The Effects of Combined Chemical Treatments on the Mechanical Properties of Three Grades of Sisal

Sameer Adnan Ibraheem,[a] Subramania Sarma Sreenivasan,[d] Khalina Abdan,[a,b,c,]* Shamsuddin A. Sulaiman,[d] Aidy Ali,[e] and Dayang Laila Abang Abdul Majid [f]

Different grades of sisal fibres (S3, STOW, and SUG) were immersed in five different treatment solutions: sodium hydroxide (NaOH) for 24 h; silane for 24 h; and NaOH followed by silane for 6, 12, and 24 h. The treated fibres were tested for bonding strength using the micro-droplet method. It was established that NaOH and silane treatments improved bonding strength with the unsaturated polyester resin that was used. However, it can be concluded that NaOH followed by silane (each for 6 h) produced the highest bonding strength compared with the other combined treatments. This is most likely because of fibre erosion caused by the chemicals in the other treatments, which causes fibres to lose the ability to bond with the resin. Fibres treated with silane had the highest bonding strength. The tensile mechanical properties, characterised using the single-fibre test method according to the ASTM standard C1557-03 (2008), showed that the NaOH treatment improved ultimate tensile strength, while the silane treatment decreased ultimate tensile strength for all sisal grades. Nevertheless, the ultimate tensile strength was reduced when the duration of the combined treatments was increased. The highest results for the mechanical properties were obtained from the combined treatments of NaOH followed by silane (each for 6 h).

Keywords: Sisal; Chemical treatment; Bonding strength; Droplet test

*Contact information: a: Biological and Agricultural Engineering Department, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor D. E. Malaysia; b: Institute of Tropical Forestry and Forest Products (INTROP) Universiti Putra Malaysia, 43400 Serdang, Selangor D. E. Malaysia;c: Aerospace Malaysia Innovation Centre (AMIC) No 3-6-01, German Malaysian Institute , Jalan Ilmiah, Taman Universiti, 43000 Bangi Selangor D. E. Malaysia; d: Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor D. E. Malaysia; e: Department of Mechanical Engineering, Faculty of Engineering, National Defence University of Malaysia, Sungai Besi, 57000 Kuala Lumpur, Malaysia; f: Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor D. E. Malaysia; * Corresponding author: khalina@upm.edu.my*

INTRODUCTION

Sisal fibre can be regarded as a natural composite comprised of 65% cellulose, 12% hemicellulose, 10% lignin, and small amounts of compounds such as ash and other minor ingredients (Rowell *et al*. 1992; Joseph *et al*. 1996). The chemical treatment of sisal fibre may contribute to the improvement of bonding between fibres and matrix. Commonly-used chemical treatments for sisal fibres are alkali, anhydrides, resorcinol, amines, silanes, and acrylate-based surface treatments. The chemical treatment of sisal fibre tends to improve the thermal, adhesive, and mechanical properties of biocomposites (Kuruvilla *et al*. 1996; Augustine *et al*. 1997; Megiatto *et al*. 2008; Kim and Netravali 2010).

Coupling agents such as silanes can significantly reduce the moisture absorption of the treated fibres by changing the surface hydrophobicity as shown in Fig. 1. Moreover, these coupling agents penetrate through the surface voids and deposit into the interfibrillar regions, thus preventing any increase in moisture (Li *et al*. 2000).

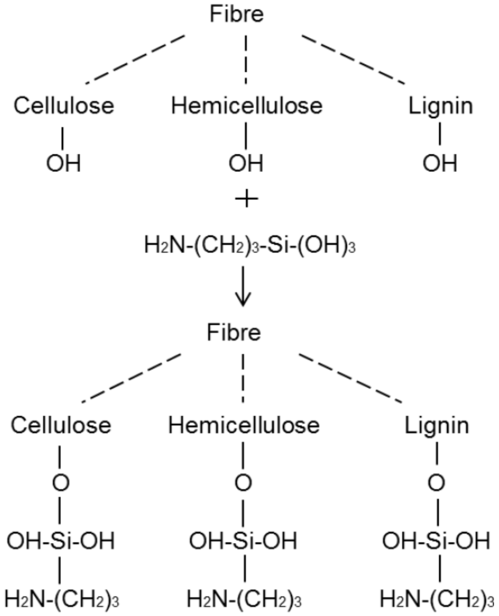

Fig. 1. Reaction of silane with natural fibers (Singha and Ashvinder 2012)

Treatment with NaOH is considered to be one of the most cost-effective and practical treatments. Moreover, it can improve the mechanical and interfacial properties of the natural fibres without toxic organic chemicals (Pimenta *et al*. 2008; Duhovic *et al*. 2009). The capability of NaOH treatment (mercerisation) to increase cellulose content by removing hemicellulose and lignin makes it a favourable treatment for enhancing the mechanical properties of natural fibres (Kim and Netravali 2010).

