

## **EFFECTS OF ALKALI TREATMENT OF BAMBOO FIBRE UNDER VARIOUS CONDITIONS ON THE TENSILE AND FLEXURAL PROPERTIES OF BAMBOO FIBRE/POLYSTYRENE-MODIFIED UNSATURATED POLYESTER COMPOSITES**

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### **Abstract**

The paper presents the effects of alkali treatment on the tensile and flexural properties of bamboo fibre/polystyrene-modified unsaturated polyester (MUP) composites. The bamboo fibres were treated using alkali (NaOH) solution with concentrations of 4, 8 and 12% (by weight). The treatment time was 0.5, 1 and 2 hours under both room and elevated temperatures (50°C). Fourier transform infrared spectroscopy, scanning electron microscopy and X-rays diffraction were conducted for characterizing the surface chemistry, surface morphologies and the crystallinity of bamboo fibres, respectively. Under room temperature treatment, the tensile and flexural properties of bamboo fibre/MUP composites increased with increasing the alkali concentration; however, they tended to decrease at high concentration and long treatment time. Under elevated temperature treatment, the optimum tensile and flexural strengths of the treated bamboo fibre/MUP composites had been obtained at low concentration and short treatment time; however, the tensile and flexural strengths was slightly lower than that under room temperature treatment.

Keywords: Bamboo fibre, Alkali concentration, Temperature, Composites, Tensile and flexural properties.

## 1. Introduction

Bamboo is one of natural fibre resources, which is abundantly available and can be harvested in 3-4 years [1]. Bamboo plantations covered 31.5 million ha in the world [2], while the bamboo product market grew around 19.7 billion USD in 2012 [3]. In the recent years, bamboo fibre is gaining great interest and has been increasingly used for manufacturing green composites. Bamboo fibre has high tensile strength (140-800 MPa), high elastic modulus (33 GPa) and low density (0.6-0.8 g/cm<sup>3</sup>) [4, 5] and is very potential for manufacturing biodegradable, low density and high specific strength polymeric composites.

The hydrophilic nature of natural fibres may have disadvantage if being used to reinforce the hydrophobic polymeric matrices [6]. Cellulose, as the main component of natural fibre, is cemented by matrix lignin and hemicellulose to have strong and rigid structures [6]. However, lignin and hemicellulose function as weak boundary layer and reduce the adhesion between fibre and polymeric materials [6]. Surface modification is necessary to improve the adhesion of fibre-polymeric materials. Shawkataly et al. [7] reported a relatively comprehensive review on the surface treatment of natural fibres was including alkali treatment, acetalation, silane treatment, benzylation treatment, acrylation and acrylonitrile grafting, maleated coupling gents, peroxide treatment, permanganate treatment, and isocyanate treatment. Among those treatments, alkali treatment was mostly used, as it could give the compromise results between the strength of the composite and the environment impact, and also often became predecessor before using another treatment.

Several surface treatments on bamboo fibres and their effects on the composite properties had been reported in literature [8-18]. Das and Chakraborty [8] investigated alkali treatment of bamboo strip up to the alkali concentration of 50%. They found that the maximum value of tensile and flexural strengths of bamboo strips was obtained at the concentrations of 20% and 15%, respectively. On their further study, Das and Chakraborty [9] focused on the effects of alkali treatment on the tensile and flexural strengths of bamboo strip/polyester using concentration up to 25%, and found that at lower concentration, the increase of tensile and flexural strengths was low, but the significant increase occurred at the concentration in the range of 10%-15%. Meanwhile, treatment at higher alkali concentration decreased the tensile and flexural strengths. The similar trend was also observed in their further study [10]; however, they used a resol matrix. Other researchers, Junior et al. [11] reported the increase of tensile strength of bamboo fibre after alkali treatment at the concentrations of 5 and 10%. The increase was mainly due to increasing the crystalline index of bamboo fibre after the alkali treatment. Wong et al. [12] studied the alkali treatment of bamboo fibre at relatively low concentrations of 1%, 3% and 5%, but with longer treatment time (24 hours) at room temperature. They found that the interfacial shear strength increased with increasing the alkali concentration, but there was an optimum concentration. Other bamboo treatments that had been reported, including hydrothermal treatment [13], heat treated bamboo [14] and other chemical treatment such as combination alkali + silane [15-17], silane + acrylation and maleic anhydride (MA) grafting [18]. Among the aforementioned surface treatments, there was no yet a specific treatment applicable for all types of bamboo fibres and for a specific matrix type.

Expandable polystyrene (EPS) foam is a low density closed cell thermoplastic, non-biodegradable and mostly used for packaging [19, 20]. The EPS foam waste is often dumped into the environment, as landfills, polluting rivers and can be harmful

for ecosystem. Recycling and reusing the EPS foam wastes are of research interest for developing other useful materials, such as to modify the unsaturated polyester resin that has many applications.

This paper investigates the effects of alkali treatment of bamboo fibres for reinforcing a polystyrene-modified unsaturated polyester resin under various conditions including alkali concentration, time and temperature treatment. This work extended and deepen our previous study [21], focusing on the flexural strength. Two environment treatments were used including room and elevated temperatures. The physical and tensile properties of the treated bamboo fibres as well as the tensile and flexural properties of bamboo fibre/modified polyester composites were investigated. Morphologies of the fracture surfaces were examined using a scanning electron microscopy (SEM).

## **2. Materials and Methods**

### **2.1. Materials**

Bamboo fibres were obtained from *Gigantochloa apus* species that were abundantly available in Lombok island, Indonesia. For matrix, the unsaturated polyester resin was used, purchased from Eternal Materials Co. Ltd (Taiwan), with a hardener of methyl ethyl ketone (MEK). The unsaturated polyester was an orthophthalic type having viscosity (at 25°C) of 350-450 centipoise, gel time of 13-23 mins and heat distortion temperature of 67°C. Expandable polystyrene (EPS) was used to modify the unsaturated polyester resin, obtained from packaging wastes. Alkali solution was obtained by dissolving a technical grade solid sodium hydroxide (purchased from PT. Brataco Chemical, Indonesia) in distilled water to obtain the alkali concentration as studied.

