

Improvement of Adhesion of PET Fibers to Rubber by Argon-Oxygen Plasma Treatment

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ABSTRACT: Polyethylene terephthalate fibers cords were modified with argon, oxygen, and successive argon/oxygen cold plasmas as a function of treatment time. Plasma treated cords were coated with resorcinol formaldehyde latex, then tested as rubber reinforcing materials. The peel strength was discussed with respect to the polar component of the surface energy and the etching of the fibers. An increased adhesion of ~ 280% was obtained with 30 min argon plasma followed by 30 min oxygen plasma, at 75 W power and 40 Pa pressure without altering the traction strength of the fibers cords. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2321–2330, 1998

Key words: plasma; poly(ethylene terephthalate); RFL adhesive; wettability; adhesion

INTRODUCTION

The many problems of adhesion between a polymer and any sort of matrices have created interest in developing new techniques to improve this adhesion by different routes. The greatest adhesion strength at a polymer–polymer interface is through a primary covalent bond, since evidently chemical bonding is one of the strongest kinds of bond one can hope to form. Various mechanisms of adhesion are considered in numerous reviews, books, and articles in the literature^{1,2} to interpret the phenomenon relying on the two traditional physical approaches of thermodynamic and molecular kinetics. These permit one to examine the structure and properties of the upper layers of the polymers relative to the strength of adhesive joints. The main conclusion of the monograph confirms that the characteristics of adhesion are simultaneously affected by two particular properties of the polymers, namely surface energy and

macromolecular mobility, whose effects appear to be directly interrelated. These factors occur in the adhesion process which should be governed by three essential mechanisms: diffusion, adsorption, and interlocking. However, the mobility and the diffusive ability of macromolecular chains across the interface lead to a strong adhesion between the polymeric materials, the diffusion being dependent on the physical state of the polymer. The diffusion of a rubbery polymer can take place at the interface more easily than in the case of a glassy polymer, where it appears to be nearly impossible. The same can be said of a crosslinked polymer, where obviously the macromolecular chain motions are considerably reduced or totally absent.

For good diffusion, the wetting, which can be also considered as a kinetic phenomenon, favors an intimate contact of the macromolecules during the migration from the surface of one polymer to that of another. Therefore, good wetting and wettability of polymers is also necessary, indeed essential, for a good adsorption mechanism leading to the formation of molecular interactions such as van der Waals interactions, acid–base interactions, and interfacial hydrogen bonds.

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Diffusion, wetting, and adsorption are all factors on the microscopic scale. For the macroscopic scale, the mechanical interlocking can be applied as a technological way to achieve optimum adsorption. It is of course well known that an increase in the roughness of a solid³ increases the interaction area and the adhesive strength; however, there is not a linear function between strength and roughness, as experimental work has confirmed.

To provide an enhanced adhesive ability, the chemical nature of the surface of the polymers situated face-to-face have to be controlled. From the literature² one can deduce two possible concepts. The first of these involves increasing the surface energy of the polymers and to achieve that, polar groups need to be incorporated into their structure. For the second concept, ensuing from the principle of interfacial energy minimization, the energy barrier at the interface should be minimized to increase the adhesive strength. These two concepts are complementary and a better understanding of experimental results is obtained when they are combined.

Techniques to modify polymer surfaces include treatment with solvents, acidic or basic solutions, mechanical abrasion, graft reactions, activated chemisorption, or plasma treatment. Generally, of these various methods, plasma surface modification delivers the best results and a high ecological conformity.⁴⁻⁶ Low-temperature plasma is a well known technique in the surface modification of polymers, which maintains the desirable properties of the bulk material. The plasma treatment changes only the chemical nature and morphology of the substrate surface, the changes being dependent upon the composition of the gaseous medium and the processing parameters. These two factors are important when regarding the problem of increasing the adhesive ability.

Indeed, the properties of the modified surfaces are highly dependent on the experimental parameters, such as the generator, radio frequency, power of the electrical discharge, pressure and nature of the gas, and the duration of the treatment. Wettability of the surface and adhesion properties vary according to the nature of the plasma treatment. The literature contains numerous examples of plasma treatment for polymer surface modification.^{7,8} In particular, plasma modification of polyethylene terephthalate (PET) polymer surfaces has been carried out by many authors and the effective adhesion of plasma-

treated PET fibers in elastomeric matrices as rubber reinforcing materials studied.