Seki (2009) examined the effects of two chemical treatments (5% NaOH for 2 h and silane for 1 h) on the flexural properties of two bio-composites (jute-reinforced epoxy and jute-reinforced polyester). For jute epoxy bio-composites, the flexural strength and flexural modulus of the jute treated with silane were higher (12% and 7%, respectively) than with alkali treatments alone (Seki 2009). Using the same alkali treatment but with different concentrations (5%, 10%, and 15%), Boopathi *et al*. (2012) investigated the effects of this treatment on Borassus fruit fibre. The FT-IR results showed a noticeable improvement in the strength of the hydrogen bonding, which led to enhancement of the mechanical properties of the fibres; the 5% alkali-treated fibres showed the highest tensile strength, while the reduction of the tensile properties for the 10% and 15%-treated fibres was caused by this strong treatment's damage to the fibres (Boopathi *et al*. 2012).

Furthermore, alkali treatments help to remove hemicellulose and lignin from the fibre surface, while silane treatment has no effect on these components. Silane treatments cover the fibre surfaces and fill the empty spaces between the microfibrils (Kabir *et al*. 2013). It has been established that differences in treatments, treatment concentrations, and durations cause a variation in the degree of the removal of impurities as well as the degree of structural perturbation (Athijayamani *et al*. 2010; Faruk *et al*. 2012; Venkateshwaran *et al*. 2013). However, it was concluded that the tensile properties of hemp fibres treated with NaOH were slightly improved compared with those of untreated fibres because of the increase in cellulose crystallinity. Nevertheless, the tensile properties of the fibres treated with several treatments (acetic anhydride, maleic anhydride, silane, and combined sodium hydroxide and silane) were slightly decreased compared with those of untreated fibres, which was believed to be the result of decreased cellulose crystallinity (Sawpan *et al*. 2011). The acidic conditions for the acid-catalysed hydrolysis of silanes were moderate, and the pH was close to that of many natural fibres. As a result, silane treatment reduced the fibres' tensile strength (Sreekala *et al*. 1997; Matuana *et al*. 1998).

The objective of this study was therefore to determine the effects of the alkali, silane, and combined treatments on the mechanical properties of the fibre and the bonding strength between the fibres and unsaturated polyester. Three grades of sisal fibres were treated with NaOH and silane for 24 h, and the durations of the combined treatment were 6, 12, and 24 h, respectively.

EXPERIMENTAL

Materials

Preparation of fibres

Three grades of sisal were used: (1) S3, with a minimum length of 0.6 m, consisting of brushed fibre. Although minor defects in colour and cleaning were allowed, it was free of barky or undecorticated fibre and knots; (2) STOW/Proper tow from the brushing machines. Free of line fibre, cuttings, dust, dirt, sweepings, and knots, with a creamy white to cream colour; and (3) SUG/Fibre that does not conform to the above-mentioned grades in terms of length, colour, and cleaning, and has a minimum length of 0.6 m.

Methods

Treatment

Three types of treatment were applied to the sisal: (1) only NaOH with 6% wt for 24 h (marked as Na); (2) silane (3-glycidoxypropyltrimethoxy silane) 6% wt as a coupling agent in which the fibres were immersed in silane for 24 h (marked as Si); and (3) a combined treatment of NaOH followed by silane for several periods of time (6, 12, and 24 h), marked as Na+Si 6, Na+Si 12, and Na+Si 24, respectively. In the combined treatment, the NaOH was applied first for each specific duration and then the fibres were washed in distilled water and followed by the silane coupling agent for same specific duration. After the immersion of the fibres for the specific type of treatment, the fibres were washed in distilled water and dried in a drying oven at 60 °C for 8 h.

Single-fibre tensile test

According to the ASTM C1557-03 (2008) standard, tests were conducted on five specimens for each sample using a 5-kN Instron Universal testing machine (USA). However, five single fibres were mounted to the grips (Fig. 2), and the diameters were measured using an optical microscope. To ensure the accuracy of the tests, ten measurements were recorded for the diameter of each specimen on the length of the strain gauge, and the mean of these ten measurements was used to determine the tensile properties. For the test, the cross-head displacement speed rate was fixed at 500 x 10^{-6} m/min.

