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THE EFFECT OF FIBRE TREATMENT USING ALKALI ON INDUSTRIAL HEMP FIBRE/EPOXY RESIN COMPOSITES

M. S. Islam[1], K. L. Pickering[1], G. W. Beckermann[1] and N. J. Foreman[2]

[1]Department of Materials and Process Engineering, The University of Waikato,
Private Bag 3105, Hamilton, New Zealand
[2]Hemptech, PO Box 46033, Herne Bay, Auckland, New Zealand

ABSTRACT

Industrial hemp fibre is a strong and renewable resource with the potential to reinforce polymers. Alkali treatment of the fibres further improves the chemical bonding and mechanical interlocking with many polymeric matrices by exposing hydroxyl groups on the fibre surface and also by roughening the fibre surface. The objective of this study was to treat the fibres with alkali to improve the performance and stability of the fibre reinforced epoxy composites. Fibres were subjected to a mild alkalisation treatment followed by single fibre tensile testing and analyses using thermal analysis (DTA/TGA), X-ray diffraction (XRD), Fourier transform infrared spectrometry (FT-IR), streaming potential analysis, and scanning electron microscopy (SEM). Aligned hemp fibre epoxy mats were manufactured from untreated and alkali treated fibres using hot and cold pressing. The strongest composite produced contained 40 wt% fibre, showing that alkalization of hemp fibres promoted the development of fibre-resin adhesion and, hence, resulted in an improvement of the mechanical properties of the composites.

Keywords: Hemp fibre, Alkali treatment, Epoxy resin.

1. INTRODUCTION

The use of cellulosic fibres as polymer reinforcement has increased over the last few years due to their low cost, low density, good mechanical properties, sustainability and biodegradability when compared to glass and aramid fibres [1]. The composites produced, compare well with glass fibre reinforced plastics in terms of recyclability, and generally with traditional structural materials, in terms of their specific mechanical properties [2].

Industrial hemp is one of the strongest and stiffest available natural fibres [3]. The major constituent of hemp fibre is crystalline cellulose which can make up 55 to 72% of the fibre mass [4]. Hemp fibre also contains hemicellulose (8-19%), lignin (2-5%) and waxy substances [4]. However, lignin, pectin and hemicellulose can degrade over time [5]. Therefore, to increase the long-term stability of hemp fibre composites and to improve interfacial bonding, researchers have attempted using various surface treatments. These include alkali treatment [6], anhydride modification [7], organosilane treatment [8], and the use of various coupling agents [9] of which alkali treatment has been found to be the most feasible [10]. Meanwhile, several researchers have reported improvement in properties of natural fibres with alkali treatment. A.K. Bledzki et al [11] applied a NaOH concentration of 22 wt%, at temperatures of 4, 10, and 20^oC to hemp fibre and a sodium hydroxide (NaOH) concentration of 29% to flax

fibres and found an improvement in fibre-matrix adhesion while H.M. Wang and R. Postle [12] applied a 1.8% NaOH solution with sodium sulphite (Na_2SO_3) and sodium carbonate (Na_2CO_3) at two different temperatures (95 and 120^oC) with a hold time of 45 and 50 minutes to remove surface impurities from Australian hemp fibres and observed a degree of reduction in lignin and pectin. Na_2SO_3 is also commonly used with alkali during the production of pulp to soften the lignin in the pulp and paper industry [13]. Alkali treatment of fibres has also been seen to increase the crystallinity [5], molecular alignment of cellulose, surface roughness of the fibre and to remove amorphous noncellulosic substances.

Both thermoset and thermoplastic polymeric materials are attractive as matrix materials for natural fibre reinforced composite production. Thermoset matrices generally have reactive functional groups that make them more compatible to hydrophilic fibre surfaces [2], with epoxies having a major advantage in that they are usually cured in two or more stages which allows preforms to be pre-impregnated with the epoxy in a partially cured state [14].

The objective here was to study the effect of alkalisation with Na_2SO_3 on industrial hemp fibre (by analysing its surface charge, morphology, crystallinity index, thermal stability, available functional groups and tensile strength) and hemp fibre/epoxy composite tensile

properties.

2. EXPERIMENTAL

2.1 Materials

Retted hemp bast fibre was supplied by Hemcore, UK. Epoxy resin R180 with an amine hardener was obtained from Fibreglass International, Australia. Analytical grade Na_2SO_3 and 98% NaOH pellets were used for the alkali treatment of the fibres.

