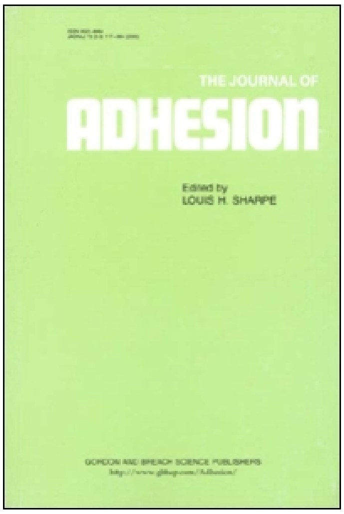

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Improvement of Interfacial Adhesion of Glass Fiber/Epoxy Composite by Using Plasma Polymerized Glass Fibers

Kutlay Sever[a]; Mehmet Sarikanat[b]; Yoldas Seki[c]; Haci Ali Gülec[d]; Mehmet Mutlu[e]; İsmail Hakkı Tavman[a]
[a] Department of Mechanical Engineering, Dokuz Eylul University, İzmir, Turkey [b] Department of Mechanical Engineering, Ege University, İzmir, Turkey [c] Department of Chemistry, Dokuz Eylul University, İzmir, Turkey [d] Department of Food Engineering, Yuzuncu Yil University, Van, Turkey [e] Plasma Aided Bioengineering and Biotechnology Research Group (PABB), Engineering Faculty, Hacettepe University, Ankara, Turkey

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Improvement of Interfacial Adhesion of Glass Fiber/Epoxy Composite by Using Plasma Polymerized Glass Fibers

Kutlay Sever[1], Mehmet Sarikanat[2], Yoldas Seki[3], Haci Ali Gülec[4], Mehmet Mutlu[5], and İsmail Hakkı Tavman[1]
[1]Department of Mechanical Engineering, Dokuz Eylul University, İzmir, Turkey
[2]Department of Mechanical Engineering, Ege University, İzmir, Turkey
[3]Department of Chemistry, Dokuz Eylul University, İzmir, Turkey
[4]Department of Food Engineering, Yuzuncu Yil University, Van, Turkey
[5]Plasma Aided Bioengineering and Biotechnology Research Group (PABB), Engineering Faculty, Hacettepe University, Ankara, Turkey

This study intends to produce plasma polymer thin films of γ-glycidoxypropyltrimethoxysilane (γ-GPS) on glass fibers in order to improve interfacial adhesion of glass fiber-reinforced epoxy composites. A low frequency (LF) plasma generator was used for the plasma polymerization of γ-GPS on the surface of glass fibers at different plasma powers and exposure times. X-ray photoelectron spectroscopy (XPS) and SEM analyses of plasma polymerized glass fibers were conducted to obtain some information about surface properties of glass fibers. Interlaminar shear strength (ILSS) values and interfacial shear strength (IFSS) of composites reinforced with plasma polymerized glass fiber were evaluated. The ILSS and IFSS values of non-plasma polymerized glass fiber-reinforced epoxy composite were increased 110 and 53%, respectively, after plasma polymerization of γ-GPS at a plasma power of 60 W for 30 min. The improvement of interfacial adhesion was also confirmed by SEM observations of fractured surface of the composites.

Keywords: Glass fiber; Interlaminar shear strength; Plasma polymerization; X-ray photoelectron spectroscopy (XPS)

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Address correspondence to Yoldas Seki, Department of Chemistry, Dokuz Eylul University, İzmir 35160, Turkey. E-mail: yoldas.seki@deu.edu.tr

1. INTRODUCTION

Polymer matrix composite materials offer tremendous advantages for applications that rely on high stiffness to weight and/or high strength to weight ratios due to their high modulus and strength coupled with low density [1]. However, composite materials have drawbacks such as poor interfacial adhesion between the fiber and the matrix resin, which is a critical factor in determining the properties of composite materials [2].

Interfacial adhesion can be improved by surface treatment of the glass fibers. Silane coupling agents have been widely applied to glass fiber to improve the interfacial adhesion between fiber and matrix and the mechanical properties of composites [3,4]. Silane coupling agents are organotrialkoxysilanes usually containing three ethoxy or methoxy groups that can condense to form covalent bonds with silanol groups on the surface of siliceous glasses. Coupling agents also contain an organofunctional tail that can react with the matrix to form a covalent bond [5]. However, a polycondensed film prepared by a wet chemical process from silane agents is heterogeneous [6] with respect to uniformity and film thickness, resulting in a deterioration of its multifunctional properties. Cech *et al.* [7] reported that, in contrast to polycondensed films, the plasma-polymerized vinyltriethoxysilane (pp-VTES) films were homogeneous and thus more suitable. Therefore, the plasma polymerization technique was chosen for the deposition of homogeneous functional films [8] as an alternative technology using the same monomer. Plasma polymerization is a technique which generates a thin polymer coating on the fiber surface [2,9,10] and improves fiber-matrix adhesion by a new polymer layer that can form strong covalent bonds between the fiber and the matrix [11]. The chemical structure of plasma polymers strongly depends on the fragmentation of the monomer [9,12]. This fragmentation depends not only on the chemical composition and structure of the monomer [12–15] but also on the polymer deposition process conditions in the glow discharge, such as power, flow rate, etc. By varying the process parameters, materials with different chemical compositions and structures can be obtained from the same monomer [12,16–19]. Polymers formed by plasma polymerization normally have a highly branched and highly cross-linked chemical structure [20]. Li *et al.* pointed out that plasma polymer films deposited from organosilicon monomers are potentially applicable as effective functional interlayers for glass fiber-polymer composites [21].

The goal of the manipulation of the interfacial chemistry is to achieve a more efficient interfacial stress transfer capability, which would result in improved mechanical properties of the composite. There are many techniques to characterize the stress transfer capability of a fiber-matrix interface, *e.g.,* the pull-out test [22,23], the transverse debond test [24], the single-fiber composite tensile test [25], interlaminar shear strength in short-beam shear specimens [26], etc. Interfacial shear strength (IFSS) is a good measurement for the effectiveness of fiber reinforcement and the macro-mechanical properties of fiber-reinforced polymer composites [27,28].

In this study, a plasma polymerization technique was used to modify the surface of glass fibers. A low frequency plasma generator was used to produce plasma polymer films of γ-glycidoxypropyltrimethoxysilane (γ-GPS) on glass fibers. To evaluate the effect of the plasma polymerization, the interlaminar shear strengths (ILSS) and IFSS of the fiber-reinforced composite materials were determined. Plasma-polymerized glass fibers were evaluated by using an X-ray photoelectron spectrometer (XPS) and fiber tensile strength. Surface morphologies of the plasma polymerized glass fibers and fractured surfaces of the composites were investigated by a scanning electron microscope (SEM).

