fraction = 0.3).

5.0 Conclusions

1. The alkali treatment of kenaf fibers partly removed hemicelluloses, lignin and other impurities from the fiber surface and made the fiber surface smoother and clearner. The interfibrillar region between the microfibrils was also well observed from the SEM micrographs. Removal of the cementing materials, i.e hemicelluloses and lignin, was evident from the FTIR and XPS results. Crystallinity index increased with the treatment but the extent of improvements after 4 and 5 hour of treatment were limited by degradation of cellulose chains and the fiber cell wall. The AFM results showed that the fiber surface roughness decreased due to the alkali treatment.

2. Alkali treated fiber composites showed superior mechanical properties to untreated fiber composites due to enhanced fiber-matrix adhesion as evident from the ILSS results. The composites, however, showed lower fracture toughness than the untreated fiber composites. This can be attributed to the strong fiber-matrix interaction that hinders the development of energy absorption mechanisms, such as debonding and fiber pull-out.

3. The uptake of water by alkali treated and untreated fiber composites was due to the uptake of water by the hydrophilic kenaf fibers. The water absorption pattern of these composites at 30 °C was found to follow Fickian behavior but at 60 and 90 °C, the composites showed non-Fickian behavior of water absorption. The tendency of the composites to absorb water decreased when alkali treated fibers were used. The results of flexural properties indicated that the properties deteriorated following water absorption or hygrothermal aging. Composites immersed at 30 °C showed better recovery (more than 95%) of the flexural properties upon redrying process than composites immersed at 60 and 90 °C. The percent of recovery of the flexural properties was less than 75% when the composites were exposed to hygrothermal aging at 60 and 90 °C due to some permanent damages introduced in the composites.

Acknowledgements

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