Improvement of the adhesion strength of PET/PMMA composite by radio frequency plasma treatment

[a]Cioffi, M. O. C., [a]Voorwald, H. J. C. and [b]Mota, R. P
[a] Department of Materials and Technology, [b] Department of Physics and chemistry
State University of São Paulo "Júlio Mesquita Filho",
Av. Ariberto Pereira da Cunha, 333 Cep 12516-410 Guaratinguetá-SP, BRAZIL.

ABSTRACT

The adhesion between polyethylene terephthalate (PET) fibres and polymethyl methacrylate (PMMA) matrix was analysed. The overall goal was to establish mechanical and chemical links between PET and PMMA, in order to increase the adhesion in their composites using cold plasma treatments. PET filaments were treated in a radio frequency (RF) plasma reactor using argon and oxygen as gas fuel. The excitation frequency was 13,56 MHz; the power of the electrical field 50 W, the pressure was set to 0,4 mbar and the treatment times were 5s, 20s, and 100s. Oxygen and argon plasmas were found to promote both chemical and mechanical anchoring by etching and sputtering mechanisms on the surface increasing fibre roughness. The mechanical strength modification of PET fibres was evaluated by pull-out tests of the treated and untreated PET monofilaments. The fibres were subsequently examined by scanning electron microscopy (SEM) to monitor changes of surface roughness. Results obtained showed that the cold plasma causes an increase of the adhesion strength of PET fibre/PMMA matrix and strong modification in the structure of the fibre surface.

Keywords: RF plasma; adhesion, PET/PMMA composite

* Corresponding author. Tel: +55-12-5252800 (r. 306); e-mail: cioffi@feg.unesp.br.

INTRODUCTION

Reinforcement of thermoplastics polymer like PET fibres/PMMA matrix composite results in a material with some improved characteristics such as low embrittlement, stability and high mechanical strength. In addition, the specific gravity of the PET fibres is 1,29 g/cm^3 less, which makes possible to produce a composite material with good mechanical properties and low specific mass. Conversely, it was recognised that the chemical inertness and the low surface energy of the PET fibres will make it difficult to achieve the adequate bond with a polymer to produce the composite[1-2]. The plasma treatment can be effective to improve the interfacial adhesion of the thermoplastics based composites[3]. By using excited-state chemistry in corona discharge, a number of polymers were modified before painting, printing and lamination[4]. Generally, oxidation on the fibre surface etched results in an increase in interfacial bond strength[5]. Gao and Zeng[6] concluded that the adhesion increases by at least four time by plasma treatment and, also, a slight decrease in the surface energy of the treated monofilaments with ageing time is observed. Because of this attractive attributes, plasma treatment of the fibre surface has been considered the prime technique for the control of adhesion in composites. However, the time of treatment is an important parameter to be considered because when it is long the fibers can be degraded and have their mechanical properties reduced. For the plasma treatment, no real increase in pull strength with treatment time was obtained for more than 5-10s[7]. In another work, it was observed that treatment time longer than 180s with argon plasma causes heavy degradation on the poly(tetrafluoroethylene) fiber surface[8]. In this work three different treatment times, 5s 20s, and 100s were used to obtain the adhesion improvement, by objecting, specifically, a treatment time with which there is an increase of the superficial energy without further degradation of the fibers. The oxygen and argon plasma were used to treat the PET in order to promote a perfect interfacial adhesion with the matrix. The experimental design was performed by pull-out test in order to investigate the adhesion of the interface PET/PMMA. SEM analysis of the pull-out specimens after oxygen and argon plasma treatment were realised.

EXPERIMENTAL

Materials

The polymethyl methacrylate resin was polymerized from the methyl methacrylate monomer by a thermal polymerization at 100ºC. The polyethylene therephthalate (PET) fiber provided by Montefiber SpA (Acerra,

Naples-Italy), has a filament diameter about 13 microns and the elastic modulus about 1 GPa.

The PET filaments were treated in a cold plasma reactor using oxygen **or** argon gases, according to the following conditions: excitation frequency was 13,56 MHz, the power of the electrical field was 50 W, the pressure of treatment was 0,3 mbar and the treatment time varied from 5 to 100 s.

For the pull-out tests in tensile mode, an INSTRON 4204 at a constant speed of 12 mm min^{-1} with a 10 N load cell, was used. The pull-out specimens were made according to Gao and Zeng.[6] As shown in Fig. 1, one end of a monofilament with 40cm in length was embedded in a disc of resin that rested in the metal cylindrical support which is attached to a base device; the other end is glued between two cardboard tabs and then fixed in a superior grip attached to the load cell of the equipment.