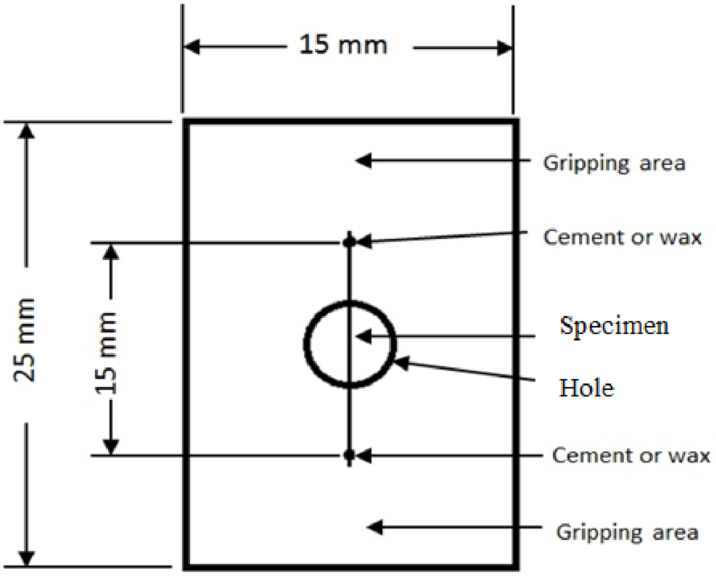

Fig. 2. Schematic of single-fibre tensile test sample

Droplet test

To determine the micromechanical bonding strength and interfacial shear strength, micro-droplet bonding tests were conducted. Five specimens for each sample were tested using a 5-kN Instron Universal testing machine (USA). The schematic of the micro-droplet test is shown in Fig. 3. The analysis was performed using Eq. (1), given below (Shito *et al*. 2002),

$$\tau = \frac{F}{\pi D L} \qquad (1)$$

where τ is the interfacial shear strength (MPa), F is the load at maximum stress (N), D is the single-fibre diameter (m), and L is the embedded length (m).

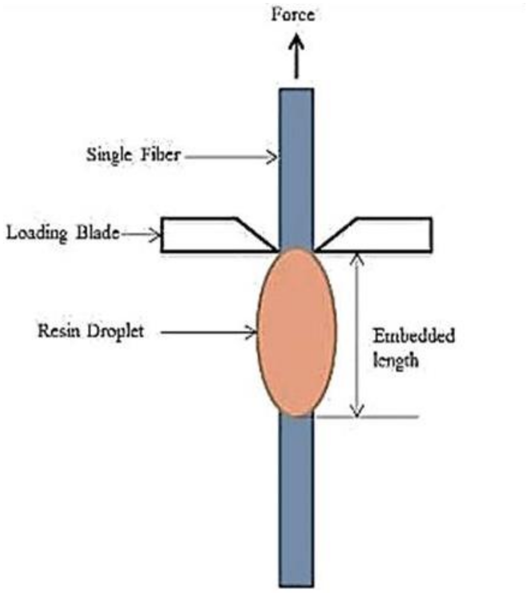

Fig. 3. Schematic of the micro-droplet test

Five specimens were tested for each grade for both treated and untreated fibres. The droplets were drawn onto the fiber from the unsaturated polyester, using pins to obtain small-size drops. A period of 24 h was allowed to pass to let the drops fully dry. The mean values of fiber diameter and droplet length were calculated. The coefficient of variation for each grade of sisal did not exceed 6%. Moreover, the diameter of the fibre was measured from the nearest point of the droplet and fibre contacts on both sides, and then marked with red colour (Fig. 4). Table 1 shows the fiber diameters and the embedded lengths (droplet length).

Table 1. Fiber Diameter and Droplet Length

	Fiber Diameter (μm)	Embedded Length (μm)
Untreated	118	1178
NaOH	100	846
Silane	133	1160
NaOH+silane 24 h	107	856
NaOH+silane 12 h	114	896
NaOH+silane 6 h	123	1011

