APPLICATION OF PLASMA POLYMERIZATION TECHNIQUE TO IMPROVE INTERFACIAL PROPERTIES OF GLASS FIBER/EPOXY COMPOSITES

Kutlay SEVER², Mehmet SARİKANAT², Yoldas SEKI², Haci Ali GÜLEÇ©
Mehmet MUTLU©, Ismail Hakki TAVMAN©

¹Department of Mechanical Engineering, Dokuz Eylül University, 35100 Bornova, Izmir, Turkey
²Department of Mechanical Engineering, Ege University, 35100 Bornova, Izmir, Turkey
©Department of Food Engineering, Yuzuncu Yil University, 65080, Van, Turkey
©Department of Chemistry, Dokuz Eylül University, 35160, Buca, Izmir, Turkey
©Department of Food Engineering, Hacettepe University, Ankara, Turkey

Abstract

In this study, plasma polymerization technique was used to modify the surface of glass fiber under various plasma powers (30, 60 and 90 W) for exposure time of 15 min to improve the compatibility between glass fiber and epoxy matrix. γ -glycidoxypropyltrimethoxysilane (γ-GPS) monomer were used for surface coating of glass fiber. Interfacial properties of composites were investigated by short beam shear test. Surface characterisation of plasma polymerized glass fiber was carried out by means of X-ray photoelectron spectroscopy (XPS). The organic/inorganic character of plasma polymerized γ-GPS (pp-GPS) glass fibers may be demonstrated by the C/Si ratio, which were obtained to be 3.7, 2.7 and 3.9 for 30, 60 and 90 W respectively. In other words, the organic character of pp-GPS glass fibers was highest at a plasma power of 90 W. From short beam shear test it has been reached that as the plasma power was increased from 30 to 90 W, interlaminar shear strength (ILSS) values increased. This indicates that the higher plasma powers exhibit the greater interfacial adhesion between glass fiber and epoxy matrix in the studied plasma power range.

Keywords: Polymer composite, Interface, Glass fiber, Plasma polymerization

1. Introduction

Advanced polymer composites have been widely utilized in structural applications due to their high specific strength and stiffness, good corrosion resistance and low thermal expansion relative to conventional metallic materials [1]. The mechanical properties of fiber-matrix composites depend not only on the properties of the fibers and matrices, but also on the nature of the fiber surface and the mechanism of load transfer from the fibers to the matrix at the interface [2]. However, composite materials have drawbacks such as poor interfacial adhesion between the fiber and the matrix resin [3]. To improve interfacial adhesion of composites, surface treatments such as silane treatments for glass fibers are widely used. Silane coupling agents are commonly applied onto glass fibers surfaces from liquid solutions in order to produce sizing, i.e. a functional film. However, it is known that the molecules of silane coupling agents have a tendency towards self-condensation, forming siloxane oligomers rather than complete bonding with the glass surface [4,5] and the density of finally formed siloxane bonds is low and the bonds are hydrolytically unstable [6]. Also, there are environmental concerns related to the disposal of chemicals after the treatment [7,8].

The low-pressure glow discharge has found a variety of important utilities in material science and engineering in recent years. Modification of surface of materials by low-pressure plasma treatment and/or deposition of nano-film has the advantage of producing very unique surface characteristics that cannot be obtained by other conventional means [9]. Also, thin films produced by plasma polymerization show suitable properties for a range of applications. The films are highly cross-linked, bond very strongly to almost every substrate and are relatively chemically and thermally stable [10, 11]. Moreover, plasma polymerized films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surface [12]. Shortly, cold plasma environments offer a unique way for modifying the chemical and physical structures of both fiber and polymer surfaces without altering the bulk structures and characteristics of these materials [13].

In the present work, we have focused on development of plasma-polymerized γ-GPS (pp-GPS) films on glass fiber for its possible application as functional interfacial layer. The plasma polymerized fibers were then characterized using an X-ray photoelectron spectrometer (XPS). The influence of plasma polymerization of glass fibers on interlaminar shear strength (ILSS) of the glass fiber/epoxy composites was investigated.

2. Experimental Details

2.1. Materials

The glass fibers (E glass, 2400 tex, mean diameter 21 μm) purchased from Cam Elyaf Corp. of Turkey. The silane coupling agent was γ-glycidoxypropyltrimethoxysilane (γ-GPS) supplied by Dow Corning Corp. under the commercial name of Z-6040. The epoxy system used was composed of two parts: R 1040 (unmodified liquid epoxy resin) and R 1048 (hardener), both supplied by Resoltech Corp., France. The resin is mixed with hardener (mixing ratio 78:22 wt %) before molding and curing.
2.2. Plasma Polymerization of γ-GPS on Glass Fibers

The pp-γ-GPS films on glass fibers were deposited using a low frequency (LF) source (Model Pico, Diener Electronic GmbH + Co., Germany) at a power of 200 W and frequency of 40 kHz. The series of depositions in this study were performed at plasma powers of 30, 60 and 90 W for 15 min. A plasma polymerization procedure was as follows: the glass fibers were put inside the vacuum chamber and then the chamber was evacuated to a pressure of 0.12 mbar. In order to bring away impurities and to ensure a uniform gas atmosphere before the plasma polymerization of γ-GPS monomer, argon gas was introduced into the chamber for 10 min at a pressure of 0.3 mbar. And then, the chamber was evacuated to approximately 0.12 mbar again. Thereafter, the monomer gas was allowed to flow through the chamber for 5 min at a pressure of 0.16 - 0.17 mbar. For each plasma polymerization treatment, the pressure and flow rates were always adjusted to the same values to guarantee similar conditions. Then, the glass fibers were exposed to plasma polymerization treatment for 15 min at plasma powers of 30 W, 60 W and 90 W. At the end of the process, argon gas was introduced into the chamber for 10 min at a pressure of 0.3 mbar to deactivate free radicals.