Figure 1 – Pull-out specimen

The thickness of the disc which determines the immersion length (*l*) of the PET monofilament in the resin disc was 3 mm. The diameter of the monofilament was measured by a scanning electron microscope and the interface area was calculated. The fibre resin adhesion τ was defined according to the expression (1):

$$\tau \equiv \frac{P}{\pi . d . l} \equiv \frac{\text{failure load}}{\text{interface area}} \qquad \textbf{(1)}$$

The surface morphology analysis was developed using a scanning electron microscope LEICA 440S. Gold coating of the samples was carried out using EMSCOPE SC 500.

RESULTS AND DISCUSSION

Adhesion

Table I indicates the results obtained for the pull-out tests with the treated and untreated fibres.

Table1 – Tensile strength and fibre/resin adhesion values of the untreated and treated PET fibres by cold plasma, obtained with pull-out tests.

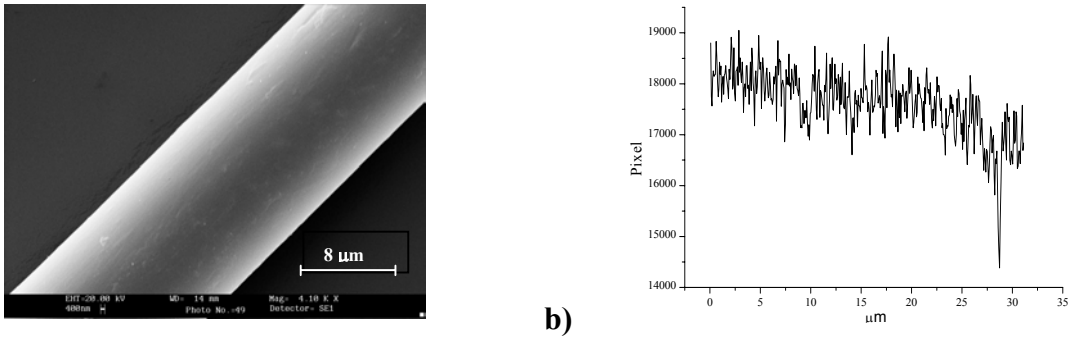
Treatment	Number of Sample	τ(MPa)	Sdt (MPa)	σmin(MPa)	σmax(MPa)	σu (MPa)
O_2 100”	4	895	116	833	1083	828
O_2 20”	8	862	96	650	975	816
O_2 5”	4	576	87	485	650	545
A_r 100”	6	931	161	668	1167	858
A_r 20”	4	792	139	650	975	748
A_r 5”	5	859	121	730	1048	829

It is possible to observe that the plasma treatments produce a significant effect on the fibre resin adhesion strength. Table I contains the number of specimens tested in each plasma treatment condition, the fibre

average tensile strength and the standard deviation, the minimum and maximum tensile strength and the fibre resin adhesion strength calculated according to equation (1). For the untreated fibre it was impossible to obtain the adhesion strength because the monofilament slighted from the resin disc as soon as the test stated. Experimental tests indicated that for all the treatment conditions the weakest point was the fibre, where the fracture occurred. In other words, the resin adhesion strength is higher than the fibre tensile strength, as shown in the Table 1. For the oxygen plasma treatment, the increase in treatment time from 5s to 20s resulted in an increase in the adhesion strength while for cold plasma treatment, the increase in the treatment time decrease the adhesion strength.

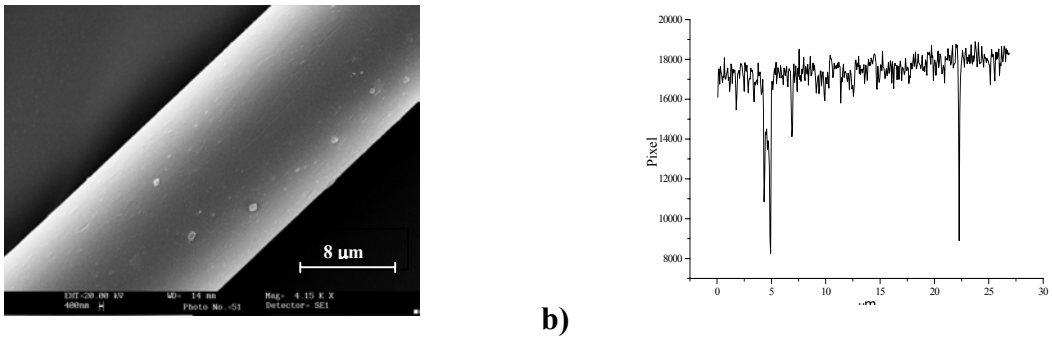
Scanning Electron Microscopy

Fibres surface of oxygen and argon plasma treated PET subsequently exposed to the matrix cure temperature, 100ºC and the roughness profile are represented in the figures 2 to 7.



