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Enhancement of the Mechanical Properties of Glass/polyester Composites *via* Matrix Modification Glass/polyester Composite Siloxane Matrix Modification

S. Erden*, K. Sever[1], Y. Seki[2], and M. Sarikanat

Department of Mechanical Engineering, Ege University, Izmir 35100, Turkey
[1]Department of Mechanical Engineering, Dokuz Eylul University, Izmir 35100, Turkey
[2]Department of Chemistry, Dokuz Eylul University, Izmir 35160, Turkey
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Abstract: Enhancement of the mechanical and vibrational properties of glass/polyester composites was aimed via matrix modification technique. To achieve this, unsaturated polyester was modified by incorporation of oligomeric siloxane in the concentration range of 1-3 wt%. Modified matrix composites reinforced with woven roving glass fabric were compared with untreated glass/polyester in terms of mechanical and interlaminar properties by conducting tensile, flexure, and short-beam shear tests. It was found that after incorporation of 3 % oligomeric siloxane into the polyester matrix, the tensile, flexural, and interlaminar shear strength (ILSS) values of the resulting composite increased by 16, 15, and 75 %, respectively. The increases in ILSS as well as in tensile and flexural properties were considered to be an indication of better fiber/matrix interaction as confirmed by SEM fractography images. Furthermore, the effect of oligomeric siloxane incorporation on the vibrational properties of the composites was investigated by experimental modal testing and the natural frequencies of the composites were found to increase with increasing siloxane concentration.

Keywords: Composites, Matrix modification, Polyester, Glass fabrics, Mechanical, Vibrational

Introduction

The mechanical performance of a fiber-reinforced composite depends basically on the fiber strength and modulus, the matrix strength and chemical stability, and the effectiveness of interface bonding between the matrix and the fiber to enable stress transfer. A well-bonded interface, which is essential for effective stress transfer from the matrix to the fiber, is a primary requirement for effective use of reinforcement properties [1-5]. The fiber/matrix interfacial adhesion is also a very important parameter in controlling the toughness of a composite material, resulting in improved final mechanical properties [6].

Generally, fiber surface treatment techniques are utilized to improve the interfacial adhesion between the fiber and the resin. The nature of the fiber surface is changed by fiber surface treatment applied during the processing of the fibers, i.e. sizing. Conventional sizings for glass fibers generally include a film former, a coupling agent, an emulsifier, an antistatic agent, etc. [7]. Silane agents applied to the glass surface as a size along with other components are designed to protect the glass fiber surface and to act as a coupling agent to promote the adhesion to a polymer matrix [8]. Hydroxyl groups of the silanes and those of the glass fiber surface can react with each other through siloxane bonding or hydrogen bonding at the interface between the glass fiber and the silane coupling agent. Therefore, interfacial adhesion can be promoted by this reaction, which indicates the adhesion process of the silane coupling agents onto a glass surface [9,10].

*Corresponding author: seckin.erden@ege.edu.tr

Another way to increase the fiber/matrix interaction or compatibility is to modify the matrix. Introducing reactive sites with higher chemical affinity toward the fibers, increasing matrix toughness, or even reducing resin viscosity to promote fiber impregnation or wetting are among the ways chosen to improve the fiber/matrix interface [11-13]. Modification of the resin by blending together with an elastomer or a thermoplastic additive to improve impact strength and fracture properties of unsaturated polyester has been reported [14-16]. But, modification of unsaturated polyester with siloxane to enhance the interfacial adhesion between fiber and matrix were rarely reported [17]. Besides, it may worth noting that the effect of matrix modification on the vibration properties of glass reinforced polyester composites has not been studied elsewhere.

Oligomeric siloxane used in this study contains alkoxy- and alkyl-functional groups, which help to improve dispersion of inorganic fillers into organic polymers such as resins/plastics and rubber and to cause better filler compatibility in organic rubbers, resins, and plastics. The alkyl functionality acts as a compatibilizer with organic polymer matrices. Therefore, oligomeric siloxane could be utilized as an additive into unsaturated polyester resin to improve interfacial adhesion between the glass fiber and polymer resin.