### **2.2. Bamboo alkali treatment**

Bamboo fibres were extracted from mature bamboo plantations, approximately in the middle part. The extraction was done mechanically using a plastic comb to remove the matrix lignin. This method produced long bamboo fibre bundles with diameter range from 0.4 to 0.6 mm. Bamboo fibres were then dried under the sun before they were chopped to obtain a fibre length of approximately 6 mm. Surface treatment was carried out by immersing bamboo fibres in alkali solution with concentrations of 4, 8 and 12% (by weight) and immersing times of 0.5, 1 and 2 hours. The alkali solution to fibre ratio was kept at 13:1 (by weight). The temperature treatment was at room temperature (approximately 28 °C) and at elevated temperature (50°C). After the treatment, the fibres were washed using fresh water to remove the alkali content from the fibres. A litmus paper was used to check the neutralised fibres. This was followed by drying under the sun for a couple days, before they were dried in the oven at a temperature of 60°C for 24 hours. The dried fibres were then kept in a sealed plastic bag to avoid absorbing water from the atmosphere before manufacturing the bamboo fibre composite specimens.

### **2.3. Manufacturing the specimens**

#### **2.3.1. Tensile specimens**

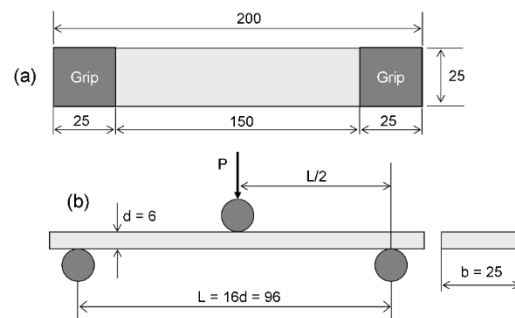
For tensile test of bamboo fibre bundles, the untreated and treated bamboo fibre bundles, 100 mm in length were placed and bonded on the paper. The diameter of

the fibre was measured using a calliper with accuracy of 0.02 mm. The measured diameter of bamboo fibre bundles was in the range of 0.4 - 0.6 mm.

For manufacturing bamboo composites, bamboo fibres were laid up randomly on the mould before the unsaturated polyester resin was poured into the mould. The mould was made of a thick steel (20 mm) covered with polyethylene sheets, with mould dimension of 200 mm×150 mm. The bamboo fibre volume fraction was kept at 20%. The unsaturated polyester resin was modified using EPS, with the content of 2% (by weight), and then it was called as a modified unsaturated polyester resin (MUP). To accelerate dissolving the EPS in the polyester resin, the EPS was ground to obtain a particles size of approximately 1 mm in diameter. The EPS and the unsaturated polyester were mixed and stirred until all EPS particles were dissolved. The hardener was added into the MUP and stirred well before pouring into the mould. The resin to hardener ratio was 100:1 (by weight). After pouring the resin into the mould, the fibres lay out were pressed and left for a day, for curing. The cured bamboo fibre/MUP composites panel was cut to obtain the tensile specimens according to ASTM D3039 [22], with dimension as shown in Fig. 1(a).

### 2.3.2. Flexural specimens

Manufacturing the flexural specimens was similar to the manufacturing of tensile specimens. However, the cured bamboo fibre/MUP composites was cut to obtain the flexural specimens according to the ASTM D790 [23], as shown in Fig. 1(b).



**Fig. 1. Dimensional of the (a) tensile, and (b) flexural specimens (not to scale). The specimen thickness is 6 mm. Unit is in mm.**

## 2.4. Mechanical testing

### 2.4.1. Tensile test

Tensile test for bamboo fibre bundles and bamboo fibre/MUP composites was conducted using a Tensilon universal testing machine with a load capacity of 10 kN. The load cell sensitivity for testing bamboo fibre bundles was 1 N. The displacement was 2 mm/min. During the test, the grip area was covered with emery paper of 100 mesh. At least three replications were made for each variable.

### 2.4.2. Flexural test

Flexural test was carried out using a Tensilon universal testing machine, similar to that for the tensile test. The test used a three-point bending method with a span length ( $L$ ) to thickness ratio ( $d$ ) was 16. The displacement rate was 2 mm/min.

## 2.5. Fourier transform infrared (FTIR) spectroscopy

Before and after alkali treatment, the fibres were examined using FTIR. FTIR test was conducted using a Perkin Elmer using transmission method with KBr pellets. The wavenumber swept was from 4000 to 500  $\text{cm}^{-1}$ .

## 2.6. Scanning electron microscopy (SEM)

A scanning electron microscopy was performed to see the morphology of the bamboo fibre before and after treatment and the morphology of the fracture surfaces of the tensile specimens. The scanning electron microscopy was carried out using a JEOL 6510 LA machine at an operating voltage of 10 kV. Before scanning, the specimen surfaces were coated using a thin gold to avoid charging of the surfaces.

## 2.7. X-rays diffraction spectrophotometry (XRD)

A XRD was used to measure the crystalline index of bamboo fibre. The XRD was conducted using X'pert Powder X-ray machine with the accelerating voltage and the current of 30 kV and 30 mA, respectively. The scanning was performed at 3 deg/min. The crystalline index (CI) of the fibre was calculated using Eq. (1).

$$CI = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (1)$$

where  $I_{002}$  is the peak intensity of lattice reflection of the 002 crystallographic plane at  $2\theta = 22^\circ$  and  $I_{am}$  is the maximum intensity of the amorphous part at  $2\theta = 18^\circ$  [24, 25].

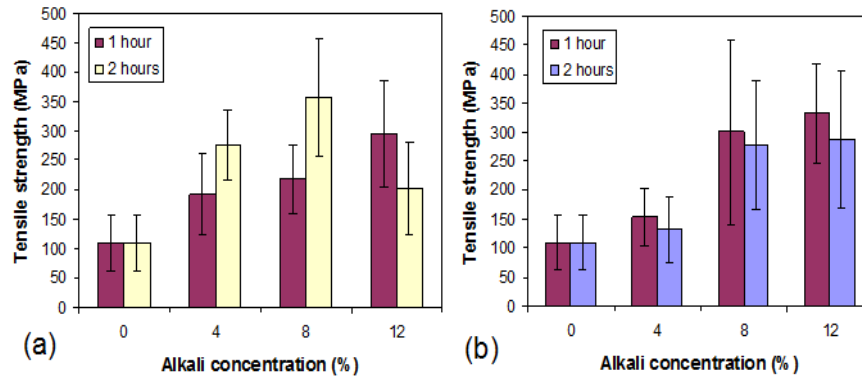
## 3. Results and Discussion

### 3.1. Tensile properties of bamboo fibres and its composites

The tensile strength of bamboo fibre bundles shown in Figs. 2(a) and 2(b) are for treatment under room and elevated temperatures, respectively. Only bamboo fibres treated at the treatment times of 1 and 2 hours were tested. The average tensile strength of this bamboo fibre in this study was in the range of 100 MPa - 350 MPa, which agreed well with the tensile strength of bamboo fibres reported in literature [4, 5, 26, 27]. For treatment time of 1 hour under room temperature, the tensile strength of treated bamboo fibres increased with the increase of concentration up to 12%. Meanwhile, for treatment time of 2 hours the tensile strength up to the concentration of 8% increased and tended to decrease afterward. Furthermore, the tensile strength for the treatment time of 2 hours up to the concentration of 8% was higher than that for the treatment time of 1 hour. The maximum increase of tensile strength was about 170% and 225% for the treatments at 12% (1 hour) and 8% (2 hours), respectively, relative to the untreated fibre.

