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Mechanical strength of cold plasma treated PET fibers

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In this work, the effects of cold plasma treatment on the mechanical strength of polyethyleneterephthalate (PET) fibers has been verified. Single fibers were treated with oxygen and a mixture of oxygen and tetrafluoroethylene in a cold plasma reactor for 30, 100 and 200 s. The single fibers were then tested in tensile mode and the mechanical strength was analyzed by using the Weibull distribution function. © *1999 Kluwer Academic Publishers*

1. Introduction

Mechanical properties of composite materials are strongly affected by the interfacial ability to transfer stresses from matrix to fibers. The nature of the interactions between the phases determines the adhesion between the matrix and the reinforcement and, as a consequence, it can result in the improvement of the mechanical properties of the composite.

Cold plasma treatment is widely used [1–3] to modify interfacial properties of polymeric materials. It can act either chemically, by introducing reactive groups on the fiber surface, and/or physically, by modifying surface morphology. Several mechanisms have been proposed to understand adhesion phenomena and its improvement, but no one satisfies completely the experimental evidence.

In this paper, the concern that a cold plasma exposure on polyethyleneterephthalate (PET) fiber surfaces could affect their mechanical properties has been considered. This topic has been treated in a large number of experimental studies on high modulus fibers, commonly employed as reinforcement in structural composites: carbon fibers, glass fibers, and polyethylene fibers. Less attention has been devoted to study degradative effects on PET fibers. Even though PET is widely studied as a material for packaging and textile applications, no experimental studies, so far as we know, have been published regarding this topic.

In this paper, statistical analysis is used to evaluate the effect of the plasma treatment on the mechanical strength of PET fibers. The necessity to use this approach is related to the presence of pre-existent defects and flaws on the surface [4]. These defects are generated during the fiber processing and, due to their nature, they produce a dispersion of data when mechanical strength is analyzed [5].

The Weibull distribution function can be considered one of the more suitable methods among the numerous ones used to analyze mechanical data of fibers. It is usually used to model the mechanical strength of metals and composite materials. The key concept of the Weibull theory is to consider a fiber of length l, as a chain constituted by n links: the natural flaw of the weakest link will determine the properties of the whole chain [6, 7]. This procedure was used to evaluate how a) the time of exposure and b) the type of gas employed affects the mechanical properties of PET fibers.

2. Materials and methods

PET fibers, supplied by Montefiber SpA (Acerra, Naples-Italy) were mounted on a special in-house built fiber holder (using a non-conductive material) and treated in a cold plasma reactor using O_2 or $CF_4 + O_2$ mixture (1 : 9, respectively); the excitation frequency was 13.56 MHz; the power of the electrical field was set at 20 W; the final pressure during treatment was 40 Pa and the treatment time was varied up to 200 s.

The plasma reactor used in this work is an internal parallel plate electrode type. The area of the ground and r. f. electrodes is 350 cm^2 for both electrodes and their distance is 3 cm. The sample is located, on the sample holder, at 1.5 cm from the electrodes.

The tensile strength of the single fiber was determined by using an INSTRON 4204 at a constant speed of 20 mm min^{-1} equipped with a 10 N load cell. The single fiber, delicately taken from yarn, was mounted on rectangular cardboard tabs with 30 mm gauge length in order to perfectly align fibers between grips (ASTM D3379-75).

Finally, the surface morphology was observed by means of a scanning electron microscopy (SEM). The microscope used was an HITACHI S-2300.

3. Results and discussion

The stress at break of the PET fiber has been statistically analyzed by using the Weibull cumulative distribution functions:

$$F(\sigma) = 1 - \exp\left\{ -\left[\frac{\sigma - \sigma_s}{\beta} \right]^{\alpha} \right\} \qquad (1)$$

where β, α and σ_s are material constants but they vary substantially with the surface condition, sample preparation and temperature: α is related to the shape of the distribution, σ_s is the largest stress at which the probability of failure is zero [8].

The analysis of the statistical distribution of the material strength is commonly performed by using the Weibull function and σ_s is usually taken equal to zero. As we will show below, this assumption is not always correct but it is a useful method for comparing data of different materials.