In this study, modification of unsaturated polyester resin with innovative oligomeric siloxane was achieved before composite fabrication. Tensile strength, flexural strength, interlaminar shear strength and vibrational properties of fabricated composites were investigated after resin modification. Also, fractured surfaces of the tensile tested composites were observed by scanning electron microscopy (SEM).

Experimental

Materials

Polipol polyester 383-T resin system (specific gravity, 1.11 g/cm^3; viscosity brookfield, 950 Pa s), which is isophthalic acid type resin, was mixed with the catalyst cobalt octoate (0.35 pph, of a 41 % solution in white spirit), the retarder 2.4-pentanedione (0.10 pph), and methylethylketone peroxide (hardener) (2.2 pph, of a 40 % dimethyl phthalate solution). Woven roving glass fabric (E-glass, 300 g/m^2) was purchased from Cam Elyaf San. A.S. (Izmir, Turkey). Oligomeric siloxane was obtained from Dow Corning Corp. under the commercial name Z-6173.

Modification of Polyester Matrix

Oligomeric siloxane used in this study was at levels of 1, 2, and 3 wt% of the glass fabrics. The oligomeric siloxane was added to polyester matrix and mixed for 5 min. Thereafter, the hardener was included into the mixture, which was then subjected to stirring for 5 min.

Manufacturing of Composite Laminates

The application of modified and unmodified polyester matrix onto glass fabric surface was carried out via hand lay-up technique. Six glass fabric layers were used to fabricate laminates with 3.5 mm thickness. Then, composite laminates were compression molded at a pressure of 120 bars at room temperature for 120 min. All composites were fabricated with about 37 % fiber volume fraction. The notations of the fabricated composites has been abbreviated as follows: Glass/polyester (GP), glass/polyester+1 % oligomeric siloxane (GP+1 %Slx), glass/polyester+2 % oligomeric siloxane (GP+2 %Slx), glass/polyester+3 % oligomeric siloxane (GP+3 %Slx).

Interlaminar Shear Strength (ILSS)

In order to determine the interlaminar shear strength (ILSS) values of the composites, short beam shear tests were conducted according to ASTM D 2344. A computer controlled Shimadzu Autograph AG-IS Series universal testing machine (Shimadzu Corp., Kyoto, Japan) was used at a crosshead speed of 1.3 mm/min. A span length/depth ratio of 5:1 was chosen. The tests were carried out at least five times and an average value was taken into consideration.

Flexure Test

Three-point bending tests were conducted to characterize the flexural properties of the glass/polyester composites following the ASTM D 790 standard. Specimens tested had a length of 100 mm and a width of 25 mm. The tests were performed by the above mentioned tensile tester using a load cell of 5 kN under three-point bending configuration. The fixture was manufactured by Shimadzu Corp. The tests were carried out at room temperature at a constant crosshead speed of 1.3 mm/min and a span length of 80 mm. At least five specimens of each composite type were tested. Flexural strength and flexural modulus values were calculated as described in [18,19].

Tensile Test

Glass/polyester composites were tested under tensile loading according to ASTM D-3039 using the above described testing machine with a video extensometer system (Shimadzu non-contact video extensometer DVE-101/201). Trapezium (advanced software for materials testing) was used for machine control and data acquisition. The tensile tests were conducted using a load cell of 100 kN at a crosshead speed of 2 mm/min at room temperature. The specimen length and width were 197 and 25 mm, respectively. At least five specimens were tested for each type of composite in order to check for repeatability. Tensile strength (σ), modulus of elasticity (E), and elongation at break (ε) values of the composites were obtained.