Various gaseous media were used for PET modification by plasma treatment. In order to increase the wettability, PET films were treated in an argon glow discharge and the residual reactivity of the surface layers was captured by exposing the film to acrylic acid in the liquid and vapor phases.⁹ Treatment with cold CO₂ plasma was found to be an excellent method to increase the surface energy,¹⁰ while ammoniac plasma, as well as nitrogen plasma, have also been investigated.^{11,12} However, oxygen is the most currently used gas in plasma treatment¹³⁻¹⁵ leading to the introduction of C—O—, C=O and COO— groups onto the PET surface. The oxygen content decreases with the plasma treatment time since the polymer surface molecules will be preferentially cracked instead of additional oxygen groups being formed.¹³ Nevertheless, it seems that oxygen plasma gives the most oxygenated PET surface, which authors still try to correlate with a better adhesion.

PET fibers and PET films have commonly been oxygen plasma-treated, resulting in a strong increase in adhesion strength with copolyester elastomeric matrices.¹⁶ Generally, the oxygen plasma-treated fibers and cords are immersed in a resorcinol formaldehyde latex (RFL) adhesive to create, upon the PET surface, an oxygenated coating more compatible with the conventional functionalized rubber, in order to achieve the adhesion.^{12,14,15}

The purpose of this article is to describe an appropriate technique to increase the wettability of PET film by argon and oxygen plasma glow discharge and combined argon-oxygen treatments in order to select suitable processing parameters. The influence of the nature of gas, the power of the discharge, and the time of treatment are all reported. An aging study has been realized on the PET films. Subsequently, PET fiber cords were treated in the same way and used as reinforcing materials in a conventional rubber. Finally, the adhesive strength was estimated and correlated to the characteristics of the plasma-treated polymer.

EXPERIMENTAL

Sample Preparation

Commercially available PET films (Hoechst Selanese; 15 μm thick) were cut into 30 \times 30 mm

size specimens, cleaned with acetone and alcohol then rinsed with deionized water. Commercially available PET cords (0.9 mm diameter, 144 g/100 m) composed of twisted fibers (25 μm diameter) were prepared in the same manner before use.

Contact Angle Measurement

Static contact angles with water and diiodomethane were measured with a Kruss G1 apparatus 5 s after the drop was deposited to avoid evaporation or absorption by the film. Ten measurements on different surface locations were averaged for each sample. The error of measurement was $\pm 1^\circ$.

Contact angles of thin fibers were best determined by dynamic analysis, using the tensiometric method, called micro-Wilhelmy technique. A single filament is suspended from an electronic microbalance (Cahn/Ventron) and then immersed into the test liquid or emerged from the test liquid. The more general form of the relationship¹⁷ for the measured force F exerted on the fiber is reduced to $F = \gamma_L \pi D \cos \theta$ with γ_L the surface tension, D the fiber diameter, and θ the contact angle.

Surface energy γ_s , and its dispersive γ_s^d and polar γ_s^p components, were calculated by the Owens method using water and diiodomethane.¹⁸ The resulting superficial tensions are respectively $\gamma_L = 72.8$ mN/m, $\gamma_L^d = 21.8$ mN/m, $\gamma_L^p = 51.0$ mN/m for the water, and $\gamma_L = 50.8$ mN/m, $\gamma_L^d = 49.5$ mN/m, $\gamma_L^p = 1.3$ mN/m for the diiodomethane, L representing the liquid.

Adhesion Measurement

The fibers cords were incorporated by hot molding (15 min at 160°C) into a conventional styrene butadiene rubber matrix (sulfur vulcanized SBR) of ~ 15 cm \times 0.6 cm \times 0.3 cm size with a delay of 30 days after plasma treatment. Two reference samples were used: an RFL noncoated cord and a plasma untreated cord. All other samples were plasma-treated with argon, oxygen, or argon; then oxygen glow discharge- and RFL-coated. All experiments were conducted on five specimens (10 cm length), with each given plasma treatment. The strength required to draw out one cord of the rubber substrate is called the peel strength. To measure this, an Instron apparatus was used, all results are given with an accuracy of ± 1 N/cord.