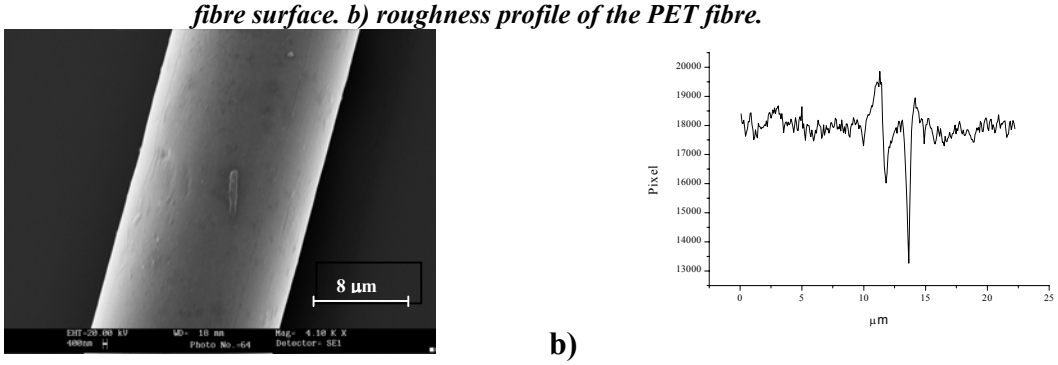
a) **b)**

Fig. 2 – Oxygen plasma treated PET fibres for 5s post heated at 100ºC a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre



a) **b)**

Fig. 3 – Oxygen plasma treated PET fibres for 20s post heated at 100ºC a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre.



a) **b)**

Fig. 4 – Oxygen plasma treated PET fibres for 100s post heated at 100ºC a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre.

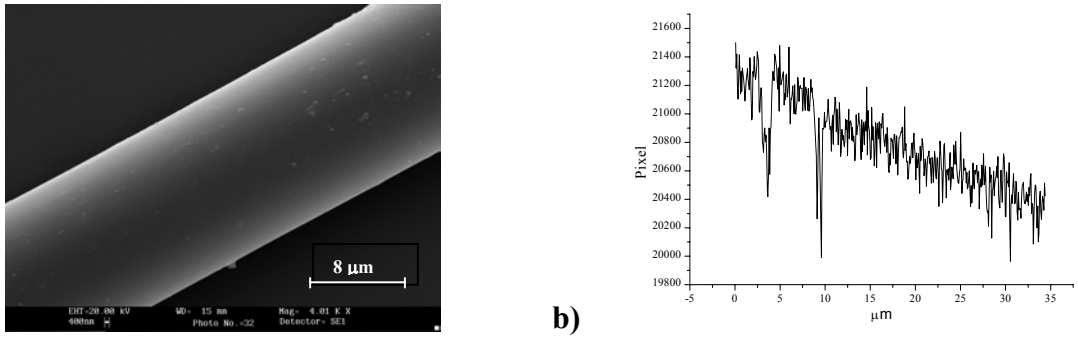


Fig. 5 – Argon plasma treated PET fibre for 5s post heated at 100ºC. a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre.

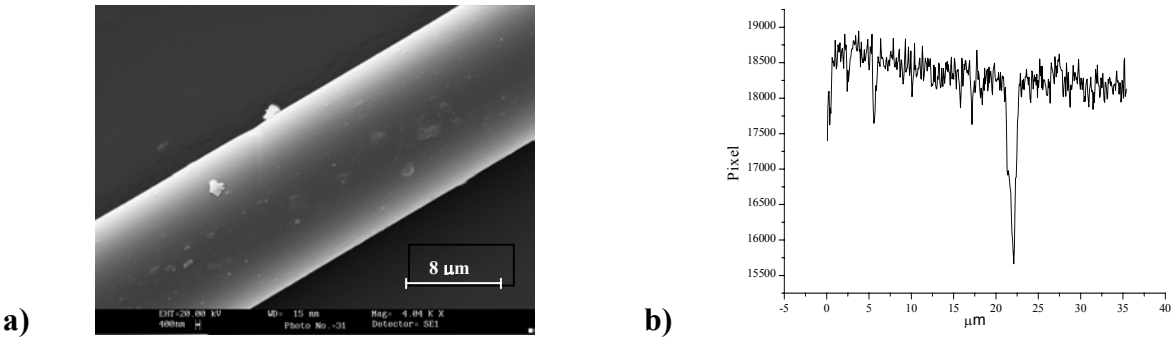


Fig. 6 – Argon plasma treated PET fibre for 20s post heated at 100ºC. a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre.

