PRODUCTION OF THERMOPLASTIC COMPOSITES FROM CARBON FIBERS TREATED BY DIELECTRIC BARRIER DISCHARGE

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Abstract
This study deals with the production and characterization of carbon-reinforced polypropylene (CF/PP) composites from carbon fibers (CFs) treated by an atmospheric pressure dielectric barrier discharge (DBD). Following the treatment the CFs were characterized by Raman spectroscopy, which demonstrated that there were no major changes in the fiber crystalline structure after the treatment. X-ray photoelectron spectroscopy (XPS) analysis revealed an incorporation of oxygen containing polar groups on the fiber surface. Atomic force microscopy (AFM) indicated that the plasma species attacked the CF surface and changed its roughness. Interlaminar shear strength test (short-beam) and subsequent observation of the composites cross-section by scanning electron microscopy (SEM) demonstrated a greater resistance to shear of the composites made with CFs treated by DBD.

1 Introduction

Fiber-reinforced composites are high-performance engineering materials widely applied in aerospace, marine and automobile industry due to their favourable properties, such as, low specific weight, high resistance to corrosion and erosion, enhanced toughness, excellent fire resistance and high mechanical strength. In the last decades carbon fibers (CFs) have been extensively used in order to improve mechanical properties of polymer composites. However, the mechanical performance of composite materials depends not only on the matrix and fiber properties, but also relays on the adhesion in the fiber/matrix interface [1]. In the production of composite material it is essential to have good adhesion between the carbon fiber and the polymer matrix [2]. Therefore, plasma processing of carbon fibers is aimed to enhance the adhesion between the composite layers without decreasing the carbon fiber mechanical resistance [3-4]. This surface modification is originated by introduction of chemical functional groups and surface morphology alteration during the treatment, without changing the structure of the fiber [5].

The DBD process has two major advantages over other types of plasma technologies: the operation at atmospheric pressure, thereby shortening the process time and reducing the

capital costs invested in equipment and the ability to be performed on an industrial scale. Studies have been undertaken in order to automate the DBD process and apply it in industrial processes [6]. Some areas that require high technology and large-scale production, such as the aerospace, marine and automobile industry [7], have adopted the DBD as a process of surface modification. Currently many different materials, such as polyester textile materials [8], twaron fibers [5], epoxy composites [9], some types of fibers such as aramid [10], polypropylene [11] and even carbon nanotubes [12] have been treated with atmospheric pressure plasmas in order to improve their surface properties.

Inside of this context, this study deals with the production of carbon fiber-reinforced polypropylene (CF/PP) composites from CFs treated by an atmospheric pressure dielectric barrier discharge (DBD). Plasma processing of carbon fibers is aimed to enhance the adhesion between the composite layers, and thus increasing the shear strength of the composite. Following the treatment the CFs were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The mechanical properties of composites samples produced from as-received and treated CFs were evaluated by interlaminar shear resistance test (short-beam) and subsequent observation of the fracture by scanning electron microscopy (SEM). A relationship between the treatment time and the shear resistance of fiber composites treated by DBD was obtained.

2 Experimental

2.1 Materials

2.1.1 Carbon Fiber

The polyacrylonitrile fibers were purchased from Hexcel Company (USA) with plain weave fabric style, containing 3000 monofilaments in each tow with epoxy coating (sizing), code AGP-193-P. Each CF monofilament has diameter of around 8 μm. The fibers were used as received.

2.1.2 polypropylene (PP)

The PP matrix was used in the form of film with 0.85 mm of thickness. It was handed over by the Polibrasil Resinas industry, it is called isotactic polypropylene with the code: PP. The material presented density of 0.95 g/cm^3 and a melting point of approximately 170 °C.

2.2 DBD treatment

The DBD reactor used in this work consists of two planar circular stainless-steel electrodes covered by a 2 mm-thick glass plate. The air gap between both dielectric layers was 4 mm. CF samples were placed on the bottom electrode, which was connected to a power supply, that consists of a high-voltage transformer (Vrms 110/20000), powered by an autotransformer Variac operating at frequency of 60 Hz. A high-voltage resistance (1 kΩ) protects the transformer in the event of electric arc. The upper reactor electrode was grounded. The DBD consists of large number of filamentary discharges randomly distributed over entire dielectric. The discharge power was set to 6.6 W and the CF substrates of 7.0 cm x 7.0 cm were placed on the glass layer covering the bottom electrode. The treatment times were set at 2, 5, 7.5 and 10 minutes while the voltage peak-to-peak amplitude was kept fixed at 35 kV.