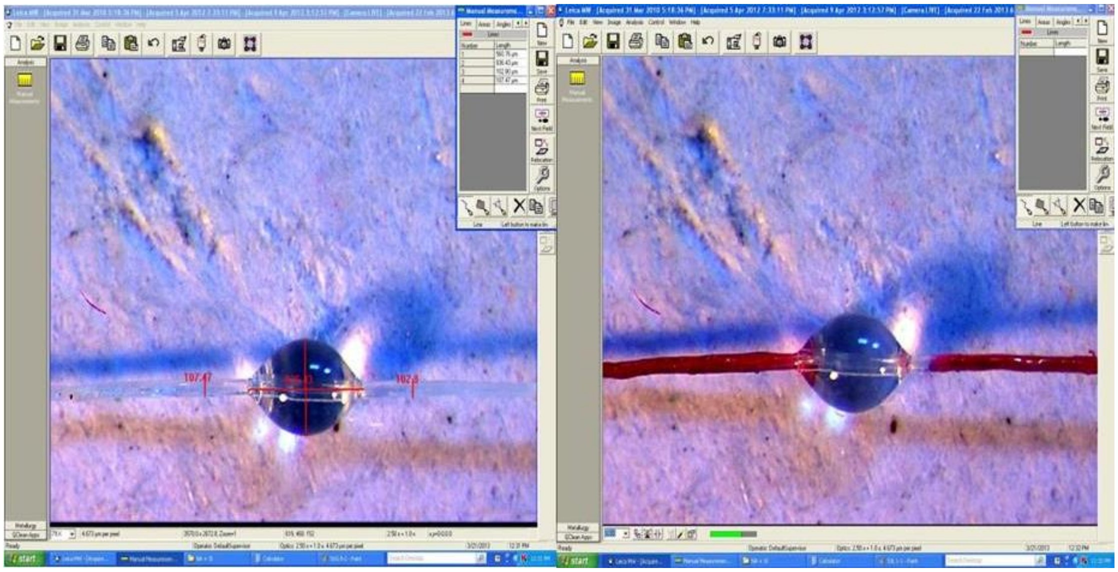

Fig. 4. Micro-droplet specimen

Transform Infrared Spectrometer (FT-IR) test

A Spectrum 100 Optica FT-IR Spectrometer (Perkin Elmer) was used to conduct FTIR analysis of the untreated and treated sisal fibers with (only NaOH, only silane (3-glycidoxypropyltrimethoxy silane), and combined treatment of NaOH followed by silane for 6 h for several periods of time (6, 12, and 24 h)).

Scanning Electron Microscopy (SEM) Characterisation

Scanning electron microscopy was used to examine the fracture surface conditions and the morphology of samples broken after the tensile tests. The analysis was conducted on a Hitachi SEM (Japan) instrument operating at an accelerating voltage of 5 kV. Samples were mounted on aluminium stubs.

RESULTS AND DISCUSSION

Single-fibre Tensile Test

Figure 5 shows the ultimate tensile strength (UTS) for all sisal grades for each type of treatment. The results were obtained from the single-fibre tensile test according to the ASTM standard ASTM C1557-03(2008). For the untreated group, Sisal STWO had the highest UTS (270.499 MPa) compared with S3 (234.747 MPa) and SUG (219.636 MPa). This was probably because of the pre-processes that were undertaken on the sisal fibres, such as combing and cleaning the fibres of impurities. However, the 24-h silane treatment reduced the value of the ultimate tensile stress for the sisal grades (STWO, S3, and SUG) by (23.46%, 34.97%, and 32.36%, respectively) compared with the untreated fibres. This reduction may have been caused by the effects of decreasing cellulose crystallinity and the acidic effects of the silane treatment (Sreekala *et al*. 1997; Matuana *et al*. 1998; Sawpan *et al*. 2011). In contrast, the alkali treatment enhanced the tensile mechanical properties for all grades of sisal and gave the highest values compared with all other treatments, as shown in Fig. 5. As expected, the alkali treatment increased the amount of cellulose by removing hemicellulose and lignin from the fibres.