2.2 Treatment of the Fibres with Alkali

The woody core of the untreated fibre was removed by hand. After weighing, fibres were placed into stainless steel canisters of 1L capacity. Pre-weighed NaOH and Na_2SO_3 solution was then poured into the canisters such that the fibre to Na_2SO_3 and NaOH solution ratio was 1:2:10 by weight. The canisters were then placed into a small lab-scale pulp digester at $120^{\circ}C$ for 60 minutes for alkali treatment of the fibres. Fibres were washed in a pulp and paper fibre washer for about 45 minutes after the alkali treatment to remove chemical residues, and to ensure a fibre pH of 7. Fibres were then dried in an oven for 48 hours at $70^{\circ}C$.

2.3 Measurement of Zeta Potential

The zeta potential of untreated and alkali treated fibres was determined in a 1.00×10^{-3} M KCl electrolyte solution at room temperature using a Mutek SZP 06 System based on the streaming potential method. The pH of the electrolyte solution was varied from 11 to 3. The pH of 11 was obtained using 0.1M KOH solution and then decreased incrementally using 0.1M HCl solution.

2.4 Scanning Electron Microscopy

The morphology of the untreated and alkali treated fibres was studied using a Hitachi S-4000 Field Emision SEM operated at 5 kV. Carbon tape was used to mount the samples on aluminium stubs. The samples were then sputter coated with platinum and palladium to make them conductive prior to SEM observation.

2.5 X-ray Diffraction

0.5 g of fibre was compressed into tablets using a hydraulic press at 20 MPa pressure. A Philips X-ray diffractometer, employing CuKα radiation and a graphite monochromator with a current of 40 mA and a voltage of 40 mV was used with a diffraction intensity in the range of 6 to 60° (2θ-angle range). The percentage crystallinity index (CrI) was determined using the Segal empirical method [15].

2.6 Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using an SDT 2960 Simultaneous DTA-TGA analyzer. A static air flow of 150 mL/min with a constant heating rate of $10^{\circ}C$/min in an open alumina crucible was maintained. The weight of the specimens was around 10mg, with a scanned temperature range of 25 to $600^{\circ}C$.

2.7 Infrared Spectra

Infrared spectra were carried out using a Fourier transform infrared (FT-IR) Digilab FTS-40 spectrometer. Untreated and alkali treated fibres were ground into small particles in liquid nitrogen and mixed and compressed with KBr into a thin disc using a hydraulic press at 8 MPa pressure.

2.8 Single Fibre Tensile Testing

Single alkali treated hemp fibres were tensile tested according to the ASTM D3379-75 Standard Test Method. Fibres were separated by hand mounted on cardboard mounting-cards with 10 mm holes punched into them to give a gauge length of 10 mm. PVA glue was used to hold the fibres in place. The fibres were then placed under an optical microscope and inspected with a calibrated eyepiece at 200× magnification to determine the average diameter of each fibre. The mounted fibres were then placed in the grips of an Instron-4204 tensile testing machine, and a hot-wire cutter was used to cut the supporting sides of the mounting cards. Tensile testing of the fibres was carried out at a rate of 0.5 mm/min using a 10 N-load cell up to the failure. Average tensile strengths and Young's moduli were obtained using the results from 25 specimens.

2.9 Composite Compression Molding

Untreated and alkali treated fibres were dried at $80^{\circ}C$ for 24 hrs and hackled to produce unidirectional fibre mats. The fibre mats were then dried at $100^{\circ}C$ for 1hr and placed in a mould. Epoxy resin was then poured on to the fibre mats followed by cold or hot pressing. A pressure of 20×10^4 kg/m^2 was used. A KOTAK press from KOHTAKI & Co.,Ltd, Japan was used.

2.10 Composite Tensile Testing

The composite mats were cut into tensile test specimens using a CNC Mill according to the ASTM D638-03 standard test method and placed in a conditioning chamber at $23^{\circ}C \pm 3^{\circ}C$ and $50\% \pm 5\%$ relative humidity. The specimens were then tested using an Instron-4204 tensile testing machine fitted with a 5 kN load cell at a rate of 5 mm/min. An Instron 2630-112 extensometer was used to measure strain. Five specimens were used for each test and tested up to the point of fracture.