The tensile strength of the PET fibers was analyzed in this work either with $\sigma_s \neq 0$ or with $\sigma_s = 0$. In the first case, these three parameters were calculated by maximizing the likelihood function, utilizing the following procedures. Experimental results were compared with the theoretical curves obtained by taking the lnln transform of $F(\sigma)$ as follows:

$$\ln \ln[1 - F(\sigma)]^{-1} = \alpha \ln(\sigma - \sigma_s) - \alpha \ln \beta \qquad (2)$$

The data are reported as $\ln \ln (1 - p_i)^{-1}$ against $\ln \sigma_i$ where p_i is connected to the experimental cumulative distribution and is calculated as $p_i = i/(n+1)$ n being the total number of experimental values, and σ_i is the statistical order (the arrangement of all the data in increasing order). After the linearization, the values of σ_s were evaluated utilizing a trial and error method and by maximizing the correlation coefficient R of the linear fitting. This value of σ_s was then utilized to maximize the likelihood function by varying the two parameters α and β. In Figs 1 and 2 is reported the effect of the parameter σ_s on the alignment of the experimental data on the straight line for untreated PET fibers and for fibers treated with oxygen for 200 s.

In each cases the decrease in both shape parameter and scale parameter means that plasma treatment initially introduces additional defects of different nature and density (β) and secondly that the distribution of defects is more nonhomogeneous.

The results of the statistical analysis are presented in Tables I and II. Here, the best Weibull parameters are reported either for $\sigma_s \neq 0$ or for $\sigma_s = 0$. The higher values of R and the lower values of χ^2 observed for $\sigma_s \neq 0$ suggests that the best correlation of the experimental

TABLE I Weibull constants calculated for the case $\sigma_s \neq 0$

O_2						
Time	α	β	σ_s	σ_m	R	χ^2
0	1.07	129	420	549	0.988	0.0710
30	2.15	211	300	552	0.997	0.0220
100	5.56	135	349	484	0.996	0.0245
200	1.26	148	320	468	0.989	0.0800
$CF_4 + O_2$						
Time	α	β	σ_s	σ_m	R	χ^2
0	1.07	129	420	549	0.988	0.0710
30	1.48	170	400	570	0.988	0.0984
100	2.99	241	300	541	0.991	0.0746
200	2.05	148	300	448	0.994	0.0477

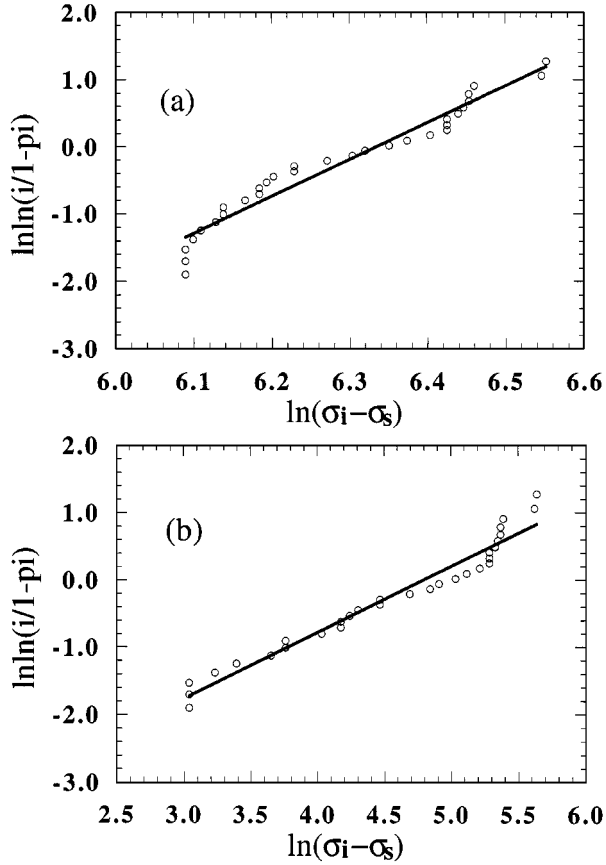

Figure 1 Linear representation of the experimental data and Weibull function of untreated PET single fibers: (a) $\sigma_s = 0$ MPa and (b) $\sigma_s =$ 420 MPa.

