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EFFECTS OF SILANE-FUNCTIONALIZED GRAPHENE OXIDE SURFACE TREATMENT ON THE MECHANICAL AND INTERFACIAL BEHAVIOR OF FLAX-EPOXY COMPOSITES

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ABSTRACT

This research investigates the impact of silane-functionalized graphene oxide (sGO) on the properties of flax single fibers and flax-epoxy composites. The functionalization of GO was achieved through chemical grafting of (3-aminopropyl triethoxysilane (APTES) onto GO sheets, resulting in APTES-functionalized GO. Characterization of sGO involved transmission electron microscopy, Fourier transform infrared spectroscopy and X-ray diffraction. Subsequently, flax fibers were dip-coated sGO at concentrations from 0.2% to 1% for durations from 30 minutes to 2 hours. Tensile performance and interfacial shear strength of flax single fibers were assessed through tensile tests and microbond tests, revealing that sGO treatment significantly improved the exfoliation and dispersion of graphene sheets. The tensile strength and modulus of sGO-treated fibers surpassed those of untreated fibers. Flax-epoxy composites treated with sGO were then prepared at the optimum level identified through single fiber tests. The Digital Image Correlation (DIC) technique provided insights into in situ strain monitoring during tensile testing, while fracture analysis by SEM elucidated the causes and nature of failure. The results demonstrated a significant enhancement in tensile strength, tensile modulus, and interfacial shear strength for fibers dip-coated for 30 minutes in a 1.0 wt% sGO solution, with increases of 32.2%, 35.5%, and 27.4%, respectively, compared to untreated flax fibers. This optimal sGO dip-coating method was then applied to flax fiber sheets for composite fabrication. The tensile strength and modulus of the resulting composites showed improvements of 10.4% and 3.7%, respectively, compared to untreated flax-epoxy composites. The study concluded that the improved dispersion and interfacial interaction in flax-epoxy composites are attributed to covalent bonds between sGO-treated flax fiber and the epoxy matrix. This research contributes valuable insights into optimizing the properties of natural fiber-reinforced composites through the functionalization of graphene oxide.

1 INTRODUCTION

Flax fiber is a natural biodegradable material that has the advantages of being cost-effective, sustainable, and has good mechanical properties such as high stiffness and tensile modulus [1], [2]. Due to its biologically sourced nature and outstanding mechanical properties, flax fiber has great potential to replace traditional fibers, such as glass fibers, in the composites industry [3]. However, its hydrophilic nature poses a challenge due to low compatibility with epoxy matrices in the composite-making process [4]. Therefore, it is essential to investigate and optimize the adhesion between the hydrophilic reinforcement and the hydrophobic matrix material through various surface treatment techniques for manufacturing composites [5], [6]. Silane functionalized graphene oxide (sGO), a derivative of graphene oxide (GO), was produced by the silylation of graphene oxide. In addition to hydroxyl,

epoxide, and carboxyl groups present on GO sheets, sGO sheets also contain silicon and amine groups. 3-aminopropyl triethoxysilane (APTES), acts as a coupling agent, is most extensively reported in the literature as saline for fiber surface treatment and has been extensively used in composites and adhesive formulations. Although a few recent studies have reported improvement of the mechanical and interfacial properties due to the grafting of APTES-GO onto fiber surfaces such as carbon [7], glass [8] and basalt fiber [9], there is a lack of research on sGO treated flax fiber composites. This research aims at overcoming the shortcoming of poor interphase adhesion between flax fiber and epoxy matrix by exploring the use of silane-functionalized graphene oxides on surface modification.

2 MATERIALS AND METHODS

2.1 Synthesis of sGO

In this study, 1 wt% GO obtained from Zentek Ltd. was silanized by APTES purchased from Sigma-Aldrich. 20g GO was dispersed in 380g DI water in a flask in a sonic bath for 60 minutes. 2.3mL of APTES was dissolved in 50 mL ethanol, which was then added to the dispersed GO after stirring for 3 minutes. The solution was heated to 70 °C and stirred at 300 rpm for 48 h. A reflux condenser was used to prevent reactant escape through steam. Vacuum filtration was used to wash the produced sGO sheets three times each with DI water, followed by ethanol. To measure the solid content of the resulting sGO in the paste form, a small amount of the paste was then dried in an oven. A bath sonicator was used to disperse sGO paste into various concentrations using DI water for 1 hour before treatment.