The traction strength of the different cords was measured with the same Instron apparatus.

Scanning Electron Microscopy (SEM)

Electron micrographs were taken with a JEOL 6300F at the Electronic Laboratory of the University of Montpellier II, France.

Low-Temperature RF Plasma Apparatus

The experimental setup used for the plasma treatments is schematically illustrated in Figure 1. Glow discharge was generated by a 13.56 MHz radio frequency generator. The energy was coupled to a pair of parallel aluminum electrodes (13 cm in diameter, 3 cm separation distance) which are situated in a closed glass reactor. Dried film samples of ~ 9 cm² are set on the bottom electrode. Each cord sample was 1 m long and was rolled on a glass support which allowed no contact between the superposed cord buckles of ~ 8 cm diameter. A vacuum was then established and the gas flow monitored with a Pirani gauge regulated in order to obtain the desired pressure. In all cases, the gas pressure was 40 Pa. Though the power is adjustable during the discharge, the power level was established and stabilized at the beginning of the treatment. When the treatment period was finished, the RF power was turned off and the system again pumped down for 20 min. Surface wettability of the films was subsequently

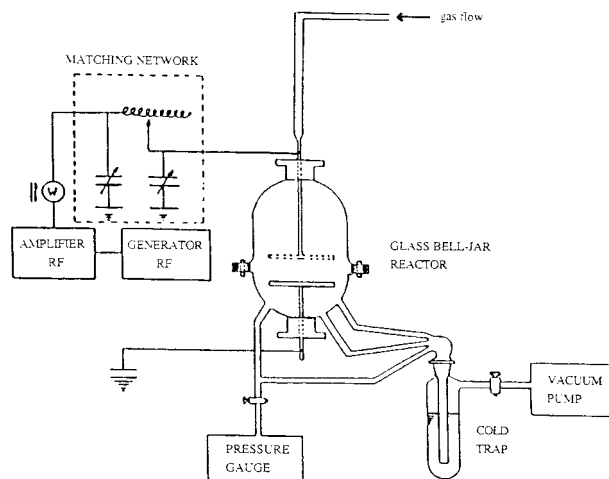


Figure 1 Experimental setup of the plasma apparatus.

Table I Different Plasma Treatments and Contact Angles $\theta_{\text{H}_2\text{O}}$ of a PET-Treated Film According to the Storage

Plasma Treatments			Contact Angle $\theta_{\text{H}_2\text{O}}$ (deg)	
Gas	Power (W)	Time (min)	1 h after Treatment	30 Day after Treatment
Argon	75	5	31	68
Argon	100	5	31	68
Argon	100	15	29	69
Oxygen	75	3	29	67
Oxygen	75	5	29	69
Oxygen	75	15	28	66
Argon/Oxygen	75	5/5	31	68

For a nontreated surface $\theta_{\text{H}_2\text{O}} = 76^\circ$.

determined at ~ 1 h, then 1 day, 4, 7, and 30 days after the end of the glow discharge treatment.

RESULTS AND DISCUSSION

One typical parameter to characterize the surface of a polymeric material is the surface free energy γ_S , which is the sum of the dispersive component γ_S^d and the polar component γ_S^p . These parameter values are obtained easily by measuring the contact angle between the PET film surface and a polar liquid (water) on one hand, and a nonpolar liquid (diiodomethane) on the other hand.¹⁸ They are commonly connected with the wettability and the hydrophilicity of the substrate surface.

A first study (Table I) showed the evaluation of

the wettability of PET plasma-treated films with respect to different experimental procedures of the plasma treatment. In all cases, the obtained water contact angle $\theta_{\text{H}_2\text{O}}$ was lower than that of untreated PET film. The value decreased from 76° to $\sim 30^\circ$ when measured one hour after the end of the plasma glow discharge. This value agrees well with the data of the literature.⁹ We can note that the power (75 W or 100 W) and the time of the treatment, from 3 to 15 min, slightly affect the $\theta_{\text{H}_2\text{O}}$ value whatever the gas used: argon, oxygen, or argon followed by oxygen. This value, $\theta_{\text{H}_2\text{O}} \sim 30^\circ$, suggested an improved wettability of the treated surface due to the oxidation. However, the value increases with storage time at ambient temperature (Fig. 2) and it attained $\sim 68^\circ$ after only five days. The measurements were continued