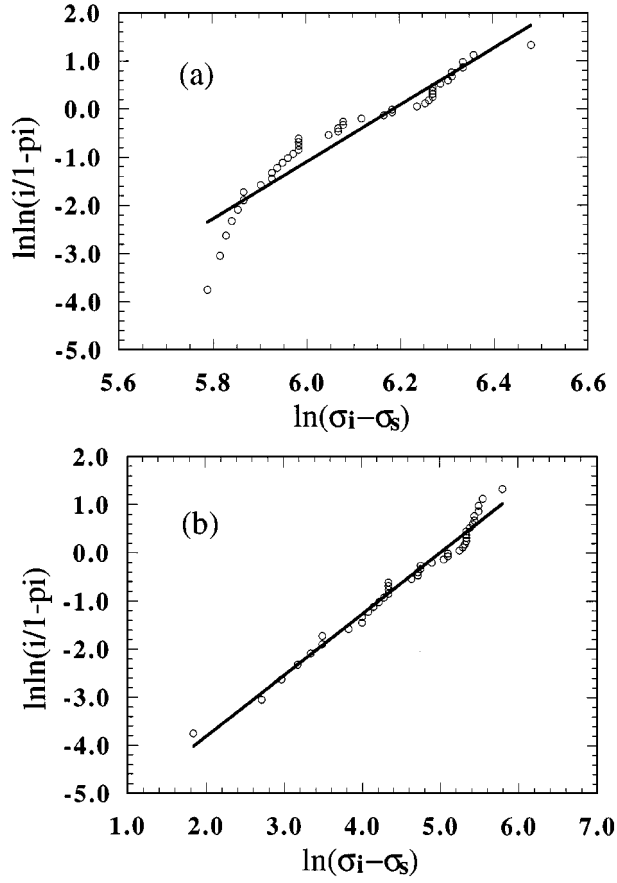

Figure 2 Linear representation of the experimental data and Weibull function of PET single fibers treated for 200 s with O_2: (a) $\sigma_s = 0$ MPa and (b) $\sigma_s = 320$ MPa.

TABLE II Weibull constants calculated for the case $\sigma_s = 0$

O_2					
Time	α	β	σ_m	R	χ^2
0	5.64	565	526	0.975	0.159
30	5.66	555	517	0.994	0.0504
100	5.56	488	557	0.987	0.104
200	4.93	484	449	0.984	0.122
$CF_4 + O_2$					
Time	α	β	σ_m	R	χ^2
0	5.64	565	526	0.975	0.159
30	6.40	579	543	0.992	0.073
100	6.84	541	509	0.989	0.099
200	5.30	478	445	0.983	0.150

data with the model can be obtained when the Weibull function includes the material constant σ_s. In this case, a good alignment of the experimental data on the straight line (Figs 1 and 2) suggests that the theoretical model is able to predict the statistical distribution of the tensile strength of the PET fibers. The lower values of σ_s of treated versus untreated samples (Table I) suggest that the minimum statistical allowable values for the tensile strength decreases when fibers are treated either with oxygen or with a mixture of oxygen and CF_4. This effect is accompanied by an increase of the shape parameter α and by a decreasing trend of the statistical mean σ_m calculated at $F = 0.5$.

Analogous comments can be drawn from the analysis carried out by using $\sigma_s = 0$ (Table II), even though the lower values of R and the higher values of χ^2 indicates a worse correlation between data and model. In Figs 3 and 4 are reported the cumulative distributions of the data regarding treated and untreated samples. The experimental data are compared with the theoretical prediction of the Weibull functions ($\sigma_s = 0$), reported in the same figures as continuous curves. Small variations are observed for treatment times up to 30 s where the values of σ_m are almost constant either for samples treated with O_2 or with $CF_4 + O_2$. PET fibers treated with oxygen for 100 and 200 s show that the plasma treatment induces a decrease of the tensile strength of the fibers. This decreasing trend is also present when oxygen is utilized in the plasma reactor in combination with CF_4. However, in the latter case, 100 s are not enough for determining a remarkable reduction of the tensile strength, as it appears in samples treated for 200 s.

The statistical analysis of the mechanical strength suggests that higher values of the treatment time induce some degradative effects that result in a lowering of the mechanical performances of the PET fiber filaments. It is not easy to explain the behavior of the tested samples because it is very difficult to demonstrate experimentally a proposed mechanism.

In our experiments we have seen degradation of mechanical properties of PET fibers but we have not detected: i) fiber diameter reduction, ii) localized defects due to plasma treatment and further iii) the degradative

