EFFECTS OF CELLULOSE NANOCRYSTALS ON THE INTERFACIAL PROPERITES OF SISAL FIBERS/EPOXY COMPOSITES

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ABSTRACT

Cellulose nanocrystal (CNC), as a new promising nanomaterial, has attracted considerable attention in recent years. In this research, electrophoretic deposition (EPD) was employed to modify sisal fibers with CNCs. Sisal fibers were treated with alkali before CNCs were deposited. With single fiber pull-out tests, the effects of alkali and CNCs on the interfacial properties of sisal fiber/ epoxy composites over a range of temperatures were investigated. The results showed that, at room temperature (RT), the interfacial shear strength (IFSS) between alkali-treated sisal fibers and epoxy resin was increased by 35%, but CNCs modification did not show any effect on the IFSS values while changing the debonding process into a stable mode and increasing the debonding frictional force. In the case of elevated temperature, the IFSS of all groups of the composites showed an inverse dependence on the temperatures. Nonetheless, the CNCs modification significantly reduced the inverse effect of temperature on IFSS owing to the formation of an interphase with improved thermo-mechanical stability.

1 INTRODUCTION

Natural fiber reinforced polymer composites have recently attracted widespread interest because of their low cost, low density, high specific strength and modulus [1]. In addition, they are renewable and biodegradable compared to other man-made reinforcing fibers. Among all the natural fibers, sisal fiber is one of the most widely used natural fibers and highly adapted to different composite manufacturing processes [2]. Due to the satisfactory mechanical performance of natural fibers, their reinforced composites have already had extensive applications in civil and automotive industries [3]. However, the mechanical properties of fiber reinforced composites also depend on the interfacial adhesion between fiber and matrix as well as stress transfer efficiency of the interface. So the potential strength and toughness of natural fiber reinforced composites have not yet been exploited because of the poor interface between hydrophilic fiber and hydrophobic polymer matrices. Many surface modification methods for natural fibers have been investigated previously to improve their interfacial compatibility with the polymeric matrices [4]. Alkali treatment is one of the most commonly used chemical treatment methods for natural fibers [5]. It removes the surface impurities such as wax, pectin, and a certain amount of lignin and hemicelluloses, which cover the external surface of the fiber cell wall [6, 7]. Stiffer natural fibers [8] and improved interfacial adhesion between natural fiber and polymeric matrix [9] could be obtained.

Natural fibers are mostly extracted from the stems or leaves of the plant in the form of long fiber bundles called technical fibers which diameters ranged from 100 to 300 μm. Every technical fiber contains numerous elementary fibers (or cell fibers) which are about 10 to 30 μm in diameter [10]. The cell wall of the elementary fiber is a composite structure of lignocellulosic material reinforced by helical microfibrillar bands of cellulose. The microfibrils possess diameters in nano-scale ranged between 10 to 50 nm. Therefore, the hierarchical structure of sisal fibers provides the possibility for obtaining nano-scaled materials to modify the properties of natural fibers and their reinforced

composites. Cellulose nanocrystals (CNCs) are highly pure crystalline material, extracted from plant, tunicate and bacteria. CNC is an ideal reinforcing material, which possesses a greater axial elastic modulus (110-220 GPa) than that of Kevlar fiber and its tensile strength (1.5-7.7 GPa) is within the range of other reinforcement materials [11, 12]. Dasong Dai et al. [13]extracted CNCs from hemp fibers and used them to modify hemp fibers with the aid of the surfactant of dodecyl trimethyl ammonium bromide (DTAB). The results showed that, by the modification of DTAB and CNCs, the tensile strength and modulus of hemp fibers were increased by 72.8% and 36.1%, respectively. It was concluded the increase of the mechanical properties might be due to the "repair" of dislocation in the fibers. However, the interfacial properties between the modified fibers and the matrix were not measured or characterized directly, even though the addition of DTAB surfactant could alter the interfacial behaviour to some extent. Bismarck et al. [14, 15] used the bacterial cellulose to modify natural fibers. By using biological technology, a hierarchical structure was produced by cultivating cellulose-producing bacteria of natural fibers, which resulted in the IFSS between sisal fiber and poly-L-lactic acid increased by 21%. But both the tensile strength and modulus of sisal fibers evidently decreased after the modification by bacterial cellulose. Our preliminary research results indicated that both the morphologies and the mechanical properties of sisal fibers showed no obvious changes by directly soaking the fibers in CNCs suspension, although lots of surface hydroxyl groups on both fibers and CNCs could form hydrogen bonds promoting the adsorption of CNCs onto sisal fibers. Therefore, it can be concluded that the strengthening effect of CNCs on the mechanical and interfacial properties of natural fiber reinforced composites is often limited by the treatment methods and the interactions between CNCs and natural fibers.