Experimental Modal Testing

Modal vibration tests are usually based on the measurement of the vibration properties of a specimen or structure. Natural frequency measurements from specimens vibrating in a single mode (e.g. rod specimens in torsional vibration or beam specimens in flexural vibration) have been used for many years to determine effective modulus and damping values, but the test procedures were typically slow and cumbersome, and the techniques were only suitable for small laboratory specimens [20]. Specimens used in this study are long, thin, cantilever beams. One end of the beam is fixed, while the other end is free (Figure 1). A typical beam used in this study has a length (L) of 25 mm, width (w) of 5 mm, and thickness (t) of 3.5 mm. A single-point excitation was adopted for the excitation of beams by applying a transient force using an impulse force hammer (086CO3, hammer sensitivity 2.17 mV/N, PCB Piezotronics, Depew, NY, USA) at one point. For response measurement, the acceleration at each point of the measuring mesh was obtained with a unidirectional piezoelectric accelerometer (KS 95B-100, voltage sensitivity 10.11 mV/m/s^2, weight 3.2 g, Metra Mess-u Frequenztechnik, Radebeul, Germany). The signals were recorded and then transferred into a personal computer through an A/D interface card (PD2-MF-16-400/14L, United Electronic Industries, Inc., Canton, USA). Fast

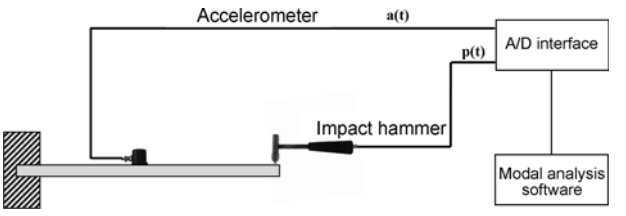

Figure 1. The experimental measurement setup.

Fourier Transform (FFT) and modal analysis software (Icats Modent Suite, ICATS, UK) were used to determine the resonance frequency of the tested beams. The experimental setup for the measurement system is shown in Figure 1. The impact hammer gave the input signal $p(t)$, and the accelerometer provided the output signal $a(t)$. Then, an FFT software calculated the frequency response functions (FRFs) between the response points and the excitation point, and then the other derived functions described the dynamic behavior of the system. The measurements were performed in the frequency bandwidth 0-1.6 kHz with a frequency resolution of 2 Hz. Each FRF was estimated by using a frequency domain average of 1024 samples.

Icats modal analysis software was used to extract the modal parameters of the beams using the ten calculated FRFs. A multi-degree-of-freedom technique was used for modal parameter estimation. The results of the modal parameter identification process were for the setting of the first three modes, including estimation of the frequency. These identified modes constituted the modal model for the beam in the frequency band 0-1.6 kHz.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM) observations of the fractured surfaces of the fabricated composites after tensile testing were carried out using a JEOL JSM 6060 (Jeol Ltd, Tokyo, Japan) at an accelerating voltage of 3 kV. Images were captured at a magnification level of 500X.

Results and Discussion

ILSS

The effect of the concentration of oligomeric siloxane on ILSS values of the composites were presented in Figure 2. The ILSS value of GP composite without oligomeric siloxane was obtained to be 25.5 MPa. After the incorporation of 1, 2, and 3 % oligomeric siloxane into polyester resin, the ILSS values of glass/polyester composite increased to 29.7, 36.8 and 44.7 MPa, respectively. It can be stated that in the studied concentration range, ILSS values increase with increasing concentration of oligomeric siloxane in polyester resin. As can be seen from ILSS results (Table 1), the greatest ILSS value belongs to GP+3 %Slx composite when compared with that of the other composites. This corresponds to an increase of 75 % in ILSS value of the glass/polyester composite. The increased ILSS values reflect a better adhesion between the fiber and the resin as a result of oligomeric siloxane incorporation. Oligomeric siloxane is known as a material with a low viscosity. Fiber/matrix interface can be improved by a reduction in resin viscosity to promote fiber impregnation or wetting [13]. Improved wetting can increase adhesive strength caused by an increased work of adhesion [11].

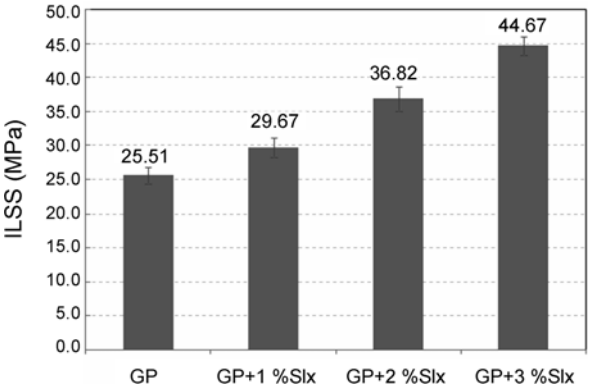

Figure 2. ILSS values of fabricated composites.