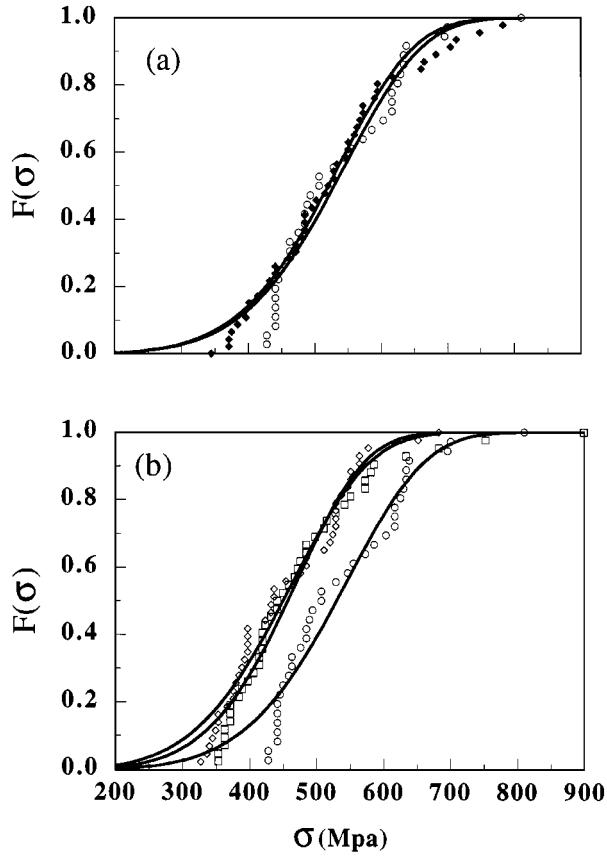

Figure 3 Cumulative distribution of the mechanical strength of PET single fibers treated with O_2: (a) untreated (○), 30 s (♦) and (b) untreated (○), 100 s (□), 200 s (◊).

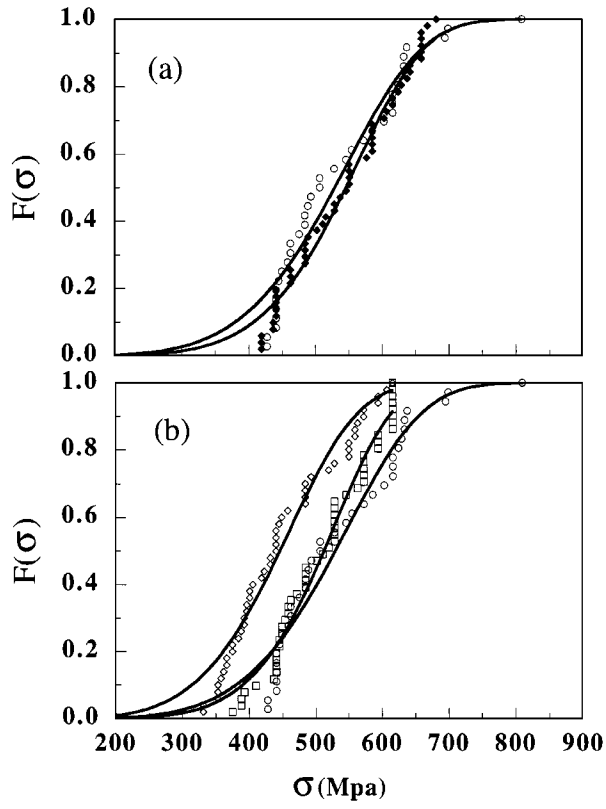

Figure 4 Cumulative distribution of the mechanical strength of PET single fibers with $O_2 + CF_4$: (a) untreated (○), 30 s (♦) and (b) untreated (○), 100 s (□), 200 s (◊).

effect is not a simple linear function of the treatment time.

SEM micrographs, reported in Fig. 5, show how the surface morphology of the PET fibers is modified by the plasma treatment. The presence of streaks and/or "islands" can be observed in both figures and this is more evident in fibers treated with CF_4–O_2 mixture. Strikes are a well known effect in the microelectronics field and during etching of polymer substrate [9] and their origin is from ionic bombardment or preferential etching. "Islands" have an unknown origin: some authors have shown that plasma produces etching and the particles observed on these surfaces can be related to the nucleating agents and other additives present in the material [10]. In our unpublished results we have demonstrate that "islands" size is not comparable with nucleating agents and other additives. It is also known [7] that plasma treatments on polymeric materials induce branching and/or cross-linking.

Further, if one takes into consideration that: i) the sample position is such that the substrate gains a floating potential, ii) very low r.f. power (0.06 W cm^{-2}), and iii) short treatment time (up 200 s) have been used, iv) ground and r.f. electrodes have the same area and v) the same effects have been detected using several types of gas; it is not possible to explain the origin of damage in terms of ionic bombardment or etching.

A possible justification for the observed reduction of the mechanical performances could be related to the formation of a thin layer on the fiber surface of a material having different physical-chemical characteristics from the bulk. The formation of this layer is due to the synergetic effect of electromagnetic radiation and a chemical reaction on the surface. The resulting reduction of the fiber strength is therefore determined by the embrittlement of the surface which could be related either to the properties of the external layer itself and/or to the presence of residual stresses induced by the different physical-chemical features between the modified layer and the unmodified core.