In this research, a more effective method named electrophoretic deposition (EPD) was employed to modify sisal fibers with CNCs. EPD is a convenient, rapid and versatile coating technique that promotes the movement of charged particles in suspension to one of the electrodes under an appropriate electric field [16]. Due to the partial esterification reaction between the sulfate and hydroxyl groups during the acid hydrolysis production of CNCs, it leads to a stable suspension of negatively charged CNCs particles, which is highly applicable to EPD process. Therefore, in the present work, attempts are made to enhance the interfacial adhesion properties between sisal fibers and epoxy by deposition of CNCs onto sisal fiber surface with EPD method. Inspired by the modified microstructures of alkali-treated natural fibers, which may facilitate the coating of CNCs, alkali treatment was applied before CNCs deposition was performed in this research. The interfacial properties between sisal and epoxy at room temperature were investigated by single fiber pull-out test. Besides, considering the sensitivity of the interface on the temperature [17-20], the IFSS was further studied with a temperature-controlled single fiber pull-out test. The tesing was performed with the aid of DMA to characterize the effect of surface treatments on the temperature dependence of interfacial adhesion.

2 MATERIALS AND EXPERIMENT

2.1. Materials

Technical sisal fibers were supplied by GUANGXI SISAL GROUP CO., LTD, which was extracted from the leaves of the sisal plant by retting followed by mechanical means using decorticators. Commercial microcrystalline cellulose (MCC) powder (particle size, 20~80 μm), sodium hydroxide (NaOH, AR) and sulfuric acid (H_2SO_4, 98 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Epoxy resin (NPEL-128), curing agent (EH-6303) and accelerator (EH-6412) (100:26:8) were provided by Nanya Electronic Materials (Kunshan) Co., Ltd.

2.2. Preparation of CNCs

CNCs were prepared by sulphuric acid hydrolysis of MCC by following the procedures reported by Cranston and Gray [21]. 20 grams of MCC were added into 200 ml of H_2SO_4 (65 wt.%) aqueous solution. The hydrolysis process was performed at 50ºC by continuously stirring (600 r/min) for 2h. Then the suspension was washed with deionized water by repeated centrifuge cycles (10 min at 10,000 rpm) until the supernatant became turbid. The colloidal suspension was then dialysed in the deionized water for a week until constant neutral pH was achieved. Finally, the CNCs sample were sonicated in

an ice bath for 10 min until a stable suspension was obtained. The concentration of CNCs in the suspension was determined by measuring the weight of freeze-dried CNCs and then diluted to 5 mg/ml for EPD procedures. The yield of CNCs was then calculated, which was about 35.9%.

2.3 Modification of sisal fibers

The sisal fibers were first washed with deionized water at 70ºC for 1h to remove some impurities and dirt, followed by a drying process in a vacuum oven at 60ºC for 6 h. The dried sisal fibers were designated as untreated fibers and were then subjected to alkali followed by CNCs treatments.

a) Alkali treatment: The sisal fibers were treated in 5 wt.% NaOH aqueous solution for 2 h at 23ºC, then washed thoroughly with deionized water and finally vacuum dried to get alkali-treated fibers.

b) CNCs modification by EPD: Both the untreated and alkali-treated sisal fibers were modified by CNCs with EPD method. Fig. 1 schematically shows the deposition procedure of CNCs onto the surface of sisal fiber. Steel plates were placed on both sides as counter electrodes with a distance of 1 cm. Because CNCs were negatively charged in the suspension, the fibers were fixed to the anode plate. 400 ml CNCs suspension (5 mg/ml) was used and DC voltage of 20 V was applied to the suspension for 5 min. Thereafter the fibers were taken out and dried at room temperature. The final obtained fibers were named CNCs modified and alkali-CNCs modified fibers, respectively.

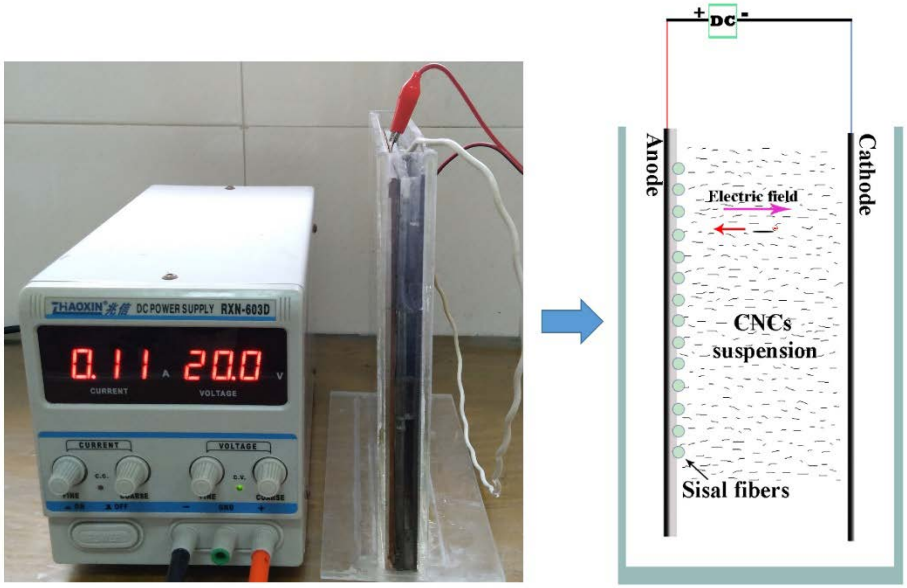

Figure 1: Photograph and schematic of electrophoretic deposition setup.

In order to determine the CNCs content of the modified fiber, mass changes of sisal fibers with different treatment were measured using a High-precision Electronic Balances (Precisa XP 205SM-DR, Switzerland; d=0.1 mg). To reduce the effect of moisture absorption of plant fibers on mass measurements, the sisal fibers were put in the climatic chamber for 12 h with constant temperature of 23ºC and humidity of 50% before weighing them.