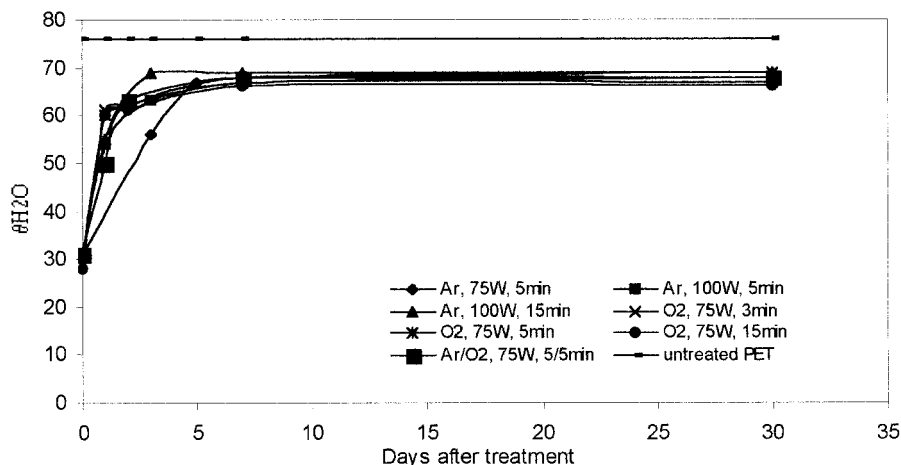


Figure 2 Contact angle $\theta_{\text{H}_2\text{O}}$ (deg) evolution of different plasma-treated PET films with storage time at ambient temperature.

Table II Different Plasma Treatments and Surface Energies γ_s , γ_s^p , γ_s^d of a PET-Treated Film

Plasma Treatments			Surface Energies (mN/m)					
			γ_s^p		γ_s^d		γ_s	
Gas	Power (W)	Time (min)	1 h after Treatment	30 Days after Treatment	1 h after Treatment	30 Days after Treatment	1 h after Treatment	30 Days after Treatment
Argon	75	5	38.0	9.9	25.8	35.0	63.8	44.9
Argon	100	5	34.9	9.9	29.8	35.0	64.7	44.9
Argon	100	15	35.1	9.2	31.1	35.6	66.2	44.8
Oxygen	75	3	33.1	10.2	34.1	35.8	67.2	46.0
Oxygen	75	5	33.3	9.4	33.7	35.1	67.0	44.5
Oxygen	75	15	34.2	11.1	33.2	34.6	67.4	45.7
Argon/Oxygen	75	5/5	33.3	10.3	32.2	33.9	65.5	44.2

For a nontreated surface $\gamma_s^p = 4.9$ mN/m, $\gamma_s^d = 40.0$ mN/m, and $\gamma_s = 44.9$ mN/m.

until 30 days after treatment, at which point the value was stable, but still less than that of a nontreated surface.

After the determination of the contact angles, the second step was to calculate the surface energy of the polymer for various treatment parameters. PET film possesses a relatively low surface energy due principally to the low polar component. Whatever the nature of the gas used during the glow discharge, the polar component was always greater than its initial value for untreated PET. A strong increase in γ_s , γ_s^p , and a decrease in γ_s^d were obtained at the end of each treatment. The respective values varied from 44.9 mN/m to ~ 66 mN/m for γ_s , from 4.9 mN/m to ~ 35 mN/m for γ_s^p , and from 40.0 mN/m to ~ 32 mN/m for γ_s^d (Table II). Thirty days after the

treatment, the polar component γ_s^p was ~ 10 mN/m. This value was stable and greater than the 4.9 mN/m corresponding to the untreated PET. The surface energy was similar to the initial value $\gamma_s = 44.9$ mN/m because the dispersive component did not raise the initial value. The improvement of the hydrophilicity appears to be permanent (Fig. 3); however, the duration of treatment (from 3 to 15 min) and the nature of the gas do not seem to be determining factors with regard to the characteristics of the PET film surface.