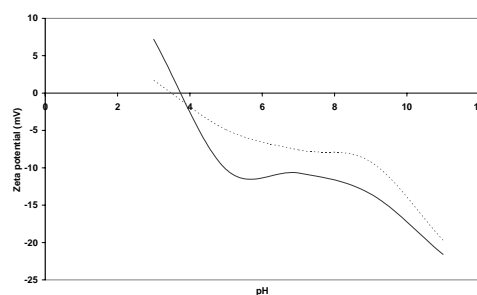## 3. RESULTS AND DISCUSSION

3.1 Zeta Potential

Fig 1. pH dependence of zeta potential of untreated (---) and alkali treated (—) fibres

Figure 1 shows the pH dependence of zeta potential

values of untreated and alkali treated fibres. It is evident from this figure that alkali treatment generally reduces the zeta potential. This might be caused by the increase in the accessibility of the dissociable functional groups in the fibre surface due to the removal of the waxy substances which obscure the fibre surface [16]. Table 1 shows the $\zeta_{plateau}$ values and iso-electric points of the untreated and alkali treated fibres.

Table 1: $\zeta_{plateau}$ value and I.E.P of untreated and alkali treated fibres.

| Sample	I.E.P	ζplateau, mV
Untreated	3.5	-7.7
Alkali treated	3.8	-11.5

A considerably lower $\zeta_{plateau}$ value (-11.5 mV) was observed for the alkali treated fibres. This may be due to an increased exposure of hydroxyl and carboxyl groups upon removal of the noncellulosic materials such as wax or lignin that would have initially covered them; hydroxyl and carboxyl groups are known to be responsible for the negative surface charge in cellulosic fibres. The slight increase in the isoelectric point by alkali treatment highlights the reduction of the acidity of the fibre surface leading to an enlargement of the double layer giving further evidence for increased hydroxyl group exposure [17] The enlargement of the double layer would also decrease the zeta potential of the solution as seen.

3.2 Scanning Electron Micrography

Figure 2 shows the scanning electron micrographs of untreated and alkali treated fibres. The untreated fibre bundles do not appear to be separated and shows some material coating likely to be the cementing materials (lignin, pectin, and waxy substances) present in fibre, as
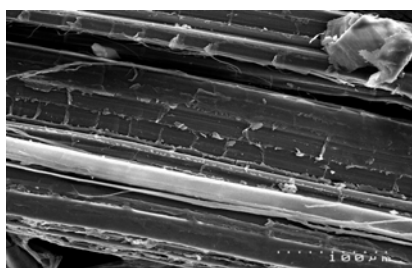
a)
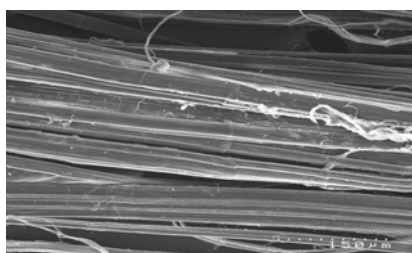
b)

Fig 2. Scanning electron micrograph of a) untreated and b) treated fibre

has been reported by other authors [18]. Alkali treatment appears to have removed much of the cementing materials and make the fibre surfaces rougher. Alkali treatment also seems to have made the fibre bundles cleaner and more separated.

3.3 X-ray Diffraction

As can be seen in Figure 3, the untreated and alkali treated hemp fibres exhibit five main peaks at 2θ-angles of 15, 16.5, 22.5, 34.5 and 46.5° corresponding to ($\bar{1}$ 0 1), ($\bar{1}$ 1 1), (0 0 2), ($\bar{2}$ 3 1) and ($\bar{4}$ 1 2) crystallographic planes of cellulose. For the untreated fibre, the peaks at 15 and 16.5^0 are merged, appearing more like one broad peak, which suggests the presence of a large amount of amorphous material such as lignin, hemicellulose and amorphous cellulose [19]. The two peaks are more separate in the case of alkali treated fibre suggesting a higher cellulose content. Assessment of the relative amount of amorphous cellulose can be carried out by using a reference point away from the crystalline peaks. Commonly this is taken at a 2θ-angle of 18.5°. As shown in Table 2, alkali treatment brings about an increase in the intensity values relating to amorphous cellulose, as well for all the intensity values of the crystalline cellulose peaks, suggesting an increase in crystalline and amorphous cellulose. This would be expected simply due to removal of non-cellulosic materials such as waxes, lignin and hemicellulose, as supported by the separation of the ($\bar{1}$ 0 1) and ($\bar{1}$ 1 1) peaks, resulting in something that is generally more rich in cellulose. However, other factors may be involved. The increase of crystalline cellulose content during alkali treatment observed elsewhere, has been explained by removal of non-cellulosic materials enabling better packing of cellulose chains. Harsher treatments have also been seen to reduce cellulose crystallinity, due to the increased exposure of hydroxyl groups which could increase the degree of swelling leading to the breakage of hydrogen bonds [19]. Here, the crystallinity index was seen to increase, indicating an increase in the ratio of crystalline to amorphous cellulose, and that the removal of non-cellulosic material and increased packing of cellulose chains, outweighs any crystalline degradation that may be occurring for the treated fibre.
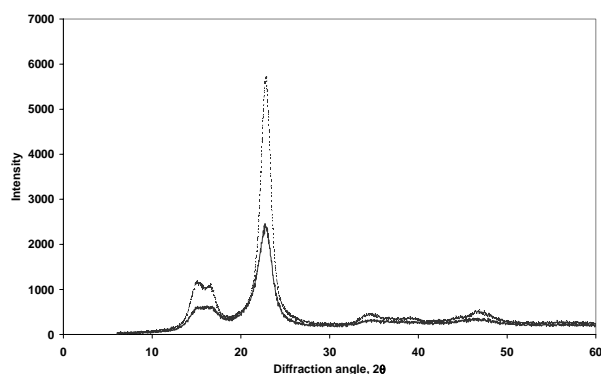