2. EXPERIMENTAL

2.1. Materials

γ-glycidoxypropyltrimethoxysilane (γ-GPS) monomer of 98.5% purity was purchased from Dow Corning Corp. (Midland, MI, USA) and used without further purification. E-glass fiber roving as reinforcement for composite materials was supplied from Cam Elyaf San. A.S. (Çayirova/Gebze-Kocaeli, Turkey). The roving contained 2400 filaments (each filament having a round cross-section and a diameter of 12 μm). The glass fibers were heat cleaned at 450°C for 1 hour in an oven before using in the plasma polymerization process. Epoxy was preferred as the matrix system for the polymer composites. A liquid epoxy resin, R1040 and hardener R1048 (mixing ratio 75:25 wt%), were provided by Resoltech, Equilleb, France. The chemical composition of the epoxy and hardener are proprietary. R1040 is known as a high-performance epoxy laminating system. The system is also suitable for casting and filament winding applications.

2.2. Plasma Polymerization

Plasma polymerization treatments were performed in a low frequency (LF) plasma generator (laboratory system PICO with 40 kHz/200 W, Diener Electronic GmbH + Co., Nagold, Germany). At first, glass fibers were placed on the ground electrode in the middle of the reactor and then the chamber was evacuated to about 0.1 mbar. At a pressure of approximately 0.1 mbar the monomer vapor was fed into the chamber. Monomer vapor was allowed to flow at a certain rate (allowed pressure difference was 0.1 to 0.16 mbar). Then, power was adjusted and the glass fibers were exposed to glow discharge. The glass fibers were modified at different powers from 30 to 90 W and at different exposure times from 5 to 30 min. At the end of the process, the generator was turned off automatically and the monomer inlet was closed manually. The chamber was fed with argon gas for 10 minutes. Finally, the chamber was evacuated to about 0.1 mbar. Argon feeding and vacuum application were applied to deactivate free radicals in the plasma atmosphere [29].

2.3. Composite Preparation

Unidirectional (UD) composites were prepared by a hand lay-up technique in a Teflon® mold. Glass fibers were pre-impregnated with matrix material consisting of epoxy and hardener in the aforementioned ratio. The impregnated glass fibers were placed in the mold cavity. Then, matrix material was poured into the mold. The composites were cured for 1 hour at 85°C. Finally, the UD composites with a length of 35 mm, width of 10 mm, and thickness of 6 mm were manufactured for each plasma polymerization treatment. All the composites were produced at a fiber volume fraction of 10% [30].

2.4. X-Ray Photoelectron Spectroscopy (XPS) Analysis

The composition of the elements in the surface region (top 6–8 nm) of the deposited layers was studied by X-ray photoelectron spectroscopy (XPS) on a Specs ESCA spectrometer (Berlin, Germany) equipped with a non-monochromatic Mg Kα radiation source at a power of 200 W and EA 200 hemispherical electrostatic energy analyzer. The base pressure in the sample chamber was controlled in the range of 10^{-9}–10^{-10} torr. The pass energies were 96 and 48 eV, for survey and high-resolution spectra, respectively. The deconvolution of the spectra was achieved by fitting the data with Gaussian (70%)-Lorentzian (30%) functions.

2.5. Single Fiber Tensile Test

The tensile strength values of single fibers were measured using a Shimadzu AUTOGRAPH AG-IS Series universal testing machine

(Shimadz, Kyoto, Japan) equipped with a 5 kN load cell. The specimens had a gauge length of 40 mm and the specimens were tested at a crosshead speed of 0.5 mm/min. At least seven samples were tested for each type of composite to check for repeatability.

2.6. Pull-Out Test

Pull out tests were performed after embedding of the fibers in the matrix for 180 min at 80°C. A Shimadzu AUTOGRAPH AG-IS Series universal testing machine equipped with a 5 kN load cell was used and the values of interfacial shear strength were obtained during single fiber pullout tests. The gauge length was 20 mm with a cross-head speed of 0.1 mm/min. In order to determine the adhesion between fiber and matrix, measurement of the interfacial shear strength (IFSS) can be accomplished by imposing a tensile load on a specimen where the fiber is embedded in the matrix [31,32]. The fiber was then loaded until it was pulled out from the matrix. The debonding force, F_{max}, the diameter, d, and the embedded length of the fibers, l_e, were determined and the interfacial shear strength (IFSS)τ_d was calculated from the following equation:

$$\tau_d = \frac{F_{\max}}{d\,\pi\,l_e}.$$

2.7. Short Beam Shear Test

According to ASTM standard D 2344, short beam shear tests were performed on a computer controlled Shimadzu AUTOGRAPH AG-IS Series universal testing machine. A three-point bending fixture had a loading pin (diameter 6.4 mm) and two support pins (diameter 3.2 mm). Samples were tested with a support span/sample thickness ratio of 4:1 and a crosshead speed of 1 mm/min. At least six samples were tested for each type of composite to check for repeatability. The apparent shear strength was then calculated as follows:

$$ILSS = 0.75\left(\frac{P_{\max}}{wt}\right),$$

where $ILSS$ is the interlaminar shear strength, P_{max} is the failure load, and w and t are the width and thickness of the specimen, respectively.

2.8. Scanning Electron Microscope (SEM) Observation

The surfaces of plasma polymerized (pp) glass fibers and the fractured surfaces of the composites were investigated by JEOL JSM 6060 scanning electron microscope (JEOL, Tokyo, Japan) at an accelerating voltage of 5 kV. In order to eliminate charging effects during SEM investigation, all samples were coated with a thin layer of gold *via* a plasma sputtering apparatus.

3. RESULTS AND DISCUSSION

3.1. X-Ray Photoelectron Spectroscopy (XPS) Analysis

Elemental compositions of the pp-glass fibers at different plasma powers and exposure times are presented in Table 1. Si/C ratios are 0.28, 0.38, and 0.24 for 30 W-15 min, 60 W-15 min, and 90 W-15 min, respectively. A more relative inorganic character was observed at 60 W for 15 min. However, the Si/C ratios for different exposure times of 5, 15, and 30 min at 60 W are 0.57, 0.38, and 0.47, respectively. The highest relative inorganic character of plasma polymerized film on the glass fiber surface was observed with the lowest exposure times (for 5 min) at 60 W [12,33]. O/C ratios obtained were 1.23, 1.56, and 0.98 at 30, 60, and 90 W, respectively. This indicates that a plasma power of 90 W leads to lower concentration of oxygen-containing groups on the surface of glass fiber. On the other hand, O/C ratios were 2.04, 1.56, and 1.83 for 5, 15, and 30 min at 60 W, respectively. More oxygen-containing groups were obtained at the lowest exposure time in the studied exposure times in this work. The plasma is fragmenting the high carbon organofunctional group, which is being removed from the treatment chamber. Because higher plasma powers break the bond, those fragmented groups are leaving the chamber. The C-Si bond possesses the lowest standard bond energy among these bonds and are firstly broken with the application of plasma power. Therefore, increasing the plasma power leads to a decrease in the relative concentration of C-Si bonds. The chemical structure of plasma polymers strongly depends on the fragmentation of the monomer [34,35]. This fragmentation depends not only on the chemical composition

TABLE 1 Elemental Compositions of Heat-Cleaned and Plasma-Polymerized Glass Surfaces

	Heat cleaned	30 W/ 15 min	60 W/ 15 min	90 W/ 15 min	60 W/ 5 min	60 W/ 15 min	60 W/ 30 min
C %	38	40	34	45	28	34	30
O %	49	49	53	44	57	53	55
Si %	13	11	13	11	16	13	14

and structure of the monomer [35] but also on the polymer deposition process conditions in the glow discharge, such as power, flow rate, etc.