The increase of alkali concentration and treatment time (in some extent) caused more and more removal of the cementing material (lignin and hemicellulose) and then increased the packing density and the cellulose crystalline [8]. After carefully checking the fracture fibre, for untreated and low alkali concentration (4 and 8%)-treated fibres, the individual fibre was pulled away from each other resulting the fibrous fracture [28]. This indicated that the interfacial bond between individual fibres in the fibre bundles was weak. The excessive alkali concentration and longer treatment time might cause deterioration of the exposed cellulose, leading to decreasing the tensile strength [8, 11, 28]. Under elevated temperature treatment,

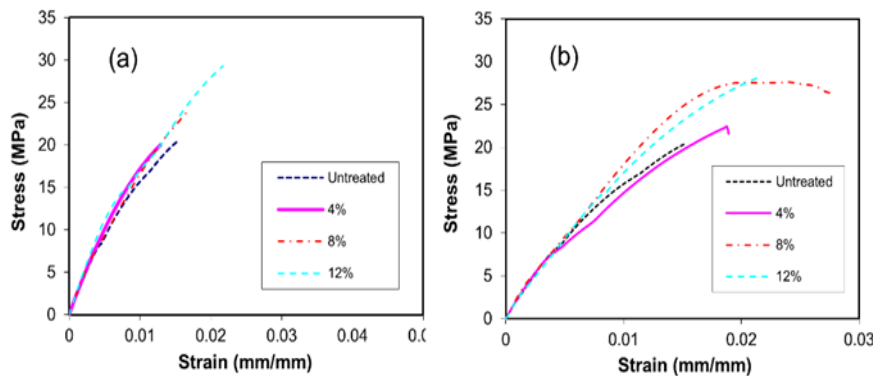
the trend of tensile strength under room temperature treatment was also observed; however, after the concentration of 8%, the increase of tensile strength for both treatment times was small. The maximum increase was about 203% and 163% for the treatments at 12% (1 hour) and 12% (2 hours), respectively, relative to the untreated fibre. Those increases were slightly lower than that of under room temperature treatment, which might be caused by more degradation of the cellulose fibre under elevated temperature treatment.



**Fig. 2. The tensile strength of bamboo fibre bundles treated under (a) room temperature, and (b) elevated temperature.**

Although the tensile strength of bamboo fibres treated at 1 and 2 hours was quite different; however, from a statistical point of view (an analysis of variance at the significance level of 5%), it was found that the effect of treatment time on the tensile strength was not significant. Nevertheless, the effect of alkali concentration was significant.

Figure 3 shows the typical stress-strain of bamboo fibre/MUP composites. The observed non-linearity of the stress-strain curves at low stress was probably due to the gradual failure process; however, the failure of most specimens occurred at the peak load.



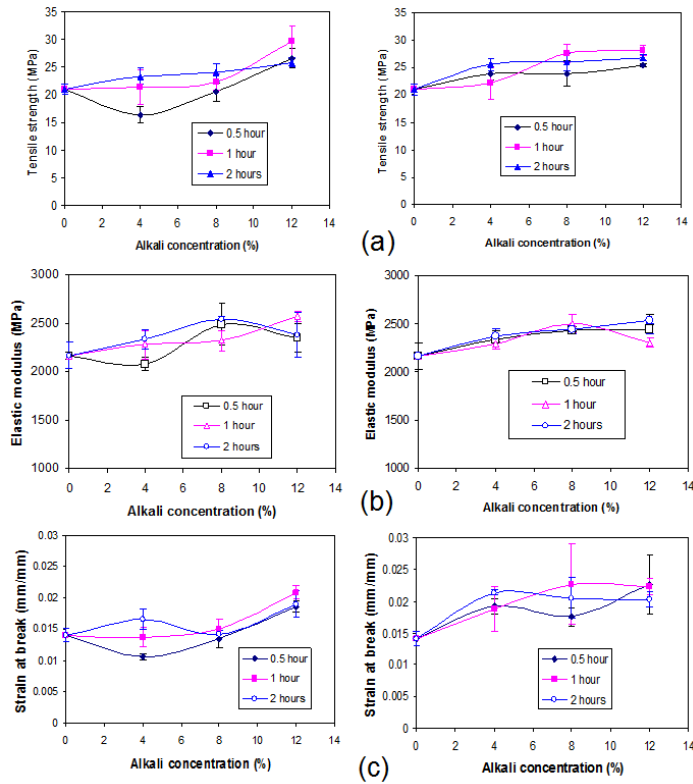
**Fig. 3. Typical stress-strain curves of bamboo fibre/MUP composites after alkali treatment under (a) room, and (b) elevated temperatures for treatment time of an hour.**

Under room temperature treatment, as seen in Fig. 4(a) (left side), the tensile strength of bamboo fibre/MUP composites tended to increase with increasing alkali concentration for all treatment times. However, an anomaly occurred at the concentration of 4% and the treatment time of 0.5 hour, in which the tensile strength was below that of the untreated bamboo fibres. It is probably because at a short treatment time and low alkali concentration, the amorphous substances such as hemicellulose and lignin were only slightly removed, and the remaining became weaker; therefore, it weakened the adhesion between the fibre and the matrix. Furthermore, alkali treatment at this low alkali concentration and short treatment time could not provide sufficient surface roughness that played an important role in the adhesion strength. There was a tendency that at low concentration (below 8%), the treatment time at least of 2 hours was more effective in increasing the tensile strength; however, for high concentration (e.g., 12%), shorter treatment time (e.g., about 1 hour) was more effective in increasing the tensile strength. The significant increase was observed after the concentration of 8% and at the treatment times of 0.5 and 1 hour, relative to the untreated fibre. While at the treatment time of 2 hours, from the untreated fibre to the concentration of 12%, the tensile strength increased smoothly. Of the combination of concentration and treatment time, relative to the untreated fibre, the maximum increase was obtained at the concentration of 12% for treatment time of 1 hour, which was approximately 40%. The increase was possibly due to the improved fibre-matrix interaction, and also the increase of fibre strength after the alkali treatment [8-10, 29]. Two key points in improving the adhesion strength are increasing the surface roughness of the treated bamboo fibre and increasing the amount of the exposed cellulose on the fibre surface. The increase of surface roughness and the exposed cellulose provide the fibre-matrix mechanical interlocking and the reaction sites with the matrix, respectively [24, 30]. Manalo et al. [29] reported that the alkali treatment increased the tensile strength of bamboo fibre/polyester composites about 10%, obtained at the alkali concentration of 6% (by volume) for the treatment time of 3 hours.