This mechanism could also explain the following points. An increase of the treatment time does not produce a progressive reduction of the mechanical performance of the fibers. When the material is subjected to the plasma treatment, there are two coexisting effects: an increase of the cross-linking density of the surface and an extension of the treatment depth. These two concurrent phenomena result in a non-linearity between damage and treatment time. The modification induced by the highly reactive plasma environment is effective only in certain ranges of time, and longer treatments do not produce additional effects. For this reason we do not observe differences in the strength distribution for fibers treated with oxygen for 100 and 200 s (Fig. 3). Moreover, if the reduction of the mechanical performances is related to the chemical modification of the external surface which includes reactions between PET and oxygen, then we should expect a decrease in the treatment efficiency when oxygen is employed together with another gas such as CF_4. In this case, 100 s are not enough to produce a significant effect on the mechanical strength, as shown in Fig. 4.

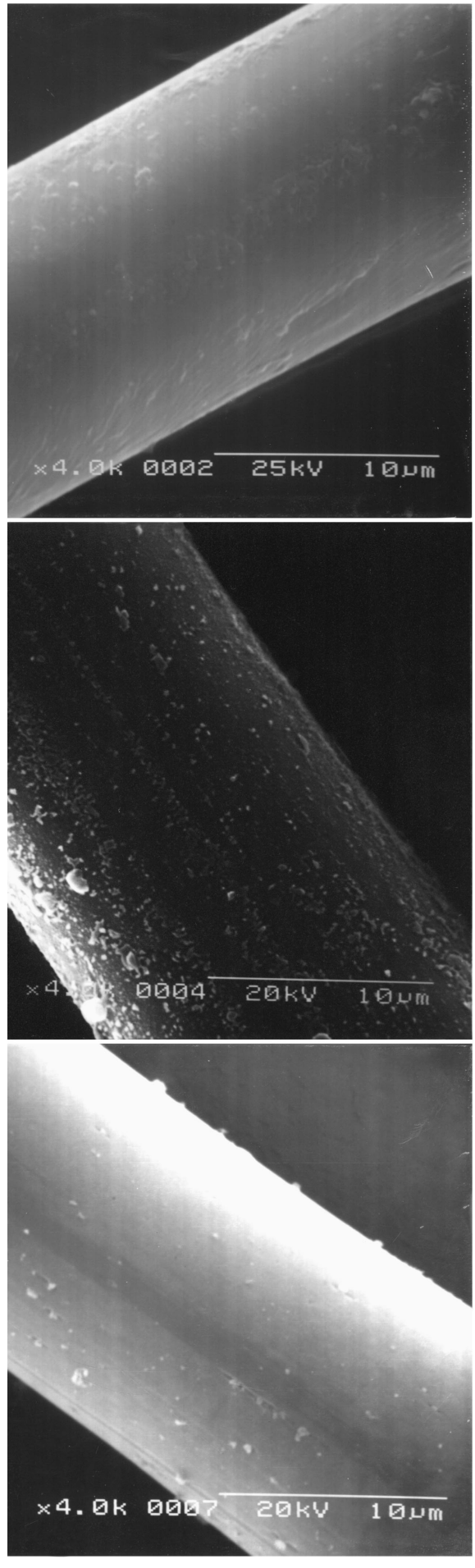

Figure 5 SEM micrograph of PET single fibers. From the top: treated with O_2 for 200 s, treated with $O_2 + CF_4$ for 200 s, untreated.

4. Conclusions

The effect of cold plasma treatment (O_2; $O_2 + CF_4$) on the statistical distribution of the mechanical strength of PET single fibers was analyzed. The results showed that degradative effects can be induced in the fibers when they are subjected to a suitable treatment time. The maximum decrease of the mechanical strength ($\sim 20\%$) was observed when plasma was applied for 200 s. Treatments with pure O_2 are more effective, compared to those with $O_2 + CF_4$, as justified by the higher reduction of the mechanical strength on fibers treated for 100 s.

The absence of an evident etching of the surface, as revealed by the SEM analysis, could not explain by itself the degradation of the mechanical properties. A possible justification of this behavior is proposed and it is based on the formation of an outer layer of chemically modified PET. This would influence the mechanism of crack initiation produced by either stress concentration effects and/or by the presence of microcracks which cannot be detected by micrography.

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