2.2 Characterization of GO and sGO

Transmission Electron Microscopy (FEI Tecnai Spirit 120kV TEM) was utilized to capture images and observe the exfoliated structures of GO and sGO. For Fourier Transform Infrared (FTIR) Spectroscopy (Bruker, INVENIO), the synthesized materials were pressed into pellets with potassium bromide and scanned to analyze the chemical bonds present in GO and sGO, as well as to determine the chemical reactions between GO and amino silane functional groups. X-ray diffraction (0-20, LynxEye detector) was used to analyze the crystalline nature of GO and sGO. GO and sGO paste were centrifuged to prevent water evaporation from the paste.

2.3 Preparation of single fiber tensile test

Five flax yarn replicates were randomly cut from a unidirectional flax fiber sheet and dip-coated with sGO at concentrations of 0.2%, 0.5% and 1% for durations of 30 minutes, 1 hour and 2 hours. According to ASTM D3822, four single flax fibers replicates were separated from five flax yarns in each treatment group using fine tweezers. A sufficient number of black construction paper frames, each measuring 25 mm by 25 mm, were prepared using a laser cutter. A 14 mm by 14 mm square was die-cut in the center to serve as the gauge length. Instron 5969 universal testing machine equipped with a 10 N load cell was used for single fiber tensile testing. Each single fiber was carefully mounted on one paper frame using tweezers and glued in place. The constant displacement rate was 0.5 mm/min. The ultimate tensile strength and modulus of elasticity were then reported. The tensile modulus of elasticity was calculated based on the middle linear phase of the stress-strain curve, as recommended by the standard.

2.4 Preparation of single fiber-epoxy microbond test

The same construction paper frames used in the single fiber tensile test were also used as sample holders for the microbond test. However, the gauge length was die-cut to 10 mm. A single glass fiber was used to apply epoxy droplets onto the mounted flax fiber, with one successfully applied droplet illustrated in Figure 1(c). After being left at room temperature overnight, the samples were transferred to an oven at 80°C for 7 hours for post-curing. A

micrometer was used to clamp the epoxy droplets while the Instron universal testing machine applied an upward vertical force to the paper frames, as depicted in Figures 1(a-b). The debonding stress-strain curve exhibited a sudden drop followed by a continuous increase, which is distinct from the curve observed when the fiber breaks. Only debonding data were selected for calculating the interfacial shear strength. The measurements of droplet size, including both length and diameter, along with fiber diameter, were taken to determine the embedded area of the fiber.

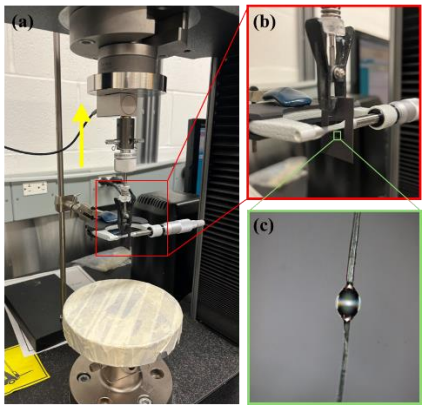

Figure 1. (a) Experimental setup for microbond testing; (b) closeup of a mounted microbond test specimen; (c). an epoxy resin droplet on a flax single fiber.

2.5 Manufacturing process of flax-epoxy composites

The 2x2 flax woven sheets were cut to dimensions 25 cm by 30 cm and dried at 105°C for 2 hours before composite processing. Epikote MGS RIMR 035C EPOXY and its corresponding curing agent Epikote RIMH 037 were bought from Westlake Ltd. Flax-epoxy composite plates were manufactured using the vacuum bagging process. Four layers of flax sheets, treated with the optimal methods identified in the single fiber tests, were positioned on a flat glass mold and sealed within a vacuum bag. A vacuum pump was then used to apply pressure to the laminates, evacuating any remaining air and inducing epoxy resin to flow into the system. This process used vacuum pressure to compress all the layers, producing a finely laminated piece. The system was left at room temperature for 24 hours, followed by post-curing at 80°C for 7 hours.