2.4 Characterization of interfacial properties between sisal fiber and epoxy

2.4.1. Single fiber pull-out test at room temperature

The preparation of single fiber pull-out test was similar to the method as described in our previous work [22]. As illustrated in Fig. 2(a), single sisal fibers were placed into a silicon rubber mould, with the embedded fiber length ranging from 200 to 600 μm. Epoxy mixed with curing agent and accelerator was then poured into the mould and cured at room temperature for 24 h. The specimens were then post-cured at 60 ºC for 2 h after they were removed from the mould. As shown in Fig. 2(b), single fiber pull-out test was then conducted with the aid of a Universal Materials Testing Machine at

a crosshead speed of 0.5 mm/min and with a gauge length of 10 mm, at room temperature of 20 ºC. The IFSS for each individual test was calculated by Equation (1).

$$\tau = \frac{P}{\pi D_f L_e} \quad (1)$$

where, P is the maximum pull-out load, the fiber diameter D_f and embedded length L_e were measured with the aid of an optical microscope.About 20 specimens were tested for each group.

2.4.2. Single fiber pull-out test at elevated temperatures

In order to investigate the temperature dependence of IFSS between sisal fiber and epoxy resin with different surface treatments, an adaptive configuration of single fiber pull-out test was built-up for Dynamic Mechanical Analyzer (DMA Q800, TA Instruments) with a customized fixture. As illustrated in Fig.2(c), the free end of the fiber was fixed on the grip with a nominal gauge length of 10 mm, and loaded in a strain rate mode with a ramp displacement of 0.5 mm/min until complete debonding and fiber pulling-out were finished. Although the pull-out tests performed with the aid of DMA could be conducted with a controlled displacement speed, the DMA device substantially continues to attempt to apply the force ramp to the moving shaft quickly in order to reach the set displacement, which would lead to an immediate end of the test as the maximum force is reached. Therefore, there is no such information recorded concerning the post-debond frictional process as could be provided by the single fiber pull-out test conducted with a Universal Materials Testing Machine. According to the data provided by the manufacturer, the glass transition temperature (T_g) of the epoxy resin is about 80ºC. Therefore, the IFSS measurements inside DMA were carried out at temperatures of 20, 40, 60 and 80ºC in this research.

To fully understand and interpret the temperature dependence of the IFSS, it was also necessary to carry out a thermomechancial characterisation of the epoxy matrix and CNC-modified epoxy. The CNC-epoxy nanocomposites were prepared by dispersing 5 wt% freezing-dried CNC powder into epoxy resin under mechanical stirring at 1400 rpm for 30min. Curing of neat epoxy and CNC-epoxy was performed as described in Section 2.5.1. The dynamic thermomechancial properties of neat and CNC-modifed epoxy was obtained by using the DMA Q800. Three-point bending configuration was used with a heating rate 3ºC/min from 30ºC to 100ºC.

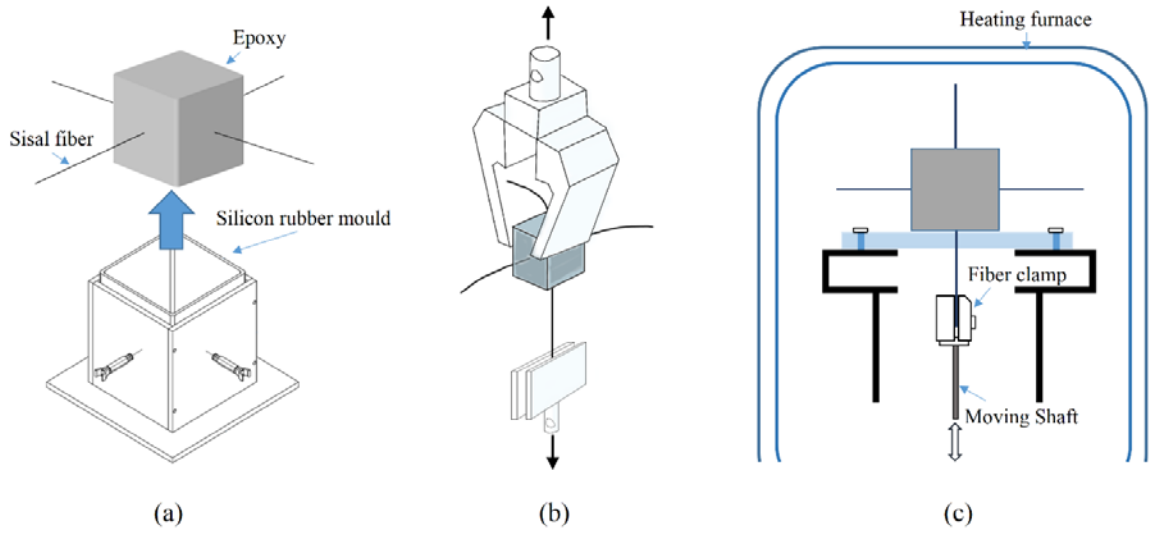

Figure 2: Schematic illustration of (a) sample preparation, (b) room- and (c) controlled-temperature testing setup for single fiber pull-out tests

2.5 Morphology characterization

The morphologies of CNCs were observed by using a field emission scanning electronic microscopy (FE-SEM, PHILIPS XL30 FEG) and a transmission electronic microscopy (TEM, Hitachi

H-600). Both optical microscope and SEM were employed to observe the surface morphologies of sisal fibers.