Under elevated temperature treatment, see Fig. 4(a) (right side), the tensile strength showed significant increase up to the concentration of 4%, and then after this concentration, the increase seemed not significant. Further, due to the data scatter, the effect of treatment time was not significant and this has been confirmed using a statistic analysis, analysis of variance, at significance level of 5%. The maximum increase of tensile strength was obtained at the concentration of 8% for the treatment time of 1 hour. This increase was lower than that of under room temperature treatment.

Under room temperature treatment, see Fig. 4(b) (left side), the elastic modulus of bamboo fibre/MUP composites increased with increasing the alkali concentration for all treatment times, following the trend of the tensile strength; however, after the concentration of 8%, it seemed not following due to the data scatter. The maximum increase was also obtained at the concentration of 12% (1 hour), which was approximately 19%, relative to the untreated fibres. Under elevated temperature treatment, see Fig. 4(b) (right side), the trend of elastic modulus was also similar to that of the tensile strength, where the elastic modulus increased smoothly up to the concentration of 12%; however, the effect of treatment time seemed not significant. Regardless the treatment time, the optimum increase of elastic modulus was achieved at the concentration of 8%, which was approximately 15%, relative to the untreated fibres. This was lower than the

increase obtained from under room temperature treatment. It was likely because the tensile strength of bamboo fibre treated under elevated temperature was lower than that under room temperature treatment. Furthermore, treatment at both high alkali concentration and elevated temperature caused the damage of fibre that led to weakening the fibre-matrix interface. Hence, the lower tensile properties of the high concentration and elevated temperature-treated bamboo fibre/MUP composite compared to that under room temperature treatment was likely due to the weakening of fibre strength and the weakening fibre-matrix interface.



**Fig. 4. (a) Tensile strength, (b) elastic modulus, and (c) strain at break of bamboo fibre/MUP composites for treated bamboo fibre under room temperature (left side) and elevated temperature (right side).**

Again, under room and elevated temperatures treatment, Fig. 4(c) at left and right side, respectively, the trend of strain at break of bamboo fibre/MUP composites seemed about following the trend as in the tensile strength. The strain at break under elevated temperature treatment tended to be higher than that of the treated bamboo fibres under room temperature treatment. Increasing the strain at break for elevated temperature treated bamboo fibre/MUP composites might be attributed to the more increase of both fibre elongation and the strength of fibre/matrix interface. Chen et al. [28] reported that the elongation of bamboo fibres increased with increasing alkali concentration and the significant increase occurred at alkali concentration higher than 15%.



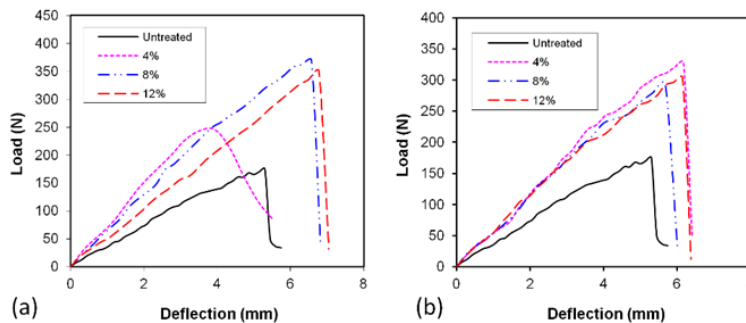
Table 1 shows the mechanical properties of Eternal MUP resin. The MUP tensile properties (tensile strength and elastic modulus) were lower than the unsaturated polyester (Reversol P9565) as reported by Ariawan et al. [25], which were 59.1 MPa and 2.91 GPa for the tensile strength and the elastic modulus, respectively. Other researcher, Manalo et al. [29] reported that the elastic modulus of AROPOL 1472/25P Infusion polyester resin was 3.1 GPa, while the flexural and tensile strength were 80.3 MPa and 30.9 MPa, respectively. Compared to the tensile properties of neat MUP (see Table 1), the maximum tensile strength of bamboo composites was only 54-62% of the MUP tensile strength, but in general, the elastic modulus was higher. Manalo et al. [29] also reported the same result for bamboo fibre/polyester composites and suggested that for randomly oriented fibres, the bamboo fibres did not act as reinforcement, but did act as filler. Furthermore, only fibres in loading direction that effectively transferred the load applied. Wong et al. [12] further emphasized that the tensile strength of bamboo fibre/polyester composite was lower than the neat polyester resin, when the fibre length was less than 10 mm at the volume fraction of 40%. In this study, the fibre volume fraction was 20% and the fibres were randomly oriented, so that the composite could not effectively transfer the load, leading to relatively low tensile properties. Using the oriented short fibre with higher volume fraction is of interest in the future work to obtain the maximum tensile properties.

**Table 1. The mechanical properties of modified polyester resin.**

Properties	Strength (MPa)	Modulus (MPa)	Strain at break (mm/mm)	Deflection at break (mm)
<b>Tensile</b>	48.30 ± 1.20	2144 ± 35	0.047 ± 0.003	-
<b>Flexural</b>	80.12 ± 10.34	2205 ± 324	-	13.04 ± 4.15