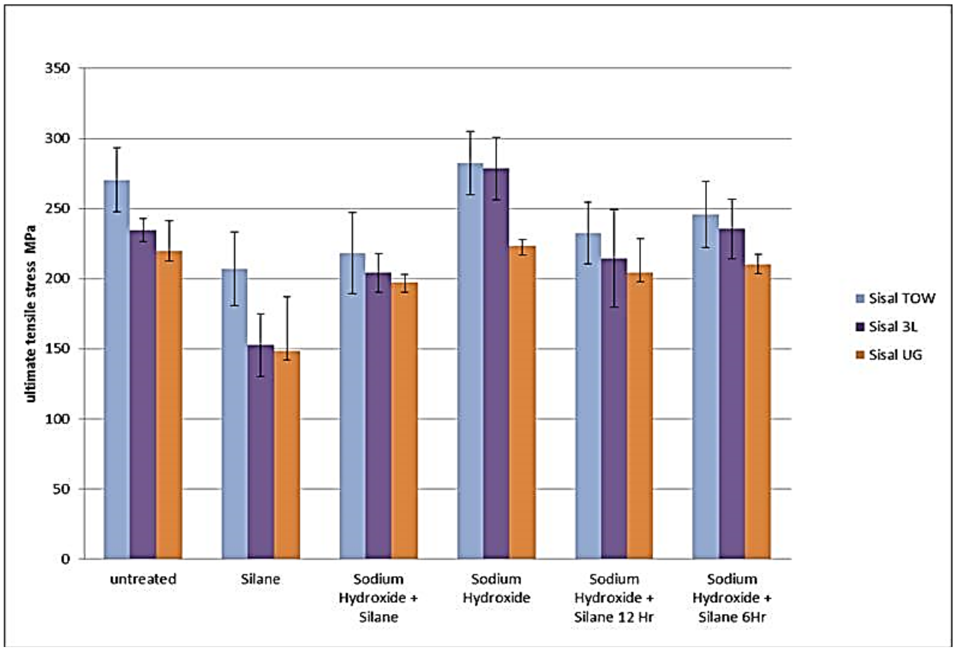

Fig. 5. Ultimate tensile stress. Data provided as the mean ± standard deviation

The combined treatments showed lower UTS compared with the untreated samples and higher UTS than the fibres that were treated with silane only. The acidic effects of the silane treatment reduced the mechanical properties of the fibres by damaging them. Silane treatment was carried out in acidic medium. This acidic medium could catalyse the cleavage of β-1,4-glycosidic bonds between the two anhydroglucose units, leading to cellulose chain scission and lowering the tensile strength. By increasing the duration of the treatments, the UTS decreased because of the decreasing pH of the fibres caused by the acidic aspect of silane; The UTS were highest for the 6h treatment duration compared with the other combined treatment durations, and reached 245.889, 235.515, and 210.450 MPa for STOW, S3, and SUG, respectively. However, when the duration of the combined treatments increased, the UTS decreased and reached their lowest values of 218.251, 204.345, and 197.418 MPa for 24 h of treatment for STWO, S3, and SUG fibres, respectively.

Droplet Test

Figure 6 shows the interfacial shear strength for all sisal grades with each type of treatment. Clearly, all types of treatment improved the interfacial adhesion and bonding between the fibre and the matrix. However, the 24-h silane treatment produced the best results for all three sisal grades, and the SUG gave the highest interfacial shear stress (6.805 MPa) compared with S3 and STOW (6.165 and 5.862 MPa). For the combined treatments, the results showed that the 6-h combined treatment achieved improvement in interfacial bonding and reached the maximum values for S3, SUG, and STOW (6.01, 6.58, and 5.571 MPa, respectively). The lowest values were given by the 24-h treatment for S3, SUG, and STOW (4.235, 2.945, and 3.898 MPa, respectively). The reductions were probably caused by the effects of the extended NaOH treatment time, which led to the removal of high amounts of lignin and hemicellulose, thus leaving behind voids that made the penetration of the coupling agent easier and with subsequent deposits into the interfibrillar regions that led to the reduction of the coupling agent's effect specifically on the surface of the fibers combined with the effects of the acidic nature of the silane coupling agent. On the other hand, NaOH treatment increased bonding between fibre surfaces and the matrix for all three grades of sisal compared to the untreated fibers.

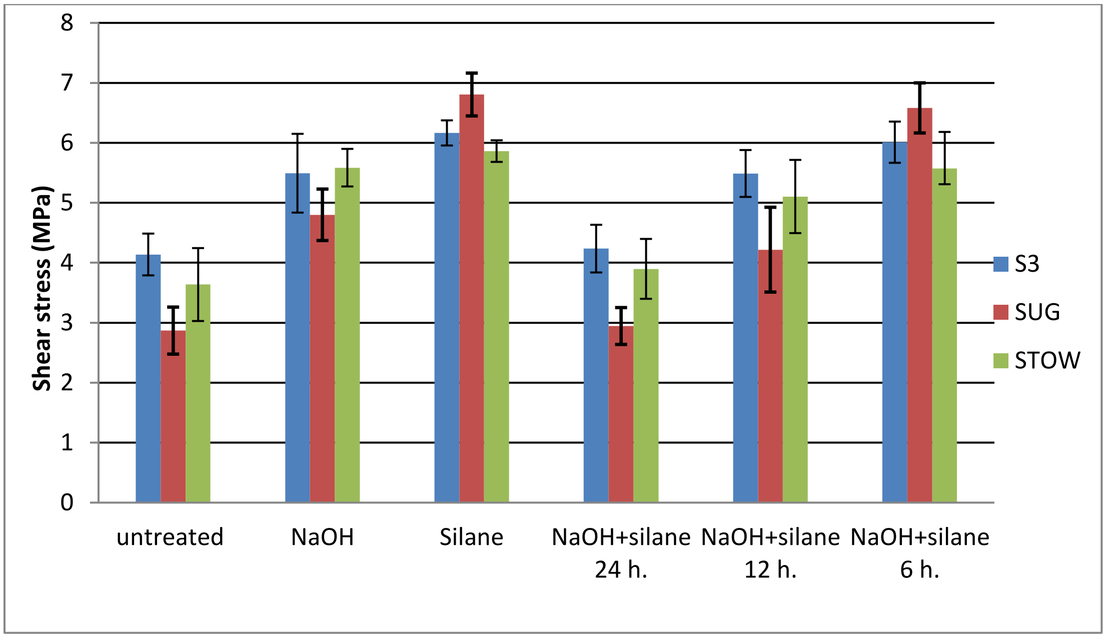

Fig. 6. Interfacial shear strength. Data provided as the mean ± standard deviation