3 RESULTS AND DISCUSSION

3.1. Size distribution and morphologies of CNCs and sisal fibers

Fig.3 shows SEM and TEM images of the prepared CNCs which displayed a rod-like structure, similar to that observed in previous studies [21]. Meanwhile, it can be seen that the size distribution of CNCs was homogeneous. The dimensions of CNCs were measured by utilizing Image-Pro Plus 6.0 software, which exhibited dimensions ranging from 300 to 500 nm in length and 15 to 25 nm in width. It can be concluded that the original MCCs (particle size: 20~80 μm) have been successfully separated into nano-sized cellulose after sulphuric acid hydrolysis.

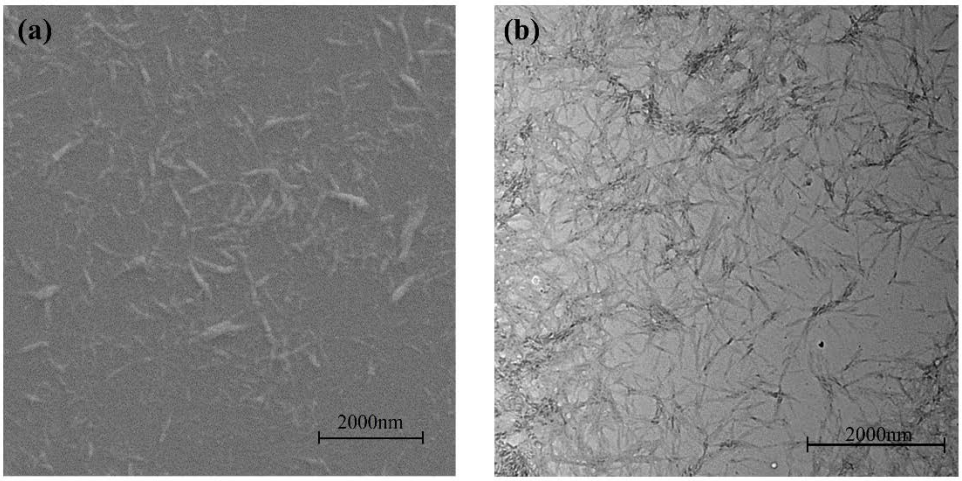

Figure 3: (a) SEM micrograph and (b) TEM micrograph of CNCs obtained by acid hydrolysis of MCCs.

Fig. 4 shows the fibrillar-like structures of the untreated and alkali-treated sisal fibers. From Fig. 4(a) and (b), it can be seen that the characteristic attachments of impurities, composed by parenchymatous cells and others constituents as waxes and pectin, were on the surface of the untreated sisal fibers. However, these impurities were partially dissolved and removed after being treated by alkali, which can be seen from Fig. 4(c) and (d). It was further demonstrated by the mass loss of 15% for alkali-treated sisal fibers (Table 1). The surfaces of alkali-treated sisal fibers were relatively clean and appeared to have a rougher texture by comparing the sisal fibers shown in Fig. 4(b) and (d), since cementing materials between fibrils could be etched away by alkali treatment[23].

Sisal fibers	Mass *I* (g)	Mass *II* (g)
Untreated	0.701	0.788
CNCs Modified	0.739 (+5.4%)	-
Alkali-treated	-	0.667 (-15.4%)
Alkiali-CNC Modified	-	0.705 (+5.7%)

Table 1: Mass change of sisal fibers modified by different treatments

Morphologies of alkali-CNCs modified fibers were compared to those of the untreated ones in Fig. 5. A coating of CNCs was clearly observed on the surfaces of the treated sisal fibers. The CNCs were uniformly dispersed and randomly oriented on the surface of fibers, which formed a dense nanocellulose layer wrapping up the surface of the sisal fibers. Compared to the untreated and alkali-treated sisal fibers, the surface roughness of fibers covered with nanocellulose layer was significantly

increased due to the randomly three-dimensional distribution of the nano-scaled CNC particles. From Table 1, it could be seen that the contents of CNCs deposited on sisal were 5.4% and 5.7% for CNC modified and alkali-CNC modified groups, respectively.

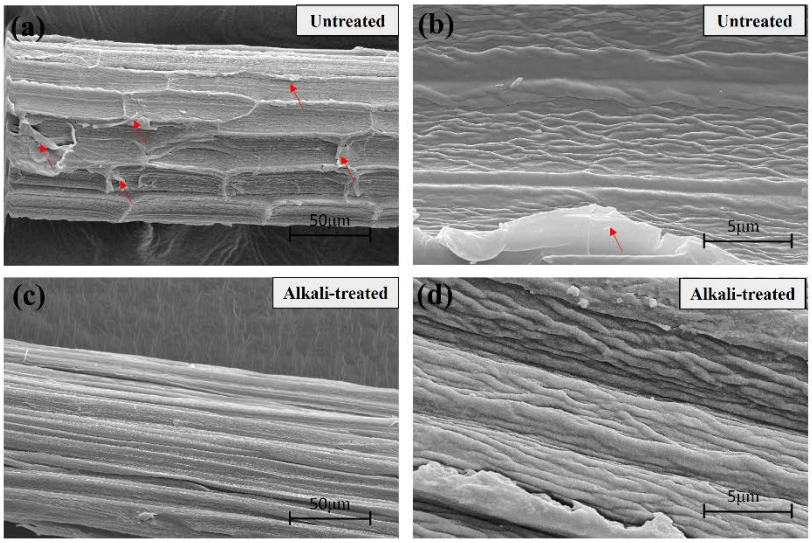

Figure 4: SEM micrographs of sisal fibers: (a) and (b) untreated, (c) and (d) alkali-treated at different magnification.