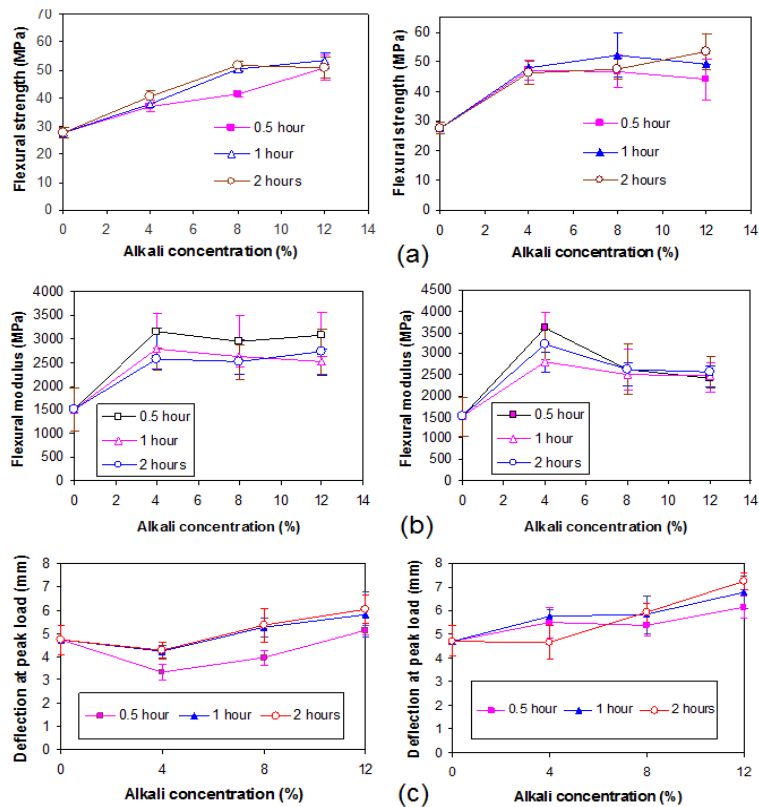
### 3.2. Flexural properties of bamboo fibre/MUP composites

Figure 5 shows the typical load-deflection curves of flexural test for bamboo/MUP composites for the selected treatment time (1 hour), under room and elevated temperatures. From those curves, it was seen that most bamboo/MUP composites did not experience significant yielding, as the curves showed linear elastic from the early loading to the peak load.



**Fig. 5. Typical load-deflection curves of bamboo fibre/MUP composites after alkali treatment for 1 hour under (a) room temperature, and (b) elevated temperature.**

The flexural strength of the bamboo/MUP composites at under room and elevated temperatures treatment is shown in Fig. 6. Under room temperature treatment, Fig. 6(a), for short treatment time (i.e., 0.5 hour), the flexural strength continued to increase up to concentration of 12%; however, for longer treatment times (1 and 2 hours), the flexural strength increased up to the concentration of 8%, then tended to be constant or slightly decreased afterward. A short treatment time did not provide sufficient time for removal of lignin and hemicellulose, but it needed higher concentration to do so. Therefore, for short treatment time, the flexural strength tended to continuously increase with alkali concentration. For longer treatment time, the flexural strength still increased with increasing alkali concentration, but there would be an optimum concentration. The optimum concentration for the treatment times of 1 and 2 hours was obtained at about 12% and 8%, respectively. As reported by Chen et al. [28] and Manalo et al. [29], treatment at high alkali concentration and long treatment time (e.g., 12% for 2 hours) tended to damage the fibre. Under room temperature treatment, the maximum increase of flexural strength compared to the untreated fibre was obtained at the concentration of 12% for the treatment time of 1 hour, which was approximately 104%. This was consistent with the highest tensile strength at this treatment. Moreover, at the concentration of 8% (the treatment time at least for 1 hour), the flexural strength had been increased by approximately 90%.



**Fig. 6. (a) Flexural strength, (b) flexural modulus, and (c) deflection at peak load of bamboo fibre/MUP composites after alkali treatment under room temperature (left side) and elevated temperature (right side).**

Under elevated temperature treatment, Fig. 6(a) (right side), at the concentration of 4% (for all treatment times), the flexural strength had increased up to 70%, relative to the untreated fibre. Further increase of the alkali concentration seemed not having significant effect on the flexural strength, even it tended to decrease at higher alkali concentration. These results were consistent with the trend of tensile strength. It seemed that the treatment under elevated temperature was able to reduce the content of lignin and hemicellulose immediately, although at low alkali concentration. Literature reported that treatment under elevated temperature in dry condition could increase the crystalline index of natural fibre [13, 14, 31]; however, in this study, the simultaneous treatment at high alkali concentration and temperature could further damage the fibre.

Under room temperature treatment, Fig. 6(b) (left side), the flexural modulus immediately increased up to the concentration of 4%, and then tended to slightly decrease up to the concentration of 12%. At low alkali concentration, the partial removal of hemicellulose and lignin improved the adhesion strength, so it increased the rigidity of the composites. As reported by Chen et al. [28], further increasing alkali concentration caused the fibres to be more wrinkles. Moreover, the elastic modulus decreased as the elongation at break increased. The tendency of increasing the fibre-matrix adhesion strength with increasing the alkali concentration could amplify the decrease of composites elastic modulus, as the fibres could be effectively elongated. As shown in Fig. 6(b) (right side), when the fibres were treated under elevated temperature, a sharp increase of flexural modulus occurred up to the concentration of 4%, and then it sharply decreased up to the concentration of 8%. Beyond the concentration of 8%, it tended to level off.

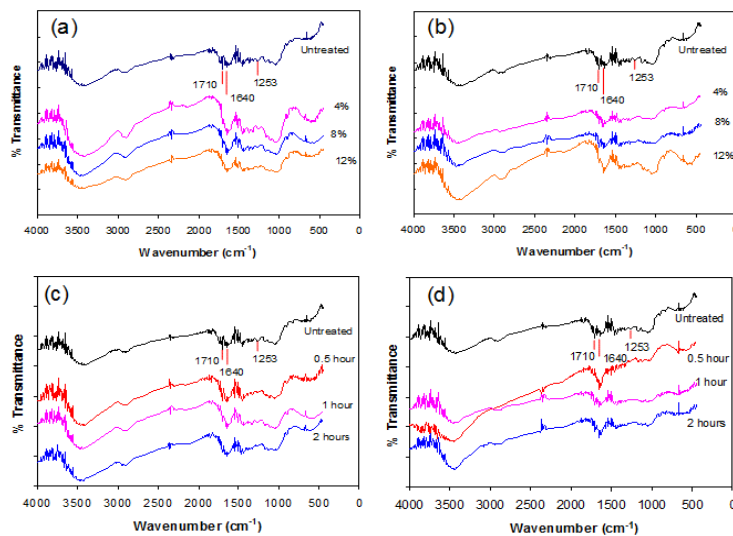
Under room and elevated temperatures treatment, Fig. 6(c) (left side and right side, respectively), generally the deflection at break tended to increase with increasing alkali concentration. However, the treatment under elevated temperature gave higher increase of the deflection at peak load, compared to that under room temperature treatment (at the same concentration). It was due to the high interfacial strength and increasing the elongation of treated fibres, and those were more apparent in elevated temperature treatment. The reason for this was similar to that in the tensile strength as discussed earlier.

