SYNTHESIS OF THERMOPLASTIC COMPOSITES FROM CARBON FIBERS TREATED BY PLASMA IMMERSION ION IMPLANTATION (PIII)

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Abstract

This paper deals with synthesis of thermoplastic composites from CFs treated by PIII processing at different treatment times, 2, 5, 10 and 15 min. The characterization of CFs samples was carried out using the following analyses: SEM, XPS, AFM and Raman spectroscopy. After this previous characterization of the CF reinforcement, the thermoplastic laminate was produced using hot compression molding technology. The laminate was characterized by Interlaminar shear test (ILSS) and SEM analysis. After the PIII treatments there was an increase in the surface roughness and an introduction of the polar groups on the carbon fiber surface. These modifications enhance the adhesion in the composites interface as confirmed by ILSS tests that show up to double increase in the shear strenght in comparison to composites obtained from untreated CFs.

1 Introduction

Composites materials are usually employed in aerospace, marine, automotive industries and for production of sporting gear. Currently, for improving the interfacial adhesion between polymeric matrix and carbon fibers (CFs) in fiber-reinforced composites different kinds of surface modification techiques have been applied [1-7]. Most of them relay on introducing polar groups and/or appreciable roughness changes on the carbon fiber surface. Plasma immersion ion implantaton (PIII) arises as an alternative surface modification process due to its advantages, such as, treating of irregularly-shaped samples, possibility of conducting treatments at different temperatures, relatively low hardware cost and also the possibility of treating a variety of materials [8]. In this work, carbon fibers were implanted by nitrogen and air PIII to modify their chemical and physical properties aiming to achieve improvement in the interfacial adhesion between carbon fiber and polypropylene matrix (CF/PP) composites. Therefore, it is necessary to derive correlations between the surface morphology and surface chemistry of the CFs and the reinforcement effect. The reinforcement effect can be estimated

by the apparent interlaminar shear strenght. Delamination or interlaminar failure is a critical failure mechanism for fiber-reinforced composites and, therefore, has already been studied extensively by other authors [9, 16]. However, by our knowlodge, there is only one work [10] that deals with the effect of nitrogen and air plasma immersion ion implantation on the properties of CFs for improvement the adhesion on the composite interface.

For analysing the interaction between the carbon fibers surface and polymer matrix (PP), the XPS, SEM, Raman e AFM analyses were performed. After these characterizations of the reinforcement, the thermoplastic laminate was processed using hot compression molding technology. This laminate was characterized by Interlaminar shear test (ILSS) and SEM analysis.

2 Materials and testing methods

2.1 Materials

2.1.1 Polypropylene (PP)

The polymeric matrix utilized in this study was polypropylene (PP) film produced by the Polibrasil Resina industry (code: RF 6146K). The material has density of 0.95 g/cm^3 and a melting point of 165-175°C.

2.1.2 Carbon Fiber(CFs)

The CFs (Hexcel Company-USA) in the form of plain weave with 3000 monofilaments per town were used. The mean diameter of 8 μm was measured from the cross section of single CF by SEM analysis. The CFs were produced by Hexcel (code: F3G282(0)"-GR) and their specific mass is 1.77 g/cm^3.

2.2 PIII Processing

The CFs samples (10 x 10 cm) were fit inside a hollow steel frames that were fixed on a sample holder for PIII processing. The CFs to be treated were immersed in nitrogen or air glow discharge plasma and pulsed with high negative voltage. Positive ions extracted from the plasma werere implanted at normal incidence into all sides of the target. The samples were treated for 2.0, 5.0, 10.0 and 15.0 minutes. All other process parameters were kept fixed: working pressure of 6x10^{-3} mbar, 200Hz pulse repetition frequency, 3.0 kV voltage amplitude and pulse width of 20 μs. The detailed description of the PIII system was given in [11].

2.3 CFs Characterization

The Atomic Force Microscope (AFM) measurements were performed using a Veeco microscope - Digital Instruments, model Nanoscope V to analyse the surface roughness of control and treated fibers. The analyzed area was 8μm x 8μm. The morphological changes on the surface of untreated and treated carbon fibers were examined by JEOL microscope; model JSM 5310. 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 using 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 C 1s 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.

The mechanical properties of composite samples produced from as-received and treated carbon fibers were evaluated by interlaminar shear resistance test (short-beam) and following observation of the fracture by SEM analysis.

2.4 Composites Manufacture

Carbon-reinforced polypropylene (CF/PP) laminates were produced by hot compression molding process. Treated and as received fibers were stacked in 15 layers, with intercalating films of PP between the fabric carbon fibers. A vacuum bag was made around this laminate in order to release the air between the composite layers (throughout pressing, the vacuum remained renovated). The laminate 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 laminates with a thickness of approximately 2.5 mm.