The narrow scan spectra of the C1 s regions were deconvoluted into the surface functional groups. High-resolution XPS spectra showing the deconvoluted C1 s envelope for different plasma powers and exposure times were given in Figs. 1 and 2, respectively. The contributions are presented in Figs. 3 and 4 for different plasma powers and exposure times, respectively. C1 s core level spectra of pp-γ-GPS film were deconvoluted into three distinct components. The first one, C1s(1), located at 284.6 eV, corresponds to the carbon atom of the

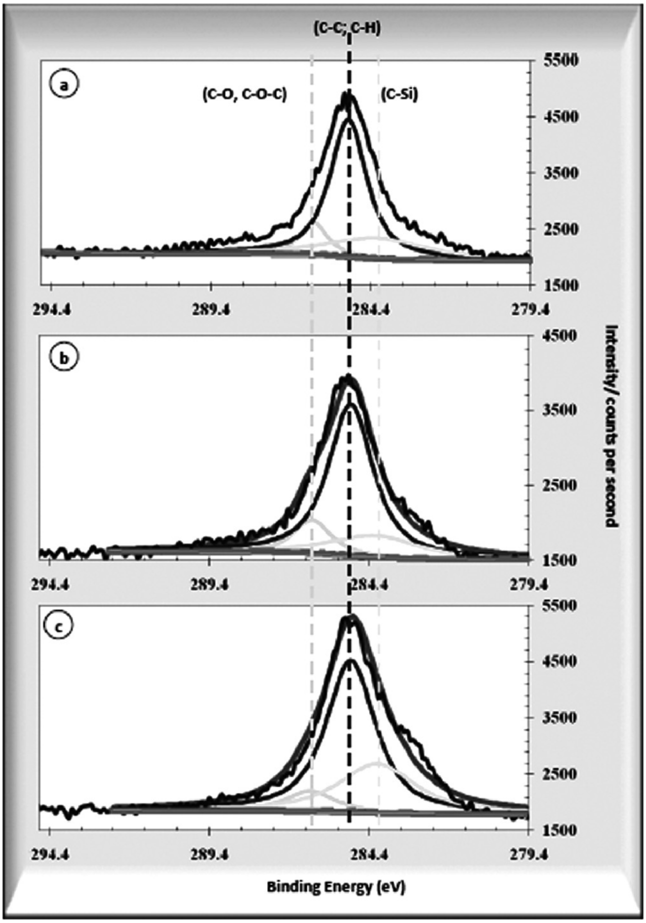


FIGURE 1 High-resolution XPS spectra showing the deconvoluted C1 s envelope for (a) 30 W-15 min, (b) 60 W-15 min, and (c) 90 W-15 min.

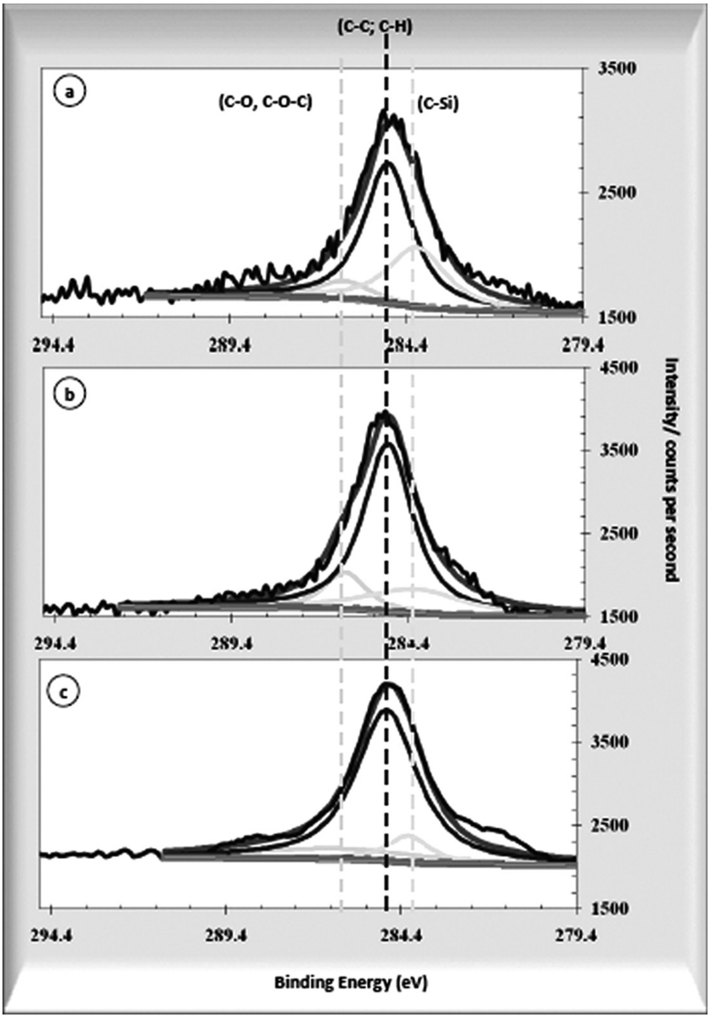


FIGURE 2 High-resolution XPS spectra showing the deconvoluted C1s envelope for (a) 60 W-5 min, (b) 60 W-15 min, and (c) 60 W-30 min.

C-C or C-H group. The second one, C1s(2), located at 286.2 eV, is attributed to the carbon atom of the C-O or C-O-C group. The third one, C1s(3), located at 284.3 eV, is assigned to the carbon atom of the C-Si group [12,36,37]. The C-O or C-O-C group increases up to 60 W. With the increase of plasma power to 90 W, the C-O or C-O-C group decreases. The C-C or C-H group shows the same trend. However, the C-Si group decreases to 19.1% for pp-glass fiber at 60 W.

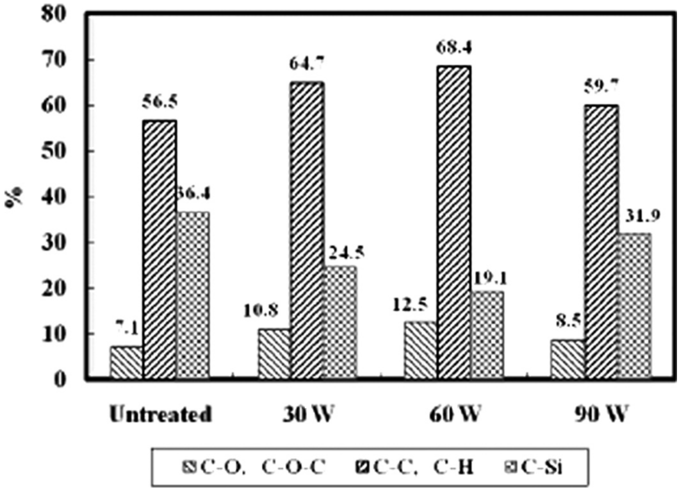


FIGURE 3 Relative percentage of C1 s on PlzP-γ-GPS glass fiber surface at different plasma powers and heat-cleaned glass fiber.