Again, similar to the tensile properties, compared to the MUP matrix, the flexural strength and the deflection at break of bamboo fibre/MUP composites were lower (see Table 1). The flexural strength and the deflection at break of bamboo fibre/MUP composites were about 34-66% and 36-54% of those of the MUP, respectively. On the other hand, in general, the flexural modulus of bamboo fibres/MUP composites was higher than the flexural modulus of MUP, as expected.

### 3.3. Fourier transform infrared (FTIR)

Figure 7 shows the FTIR spectra of the untreated and treated bamboo fibres. All of the FTIR spectra show peaks at wavenumbers of 3800-3300  $\text{cm}^{-1}$ , 1710  $\text{cm}^{-1}$ , 1253  $\text{cm}^{-1}$ . A broad peak at wavenumbers in the range of 3800 - 3300  $\text{cm}^{-1}$  was associated with O-H stretching, while the peak at wavenumber of 1710  $\text{cm}^{-1}$  was associated with C=O vibration in pectin and hemicelluloses [28, 32, 33]. The peak at wavenumber of 1253  $\text{cm}^{-1}$  was associated with C-O stretching vibration in lignin [11]. After alkali treatment at the concentration of 4% for 1 hour under room temperature, the peak intensity at wavenumbers of 1710 and 1253  $\text{cm}^{-1}$  reduced, and the reduction increased with the

increase of alkali concentration. At the concentration of 12%, the peak at wavenumber of  $1710\text{ cm}^{-1}$  was almost vanished, indicating that the hemicellulose was almost thoroughly removed. While the peak at wavenumber of  $1253\text{ cm}^{-1}$  that corresponded to the lignin was only partially removed, as the peak intensity only reduced, but not completely vanished. When the alkali treatment was conducted under elevated temperature, the reduction of intensity of both peaks had been observed at low concentration (4%); however, the reduction was more apparent at the peak at wavenumber of  $1253\text{ cm}^{-1}$ . The peak intensity at wavenumber of  $1710\text{ cm}^{-1}$  reduced, but it was still detected at the concentration of 12%. This meant that the content of lignin, hemicellulose and pectin in the bamboo fibres decreased with the increase of alkali concentration. The lignin was likely more sensitive to the temperature, whereas the hemicellulose was more sensitive to the concentration. The similar trend was observed for the effect of treatment time, as seen in Figs. 7(c) and (d). With increasing the treatment time, at the constant alkali concentration of 8%, the reduction of intensity of both peaks increased and it was more apparent under elevated temperature treatment. At the treatment time of 2 hours, the highest reduction of peak intensity occurred at the wavenumbers of  $1710\text{ cm}^{-1}$  and  $1253\text{ cm}^{-1}$ . It was expected, as the longer treatment time provided sufficient time for alkali to dissolve most of the alkali sensitive substances.



**Fig. 7. FTIR spectra of treated bamboo fibres showing the effect of alkali concentration (a) under room and (b) elevated temperatures, respectively, for treatment time of 1 hour, while (c) and (d) showing the effect of treatment time under room and elevated temperatures, respectively, at the concentration of 8%.**

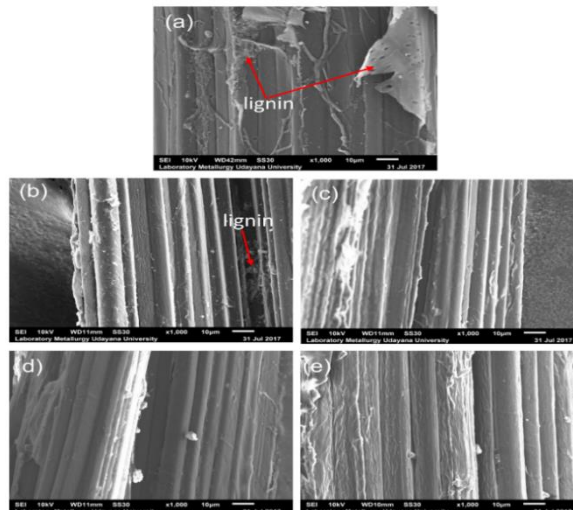
Beside the two peaks at wavenumbers of  $1710$  and  $1253\text{ cm}^{-1}$ , there was a peak at wavenumber of  $1640\text{ cm}^{-1}$ . The wavenumber of  $1640\text{ cm}^{-1}$  was associated with the absorbed water in the crystalline cellulose [15, 34]. Under room temperature treatment at the concentration of 4%, the peak transmittance tended to decrease (the absorption increased), relative to the untreated fibre, but it then tended to increase with increasing both alkali concentration and treatment time. This meant that at the concentration of 4% (treatment time of 1 hour), the absorbed water in crystalline cellulose likely increased, and then it decreased with further increasing alkali concentration. On the other hand, under elevated temperature treatment, the peak

transmittance tended to decrease with increasing alkali concentration, indicating more water in the crystalline cellulose. This behaviour was also reported by Kim et al. [15] and Das and Chakraborty [33]. The effect of treatment time on the peak of  $1640\text{ cm}^{-1}$  under room and elevated temperatures treatment was approximately similar to the effect of concentration under the same treatment condition. However, the effect of treatment time on the peak transmittance under elevated temperature was not as apparent as that the treatment under room temperature treatment.