2.5 Interlaminar shear resistance test

Interlaminar shear resistance test were conducted to evaluate the effect of the PIII treatment on the adhesion between CFs and the polymer matrix (PP). The tests were performed according to D 2344/D 2344M standard [12]. Ten samples of 2.5mm x 5.0mm x 15.0mm 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).

$$P = 0.75 \times \frac{F}{w \times t} \qquad (1)$$

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 the standard [12] 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 Carbon fibers characterization

SEM micrographs of all PIII-treated samples show some modifications on the CFs surface after the treatment. Figure 1 shows the images for untreated and air/nitrogen PIII treated CFs for 5 min. The micrograph depicts narrow grooves in the longitudinal directon on the untreated CFs (Figure 1a), originated from its manufacturing while heterogeneity was observed on the treated samples (Figure 1b-c). One can observe small particles distributed on the entire treated CFs surface that were possibly produced due to the sputtering during the PIII processing. The sputtering can remove the layer (sizing) that cover the untreated CFs and subsequently redeposit some material on the surface as inferred by other authors [13].

Consequently, there was an increase in the surface roughness, which was confirmed by AFM results for both treatments (Table 1 and Figure 2).

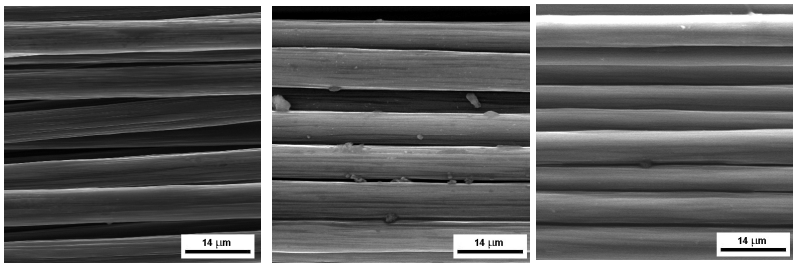

Figure 1: SEM images: a) untreated CF. c) Air-PIII treated CF at 5 min. c) N-PIII treated CF at 5 min.

The rms roughness (Rq) increased up to 6.5 times for N-PIII treated sample at 5 min. compared to the untreated one (Rq=14 nm). For the sample treated in air for 2 min, the roughness is up to 5.5 times higher than the one of the untreated specimen. However, as the treatment time further increases, the implantation dose is intensified and a decrease of the roughness is observed, as can be seen in Table 1.

Time of treatment (min)	**Roughness (Rq in nm)**	
	Nitrogen	**Air**
Untreated CF	14.00	14.00
2	25.10	76.50
5	90.90	40.3
10	46.90	68.5
15	14.00	40.5

Table 1. Roughness values of CFs

Figure 2 presents the AFM images for an as received sample and a nitrogen PIII-treated sample for 5 min. SEM and AFM results were reported by Silva et al. in [10], where the effect of nitrogen and air plasma immersion ion implantation treatment on the properties of carbon fiber were investigated.

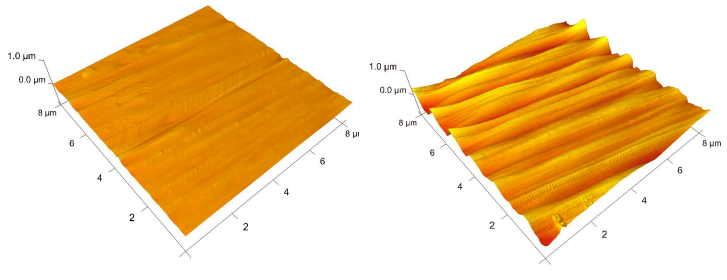

Figure 2: AFM images: a) untreated CF. b) N-PIII treated CF for 5 minutes.

The surface chemical composition of the CF samples was investigated by XPS analysis and the results are presented in the Table 2. Generally, the XPS analysis of all PIII-treated samples detected an increase of the nitrogen content with the treatment time. For the 15 min PIII-treated CFs, the nitrogen content was about 50% higher than the one of the untreated CF (4.2%) while the oxygen content decreases around 20% as compared to the control sample (29.4%). Additionally, an increase of the oxygen content (~6%) was also observed for air-PIII treated sample at 15 minutes in comparison with the untreated specimen (~24 at.%). These surface modifications would enhance the wettabillity of CFs, thus intensifying the adhesion to the composite interface as inferred in [10].

Time of treatment (minutes)	**C (at %)**	**O (at. %)**	**N (at %)**
	Air-PIII Treatment		
Control	72.3	24.1	3.7
2	69.2	26.8	4.1
5	69.1	26.7	4.2
10	68.0	27.4	4.6
15	69.6	25.6	4.8
	N-PIII Treatment		
Control	66.4	29.4	4.2
2	71.2	25.5	3.3
5	70.0	26.1	3.9
10	69.7	26.1	4.2
15	70.2	23.5	6.3

Table 2. Surface composition of CFs

Raman spectra of all carbon fibers (untreated and treated ones) exhibit the characteristic D (disordered) and G (ordered or graphitic) bands located at about 1376 cm^{-1} and 1594 cm^{-1}, respectively. The difference between the peaks positions and areas of treated and the untreated fibers is insignificant. Therefore, one can conclude that there was not a significant change in the crystalline structure of carbon fiber after the PIII treatment. These results are close to those presented by other authors [1, 14], who studied the treatment of carbon fibers by other types of plasma.