Transform Infrared Spectrometer (FT-IR) test

Figure 7 shows the results of FTIR analysis. The peak in the range of 3300 to 3500 cm^{-1} and a peak at 1610 cm^{-1} are due to the characteristics axial vibration of hydroxyl group of cellulose, the peak at around 1010 cm^{-1} is due to the associated hydrogen group (Mohan *et al*. 2012). The peak at around 1259 cm^{-1} is due to G ring stretching (Fan *et al*. 2012), and 1378 cm^{-1} is attributable to CH_3 symmetric deformation. The band located at 1257 cm^{-1} disappears in the fibers treated with NaOH. This has been associated with the mercerization of lignocellulosic fibres, and it also can indicate that peaks near 1250 cm^{-1} are related to residual unhydrolysed Si–ethoxy–methoxy groups and their small intensity indicating minor presence in the silane-treated fibers (Herrera-Franco and Valadez-González 2005).

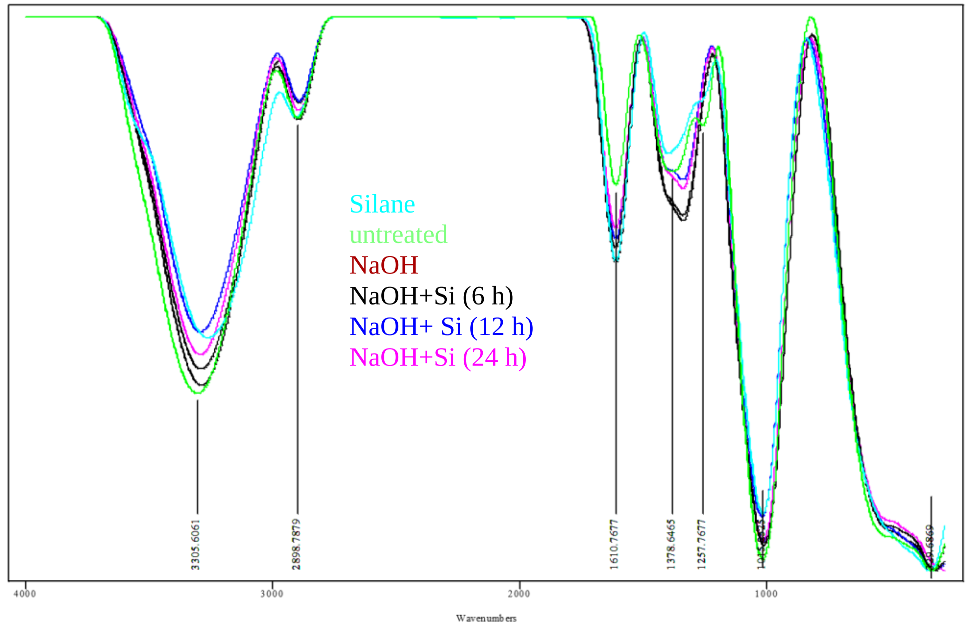

Fig. 7. FTIR spectra for untreated and treated fibers

Scanning Electron Microscopy

Figure 8A shows SEM micrographs for untreated and treated S3 fibres. For all untreated samples (A1, B1, and C1) it is possible to see the impurities on the fibre surfaces and how the waxy and lignin layers cause the surfaces to be smooth. This may lead to reduced adhesion and reduced wettability between the fibres and the polymer.

Figures 8A2, 8B2, and 8C2 show how the NaOH treatment changed the surface of the fibre to make it rougher by removing all alkali-soluble fractions such as wax and lignin, besides removing high amounts of minor constituents. Although the treatment with silane coated the surfaces of these fibres, the treatment had no effect on removing impurities, lignin, or wax, and tended to leave the fibre surfaces smooth, as can be seen in Figs. 8A3, 8B3, and 8C3. However, silane did increase adhesion between the fibres and polymer due to the increase in functional groups on the fibres that could react with the polymer and thus change the hydrophilic nature of the fibres.

Figures 8A4, 8B4, and 8C4, which represent the combined treatment, show that there was a slight improvement in terms of surface roughness and surface morphology compared with untreated fibres, due to the effect of the NaOH treatment by removing wax and lignin. The silane treatment would be changing the hydrophilic nature of the fibres.