The C-Si group increases to 31.9% with the increasing of plasma power to 90 W. The effect of exposure time at 60 W can be seen in Fig. 4. As can be seen from Fig. 4, the C-O or C-O-C group increases from 7.1%

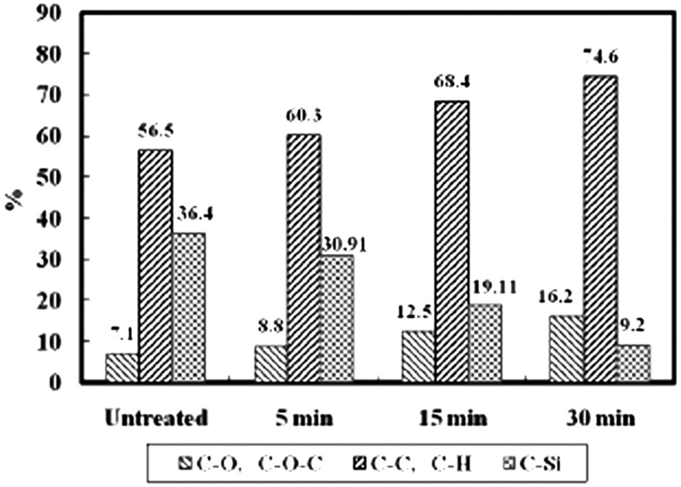


FIGURE 4 Relative percentage of C1 s on pp-γ-GPS glass surface at different exposure times at 60 W and heat-cleaned glass fiber.

for heat cleaned glass fiber to 16.2% for pp-glass fiber at 90 W. The same trend was observed for the C-C or C-H group.

In contrast to this, the C-Si group decreases from 31.9% for the pp-glass fiber at 90 W to 24.5% for the pp-glass fiber at 30 W. C-Si bonds are broken with the increase of plasma power during plasma polymerization of γ-GPS onto glass fibers. The C-Si bond, which possesses the lowest standard bond energy among these bonds, are firstly broken with the application of plasma power. Therefore, increase of plasma power leads to decreasing relative concentration of C-Si bonds.

The narrow scan spectra of the Si2p regions were deconvoluted into the surface functional groups. High-resolution XPS spectra showing the deconvoluted Si2p envelope for different plasma powers and exposure times are shown in Figs. 5 and 6, respectively. Close examination of the Si2p spectrum shows peaks at 103.4, 102.8, 102.1, 101.5, and 100.9 eV corresponding to Si-$(O)_4$, $(R)_1$-Si-$(O)_3$, $(R)_2$-Si-$(O)_2$, $(R)_3$-Si-$(O)_1$, and Si-$(R)_4$, respectively [37]. The contributions at different plasma powers and exposure times are given in Tables 2 and 3, respectively.

The percent contribution of the Si-$(O)_4$ group was 9.2% for pp-glass fiber at 30 W. With increase of plasma power from 30 to 90 W, the relative amount of the Si-$(O)_4$ group decreases to 2.1% for pp-glass fiber. However, the relative contribution of the $(R)_1$-Si-$(O)_3$ group was found to be 25.6% at 30 W. Increasing the plasma power from 30 to 90 W increased the relative contribution of $(R)_1$-Si-$(O)_3$ to 62.3%. The contributions of other groups decrease with the increase of plasma power from 30 to 90 W. As can be seen from Table 2, the relative contribution of Si-$(O)_4$ was found to be 9.7% after plasma polymerization for 5 min. The relative amount of the Si-$(O)_4$ group decreases with increased plasma exposure times. The relative contribution of the $(R)_1$-Si-$(O)_3$ group increases with the increase of plasma exposure time from 5 to 30 min. However, the relative amounts of $(R)_2$-Si-$(O)_2$, $(R)_3$-Si-$(O)_1$, and Si-$(R)_4$ groups decreases at high plasma exposure times. The relative contribution of the Si-$(R)_4$ group after plasma polymerization of glass fiber for 30 min was 1.2%. It can be said that the relative amounts of Si-C bonds decrease with increasing plasma exposure time. It is an expected result because of the fact that Si-C bonds are broken firstly.

3.2. SEM Observations of pp-Glass Fibers

We used the scanning electron microscope (SEM) for investigation of the surface morphology of pp-glass fibers. SEM micrographs of the plasma-polymerized glass fibers at different plasma powers and

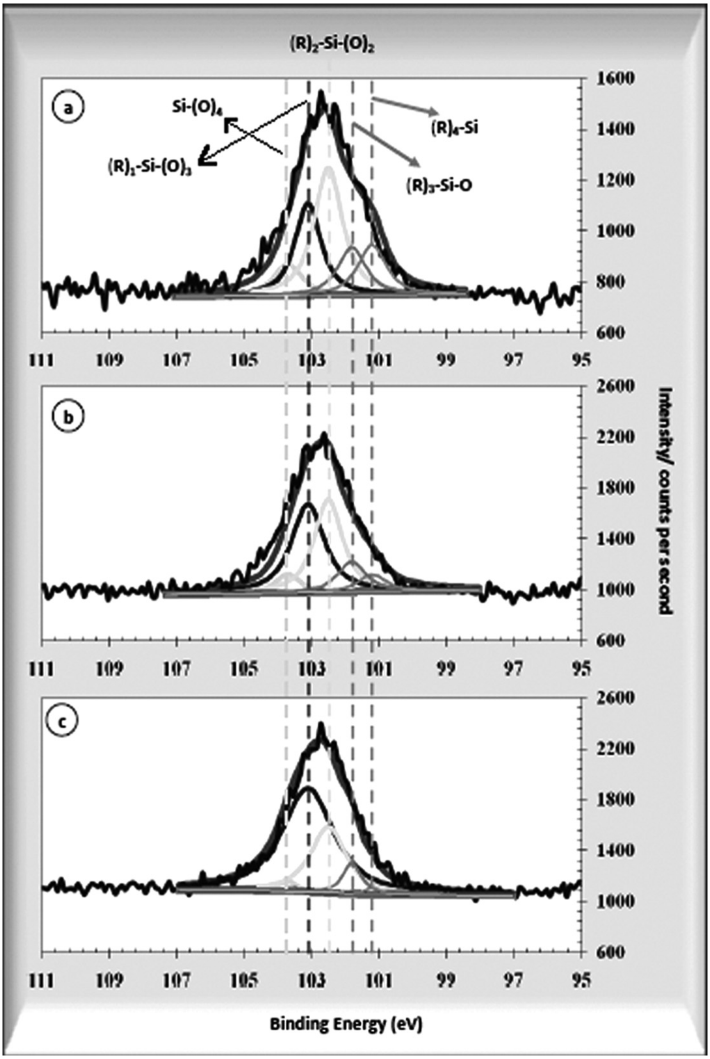


FIGURE 5 High-resolution XPS spectra showing the deconvoluted Si2p envelope for (a) 30 W-15 min, (b) 60 W-15 min, and (c) 90 W-15 min.

exposure times can be seen in Figs. 7 and 8. The SEM micrographs could easily verify the difference between heat-cleaned glass fiber and plasma-polymerized fibers (Figs. 7 and 8). Figure 7a shows the micrograph of the heat-cleaned glass fiber. The surface of the fiber is smooth and uniform. This type of morphology does not enable a mechanical interlocking mechanism. As can be seen from Figs. 7b–d and 8a–c,