Flexure Test

The flexural properties of the fabricated glass/polyester composites were presented in tabular form using the calculated average values and their standard deviations (Table 1). As seen in Figure 3, the flexural strengths of the modified polyester composites increased with increasing siloxane concentration in polyester. The flexural strengths of the modified polyester composites were enhanced by 10, 12, and 15 % for GP+1 %Slx, GP+2 %Slx, and GP+3 %Slx, respectively, when compared to that of GP. It is clearly seen that 3 % siloxane modified polyester composite showed the highest improvement in terms of flexural strength, which increased from 346.1 MPa for GP to 399.4 MPa for GP+3 %Slx. The flexural strength of fiber reinforced composites depends on the fiber/matrix adhesion as well as the strength of each component [21]. Therefore, this increase in flexural strength may be an indication of better adhesion between the glass fabric and the modified polyester. Besides, the flexural modulus value of GP composite is enhanced by 6.4, 9.4, and 13.4 % as a result of matrix modification using 1, 2, and 3 % oligomeric siloxane, respectively (Table 1).

Table 1. Mechanical properties of fabricated composites (the data quoted are all average results taken from a minimum of five tests)

Composite	Tensile strength (MPa)	Modulus of elasticity (GPa)	Elongation at break (%)	Flexure strength (MPa)	Flexure modulus (Gpa)	ILSS (MPa)
GP	341.5±20.6	15.0±3.4	3.1±0.6	346.1±23.1	16.6±0.5	25.5±1.2
GP+1 %Slx	375.7±21.1	15.7±2.5	3.3±0.3	379.2±23.4	17.7±0.7	29.7±1.4
GP+2 %Slx	387.7±23.2	17.2±3.0	3.6±0.3	387.6±24.3	18.2±0.6	36.8±1.8
GP+3 %Slx	395.8±23.9	18.0±3.0	3.9±0.4	399.4±22.4	18.8±0.7	44.7±1.4

*The values after the (±) in all the tables refer the standard uncertainty of the measurement.

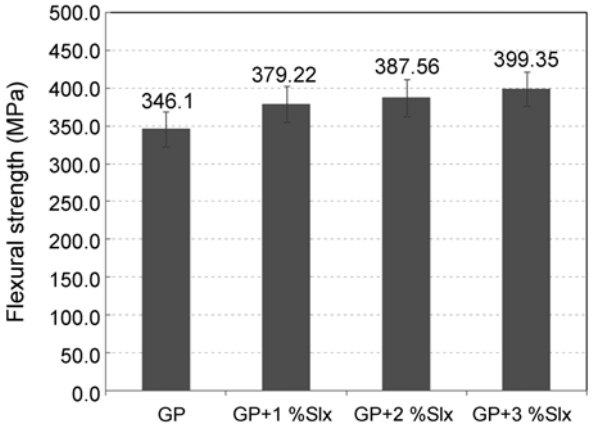

Figure 3. Flexural strength values of fabricated composites.

It can be obviously seen that GP+3 %Slx composite exhibited the best flexural modulus and strength among all the studied composites. From these results, it can be proposed that addition of oligomeric siloxane into polyester resin may improve the wettability of the glass fabric by the matrix system and hence increase the composite flexural properties.

Tensile and Modal Testing

Tensile strength and the modulus of elasticity values for GP, GP+1 %Slx, GP+2 %Slx and GP+3 %Slx were presented in Figure 4 and Table 1, respectively. From Figure 4, it is seen that the matrix modification by oligomeric siloxane in the concentration range of 1-3 % (w/w) improved the tensile strength of glass-polyester composites. Increases of 10, 14, and 16 % in tensile strength values for GP+1 %Slx, GP+2 %Slx and GP+3 %Slx were obtained, respectively. It is obvious that GP+3 %Slx composite exhibited the highest tensile strength, which increased from 341.5 MPa for GP to 395.8 MPa for 3 % siloxane modified polyester composite.