These preliminary results guided the selection of the experimental parameters used for the plasma treatment of the PET fibers. Essentially, the time of treatment was increased in order to find an equilibrium between the control of the degradation, then the roughness of the polymer sur-

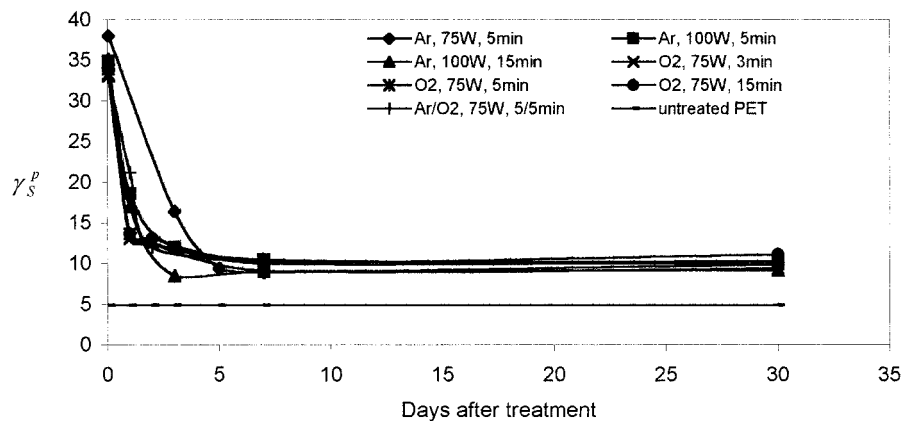


Figure 3 Evolution of γ_s^p surface energy polar component of different plasma-treated PET films with storage time at ambient temperature.

Table III Different Plasma Treatments and Contact Angle $\theta_{\text{H}_2\text{O}}$ of a PET-Treated Fiber

Plasma Treatments			Contact Angle $\theta_{\text{H}_2\text{O}}$ (deg)
Gas	Power (W)	Time (min)	30 Days after Treatment
Argon	75	5	69
Argon	75	30	70
Argon	75	60	65
Oxygen	75	5	67
Oxygen	75	30	73
Argon/Oxygen	75	5/5	74
Argon/Oxygen	75	15/15	55
Argon/Oxygen	75	30/5	73
Argon/Oxygen	75	30/30	63

For a nontreated fiber $\theta_{\text{H}_2\text{O}} = 79^\circ$.

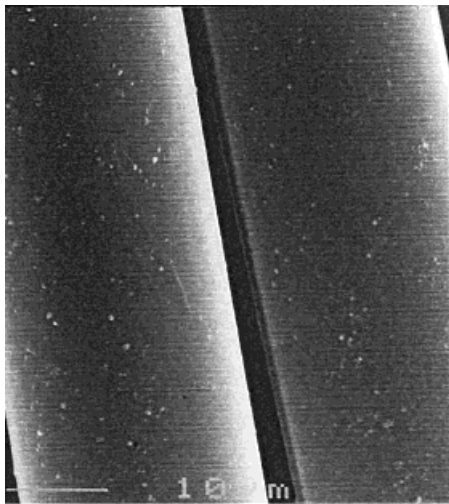
face, and the improvement of the wettability and the polar component. Table III shows that an increased duration is necessary to obtain a real modification of the surface wettability. Finally, the selected parameters, power of 75 W, argon 15 min followed by oxygen 15 min (argon/oxygen 15/15 min), give the lowest $\theta_{\text{H}_2\text{O}}$ value $\sim 55^\circ$, measured 30 days after the treatment. Contrary to what was discovered for the film samples, the polar component of the fiber surface energy was sensitive to the nature of the gas and the time of treatment. The γ_s^p values ranged between 9.8 mN/m while 22.5 mN/m and the γ_s^d value kept nearly constant (Table IV). With an argon/oxygen 15/15 min treatment, γ_s^p increases from 7.5

mN/m for the untreated fiber to 22.5 mN/m for the treated one. These selected parameters allowed one to verify the surface etching and the polar groups grafting to give a best hydrophilicity. Figures 4 and 5 show the SEM of untreated and plasma-treated fibers. We can note the relationship between the nature of the gas and the morphology of the surface. The untreated PET fiber surface displays some irregularities and defects which are due to the working up. They are easily visible at magnifications of 20,000 as well as 1200 (Fig. 4). For an argon plasma treatment of 5 min duration and 75 W power, the surface appears to be slightly bombastic with unequally etched zones [Fig. 5(a)]. The removal of the surface layer leads