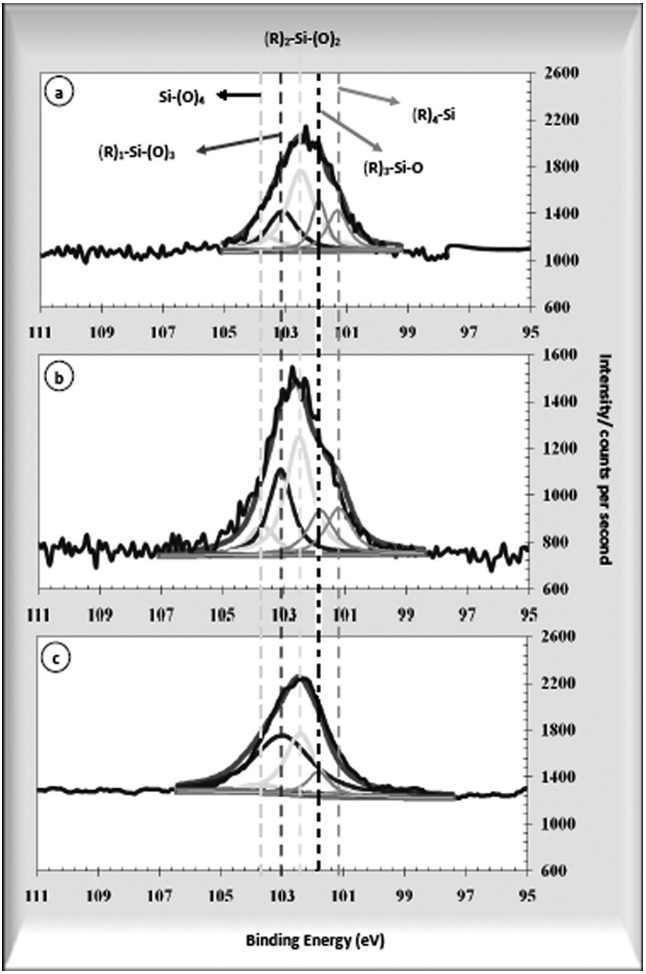


FIGURE 6 High-resolution XPS spectra showing the deconvoluted Si2p envelope for (a) 60 W-5 min, (b) 60 W-15 min, and (c) 60 W-30 min.

TABLE 2 Relative Percentage of Si2p on Glass Fiber Surface at Different Plasma Powers for 15 min

	Si-(O)$_4$	(R)$_1$-Si-(O)$_3$	(R)$_2$-Si-(O)$_2$	(R)$_3$-Si-(O)$_1$	Si-(R)$_4$
Heat-cleaned	10.2	15.6	42.6	15.9	15.8
30 W	9.2	25.6	37.0	13.8	14.5
60 W	6.3	39.6	35.8	11.8	6.6
90 W	2.1	62.3	27.6	6.9	1.2

TABLE 3 Relative Percentage of Si2p on Glass Fiber Surface for Different Exposure Times at 60 W

	$Si\text{-}(O)_4$	$(R)_1\text{-}Si\text{-}(O)_3$	$(R)_2\text{-}Si\text{-}(O)_2$	$(R)_3\text{-}Si\text{-}(O)_1$	$Si\text{-}(R)_4$
Heat-cleaned	10.2	15.6	42.6	15.9	15.8
5 min	9.7	21.3	39.7	14.1	15.2
15 min	6.3	39.6	35.8	11.8	6.6
30 min	4.7	55.5	29.7	8.6	1.6

the surfaces of the plasma-polymerized glass fiber at different plasma powers and exposure times are not smooth and uniform. In Figs. 7b–d, the SEM micrographs show fragments of γ-GPS adhered to the fiber surface at several points. It is probable that the plasma-polymerization of glass fibers creates different bonding sites that promote adhesion between glass fibers and epoxy matrix. From the SEM micrographs of glass fibers plasma polymerized at 90 W for 15 min (Fig. 7d), formation of some cavities during plasma polymerization can be seen. This may create a surface roughness. As can be seen from Fig. 8, the glass fiber surfaces become rougher as a result of plasma polymerization of glass fibers. Rough surfaces increase the number of anchorage points, thus offering good fiber-resin mechanical interlocking [38,39]. It is well known that the mechanical interlocking

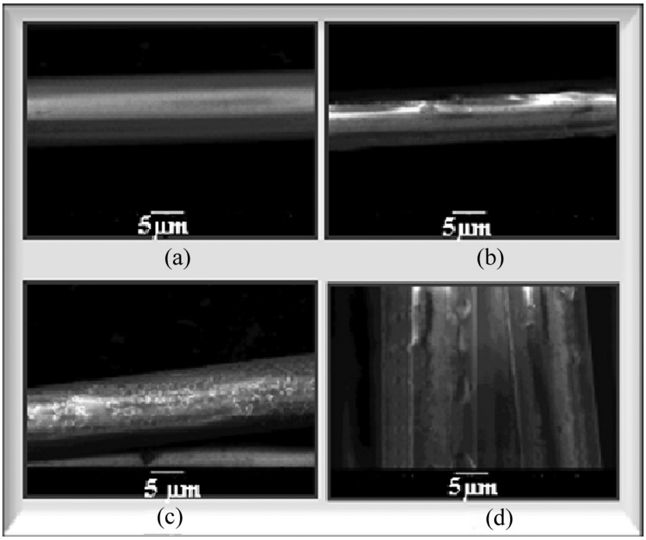


FIGURE 7 SEM micrographs of plasma polymerized glass fibers: (a) heat-cleaned, (b) 30 W-15 min, (c) 60 W-15 min, and (d) 90 W-15 min.

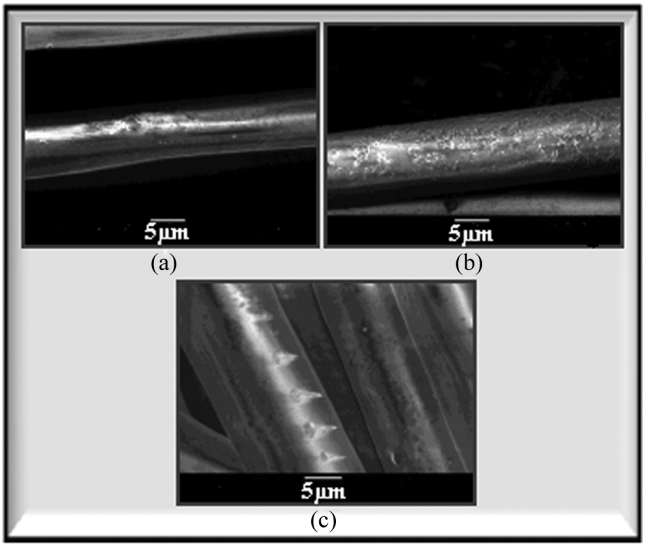


FIGURE 8 SEM micrographs of plasma polymerized glass fibers: (a) 5 min-60 W, (b) 15 min-60 W, and (c) 30 min-60 W.

mechanism between fiber and matrix resin plays a key role in improving the interfacial adhesion of fiber-reinforced polymer matrix composites.