2.6 Composite tensile test

An Instron universal testing machine was used for the tensile performance characterization while the digital image correlation (DIC) technique monitored in-situ strain during tensile testing. Tensile strength, modulus, and strain at failure were measured according to the ASTM D3039 standard, using a speed of testing of 2 mm/min. Samples gauge length was 150 mm long by 25 mm wide; the thickness of each sample was the origin thickness given by the composite processing conditions. Three sample replicates were used for each test.

3 Results and Discussion

2.2 Characterization of GO and sGO

The surface morphology of GO and sGO was observed with TEM, as shown in Figure 1a. Both GO and sGO appear as dark, thin sheets with exfoliated and wrinkled surface morphologies. Similarly, Yan et al. [10] reported that the transparency of sGO sheets decreases after modification with APTES. The rough and wrinkled surface morphology

of sGO sheets enhances their compatible interaction. Figure 1b shows the FTIR spectra of GO and sGO. In the FTIR spectrum of GO, peaks at 3422, 2963, 2924, and 1624 cm^{-1} correspond to OH stretching vibrations, CH_2 stretching vibrations, CH stretching vibrations, and C=O stretching vibrations respectively. In the FTIR spectrum of sGO, new peaks at 1198 cm^{-1} and 1036 cm^{-1}, resulting from Si-O-Si and Si-O-C stretching, indicate the presence of APTES on sGO. Furthermore, a new peak at 1354 cm^{-1} (N-H stretching vibration) indicates the formation of NH-C bonds resulting from the reaction between the epoxide group of GO and the amine group of APTES [11]. Figure 2c shows the XRD patterns of GO and sGO. GO exhibits a diffraction peak at 2θ = 14.07°, corresponding to an interlayer spacing of 0.63 nm. After the chemical conversion of GO with APTMS, the XRD pattern of sGO only shows a small peak at 2θ = 32.43°, indicating a reduced interlayer spacing of 0.28 nm. This suggests the removal of oxygen-containing groups and the intercalation of functional groups into the graphene layers [12]. These results confirm that the surface of GO was successfully functionalized with silane. Zhi et al. [11] also observed a similar sGO flat XRD pattern and they concluded that the functionalization of exfoliated GO with APTES results in sGO exhibiting no diffraction peak, suggesting a 3D disordered structure due to the strong association of APTES's amine group with GO sheets and the hydrolysis and condensation of APTES's ethoxy groups, forming Si-O-Si bridges.

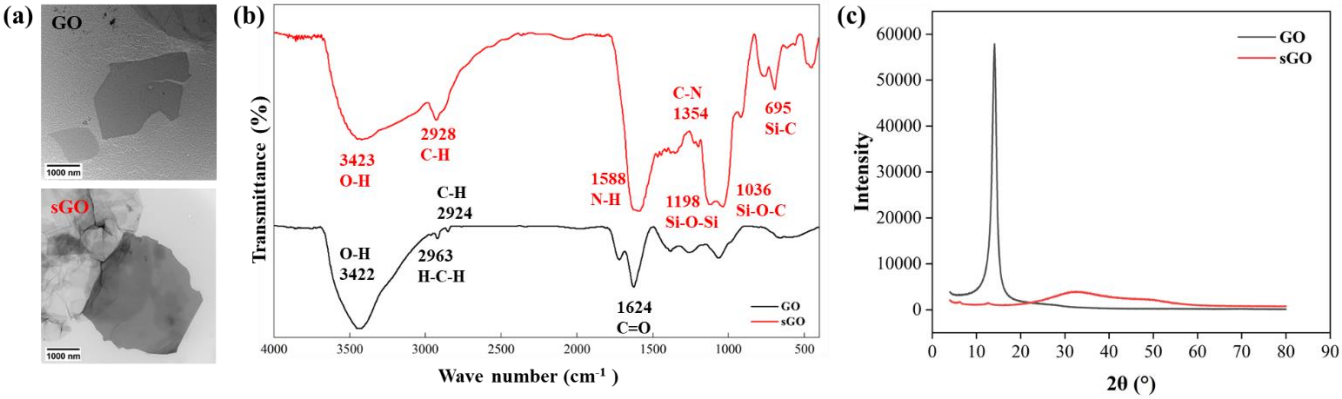

Figure 2. (a) TEM images at x9300 magnification of GO sGO sheets; (b) FTIR spectra and (c) XRD patterns of GO and sGO.