2.3 Composite Manufacture

Carbon fiber-reinforced polypropylene (CF/PP) composites were produced by hot compression molding process. Treated and as received fibers (7.0 cm x 7.0 cm) were stacked in 15 layers, with intercalating films of PP between the fabric carbon fibers. A vacuum bag

was made around these laminate in order to release the air between the composite layers (throughout pressing, the vacuum remained renovated). The laminates of CF/PP were placed in a press, Solab model SL - 11, and heated to 180 °C. A pressure of 2 MPa was applied, and the material remained in that condition for one hour. Then the heating was turned off and the material naturally cooled to room temperature. This procedure produced composite laminates with a thickness of approximately 2.5 mm

2.4 CF Characterization

Atomic Force Microscope (AFM) measurements were performed using a Veeco microscope - Digital Instruments, model Nanoscope V to assess the surface roughness of control and treated fibers. The analysis was performed in air and under the microscope operating in the intermittent contact ("Tapping Mode") with the silicon tip 50 N/m vibrating at a frequency of 0.5 Hz. The analyzed areas were of 8.0μm x 8.0μm size and the topography was characterized by rms roughness (Rq), automatically calculated by software supplied with the equipment. Raman spectra of the samples were obtained by a Raman imaging microscope system (Renishaw System 2000) with Ar^+ laser (λ=514.5 nm) as an excitation source. The radiation penetration depth is estimated to be ~5.0 μm. The surface chemical characterization was carried out by X-ray photoelectron spectroscopy on a Kratos XSAM 800 spectrometer, using Mg Kα radiation and fixed analyzer transmission mode (80 and 40 eV pass energies for the wide scan and detailed spectra, respectively). The spectra were referenced to the C1s line (binding energy, BE=285.0 eV) of the hydrocarbon type carbon. Data acquisition, quantification and peak fitting were performed with the Kratos Vision 2 software.

2.5 Carbon fiber-reinforced polypropylene (CF/PP) Characterization

Interlaminar shear resistance test were conducted to evaluate the effect of the DBD plasma treatment on the adhesion between CFs and the polymer matrix (PP). The tests were performed according to the D 2344/D 2344M–00 [13] standard. Ten samples of 2.5 mm x 5.0 mm x 15.0 mm were cut and tested in a universal testing machine Shimadzu, model Autograph AG-X. The peak force was recorded and the shear strength of the composites was calculated by the equation (1).

$$P = 0.75 \times \frac{F}{w \times t} \tag{1}$$

Where P is the short-beam strength (MPa), F is the maximum load observed during the test (N), w is the measured specimen width (mm) and t is the measured specimen thickness (mm). The purposes of this characterization are: first to evaluate if there was actually a shear failure in the tested composites (to be able to validate the test in accordance with standard [13]) and second to determine which was the failure mechanism: cohesive or adhesive. The analysis of scanning electron microscopy were made with the JEOL microscope, model JSM 5310.

3 Results and discussions

3.1 Raman spectroscopy

The main reason for using this technique is to verify whether there were any changes in the positions of order (G) and disorder (D) peaks, indicating a modification in the atomic structure of the fiber. The treated and untreated CF samples were analyzed and detected Raman spectra are presented in Figure 1.

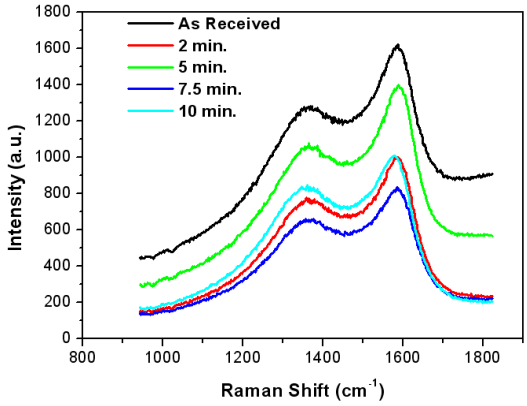

Figure 1. Raman spectra of carbon fibers untreated and DBD treated at different times

Examining the spectra and comparing the positions of the peaks, can be concluded that the D and G bands centered at 1368 and 1573 cm^{-1}, respectively, are very close to the ones cited in the literature [14, 15]. The values of D/G ratios were determined (Table 1) and a slight increase was observed. So despite the plasma treatment, no significant changes in the D and G bands positions could be observed. Therefore it can be concluded that the plasma treatment induced no substancial changes in the bulk structure of the fiber, as also inferred by other authors [16].