These enhancements may be explained by considering the improvement in the adhesive characteristics between glass fiber and polyester matrix. Due to the fact that oligomeric siloxane contains alkoxy and alkyl functional groups, dispersion of polyester onto the glass fabric may be improved causing better wetting of the fabric by the matrix. Therefore, glass fiber/modified polyester composites exhibit superior tensile strength.

As summarized in Table 1, moduli of elasticity of the composites increase as the added siloxane amount increases in the concentration range of 1-3 % (w/w). The increases in moduli of elasticity were determined to be 5, 15, and 20 % for GP+1 %Slx, GP+2 %Slx and GP+3 %Slx, respectively, when compared to that of the unmodified composite.

Table 1 shows the changes in the elongation at break values for the different composite specimens. Glass fabric/modified polyester composites exhibit increased elongation at break values when compared to that of the glass fabric/unmodified polyester composite. It is obviously seen that the incorporation of siloxane into polyester matrix induces increases of 7, 18, and 29 % in elongation at break values for GP+1 %Slx, GP+2 %Slx and GP+3 %Slx, respectively. The increases recorded in tensile strength and values of elongation at break of the specimens indicate an increase in toughness of the composites with increasing concentration of oligomeric siloxane [17]. It was also previously mentioned that increase in tensile strength and modulus may be a result of improved adhesion between fiber and matrix, pointing out a stronger interface, which allows better stress transfer between the constituents of the composite [22]. Therefore, when the above findings are evaluated, it is evident that matrix modification increases the tensile properties of the composites.

Additionally, as a result of the natural frequency measurements, Figures 5, 6, and 7 were presented to show the effect of the concentration of oligomeric siloxane on the changes in first, second, and third fundamental natural frequencies of the composite beams, respectively. As obviously seen in the figures, natural frequency increases as the concentration of oligomeric siloxane increases. This finding can be explained by the increase in modulus of elasticity as the natural frequency (w_n) is a function of the beam stiffness. It has been shown before that the stiffness and elastic moduli of composite materials correlate directly to the changes in

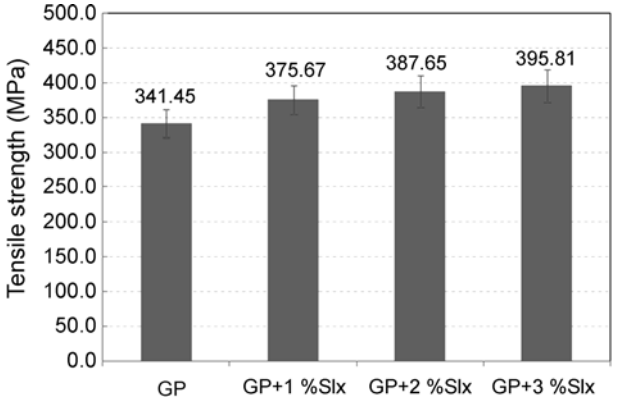

Figure 4. Tensile strength of fabricated composites.

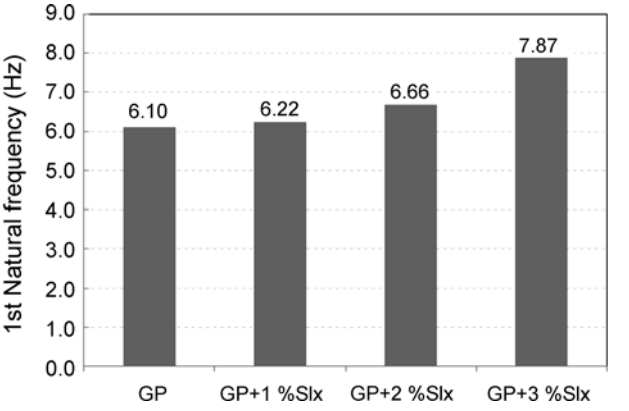

Figure 5. 1st natural frequency of fabricated composites.