3.1 Single Flax fiber mechanical properties

Figure 3a–b illustrates the impact of sGO treatment on the tensile properties of single flax fibers. The tensile strength and modulus of untreated flax fibers were measured at an average 30.29 GPa and 738.23 MPa, respectively. The modulus is lower than in previous studies, which reported an untreated flax Young's modulus of 50.7 GPa. [13]. This discrepancy is attributed to the removal of impurities (e.g., wax and extractives) from the unidirectional fibers purchased from ampliTex BcompTM, which reduces tensile modulus. The tensile strength and modulus exhibited the highest increases of 32.21% and 35.54%, respectively, for a 1% sGO treatment for 30 minutes. This was followed by a 0.2% sGO treatment for 2 hours, which resulted in increases of 20.47% and 9.73%, respectively. However, for other conditions such as a 0.5% sGO treatment for 2 hours, the tensile modulus decreased significantly, possibly due to sGO solid agglomeration forming a rigid and sharp coating layer that could damage the fiber upon drying.

Interfacial shear strength (IFSS) is crucial for evaluating the performance of fiber-reinforced composites. Strong interfacial bonding ensures efficient load transfer from the matrix to the reinforcement, thereby reducing stress concentration and enhancing overall mechanical properties. The microbond test measured the IFSS at the flax/epoxy interface. Figure 3c shows the lowest IFSS value of 21.32 MPa at the untreated flax/epoxy interface, indicating poor compatibility between the flax fibers and epoxy matrix. Significant improvements in IFSS were observed after dip-coating the fibers with sGO. Fibers coated with 1 % sGO for 30 minutes exhibited an IFSS of 27.16

MPa, a 27.44% increase compared to untreated fibers. Fibers coated with 0.2% sGO for 2 hours demonstrated an IFSS of 27.97 MPa, representing a 31.24% improvement. These findings highlight the effectiveness of sGO dip-coating in enhancing single fiber tensile performance and improving the interfacial bonding of flax/epoxy composites.

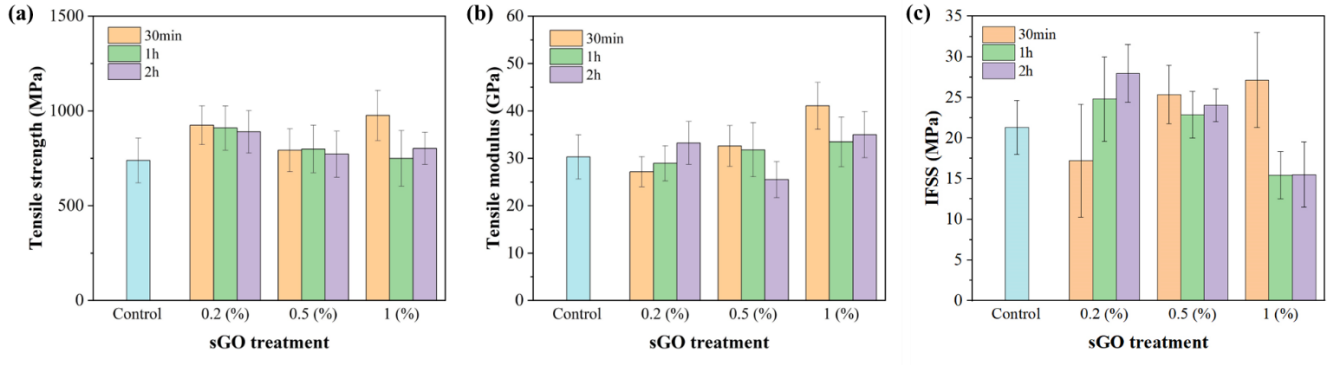

Figure 3. (a) The average tensile strength, (b) tensile modulus, and (c) interfacial shear strength of single flax fibers. Error bars indicate the 95% confidence intervals. The number of data points: 20 replicates for each column.

3.2 Flax-epoxy Composite mechanical properties

Results from single fiber mechanical tests indicate that 0.2% sGO 2 hours and 1% sGO 30 minutes were the two optimum treatment methods for flax single fiber. To determine which treatment is the superior treatment between the two, the influence of sGO on the mechanical properties of flax-epoxy composites was evaluated. Figure 4(a) shows the tensile stress-strain curves of the composites coupons with control sample, 0.2% sGO 2 hours and 1% sGO 1h, respectively. As shown in Figure 4(a), the value of the sGO composite is higher than that of the control. This suggests that the tensile modulus of the composite is enhanced by sGO surface treatment. Among these composites, the 1% sGO-treated composite exhibited the highest values of tensile modulus and tensile strength, with a 10.4% increase in tensile strength, a 3.7% increase in tensile modulus and a 21.26% increase in strain to failure compared to the control sample.