### 3.4. Scanning electron microscopy results

#### 3.4.1. Morphologies of bamboo fibre

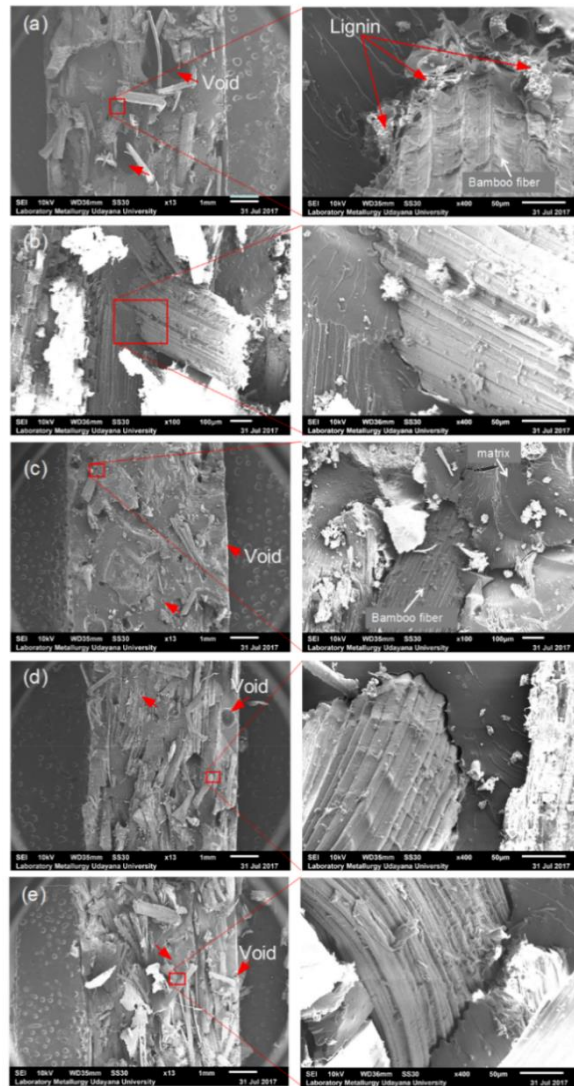
Figure 8 shows the SEM micrographs of bamboo fibres at the selected concentration and at the same treatment time (1 hour), under both room and elevated temperatures. It can be seen in Fig. 8(a) that for the untreated fibre, the surface of fibres was covered by lignin matrix and other non-crystalline substances. Under room temperature treatment at the concentration of 4% for 1 hour, see Fig. 8(b), the individual fibres were seen, but they might still contain lignin and hemicellulose as confirmed using FTIR. With increasing alkali concentration, for example at the concentration of 12% (at the same treatment time), there was a tendency that the individual fibres started to detach from the bundle, see Fig. 8(c) or the fibre bundles became fibrous. Because this study used fibre bundles rather than individual fibre; therefore, lignin and hemicellulose that bonded the individual fibre might still exist in the inner of fibre bundles and they were detected using FTIR. Furthermore, the removed lignin and hemicellulose on the surface of fibres reduced the size of both fibre bundles and the alkali exposed individual fibre. This increased the surface roughness of the fibre as the fibre became smaller. As seen in Fig. 8(d), under elevated temperature treatment at the concentration of 4%, the fibre surface looked cleaner than that of under room temperature treatment, at the same concentration. It likely indicated that most lignin had been removed but referring to the FTIR spectrum, Fig. 7(b), hemicellulose might still exist. At the concentration of 12%, Fig. 8(e), the fibres became rough, indicating that the fibres started to degrade.



**Fig. 8.** SEM images of (a) untreated bamboo fibres and treated at concentrations of (b) 4%, (c) 12% under room temperature, (d) 4% and (e) 12% under elevated temperature.

### 3.4.2. Morphologies of tensile fracture surfaces of bamboo fibre/MUP composites

Figure 9 shows the SEM micrographs of the tensile fracture surfaces of bamboo fibre/MUP composites. It was observed in Fig. 9(a) that for the untreated fibre, at low magnification, the fibres appeared to be pulled out from the matrix, indicated by longer fibre and some holes in the surfaces. Using high magnification, it was seen that the fibre was surrounded by lignin, shown by long red arrows in Fig. 9(a) (right). In this case, lignin functioned as weak boundary layer that prevented the matrix to have strong adhesion with fibres, so that it could not fully transfer the load.



**Fig. 9.** SEM micrographs of tensile fracture surfaces of bamboo fibre/MUP composites (a) untreated, and treated at concentrations of (b) 4%, (c) 12% under room temperature, and (d) 4% and (e) 12% under elevated temperature.

Under room temperature treatment at the concentration of 4% for 1 hour, as seen in Fig. 9(b), the fracture surface was mostly dominated by the fibre fracture. Using higher magnification, it was clear that hemicelluloses and lignin have partially been removed from the fibre. Although void was observed surrounding the fibre; however, there was no significant slip between the fibre and the matrix, indicating a good bonding between matrix and fibre. Nevertheless, the increase of tensile strength was not yet significant at this concentration. With increasing the concentration up to 12% for 1 hour, the fracture surface was also dominated by the fibre fracture. At higher magnification, it was observed that the matrix deformed around the fibre, indicating high fibre-matrix interfacial strength. It was expected, as at this treatment, the tensile strength of bamboo fibre/MUP composites was the highest.

Treatment under elevated temperature could accelerate removal the lignin, hemicellulose and other non-crystalline substances from the fibre. As shown in Fig. 9(c), at the concentration of 4% for 1 hour, the fibres looked clean, showing the exposed individual fibres. The exposed individual fibres increased the contact surface area between matrix and fibre, leading to high bonding strength. Finally, the high bonding strength increased the tensile strength of its composites, compared to the untreated fibres. At the concentration of 12%, as seen in Fig. 9(d), the degradation of bamboo fibres might have been occurred, indicated by the serrated surface of the bamboo fibre. Nevertheless, the tensile strength indicated the highest. This could be higher contact surface area and higher bamboo's tensile strength.

For most of specimens, voids due to the trapped air during manufacturing were observed, shown by short red arrows in Fig. 9. The voids functioned as a stress raiser that could cause premature failure of the specimens. The large variations in the tensile properties could be caused by the existence of those voids.

### 3.5. X-rays diffraction (XRD)

Figure 10 shows the XRD spectra of the untreated and treated bamboo fibres. The peaks at  $2\theta = 16.2^\circ$  and  $22.2^\circ$  are attributed to the reflection at the 101 and 002 crystallographic planes, respectively. It can be seen that for the untreated fibre, there were peaks at  $16.2^\circ$ , and  $22.2^\circ$  and  $38.9^\circ$ . The peaks at  $16.2^\circ$  and  $22.2^\circ$  corresponded to the cellulose I that had the preferred orientation of crystallites along the fibre axis [28, 35], while the peak at  $38.9^\circ$  was associated with amorphous cellulose [36]. Cellulose I consist of one-chain triclinic cellulose  $I_\alpha$  and two-chain monoclinic cellulose  $I_\beta$  unit cells, and the ratio of  $I_\alpha$  to  $I_\beta$  depends on the origin of cellulose resources [37]. For this bamboo species, as shown in Table 2, the ratio of  $I_\alpha$  to  $I_\beta$  for the untreated fibre was 0.59, and after treatment at the concentrations of 4% and 12%, under room temperature, the ratio increased to 0.67, and 0.91, respectively. At the concentration of 4%, the percentage crystalline of  $I_\alpha$  and  $I_\beta$  slightly increased and decreased, respectively; however, at the concentration of 12%, the percentage crystalline of  $I_\alpha$  and  $I_\beta$  decreased significantly. Liu and Hu [38] reported that at the concentration of 12%, the cellulose I started to transform to cellulose II, which was more stable than cellulose I, shown by peaks at  $12.2^\circ$ , and  $20.1^\circ$ . However, in this study, the transformation from cellulose I to cellulose II could not be clearly identified. Therefore, other possible explanation was partial removal of lignin and hemicelluloses, which affected the crystalline index. For the treatment under elevated temperature, instead of increasing, the ratio of  $I_\alpha$  to  $I_\beta$  tended to more decrease with increasing concentration. For example, at the

concentrations of 4% and 12%, the ratio of  $I_\alpha$  to  $I_\beta$  was 0.70 and 0.55, respectively. This indicated that for alkali treatment under elevated temperature, the cellulose crystalline tended to exist in the form of cellulose  $I_\beta$ , which was more stable than cellulose  $I_\alpha$  [39].