3.2 X-ray photoelectron spectroscopy (XPS)

The XPS is an important surface characterization technique. This analyses was used to asses the influence of the DBD treatment on the chemical composition of the CFs surfaces. According to the results presented in Figure 2a, the C-content of the surface slightly decreases with treatment time from 77.6 to 74.8 at. %. Simultaneously, the oxygen content of the surface gradually increases from 18.4 to 20.9 at. %. There is also an incorporation of nitrogen upon air DBD-treatment. Its amount ranges from 4 to 4.5 at. %. In other words, the CF chemical composition does not seem to change significantly with the treatment time.

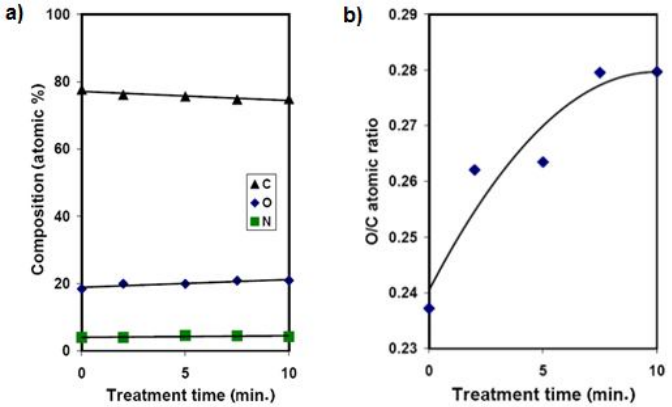

Figure 2. (a) Surface chemical composition of carbon fibers as a function to DBD treatment time (b) The ratio O/C on the surface of the carbon fiber in relation to DBD treatment time

The O/C atomic ratio of the surface layer grows with treatment time tending to saturation beyond 10 min. (Figure 2b). This fact indicates that the concentration of oxidized species increases on the carbon fiber surface due to the plasma exposure, and also the concentration of C-C and C-H species is reduced. According to some authors [17] in the DBD processing, energetic species from the plasma (electrons, uv-photons etc.) break preferentially C-C and

C-H bonds, then oxygen is added on the polymeric surface by formation of polar groups: C-O, C=O and C-H-O. This process leads to enhanced surface energy.

Figure 3 summarizes the results from deconvolution of the C1s peak with the variation of DBD treatment time. A decrease in the relative intensity of the C1 Component (285.0 eV, carbon in C-C and C-H type bonds) from 49.4 to 43.6 % can be observed. The relative intensity of the C2 component at 286.7 eV (Mainly C-O, but also some C-N type bonds) grows from 41.3 to 44.6 %, as also seen in [18]. Finally, the C3 Component (289.4 eV, carboxyl and/or ester type or similar bonds) tends to increase slightly.

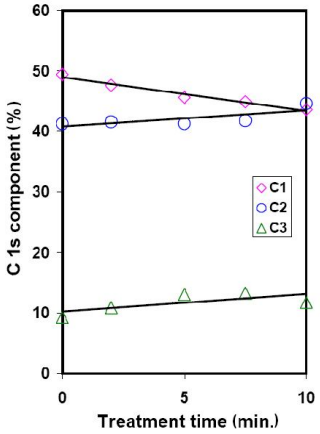

Figure 3. Evolution of the components of the C1s peak versus time of DBD treatment (C1) C–C, C–H; (C2) C–O, C–N; (C3) O=C−O

Both, the increase in C2 component and the oxygen incorporation, evidenced by the increase of the O/C, indicate that the DBD treatment turns the CF surface more polar with an enhanced surface energy, as also observed by other plasma treatments [14, 18]. So the DBD treatment of CF would contribuit for a stronger fiber/matrix interface, fact confirmed by Interlaminar shear strength test.

3.3 Atomic force microscopy (AFM)

The surface roughness of the carbon fibers was analyzed by the AFM analyses. The root-mean-square values (Rq) are presented in Table 1.

Time of Treatment (min.)	Rq roughness (nm)	D/G ratio
0	14	2.2
2	37	2.5
5	15	2.4
7.5	38	2.5
10	14	2.7

Table 1. Some properties of carbon fibers at different DBD treatmet times

The roughness varies with DBD treatment time, as shown in Table 1. The surface roughness increased from 14 nm for the untreated sample up to approximately 38 nm for samples treated at 2 min and 7,5 min. A non monotonic behaviour of the roughness with the increase of the treatment time was observed. This finding was also noted by Silva et al [18]. They investigated the effect of nitrogen and air plasma immersion ion implantation on carbon fibers. The variation of the roughness is due to the plasma etching during the DBD treatment.