2.3. Composite Fabrication

The epoxy resin and hardener mixture were applied onto the untreated and the plasma polymerized glass fibers by a hand lay-up technique. Unidirectional (UD) glass fibers reinforced epoxy composites with width of 12 mm, thickness of 6 mm and length of 35 mm were fabricated in a teflon mold for each plasma polymerization treatment, which was then cured for 3 h at 90ºC.

2.4. X-Photon Spectroscopy (XPS) Analysis

The surface chemistry of the untreated and plasma polymerized glass fibers was determined by X-ray photoelectron spectroscopy (XPS) using a Specss Esca instrument (Germany). The spectrometer was equipped with a non-monochromatic Mg Kα radiation source at a power of 200 W at 10 kV. The spectra were collected using Mg Kα radiation source and EA 200 hemispherical electrostatic energy analyzer. All measurements took place at operating pressures of less than 10⁻⁸ torr.

2.5. Interlaminar Shear Strength (ILSS) Testing

According to ASTM standard D 2344, ILSS tests of UD composites were performed on a computer controlled Shimadzu AUTOGRAPH AG-G Series universal testing machine. A sliding roller three-point bending fixture includes a loading pin (diameter 6.4 mm) and two support pins (diameter 3.2 mm). The test fixture was mounted in a 5-kN capacity, screw-driven load frame. For the ILSS tests of the composite, a support span/ sample thickness ratio of 5:1 at a constant speed of 1.3 mm/min was used. At least four samples were tested for each type of UD composite to check for repeatability.

3. Results and Discussion

3.1. XPS Analysis

In order to evaluate surface composition of glass fibers, XPS analyses of plasma polymerized (pp)-glass fibers were investigated. The elemental composition of pp-glass fibers was obtained from the integral intensities of the C1s, O1s, and Si2p signal of the XPS spectra recorded. The theoretical composition of γ-GPS monomer is one silicon atom, five oxygen atoms and nine carbon atoms; that is, the O/C, C/Si and O/Si ratios are 0.56, 9 and 5, respectively. The atomic concentration of pp- glass fibers were summarized in Figure 1. The compositions of C atoms of pp glass fiber are 40.4, 34.4 and 44.8 % for 30, 60 and 90 W, respectively. The atomic concentrations of O atoms were obtained to be 48.7, 52.8 and 43.8 % for 30, 60 and 90 W, respectively. The greatest O content was observed at a plasma power of 60 W for 15 min. The contents of Si atom seem to be 10.9, 12.8 and 11.4 % for 30, 60 and 90 W, respectively. The O/C, C/Si and O/Si ratios for each type of fiber were given in Figure 2. It can be seen that the O/C ratio for untreated fiber seems to be 1.5. The ratio of oxygen atoms to carbon atoms was highest for 60 W. The smallest O/C ratio was observed at 90W. The organic/inorganic character of pp-GPS glass fibers may be expressed by the C/Si ratios, which are 3.7, 2.7 and 3.9 for 30, 60 and 90 W respectively. The C/Si ratio of monomer is 9. Probably it indicates that the monomer is highly fragmented in the discharge, some fragments are probably evacuated and a carbosiloxane network may be formed. The organic character of pp-GPS glass fibers was highest at 90 W. Additionally, inorganic character of pp-GPS glass fibers was the highest at 60 W. The O/Si ratio seems to be the highest for 30 W. It can be noted that when plasma power increases, O/Si ratio decreases. Cech et al., (2003) used Hexamethyldisiloxane (HMDSO) and vinyltriethoxysilane (VTES) monomer vapors for plasma polymerization of thin films which were deposited on microscope slides, silicon wafers and glass fibers. They reported that plasma polymers deposited at high power are unstable in a chemical and physical sense showing the aging effect, which is unsuitable for most applications.

Figure 1. Atomic Concentration of pp-GPS glass fiber surface
In order to evaluate the interfacial adhesion of the composite, we have compared the ILSS values of pp-glass fibers reinforced epoxy composites. ILSS results of plasma polymerized glass fibers (at different plasma powers) reinforced epoxy composites were shown in Figure 3. From this figure, it is seen that the plasma polymerization of glass fibers with γ-GPS improves the ILSS values of glass fiber-epoxy composites. For better adhesion of glass fibers to epoxy matrix, plasma polymerization of glass fibers with γ-GPS monomer at a plasma power of 90 W for 15 min may be more suitable.

Figure 3. The effect of plasma power on ILSS

4. Conclusion

From XPS Analysis it is inferred that plasma polymerization of γ-glycidoxypropyltrimethoxysilane on the surface of glass fibers at different plasma powers (30, 60, 90 W) for 15 min were carried out successfully. Interlaminar shear stress (ILSS) values showed that at higher plasma power (90 W in this study) causes better adhesion between glass fiber and epoxy matrix.