3.3. Single Fiber Tensile Test

To find out how the treatment of plasma polymerization affects the strengths of treated fibers, tensile strengths of glass fibers were determined using a tensile test. In Figs. 9 and 10, the tensile strengths of heat-cleaned and pp-glass single fibers are given. As can be seen in Fig. 9, considerable decrease in tensile strength was observed at 90 W. The strength of heat-cleaned fiber was 1.7 GPa and after subjecting to high plasma power (90 W), the fiber strength decreased to 1.2 GPa. Approximately a 30% decrease in tensile strength of pp-glass fiber at 90 W was observed when compared with that of heat cleaned glass fiber. It can be said that high plasma powers (especially 90 W in this study) degrades the fiber and weakens the fiber strength.

Figure 10 shows fiber tensile strength values as a function of exposure time under a plasma power of 60 W. Fiber tensile strength of untreated glass fiber was 1.7 Gpa. After plasma treatment, fiber strengths were 1.7, 1.6, and 1.5 Gpa for plasma exposure times of 5,

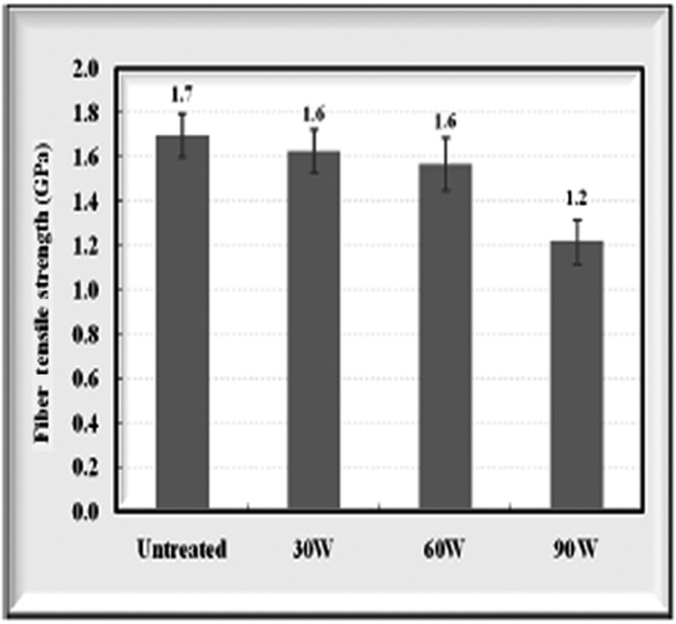


FIGURE 9 Fiber tensile strength values as a function of plasma power under an exposure time of 15 min.

15, and 30 min, respectively. It can be reported that increasing the exposure time of plasma treatment decreases the fiber strength.

3.4. Pull-Out Test

Figures 11 and 12 show the influence of the plasma power and exposure time on the interfacial shear strength. As can be seen in Fig. 11, the single fiber pull-out value for heat cleaned fiber was 36.6 MPa. IFSS values increased up to 60 W. The IFFS values of pp-glass fiber at 30 W-15 min and at 60 W-15 min in comparison with that of the heat-cleaned glass fiber increased approximately 12.8 and 37.4%, respectively. Conversely, The IFSS value decreased to 39.5 MPa for pp-glass fiber at 90 W.

As can be seen from Fig. 4, the increases in IFSS values were compatible with the increases in C-O, C-O-C and C-C, C-H groups on the surface of the glass fibers. It is probable that interaction of the epoxy matrix with C-O, C-O-C and C-C, C-H groups determines the strength of adhesion between the glass fibers and the epoxy matrix. Strong bonding may be possible between pp-glass fibers and epoxy matrix.

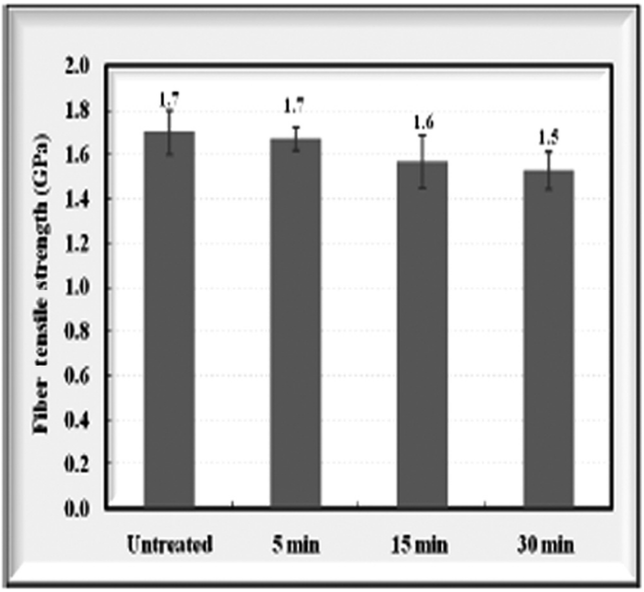


FIGURE 10 Fiber tensile strength values as a function of exposure time under a plasma power of 60 W.

As can be seen from Fig. 12, the IFSS values for pp-glass fiber at 60 W-5 min, 60 W-15 min, and 60 W-30 min are 42.6, 50.3, and 56.1 MPa, respectively.

3.5. Short Beam Shear Test

Interlaminar shear strength values of glass fiber/epoxy resin composites were determined to evaluate the effect of plasma polymerization on fiber-matrix interface properties of the composites. The effect of plasma polymerization of γ-GPS on the ILSS of the glass fiber-reinforced epoxy composites is shown in Figs. 13 and 14. It is seen in Fig. 13b that the ILSS values of the composites increased with increasing exposure time at a plasma power of 60 W. The ILSS value of heat-cleaned glass fiber-reinforced composite was 8.1 MPa, while it increased to 9.8, 14.9, and 17.0 Mpa, increments of about 21, 84, and 110%, after plasma polymerization using γ-GPS for 5, 15, and 30 min at plasma power of 60 W, respectively. Namely, the maximum ILSS was obtained for an exposure time of 30 min at 60 W. This indicates the greatest adhesion between glass fiber and epoxy matrix. As was noted above, the relative concentrations of C-O, C-O-C and C-C,

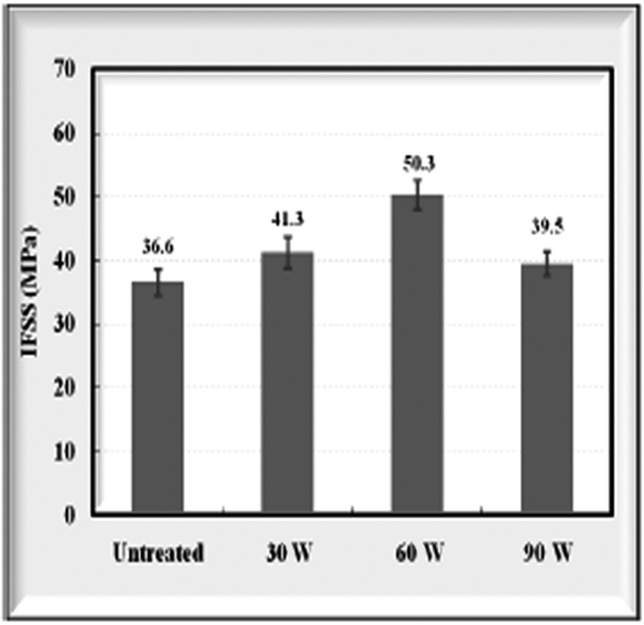


FIGURE 11 The influence of the plasma power under exposure time of 15 min on the interfacial shear strength (IFSS).