Since the surface roughness does not grow linearly with the treatment time (behavior also seen in [18]), it is necessary to optimize the treatment time in order to obtain a greater adhesion between the fiber/polymer matrix.

3.4 Interlaminar shear strength test (short-beam)
The results of the ILSS analyses are shown in Figure 4.

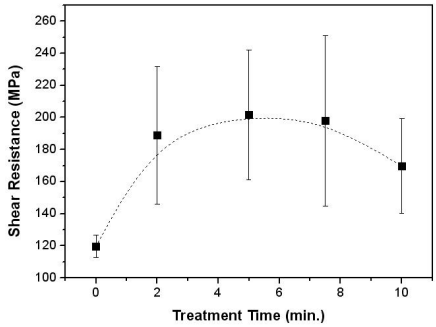

Figure 4. Interfacial shear strength of the CF/PP composites as a function of DBD treatment

As can be observed in Figure 4, there is an enhancement of the shear strength from 120 MPa up to 200 MPa for the sample treated for 5 min (an increase of 67%). Following this increase an opposite tendency took place leading to a reduction of shear strength to about 170 MPa for the 10 min. treated sample. This fact is explained by the combination of two phenomena that influence the shear strength: the increase of the roughness and the introduction of polar groups on CF compete with the decrease of the mechanical strength of the fiber, promoted by the etching. However it is important to emphasize that despite this shear strength reduction, the composites still keep a higher resistance than the untreated one.

The mechanism of CF plasma modification can be explained as follows: the CF surface is attacked by the plasma and the aromatic bonds in the basal plain are broken and atoms are added on the surface. As a result number of active sites on the CF surface is achieved, thus enabling strong adhesion to the resin, like observed in [19]

3.5 Scanning electron microscopy (SEM)
Figure 6 presents the images of the composites cross section. The image of the composite before the shearing test, (figure 5(a)) does not exhibit voids and cracks. The figure 5(b) presents the composite after the shear test. It helps to elucidate one of the objectives of this characterization, that the composites really failed by shear, so the standard is valid. This finding is very important, as shown in [20].

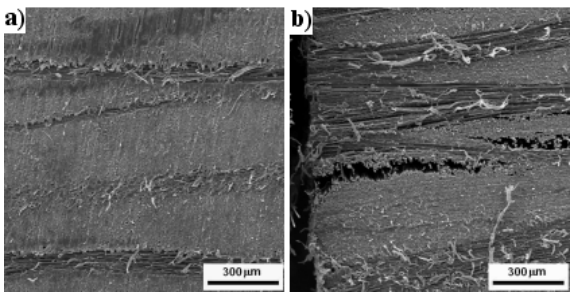

Figure 5. Composite 5min DBD treated (a) not sheared (b) sheared

Figure 6 answers the second objective of this characterization. In this case, it can be observed that the mechanism of failure is adhesive because of the visible detachment of the fiber from the matrix. Therefore, despite the enhanced adhesion between CF/PP, promoted by the treatment, the failure occured in this critical region.

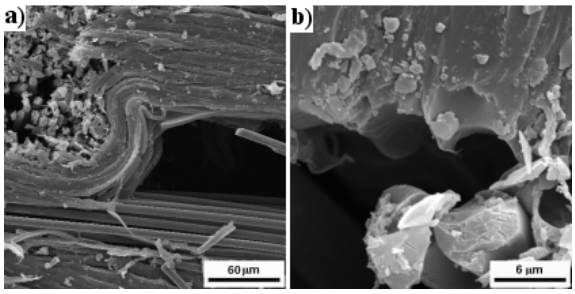

Figure 6. Detachment of the PP from the carbon fiber (a) 2min treatment (b) 5min treatment

4 Conclusions

Thermoplastic composites materials with carbon fibers treated by air dielectric barrier discharge (DBD) using different processing times have been obtained. Surface structural modification happened during the DBD treatment. This behaviour was confirmed by AFM results, which showed a variation of surface roughness. Furthermore, Raman spectroscopy analysis showed that there were no significant changes in the fiber atomic structure after the treatment. The XPS results demonstrated an increase in the O/C of the fiber surface that was caused by the introduction of polar groups on the fiber. For all obtained composites the shear strength tests showed an improvement in the fiber/matrix adhesion. The best composite improvement was reached at 5min. DBD treatment, beyond this treatment time the shear strength declines because of reduction in mechanical strength of the fiber, due to treatment. SEM images showed that there actually was shear in the tested samples, and in spite of increased adhesion in CF/PP interface the failure mechanism still happened by adhesion. In conclusion, DBD treatment of CF proved to be a useful tool for increasing the shear strength of composites.

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