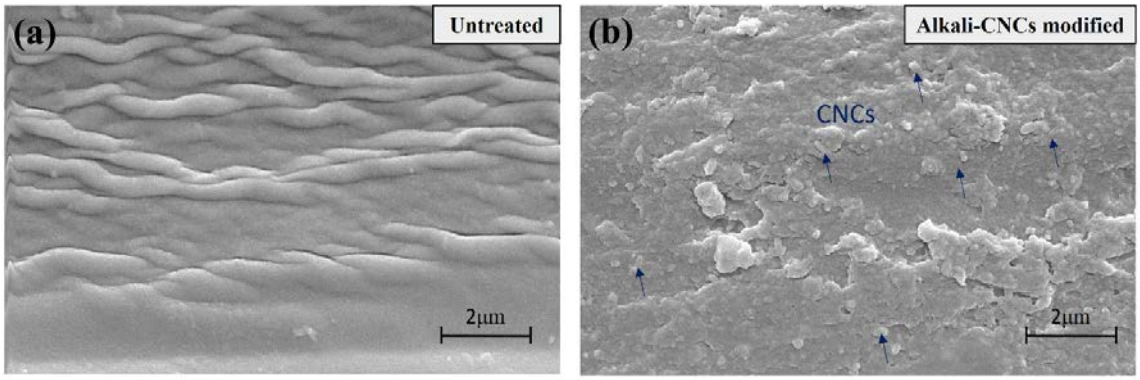

Figure 5: SEM micrographs of sisal fibers: (a) untreated, (b) alkali-CNCs modified.

3.2 Interfacial properties between sisal fiber and epoxy resin

The load-displacement curves obtained from single fiber pull-out tests for treated and untreated sisal fibers from epoxy resin at room temperature are given in Fig. 6. Two obviously different types of load-displacement curves were observed. For untreated and alkali-treated groups, the debond process were typically unstable. While with the addition of CNCs, the pull-out process turned into a relatively stable one, which attributed to a mainly mechanically bonded interface as described by Kim et al. [24]. It illustrated that CNCs modification rendered extremely rough surface for both untreated and alkali-treated sisal fibers (Fig. 5 (b)), which could form extra nano-scaled mechanical interlocking at the interface between fibers and matrix.

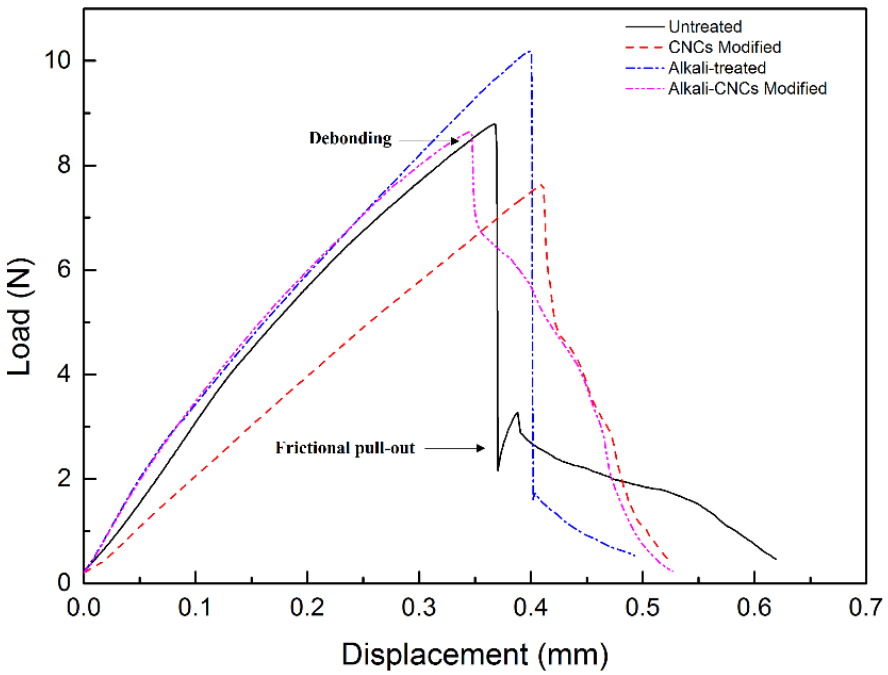

Figure 6: Load-displacement curves obtained from single fiber pull-out tests for sisal reinforced epoxy composites with different surface modifications.