Fig 3. X-ray diffraction pattern of untreated (——) and alkali treated (----) fibres

Table 2: The crystallographic planes at various intensities (XRD counts) and 2θ-angles, and the crystallinity indices of untreated and alkali treated fibres.

Sample	2θ-angle (°)	Intensity of XRD	h k l	CrI (%)
Untreated	15	571	$\bar{1}$ 0 1	83.8
	16.5	566	$\bar{1}$ 1 1	
	18.5	370	Amorphous	
	22.5	2298	0 0 2	
	34.5	296	$\bar{2}$ 3 1	
	46.5	356	$\bar{4}$ 1 2	
Alkali treated	15	1146	$\bar{1}$ 0 1	91.9
	16.5	1061	$\bar{1}$ 1 1	
	18.5	390	Amorphous	
	22.5	4842	0 0 2	
	34.5	450	$\bar{2}$ 3 1	
	46.5	506	$\bar{4}$ 1 2	

3.4 Thermal Analysis

The DTA and TGA curves of untreated and alkali treated fibres are shown in Figures 4 and 5 respectively. The DTA curves for untreated and alkali treated fibres
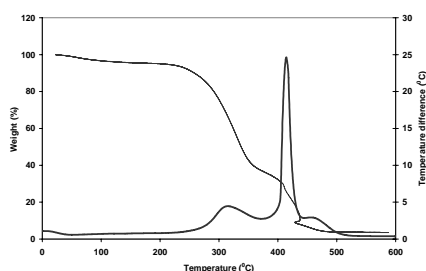
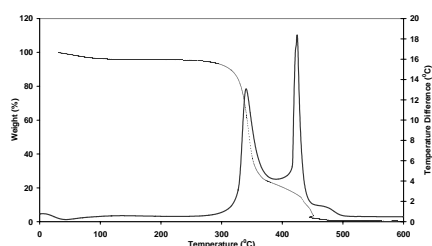Fig 4. DTA (—) and TGA (—) curves for untreated fibre in static air flow.

Fig 5. DTA (—) and TGA (—) curves for alkali treated fibre in static air flow

both show an endotherm around 60°C due to the evolution of adsorbed moisture. At higher temperatures there are two exotherms. The first exotherm has a peak temperature of 318°C for untreated fibre and 363°C for alkali treated fibres and is likely to be caused by the decomposition of cellulose leading to the formation of volatile products [20]. The second exotherm has a peak temperature of 436°C for untreated fibre and 450°C for alkali treated fibres and is expected to be due to the

oxidation of volatile and charred products. The increase in the first and second exothermic peak temperatures for alkali treated fibres indicates their higher thermal stability. The onset, peak and final temperatures of the endotherm and both exotherms described for the alkali treated fibre are higher than for the untreated fibres as shown in Table 3. The temperature at which specific weight losses have occurred are summarised in Table 4 and are shown to be consistently higher for alkali treated fibres compared to untreated fibres. Therefore, it is clear from the results that alkali treatment increases the thermal stability of the fibres.