As seen in Fig. 10, for all treatment conditions, there was no shifting in the angle of peaks but the intensity decreased. This indicated that there was no cellulose crystalline transformation, but the crystalline index increased. Relative to the untreated fibre, the crystalline index for the 4% treated fibres increased by about 10.5% (from 23.6% to 32.1%), but the crystalline index for the 12% treated fibre (32.75%) was only slightly higher than the 4% treated fibre. The increasing of crystalline index was likely due to the removal of hemicelluloses and lignin, so that the cellulose chain pack became closer and dense, indicated by decreasing d-spacing (see Table 2) [8].

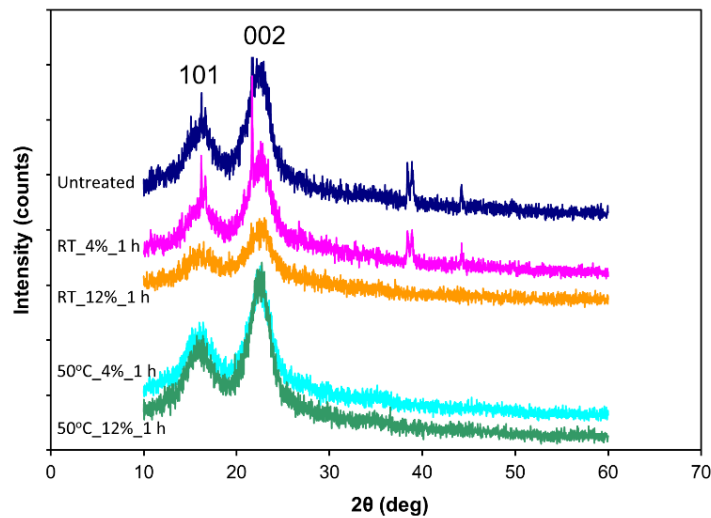


Fig. 10. The XRD spectra of bamboo fibres.

Table 2. Crystallinity of bamboo fibre.

Cellulose type	Treatment				
	UT	4%, 1 h (RT)	12%, 1 h (RT)	4%, 1 h (50°C)	12%, 1 h (50°C)
Cellulose $I_\alpha$ (%)	37.3	40	31.3	28.1	24.9
Cellulose $I_\beta$ (%)	62.7	60	34.3	39.9	45.4
Crystalline index (CI) (%)	23.6	32.1	32.75	24.3	23.3
d-spacing (Å)	3.95948	3.93187	3.93216	3.93216	3.93787

UT = untreated, RT= room temperature, h = hour

On the other hand, under elevated temperature treatment, compared to the untreated fibre, the crystalline index of the 4% treated fibre slightly increased to 24.3%, but at the concentration of 12%, the crystalline index slightly decreased to 23.3%. This indicated that for alkali treatment under elevated temperature, degradation of cellulose might have been occurred at low concentration, and the degradation increased at high alkali concentration. Das and Chakraborty [8]



suggested that at high alkali concentration, there was a tendency for the cellulose molecular structures to be randomness. Furthermore, Liu and Hu [38] suggested that treatment at high alkali concentration and high temperature tended to increase the size of hydrated hydroxide ions, so that it reduced the adsorption of alkali in the cellulose structure. This resulted in decreasing the crystalline index. Nevertheless, we believed that as the surface topography of the 12% treated fibres became cleaner and rougher under elevated temperature than that of under room temperature treatment, the cellulose degradation might be more reasonable for decreasing the crystalline index.

#### 4. Conclusions

Alkali treatments of the bamboo fibres had been carried out to improve the fibre-matrix interaction of bamboo fibre/polystyrene-modified unsaturated polyester resin (MUP) composites. Characterization of the physical and tensile properties of bamboo fibres as well as the tensile and flexural properties of bamboo fibre/MUP composites also had been conducted. Some keys finding are following:

- Combination of FTIR analysis, SEM and X-rays diffraction can indicate the removal of hemicellulose, lignin and other amorphous substances from bamboo fibre.
- Under room temperature treatment, the tensile and flexural properties of bamboo fibre/MUP composites tended to increase with increasing alkali concentration, but high concentration (12%) and longer treatment time (2 hours) tended to decrease the tensile and flexural properties. Meanwhile, under elevated temperature treatment, the optimum tensile and flexural properties had been obtained at lower alkali concentration (4%) and short treatment time (0.5 hour). Therefore, treatment at low alkali concentration under elevated temperature was suggested to minimise the environment impact and to reduce the production time in manufacturing the natural fibre composites. Utilising the expandable polystyrene waste for composite manufacturing can help overcoming environmental problems.

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#### Nomenclatures

$b$	Width of the flexural specimen (Fig. 1), mm
$C$	Carbon atom
$CI$	Fibre crystalline index, %
$d$	Thickness of the flexural specimen (Fig. 1), mm
$H$	Hydrogen atom
$I_{am}$	Maximum intensity of the amorphous part, counts
$I_{002}$	Peak intensity of the 002 crystallographic plane reflection, counts
$I_a$	One-chain triclinic cellulose

$I_{\beta}$	Two-chain monoclinic cellulose
$L$	Span length of the flexural specimen (Fig. 1), mm
$O$	Oxygen atom
$P$	Applied load (Fig. 1), N
<b>Greek Symbols</b>	
$\theta$	Incident angle of X-rays beam, degree
<b>Abbreviations</b>	
ASTM	American Society of Testing Materials
EPS	Expandable Polystyrene
FTIR	Fourier Transform Infrared
GPa	Giga Pascal
KBr	Potassium Bromide
MA	Maleic Anhydride
MEK	Methyl Ethyl Ketone
MPa	Mega Pascal
MUP	Modified Unsaturated Polyester
NaOH	Sodium Hydroxide
RT	Room Temperature
SEM	Scanning Electron Microscopy
USD	United States Dollar
UT	Untreated
XRD	X-rays Diffraction

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