From the load-displacement curves obtained from single fiber pull-out test, the IFSS of each group was calculated and shown in Fig. 7. It can be seen that the IFSS of alkali-treated group was considerably higher than that of the untreated one, increased by 35%. The mechanisms have already been revealed that the removal of surface impurities of parenchyma and some waxy substances from sisal fibers was advantageous to fiber-matrix adhesion, as it improves the wetting ability and mechanical bonding [9, 25]. However, the existence of CNCs on the surface of fibres did not show any effect on the IFSS between sisal fiber and epoxy resin, the IFSS between CNCs or alkali-CNCs treated sisal fibers and epoxy was almost the same with those of untreated or alkali treated ones.

According to theories of adhesion on fiber reinforced composites [26, 27], there are several types of bonding which include adsorption and wetting, electrostatic attraction, chemical bonding, and mechanical interlocking. From the above discussion, the interfacial adhesion between untreated or treated sisal fiber and epoxy resin in this study can be mainly attributed to two kinds of mechanisms involving adsorption and wetting, and mechanical interlocking. The mechanism of adsorption and wetting is primarily influenced by the compatibility of fiber and matrix, and mechanical interlocking is significantly dependent on the degree of surface roughness of the fibers. It is well-known that highly hydrophilic CNCs are poorly compatible with the hydrophobic epoxy, which obviously weakened the interfacial adsorption and wetting mechanism. In addition, the relatively weak non-covalent interactions between CNCs and sisal fibers could further influence the interfacial adhesion [28]. However, the rough and hierarchical structures of sisal fibers modified with CNCs greatly promoted mechanical interlocking with epoxy resin. Therefore, the two interfacial influencing mechanisms balanced each other and resulted in unchanged IFSS between groups with and without CNCs modification. However, such rough and hierarchical structures could remarkably improve the post-debond frictional pull-out force, which led to no significant load drop after complete debonding, as shown in the load-displacement curves obtained from single fiber pull-out tests (Fig. 6). It demonstrated that the surface of sisal fibers modified with CNCs was much rougher than that of untreated or alkali-treated fibers, which was primarily beneficial from the ultra-high specific surface area of CNCs coated sisal fibers. Bismarck et al. [15] reported that the surface area of bacterial cellulose coated fibers increased by as much as 8 times compared to that of neat sisal fibers. It would enhance the mechanical interlocking interaction between fibers and matrix, which was further verified

by the SEM micrographs of pulled-out fibers surfaces as shown in Fig. 8. It is observed that lots of resin residues were adhered to the surface of fibers modified with CNCs, whereas, untreated and alkali-treated groups are relatively smooth and clean. Sreekumar P reported that the high frictional force could result in a significant increase in the energy absorption capacity of the composites so as to improve the corresponding impact properties [29].

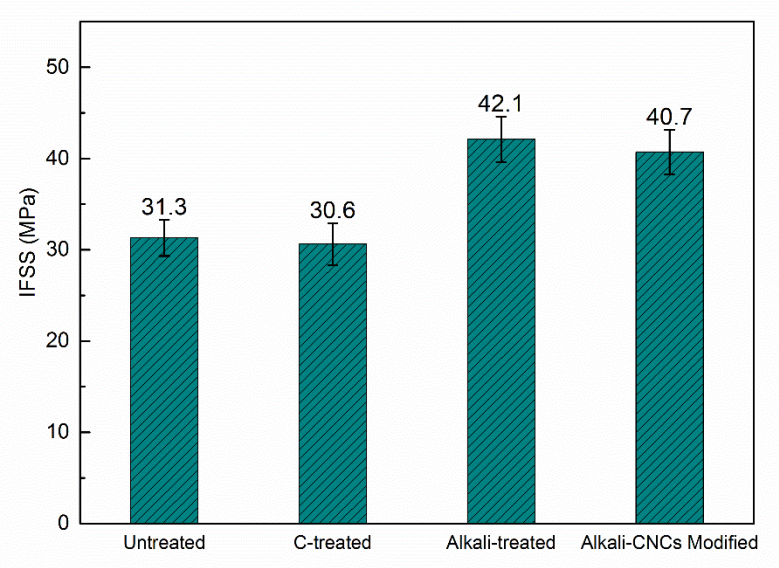

Figure 7: Interfacial shear strength between sisal fiber and epoxy resin by different fiber surface modifications.