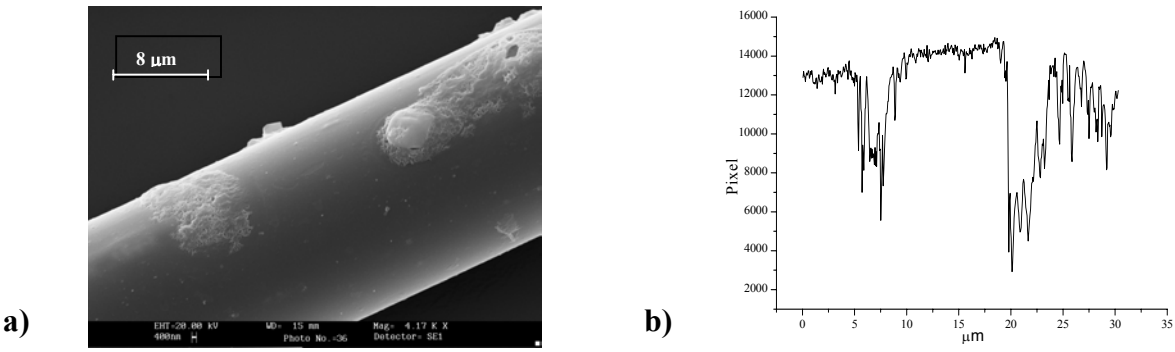


Fig. 7 Argon plasma treated PET fibre for 100s *post heated at 100ºC*. a) scanning electron microscopy of the fibre surface. b) roughness profile of the PET fibre.

Figures 2a to 7a represent the fracture surface of oxygen and argon plasma treated from 5s to 100s and post exposed to the matrix cure temperature, 100ºC. Roughness profile obtained through the scanning line method are represented in figures 2b to 7b and average distances of the roughness interval, for each condition, were calculated. The distances of the roughness interval (D_{ri}) for the oxygen plasma treated PET fibres from 5s to 100s post exposed at 100ºC were 0,44µm, 0,45µm and 0,57µm, respectively and for the argon plasma treated PET fibres from 5s to 100s post exposed at 100ºC were 0,59µm, 0,65µm and 0,99µm. As a comparison parameter, it is important to remember that D_{ri} is equal to 0,55 µm for the untreated fibres. Higher D_{ri} means less roughness peaks in the reference unit length; closely spaced surface defects are associated to low values of D_{ri}. On the other hand, surface analysis from figure 2a to 7a shows an intense

surface degradation on the fibres subjected to argon plasma. Roughness profile represented in figure 7b for argon plasma treatment 100s and post heated at 100°C confirms the significant reduction in the average tensile strength.

CONCLUSIONS

- The plasma treatments produce a significant effect on the fibre resin adhesion strength;
- For the untreated fibre it was impossible to obtain the adhesion strength due to the inertness and the low energy of PET fibres surface;
- For all treatment conditions the weakest point was the fibre, where the fracture occurred attesting that the fibre/resin adhesion strength is higher than the fibre tensile strength;
- The distance of roughness interval (D_{ri}) was a parameter obtained through the use of Scion Image Program and used to associate fibre surface condition after cold plasma treatment and average tensile strength. For oxygen and argon cold plasma treated fibres, D_{ri} is lower in comparison to the untreated fibres which explains decrease in the tensile strength. In some cases, higher roughness depth enhance stress concentration effects and influences mechanical behaviour.

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REFERENCES

1. WEIDNER et al, *J. applied pol. Sci. : Part A: Pol. che,*. 36, (1998) 1639-1648.
2. GOULD, S.A. C., SCHIRALDI, D. A. & OCCELLI, M. L. *J. applied pol. sci.* (1998) 1237-1243.
3. BLACKMAN, B. R. K., KINLOCH, A. J. & WATTS, J. F. *Composites*, 25/5 (1994) 332-341.
4. KILL, G., HUNTER, D. H. & McINTYRE, N. S. *J. pol. sci.: part A pol. che.*, 34 (1996) 2299-2310.
5. JANG, B. Z. *Comp. sci. Tech*. 44 (1992) 333-349.
6. GAO, S. & ZENG, Y. *J. applied pol. sci.* 47, (1993) 2065-2071.
7. OCCHIELLO, E. et. al. *Composites*. 23/3 (1992) 193-200.
8. INAGAKI, N., TASAKA, S. & GOTO, Y. J. applied pol. Sci. 66(1997) 77-84.