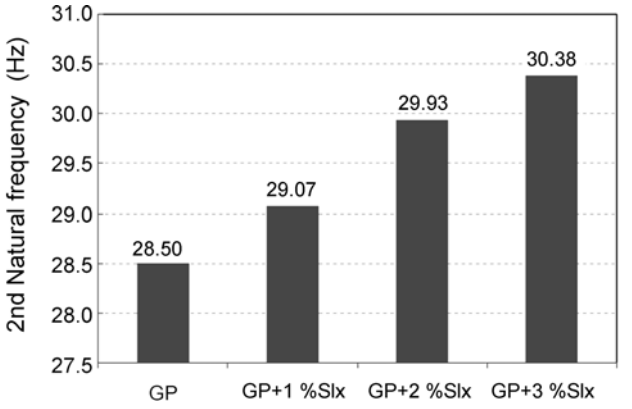

Figure 6. 2nd natural frequency of fabricated composites.

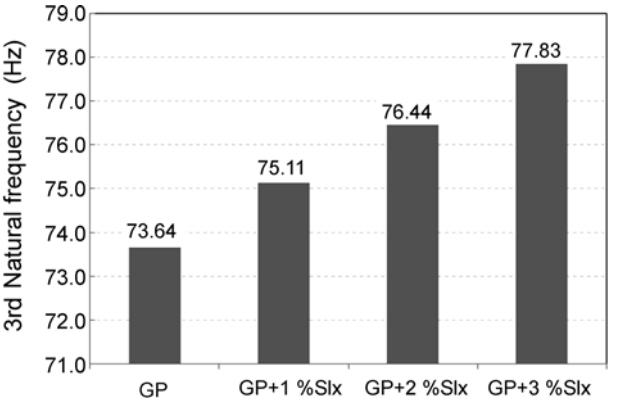

Figure 7. 3rd natural frequency of fabricated composites.