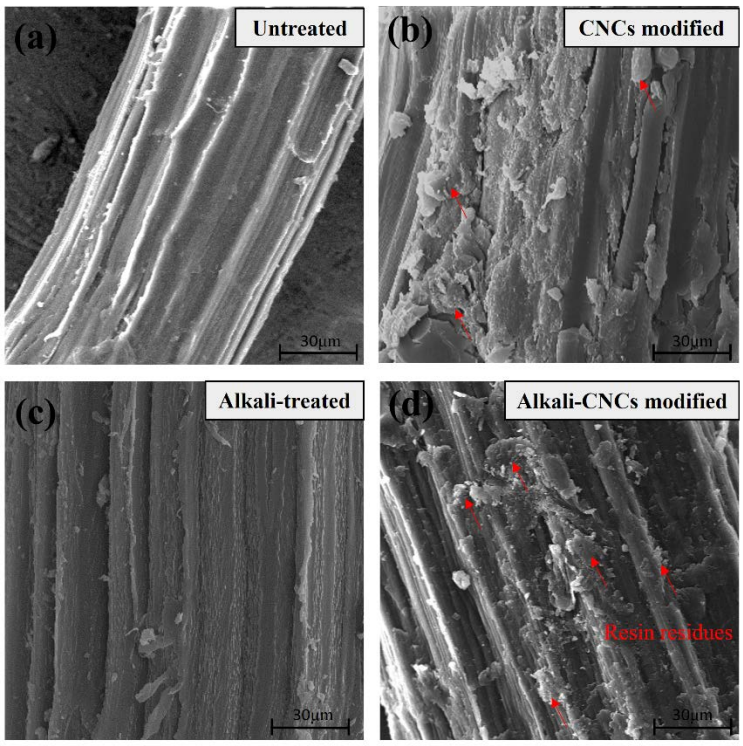

Figure 8: Surface morphologies of the pulled-out sisal fibers with various treatment: (a) untreated, (b) CNC modified, (c) alkali-treated and (d) alkali-CNCs modified.

3.3. Effect of fiber surface treatments on the temperature dependence of the IFSS

IFSS between sisal fiber and epoxy resin obtained at different temperatures were summarized in Fig. 9. Compared to the IFSS obtained by the Universal Materials Testing Machine as shown in Fig. 7, DMA measurements gave very consistent results, which confirmed the feasibility and validity of the IFSS obtained by DMA. It can be observed that there existed a significant temperature dependence of IFSS between all the sisal fibers and epoxy resin by showing a gradually decreased value with the increase of the temperature. The IFSS of untreated groups dropped from 31 MPa at 20ºC to just 7 MPa at 80ºC. For alkali-treated group, the decrease of the IFSS at the studied temperature range was similar to that of the untreated groups. Similar results have been reported from fragmentation tests on carbon- [18, 20] and glass- [19] epoxy interfaces. However, with regard to the groups modified with CNCs, it can be observed that the decrease of IFSS versus temperature was much lower than that of the untreated and alkali-treated groups. It showed that the IFSS of alkali-CNCs modified group still remained 20 MPa at 80ºC, while dropped to 12 MPa for alkali-treated group. The IFSS between CNCs modified or alkali-CNCs modified sisal fibers and epoxy resin decreased 58% and 47%, respectively with the temperature increasing from 20 ºC to 80 ºC, while IFSS decreased 77% and 70%, respectively for their counterparts without CNCs treatment. It illustrated that CNCs modification on the interface effectively reduced the impact of temperature on the IFSS.

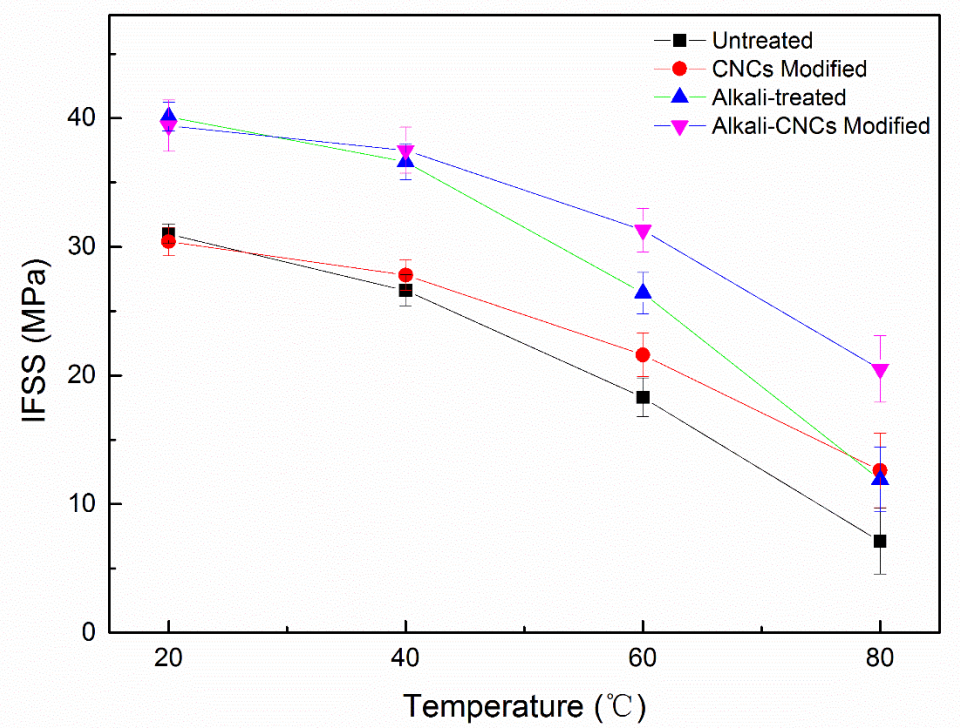

Figure 9: Comparison of the IFSS between sisal fiber and epoxy resin versus temperature

The decrease of IFSS with increasing temperature can be explained by the reduction in mechanical properties of the matrix, which exhibited a well correlation with temperature dependence of modulus [19, 30], shear strength [20], and tensile strength [18] of the matrix. The thermal-mechanical properties of the bulk matrix was exhibited in Fig. 10 (a) which showed the typical DMA results for the storage modulus (E') of epoxy across temperature range. In Fig. 10 (b), the correlation between the decrease of IFSS and matrix storage modulus was further examined, where the normalised IFSS data was plotted directly against the corresponding normalised matrix modulus. It can be found that the decrease trend in IFSS was significantly consistent with the decrease in matrix storage modulus. The decrease in mechanical properties can be essentially explained by the increased molecular mobility in the resin especially as temperature approaches the T_g. In regard to the decrease in IFSS, the higher mobility of the polymer chains will facilitate the deformation of the matrix at the interface subjected to

shear stress, consequently leading similar decreasing trends between IFSS and matrix storage modulus.