3.2 Polypropylene/CFs composites characterization

Interlaminar shear strength (ILSS) test was conducted to evaluate the effect of the PIII treatment on the adhesion between CFs and the polymer matrix (PP). Figure 4 depicts the values obtained from this test for N-PIII treated samples. As can be seen in the Figure 4, there was an increase of the interlaminar shear strenght for all composites obtained from PIII-treated carbon fibers in comparison with that obtained from untreated CF (121.3 MPa). However, the higher ILSS values (235.7 MPa and 193.5 MPa) are attributed to the composites obtained from N-PIII-treated CFs at 5 min. and 2 min., which exhibit an increase of the interlaminar shear strenght about 94% and 60%, respectively. For the samples treated at a higher treatment time (≥ 5 min.), the ILSS values tend to decrease. This behavior is in agreement with the roughness values obtained from the AFM measurements, because an

decrease of the roughness was also observed at these treatment times. This fact can be explained by the more intense sputtering that occurs for the longer PIII processing time.

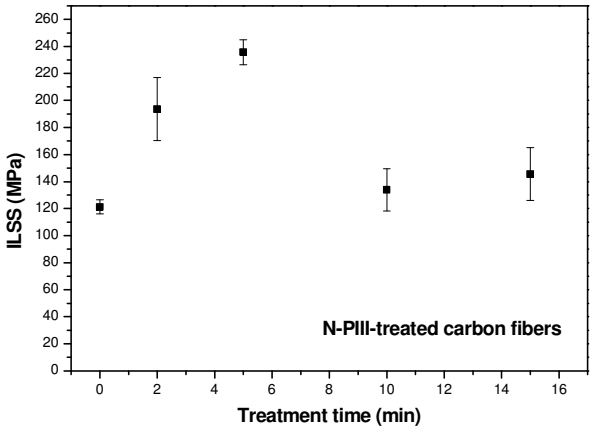

Figure 4. Interfacial shear strength of the CF/PP composites as a function of N-PIII treatment time.

Thus, the main factor that promotes better adhesion on the PP/CFs interface of the obtained composites is the roughness due to the better mechanical ancorage between the individual plies of the composite without decrease of the carbon fiber mechanical resistance as inferred by other authors in [7, 15].

From the XPS results, the highest nitrogen (6.3%) and oxygen contents (29.4%) were achieved for CFs treated at 15 min. and for untreated CFs, respectively. The polar groups on the CFs surface do not contribute significantly to the adhesion in the composite interface since they do not improve interlaminar shear strenght for these cases, as can be seen in the Figure 4. Furthermore, their roughness values for the obtained composites are low, which is not favorable for good adhesion on the composite interface.

After the thermoplastic laminates were processed, their cross sections were examined by scanning electron microscopy (SEM), as can be observed in Figure 5.

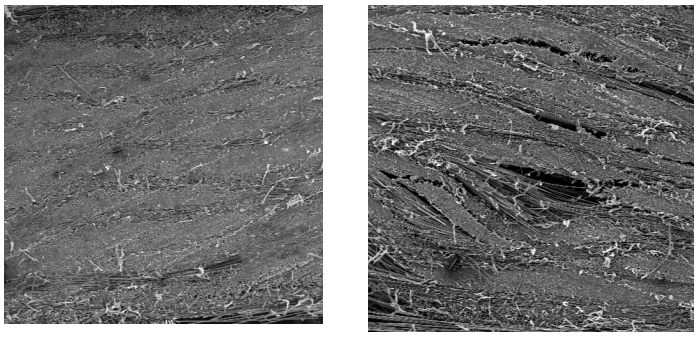

Figure 5: N-PIII-treated composites: (a) not sheared (b) sheared

The image of the cross section composite obtained from 5 min treated CFs before the ILSS test (Figure 5a) presents homogeous features without the presence of voids and/or cracks. While for the same composite after the ILSS test, a typical image of the sheared composite was noted (Figure 5b) characterized by the presence of darker voids and/or cracks distributted among the plies in the composite. This behavior was found for all PIII-treated composites that is in agreement with the study presented in [9], in which the authors investigated the mechanical behavior of carbon fiber reinforced polyamide composites.

4 Conclusions

Thermoplastic composites from carbon fibers treated by nitrogen and air PIII using different treatment times have been obtained. Raman spectra showed insignificant differences in D and G bands, indicating no changes in the crystalline structure of carbon fibers after the PIII process. AFM e SEM results confirmed the surface modification of carbon fibers after the treatment. There was an increase of surface roughness for both PIII treatments that contributes for producing more resistant composites by enhancing the mechanical anchorage between the polimeric resin and the carbon fiber. These features were confirmed by ILSS tests because there was an increase of the interfacial shear strenght up to 94% for the samples treated at 5 min. On the other hand, the introduction of nitrogen and oxygen was also detected by XPS analysis. However, the added elements are in small quantities and do not substantially contribute to the adhesion on the composite interface. Therefore, the PIII treatment showed as an alternative and efficient method for enhancing the adhesion between polypropylene and carbon fibers in the composite production.

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6 References

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