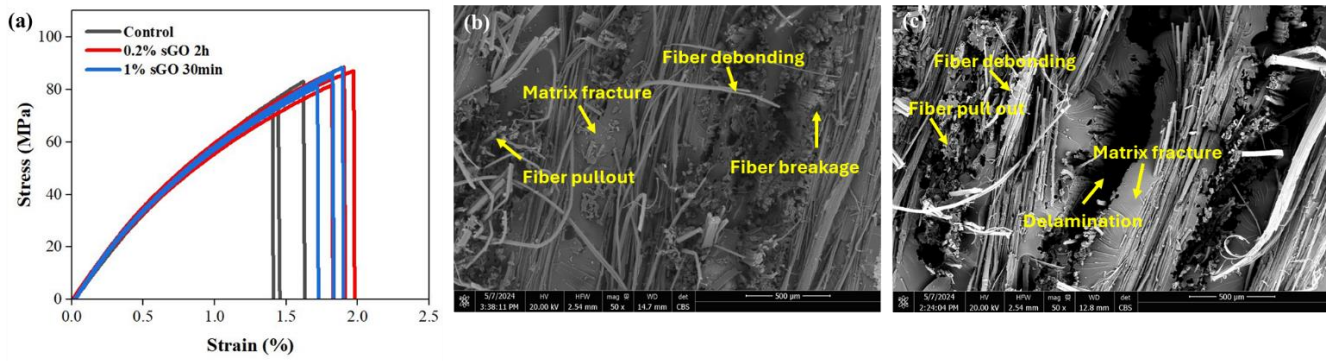

Figure 4. (a) Stress-strain curves for flax-epoxy composites tensile test coupons; (b) SEM images of flax-epoxy composites showing the representative fracture surface for the control group and (c) sGO treated groups at 500 µm magnification (50 X).

To better understand the interface behavior and enhancement mechanism of sGO-treated composites, the fracture surfaces were examined using SEM. Figure 4(b) shows the fracture micro mechanism of the control group. Both

control and sGO-treated composites exhibited matrix fracture, fiber breakage, fiber pull-out, and fiber debonding. The use of twill weave fiber sheets in composite manufacturing resulted in significant fiber debonding, as illustrated in Figure 4(b), where fibers easily detached from the fiber bundles. Following sGO treatment, the granulated sGO solids formed a brittle coating layer on the flax sheets, effectively reducing fiber debonding. However, this treatment also increased the brittleness of the fiber sheets, leading to delamination observed in the fractograph. While this brittle coating contributed to improved tensile strength and strain to failure of the composites, the increased brittleness did not significantly enhance the tensile modulus.

4 Conclusions

In conclusion, sGO was created by treating GO with APTES, which contains multiple amine, epoxy, and alkyl functional groups. The FT-IR spectra confirmed the silanization of the GO surface through the loss of carboxyl and epoxide groups and the appearance of Si-O-C, Si-O-Si, and NH-C bonds. Furthermore, the shifting diffraction angles in the XRD peaks demonstrated successful interactions between the silane molecules and the GO's functional groups. Tensile strength and tensile modulus for fibers dip-coated for 30 minutes in a 1.0 wt% sGO solution were increased by 32.2%, and 35.5 % compared to untreated flax fibers. After the dip-coating of sGO to flax single fiber and flax sheets/epoxy composite, the interfacial shear strength was increased by 27.4 %. This suggests that the presence of amine, epoxy, or alkyl groups played a crucial role in enhancing the interfacial interactions between the flax fibers and the epoxy adhesive. Furthermore, the 10.4% and 3.7% increase in tensile strength and tensile modulus of the sGO-treated flax-epoxy composites showed that the addition of sGO to the bonding areas of the epoxy-based composites effectively increased the bonding strength. Therefore, sGO surface treatment is considered a promising method for fabricating flax-epoxy composites. Future studies should explore sGO-mixed epoxy resin to prevent excessive brittleness in flax fiber sheets and compare its effectiveness with sGO surface treatment.

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