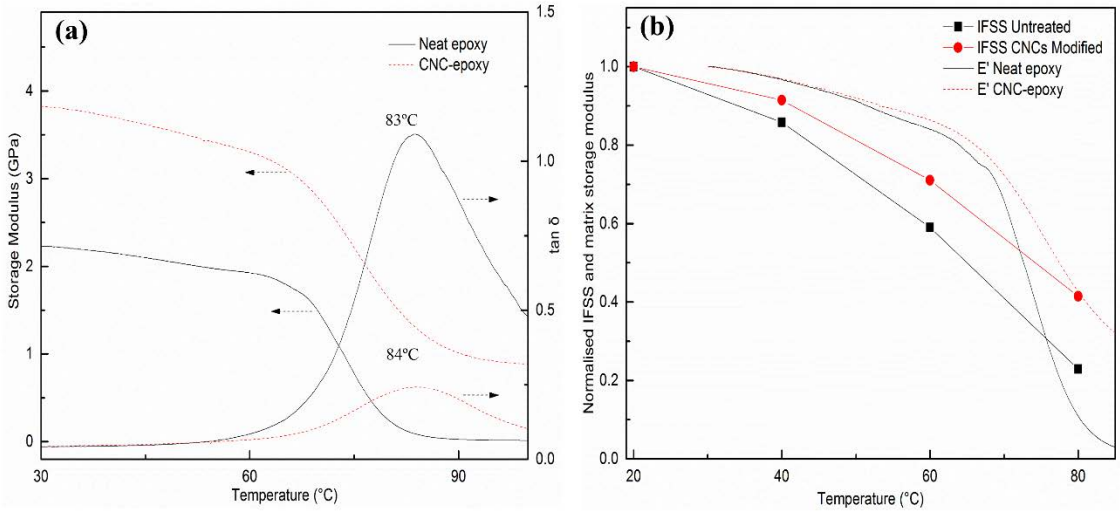

Figure 10: (a) DMA curves of neat and CNC-modified epoxy, (b) Comparison of the normalised IFSS and normalised matrix storage modulus

Moreover, in Fig. 10 (a) and (b), we can recognize that the decreasing trends of storage modulus for neat and CNC-epoxy matrix were obviously different, which correlated so well with the distinguishing variation trends of IFSS for untreated and CNC-modified interface. Comparing to neat epoxy, the storage modulus of CNC-epoxy showed obviously lower temperature dependence. It can be attributed to high thermal-mechanical properties of CNCs and the restriction of polymer chain movement due to the effective interactions between the nanoparticles and matrix [31, 32]. As discussed before, the surface of sisal fibers covered with CNC layer exhibited a rough and hierarchical structure (Fig. 5), which promoted the mutual penetration between CNCs and the matrix, and finally generated a particular interphase closely resembling the CNC-epoxy nanocomposite. The CNCs of the nanocomposite constrained matrix deformation in their longitudinal direction [33]. Therefore, it was believed that there existed an interphase of higher modulus than the bulk matrix in the case of CNC-modified sisal fiber systems. As a consequence, the inverse effect of temperature on IFSS was significantly reduced by CNC modification.

In this study, at the temperature around T_g, the IFSS values of CNC modified groups still retained ~50% of that at RT, which is less than 30% for groups without CNC modification. And the high retention of IFSS is beneficial to promoting the overall performance of composites at elevated temperature. It is well accepted that the composite mechanical properties, such as in-plane and interlaminar shear strengths, transverse tensile and flexural properties, impact strength and Mode I/II fracture toughness, strongly depend on the adhesion of interface [34-36]. So the temperature dependence of these macro properties of composites was directly correlated with the deteriorated interfacial properties. Kim et al. reported that, as the IFSS decreased 35.5% with the temperature rising to 130ºC, the transverse tensile and flexural strength of CF-PEI laminates decreased 37.1% and 36.4%, respectively. And the weakened interface at elevated temperatures made delamination more likely to initiate at the fiber/matrix interface, leading to decreased values of initial G_{IC} and G_{IIC} [36]. So it can be inferred that, with the CNCs modification at the interface, sisal/epoxy composites may have a relatively larger working temperature range due to the higher thermo-mechanical stability of the CNC-modified interface.

4 CONCLUSIONS

EPD method was successfully employed to deposit CNCs onto sisal fibers.With alkali treatment, the IFSS between sisal fiber and epoxy resin was improved by 35%. Hydrophilic CNCs weaken the interface compatibility between fibers and epoxy, which slightly decreased their IFSS, however, remarkably improved the post-debond frictional pull-out force due to the large surface roughness of fibers. The IFSS between sisal fibers and epoxy resin decreased with the increase of the temperature, no matter the fibers were treated or not. However, the existence of CNCs greatly improved the thermo-mechanical stability of the interface between sisal fiber and epoxy resin due to the improved mechanical properties of the epoxy resin at the interfacial region.

ACKNOWLEDGEMENTS

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