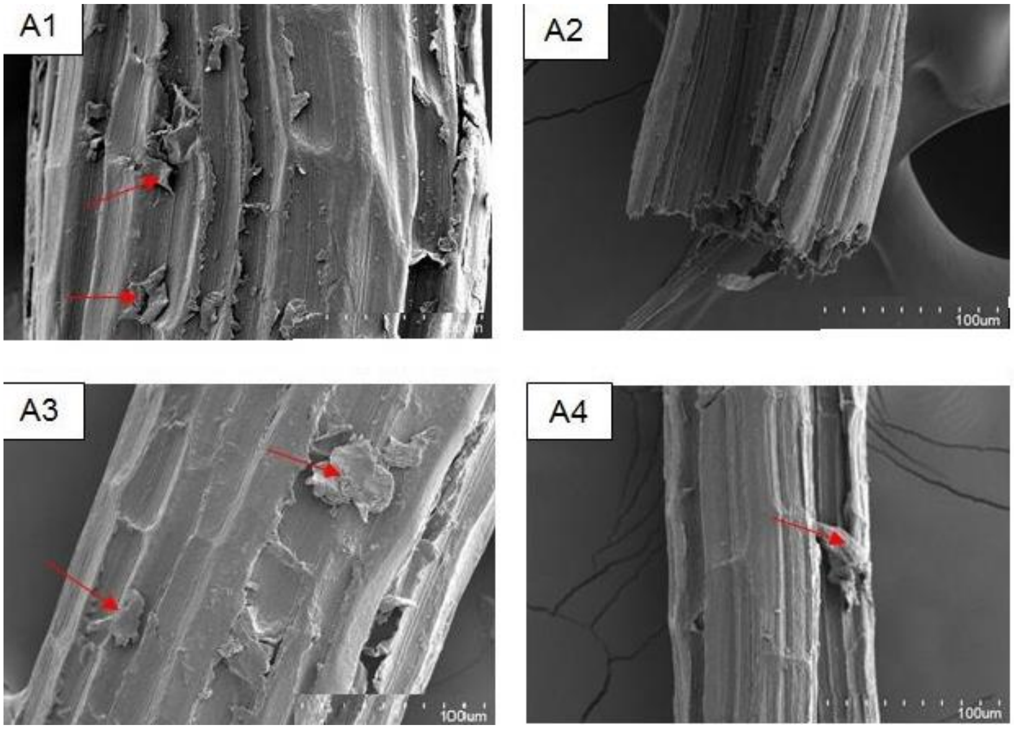

Fig. 8A. SEM images S3. (A1) Untreated sisal, (A2) sisal treated with NaOH, (A3) sisal treated with silane, and (A4) sisal treated with NaOH followed by silane. Arrows denote impurities on the samples

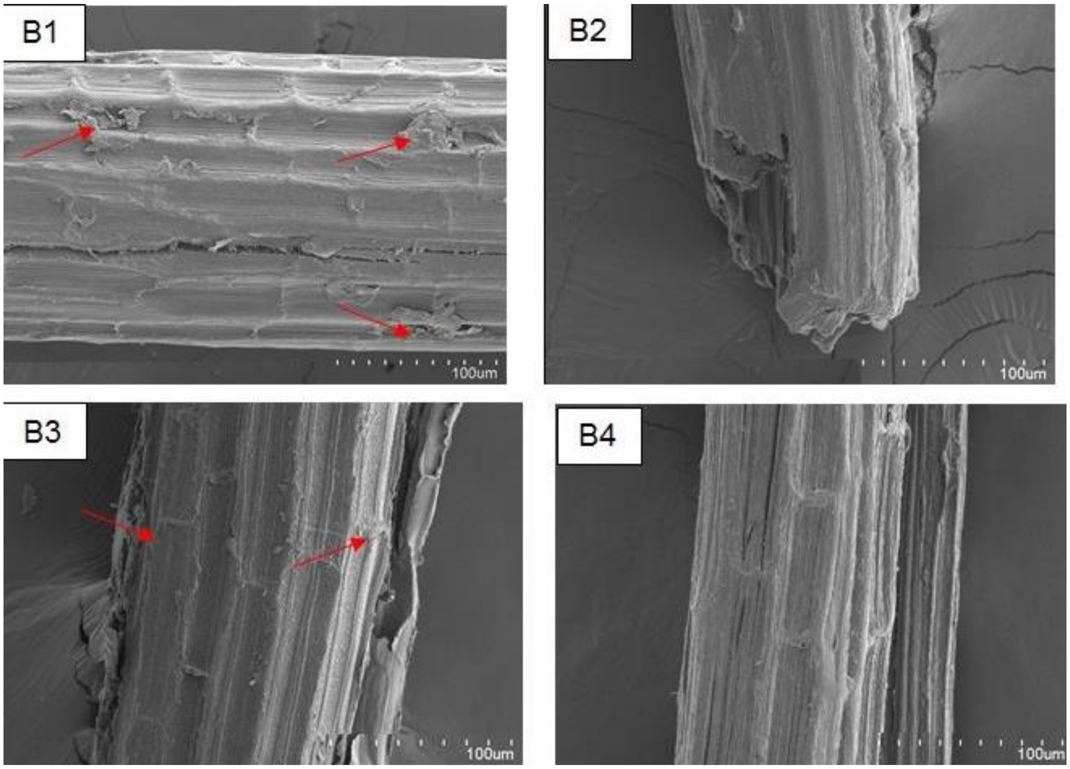

Fig. 8B. STOW (B1) Untreated sisal, (B2) sisal treated with NaOH, (B3) sisal treated with silane, and (B4) sisal treated with NaOH followed by silane. Arrows denote impurities on the samples