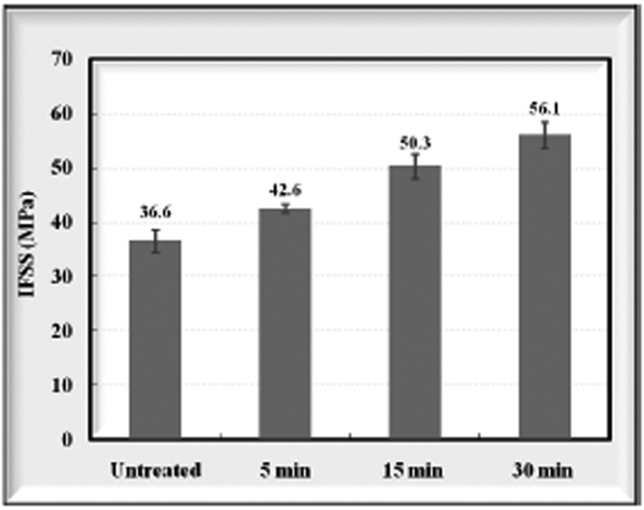
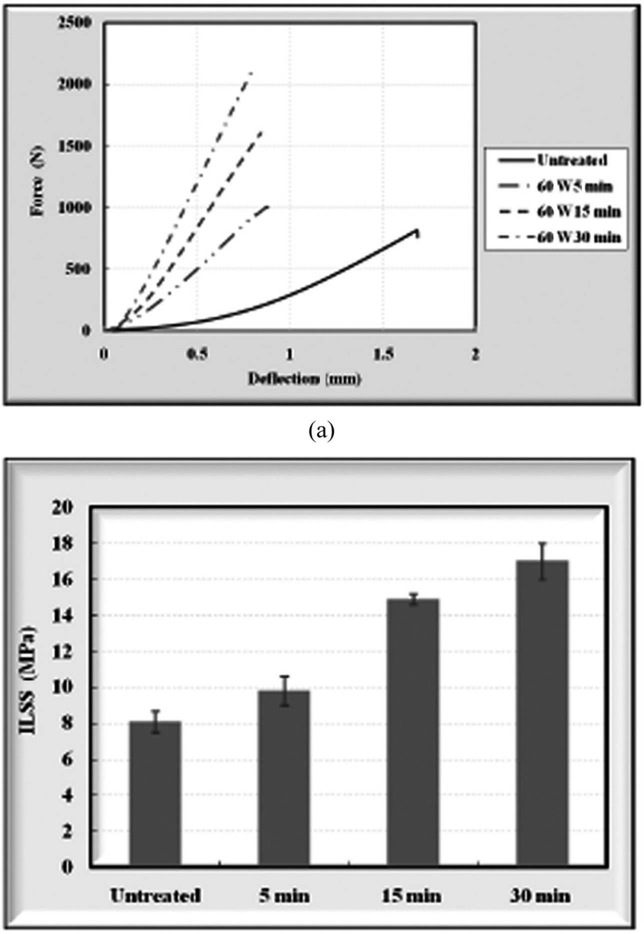


FIGURE 12 The influence of the exposure time under plasma power of 60 W on the interfacial shear strength (IFSS).



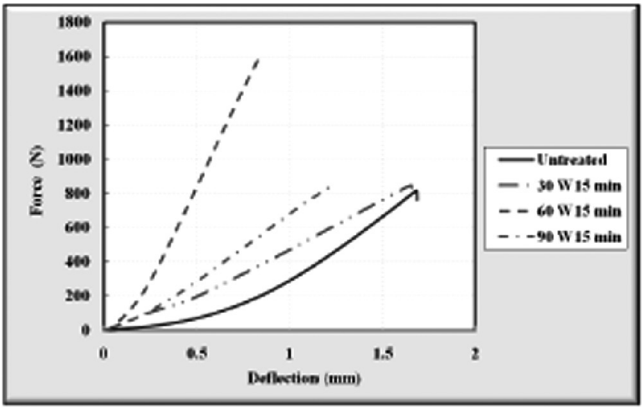
(a)

(b)

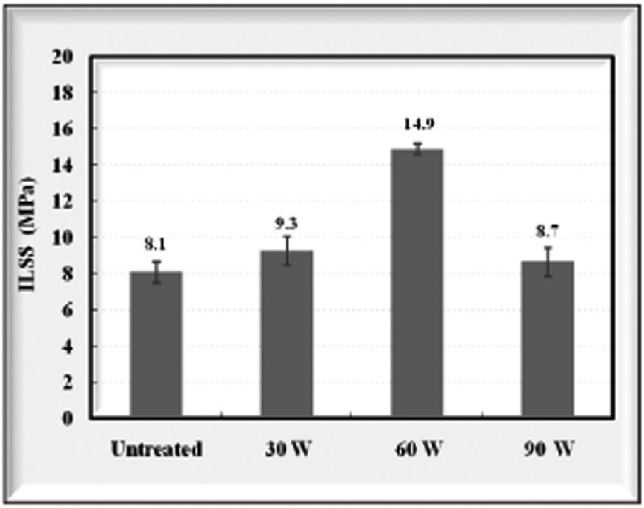
FIGURE 13 (a) Force-deflection curve and (b) ILSS values of the composites as a function of exposure time under a plasma power of 60 W.

C-H groups were found to be 16.2 and 74.6%, respectively, at 60 W for 30 min and these are the greatest values in the studied range. It is interesting to note also that the relative concentration of the C-Si group (19.1%) at 60 W for 30 min was the lowest value among the C-Si groups.

Force-deflection plots at different exposure times and plasma powers are presented in Figs. 13a and 14a, respectively. Figure 14b shows the ILSS values of pp-glass fiber/epoxy composites as a function of plasma power for an exposure time of 15 min. As can be seen from



(a)



(b)

FIGURE 14 (a) Force-deflection curve and (b) ILSS values of the composites as a function of plasma power under exposure time of 15 min.

Fig. 14b, the maximum ILSS was observed at a plasma power of 60 W and the ILSS of the composite showed 84% improvement compared with that of the heat-cleaned fiber. However, it decreased from 14.9 to 8.7 MPa when the plasma power was 90 W. The drop in strength at 90 W may be attributed to surface degradation due to excess treatment and the formation of a weak boundary layer [40]. It is well known that there are two major processes with opposite effects which occur simultaneously in plasma treatments, leading to the removal of materials and the deposition of materials, respectively. Both processes can change the surface topography of a substrate exposed to plasma [41,42]. Plasma treatment may cause damage on the fiber surface and thus decreases fiber strength. Increase in power and time lead to more damage on the fiber surface, resulting in a larger decrease in fiber strength. Therefore, some researchers proposed that high power input is the dominant factor to degrade the strength of fibers [41].