The Broido method [21] was used to evaluate the activation energy (E_a) and frequency factor (a constant indicating the number of collisions required for reactions to occur) of untreated and alkali treated fibres. Using the Broido equation, plots of $\ln[\ln(1/y)]$ vs $1/T$ (Broido plots) for second and third stages of thermal degradation were plotted for which examples are shown in Figures 6 and 7. The activation energy and frequency factors were calculated from the slopes and intercepts of these plots, respectively, and are given in Table 3. Activation energies (E_a) for the first exothermic peak for the untreated and alkali treated fibres also show increased thermal stability of the alkali treated fibres, with higher values of activation energy (110 kJmol^{-1}) and frequency factor (1.62×10^7 s^{-1}). For the second exothermic peak, the activation energy and frequency factor are both lower for the alkali treated fibre. This could be due to the increased potential for the production of more stable lignocellulosic groups in the more lignin reach untreated fibre at higher temperatures [22].
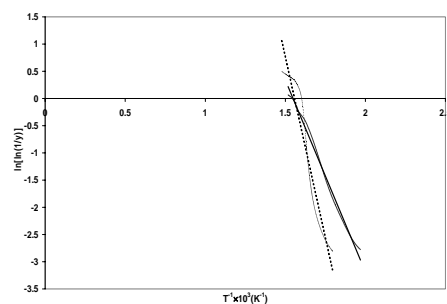
Fig 6. Broido plots for the second stage of thermal degradation for untreated (—) and alkali treated (----) fibres.
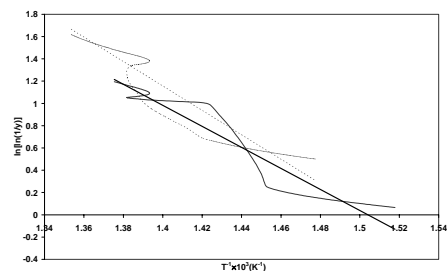
Fig 7. Broido plots for the third stage of thermal degradation for untreated (—) and alkali treated (----) fibres.

Table 3: DTA thermograms, activation energy and frequency factor for second and third stages of thermal degradation for untreated and alkali treated fibres.

Sample	Temperature (°C)			Degradation stage	Nature of Peak	E_a (kJmol^{-1})	Z (s^{-1})
	Onset	Peak	Final				
Untreated fibre	23	58	90	First	Endo	----	----
	225	318	374	Second	Exo	58.63	6.43×10^2
	374	436	445	Third	Exo	78.47	12.06×10^3
Alkali treated fibre	33	62	98	First	Endo	----	----
	283	363	403	Second	Exo	110.39	1.62×10^7
	403	450	465	Third	Exo	31.99	1.77×10^1

Table 4: Weight losses of untreated and alkali treated fibres at various temperatures.

Weight Loss (%)	Untreated (°C)	Alkali treated (°C)
10	258	314
20	291	331
30	309	338
40	324	342
50	337	345
60	351	370
70	400	392
80	426	428
90	437	472
100	483	588

3.5 Infrared Spectra

Figure 8 shows the FT-IR spectra of untreated and alkali treated fibres for which there is a summary of the most significant peaks in Table 5. For the untreated hemp fibre, peaks in the region of 3629-3796 cm^{-1} commonly related to stretching vibrations of OH groups, were found to shift slightly to 3619-3795 cm^{-1} for treated fibres, supporting the possibility of increased availability of hydroxyl groups. Removal of hemicellulose of alkali treated fibres is suggested by two sharp peaks at 1718 and 1735 cm^{-1} for untreated fibres which are likely to be due to the C=O stretching vibration of carboxylic acid and ester groups present in hemicellulose. These are found to be reduced in intensity for alkali treated fibres.

Further evidence is provided by the reduction of the peak intensity and peak shift from 2921 cm^{-1} for untreated fibres to 2929 cm^{-1} for alkali treated fibres. Reduction in the peak intensities between 1448-1534 cm^{-1} especially for an intense peak at 1507 cm^{-1} associated with the bending of C-H bond in the aromatic ring present mostly in lignin compounds, suggests the removal of significant amount of lignin by alkali treatment. The peak at 890 cm^{-1} for untreated fibre is characteristic of the β-glycoside linkage between cellulose monosaccharides and undergoes a shift to 895 cm^{-1} with higher intensities for alkali treated fibres. This may be due to the rotation of the glucose residues around the β-glycosidic bonds which indicates the chemical modification of the alkali treated fibres as reported by other authors [23].

3.6 Single Fibre Tensile Testing

It can be seen from Table 6 that alkali treatment reduces the strength of the single fibre of the untreated hemp fibre [24]. This might be due to a degree of degradation of cellulose chains upon alkali treatment.

Table 6: Single fibre tensile test results of untreated and alkali treated fibres.