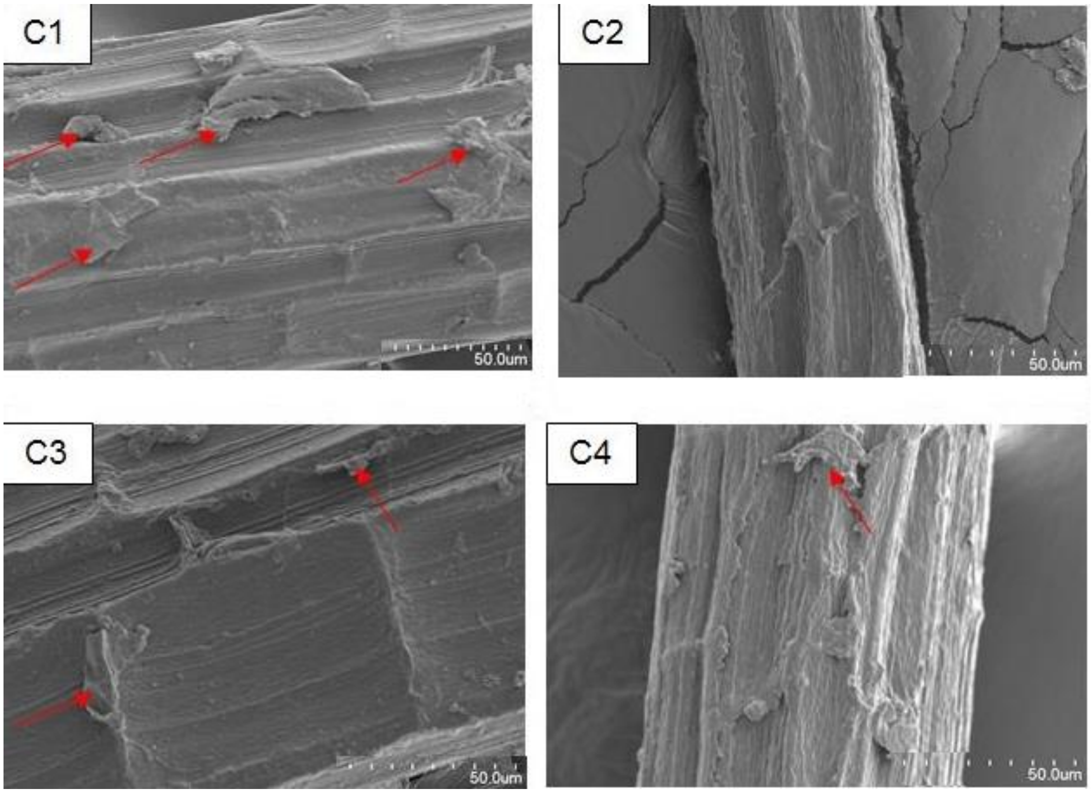

Fig. 8C. SUG (C1) Untreated sisal, (C2) sisal treated with NaOH, (C3) sisal treated with silane, and (C4) sisal treated with NaOH followed by silane. Arrows denote impurities on the samples.

CONCLUSIONS

1. Silane treatments reduced the tensile mechanical properties for all grades of sisal fibres because of their acidic effects. In contrast, NaOH treatment increased the ultimate tensile strength for all grades of sisal and show the highest values compared to the untreated and treated fibers with silane and with combined treatments.
2. The increase in the duration of the combined treatment was responsible for decreasing the tensile properties of sisal fibres, which demonstrated the acidic effect of the silane treatment on natural fibres.
3. All types of treatment increased the interfacial shear strength between the fibres and the polymer compared with untreated fibres. However, the silane treatments produced the best results. The reduction of the duration of combined treatments increased the interfacial shear stresses.
4. The FTIR analysis indicated effects of the alkali treatment on removing the lignocellulosic fibres and the presence of unhydrolysed Si–ethoxy–methoxy groups and their small intensity

ACKNOWLEDGMENTS

The authors wish to thank the Sri Jentayu Sdn Bhd company for supplying the sisal fibres used in this study. The authors also wish to thank the School of Graduate Studies, Universiti Putra Malaysia, for supporting this study.

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Article submitted: July 22, 2014; Peer review completed: November 6, 2015; Revised version received: August 25, 2016; Accepted: August 26, 2016; Published: September 7, 2016.
DOI: 10.15376/biores.11.4.8968-8980