It can be also noted that ILSS results showed the same trend as the IFSS results. Plasma polymerization of the surface of glass fiber with γ-GPS improves not only the IFSS but also the ILSS values of the glass fiber/epoxy composite.

In a study by Cech [30], it was reported that by plasma polymerization of vinyltriethoxysilane (VTES), the ILSS value of the composite increased with the effective plasma power by more than 112% compared with the untreated fibers. Strong bonding could be possible between the interlayer (thin film) and the polymer matrix *via* chemical bonds as the hydroxyl groups at the film surface could react with the resin during polymerization.

As a result, the ILSS indicates that plasma polymerization of γ-GPS on glass fiber can improve adhesion between the glass fiber and the epoxy matrix.

3.6. SEM Observations of pp-Glass Fibers/Epoxy Composites

SEM micrographs of the fractured surfaces of plasma polymerized glass fiber/epoxy composites are shown in Figs. 15 and 16. Figure 15a represents the fracture surface of the heat-cleaned glass fiber/epoxy composite. SEM analysis was conducted to investigate the fracture morphology of the composites depending on the plasma polymerization conditions of the glass fibers. There was a marked difference in fracture surface topography between heat-cleaned glass fiber-reinforced epoxy and plasma-polymerized glass fiber-reinforced epoxy composites. From Fig. 15, it can be seen that heat-cleaned glass fibers were pulled out from the epoxy matrix and that the surfaces of the fibers were smooth and clean with no resin matrix adhered. A large amount of fiber pull-outs and clean fiber surfaces demonstrate that interfacial adhesion between heat-cleaned glass fiber and epoxy matrix was very weak. The fracture of heat-cleaned glass fiber-reinforced epoxy composite occurred at the interface between fiber and matrix and the interface structure cannot transfer stress effectively [43].

In the case of pp-glass fiber-reinforced epoxy composites, better adhesion was observed between the fiber and matrix as seen in

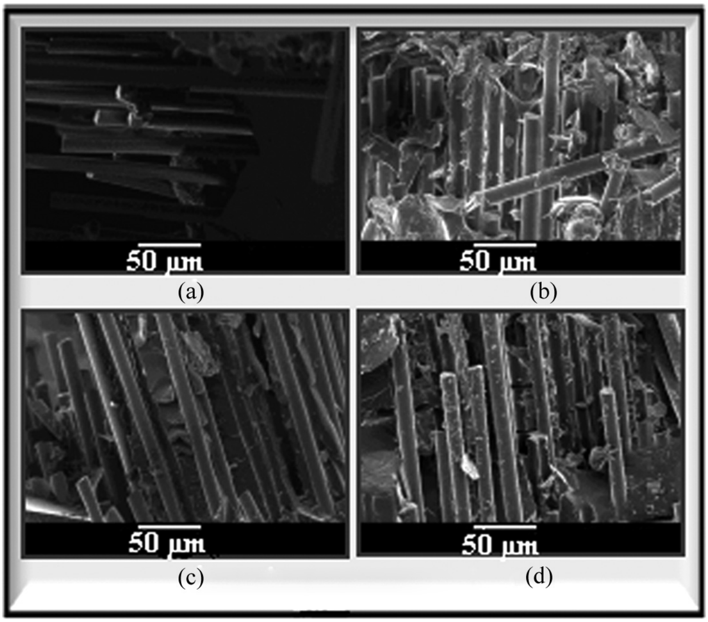


FIGURE 15 SEM micrographs of glass fiber/epoxy composite: (a) heat cleaned, (b) 30 W-15 min, (c) 60 W-15 min, and (d) 90 W-15 min.

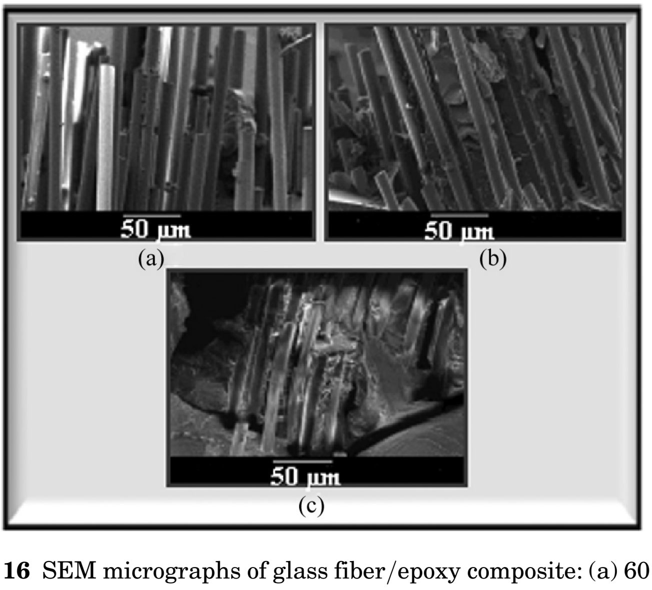


FIGURE 16 SEM micrographs of glass fiber/epoxy composite: (a) 60 W-5 min, (b) 60 W-15 min, and (c) 60 W-30 min.

Figs. 15b–d and 16a–c. It is obvious that when compared with surfaces of heat-cleaned fiber (Fig. 15a), the pp-fiber surfaces (especially, Figs. 15b,d) were covered with larger quantities of resin matrix and a greater number of fibers appeared to be embedded in the epoxy matrix after failure, indicating a higher fiber/matrix adhesion. Moreover, the surface of the pp-glass fibers is not as clean as the surface of the heat-cleaned glass fibers. However, as far as the SEM micrograph for 60 W-5 min (Fig. 16a) is concerned, the fiber surface (Fig. 15a) is almost similar to that of the heat-cleaned glass fiber. This may be due to fact that fiber surfaces were subjected to relatively short plasma exposure time.

4. CONCLUSION

Plasma polymerization of γ-GPS on the surface of glass fibers was carried out successfully by using a low frequency plasma generator. Deconvolution of XPS spectra of pp-glass fibers showed that relative concentrations of C-O, C-O-C (16.2%) and C-C, C-H (74.6%) groups was greatest at 60 W for 30 min in the studied range. It is interesting to note also that the relative concentration of the C-Si group (19.1%) at 60 W for 30 min was the lowest value among the C-Si groups. It may be proposed that interaction of epoxy matrix with C-O, C-O-C and C-C, C-H groups is responsible for the strength of adhesion between glass fibers and epoxy matrix. SEM observations of pp-glass fibers showed that the glass fiber surfaces become rougher as a result of plasma polymerization of glass fibers. Rough surfaces offer good fiber-resin mechanical interlocking. The maximum ILSS value was obtained at 60 W-30 min. IFSS results were shown to be agreement with ILSS results. These results indicate that the greatest interfacial adhesion between glass fiber and epoxy matrix occurred at 60 W-30 min. The strength of the glass fibers decreased at higher plasma powers. SEM micrographs of fracture surfaces of pp-glass fiber-reinforced epoxy composites confirm the improvement of adhesion between glass fibers and epoxy matrix as a result of plasma polymerization of glass fibers. As a result, plasma polymerization of γ-GPS on the surface of glass fibers at a plasma power of 60 W for an exposure time of 30 min are the most efficient parameters in the studied range for improvement of interlaminar shear strength of glass fiber/epoxy composite.

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