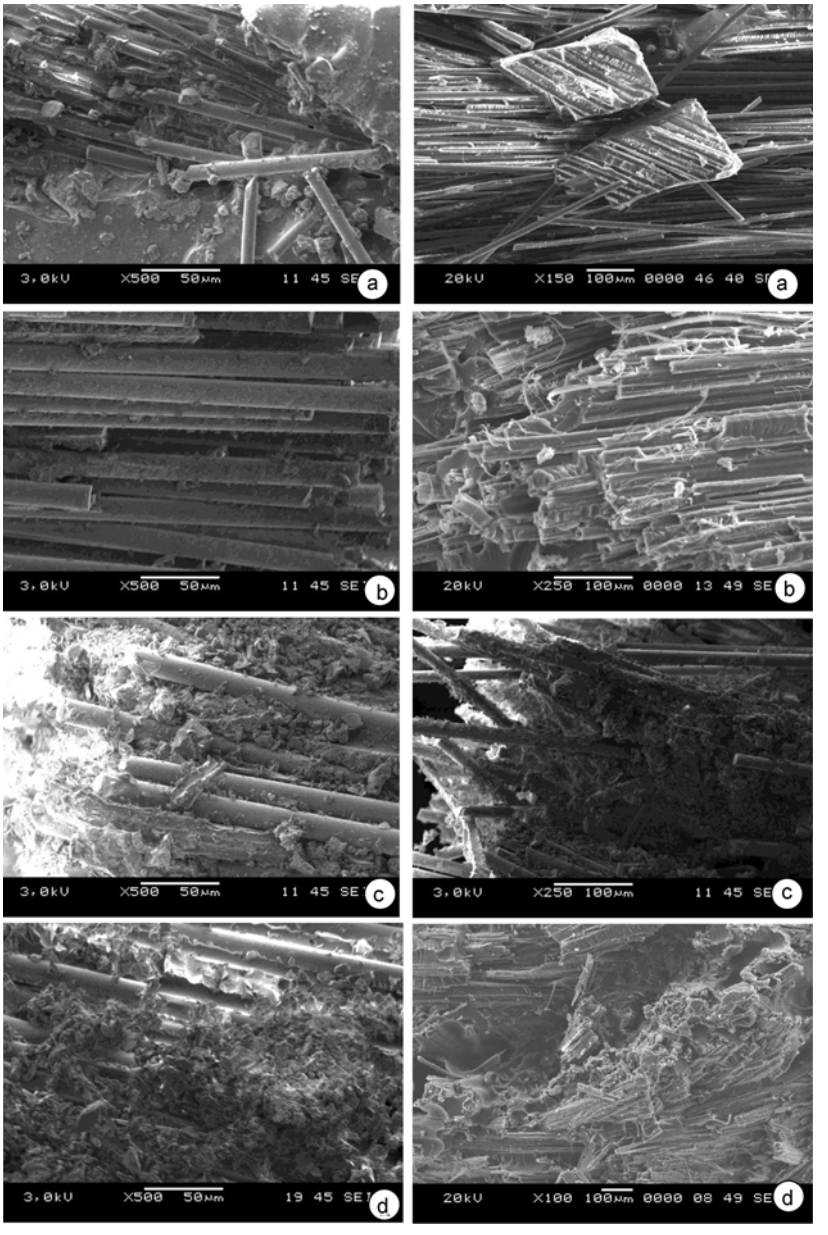

Figure 8. SEM images of tensile fracture surface of (a) glass/polyester (GP), (b) GP+1 %Slx, (c) GP+2 %Slx, and (d) GP+3 %Slx.

natural frequencies during modal vibration response [23].

SEM Analysis

SEM micrographs of the fractured surfaces of the composites were captured to visualize the fiber/matrix adhesion in glass fiber reinforced polyester composites. Both high-(500X) and lower-magnification-level images were attached for each composite type in Figure 8.

A fiber pullout failure mechanism was observed in the particular case of the unmodified polyester composite (Figure 8(a)). In addition, as can be seen in Figure 8(a), very little amount of polyester resin was found to adhere onto the fiber surfaces in the facture site of the composite, suggesting poor interfacial bonding between the glass fiber and the unmodified polyester matrix. This was also confirmed by the grooves seen in the polyester matrix as a result of fiber pullout. These features suggest poor interfacial bonding between the glass fiber and the unmodified polyester matrix.

The comparison of the SEM micrographs of the modified (Figure 8(b)) and unmodified polyester composites (Figure 8(a)) demonstrates that the siloxane modified polyester composites exhibited a greater amount of polyester resin adhered to the fiber surfaces. Moreover, for the cases of glass/polyester composites with the addition of 2 and 3 wt% oligomeric siloxane, the broken fibers are obviously seen to be embedded in the polyester resin (Figures 8(c) and (d)). Therefore, it is evident by the SEM observations performed on the fractured specimens that the interfacial adhesion between the glass fiber and unsaturated polyester resin has been improved via modification of the resin by incorporation of siloxane.

Conclusion

The effect of matrix modification on the mechanical and vibrational properties of glass/polyester composites was investigated. Oligomeric siloxane, which was varied within the range 1-3 % (w/w), was used to modify the unsaturated polyester. Composites of modified and unmodified polyester reinforced with woven roving glass fabric were compared in terms of mechanical, interlaminar, and vibrational properties. Tensile, flexural, short-beam and modal tests showed improvement in composite properties with increasing concentration of oligomeric siloxane in polyester. Experimental data demonstrated that 3 % oligomeric siloxane incorporation resulted in the most effective modified composite. The tensile strength increased from 341.5 to 395.8 MPa while the modulus of elasticity seemed to change marginally. Flexural strength changed from 346.1 MPa up to 399.4 MPa while ILSS was found to increase from 25.5 to 44.7 MPa. These improvements in ILSS as well as in tensile and flexural strengths may be an indication of better fiber/matrix interaction. SEM images also confirmed enhanced interfacial adhesion as the more the siloxane was incorporated, the more the glass fibers were embedded in polyester. Furthermore, with increasing oligomeric siloxane incorporation, the vibrational properties of the composites were seen to improve. It was shown that the 1st natural frequency of the composites increased from 6.10 to 7.87 Hz while the 2nd and 3rd natural frequencies also increased.

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