Sample	σ (MPa)	s.dev (MPa)	E (GPa)	s.dev (GPa)
Untreated	514	275	24.8	16.3
Alkali treated	463	120	30.7	15.1

Table 5: FT-IR transmittance peaks of untreated and alkali treated fibres

Transmittance (cm^{-1})		Bond type
Untreated	Alkali treated	
3629-3796	3619-3795	O-H stretching relating to hydrogen bonding
2921	2929	C-H stretching vibration in cellulose and hemicellulose
1735, 1718	1719, 1735	C=O stretching of carboxylic acid or ester
1654	1654	C=C stretching
1448-1534	1460, 1518, 1522	C-H bond in aromatic ring present in lignin component
1437	1438	CH$_2$ bending in lignin
1384	----	C-H bending
1070 1152	1080	C-C stretching
890	895	C-H stretching for β glycosidic linkage

a)

b)

Fig 8 . FT-IR spectra of a) untreated and b) alkali treated fibres

3.7 Composite Tensile Testing

Results of composite tensile testing are summarised in Table 7. It is evident from the results that alkali treatment increases the tensile strength and Young's modulus to a great extent. It is reported in the literature that epoxy resin has active groups known as epoxide or hydroxyl groups to produce network structures with the active hydrogen atoms of diamine hardener [14]. It is very likely that those epoxide groups and the active hydrogen groups of the hardener can react well with the free hydroxyl groups of cellulose present in hemp fibres. Alkali treatment removes weaker non-cellulosic fibre components such as lignin, pectin and hemicellulose. Hemicellulose and pectin are amorphous compounds that need to be removed to separate individual fibres from their fibre bundles, and lignin is known to photodecompose when exposed to ultra-violet light [5]. Alkali treatment also causes fibre swelling, which exposes more hydroxyl groups on the fibre surface to chemical bonding with the matrix, and roughens the fibre surface to improve mechanical interlocking. Increases in the chemical bonding and mechanical interlocking directly result in composite strength improvements. It was also observed that composites cured at $120^{o}C$ had greater tensile strengths compared to those cured at room temperature. This is thought to be due to better fibre wetting with epoxy resin at higher temperatures.
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Table 7: The tensile properties of the untreated and alkali treated hemp fibre reinforced aligned epoxy composites.

Sample	Room temperature cure				$120^{o}C$ cure			
	σ (MPa)	s.dev (MPa)	E (GPa)	s.dev (GPa)	σ (MPa)	s.dev (MPa)	E (GPa)	s.dev (GPa)
Untreated	33.8	2.6	3.7	0.3	35	3.2	4.3	0.8
Alkali treated	64.3	1.5	8.6	0.4	91	13.3	11.1	1.7

4. CONCLUSIONS

Industrial hemp fibre was treated using an alkali solution. This was found to remove non-cellulosic surface impurities and appears to expose relatively more hydroxyl groups on the fibre surface compared to the untreated fibres as found from analysis of the results of different characterization methods. FT-IR studies also showed that alkali treatment was responsible for various chemical changes on fibre surfaces including reduction of lignin and hemicellulose. Surface topography was also found to change and the fibres became more separated and clean due to the removal of the non-cellulosic cementing materials. In alkali treated fibres, an increase in the crystallinity was seen from the crystallinity index obtained by X-ray diffraction. The thermal stability of the alkali treated fibres was observed to improve as seen from TGA/DTA thermograms and values of activation energy and frequency factor. Alkali treatment reduced the fibre strength, as can be seen from the single fibre tensile test results. However, the removal of non-cellulosic surface impurities resulted in stronger composites consistent with enhanced chemical bonding and mechanical interlocking between the reinforcing fibres and epoxy resin matrix.

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6. NOMENCLATURE

Symbol	Meaning	Unit
T	Temperature	(K)
θ	Diffraction angle	(^{0})
y	Mass fraction	--
CrI	Crystallinity index	(%)
ζ	Zeta potential	mV
E_a	Activation energy	(kJmol^{-1})
Z	Frequency factor	(s^{-1})
σ	Tensile stress	(MPa)
E	Young's modulus	(GPa)
s.dev	Standard deviation	(MPa and GPa)

7. MAILING ADDRESS

Dr. K. L. Pickering
Department of Materials and Process Engineering
The University of Waikato
Private Bag 3105, Hamilton, New Zealand
Phone: [+64] (7) 838 4672
Fax: [+64] (7) 8384835
E-mail: klp@waikato.ac.nz, msi2@waikato.ac.nz