Table IV Different Plasma Treatments and Surface Energies γ_s , γ_s^p , γ_s^d of a PET-Treated Fiber

Plasma Treatments			Surface Energy (mN/m) 30 Days after Treatment		
Gas	Power (W)	Time (min)	γ_s^p	γ_s^d	γ_s
Argon	75	5	12.6	27.4	40.0
Argon	75	30	12.3	27.7	40.0
Argon	75	60	15.1	27.6	42.7
Oxygen	75	5	14.3	25.9	40.2
Oxygen	75	30	10.6	27.2	37.8
Argon/Oxygen	75	5/5	9.8	27.2	37.0
Argon/Oxygen	75	15/15	22.5	25.5	48.0
Argon/Oxygen	75	30/5	10.2	27.7	37.9
Argon/Oxygen	75	30/30	16.5	27.3	43.8

For a nontreated fiber $\gamma_s^p = 7.5$ mN/m, $\gamma_s^d = 27.5$ mN/m, and $\gamma_s = 35.0$ mN/m.



(a)



(b)

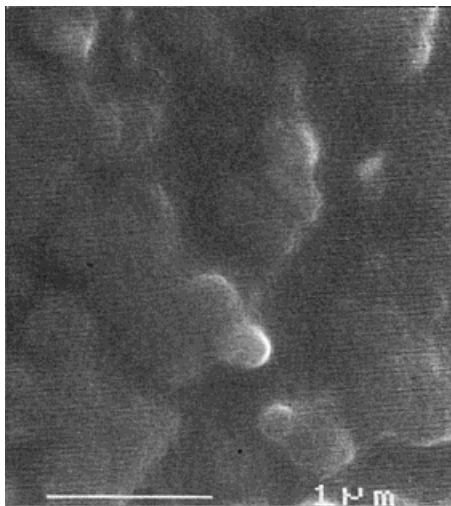
Figure 4 Scanning electron micrographs of untreated PET fiber. (a) $\times 1200$; (b) $\times 20,000$.

to an increase in the roughness, which is more and more apparent as the treatment time increases (photographs not shown). This effect is more strongly marked when oxygen gas is used [Fig. 5(b)]. The last photograph [Fig. 5(c)] suggests the associated effects of an argon treatment followed by an oxygen treatment. The roughness of this surface is widely different from those treated with only argon or oxygen and far more accentuated than that of the untreated fiber surface.

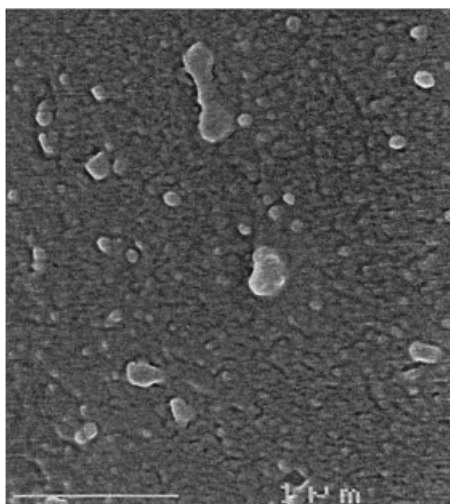
The plasma-treated fibers were tested as rubber reinforcing materials according to the elementary method described in the experimental sec-

tion. The goal of this article was only to verify whether the various plasma treatments we have carried out were able to activate the fiber surface to make it more receptive to adhesive. The adhesion comparison tests were realized with plasma treated fibers cords which were immersed in the usual RFL adhesive. A proof which was not adhesive-coated was used as a reference for each plasma treatment. The results of the previously definite peel strength are gathered in Table V. When the cords were not RFL-coated before plasma treatment, the improvement of the adhesion was not significant. The increase of the peel strength was very weak from 16 N/cord for the reference cord to 18 N/cord whatever the kind of treatment. The 25 N/cord peel strength value of the RFL coated but untreated cord shows that, of course, RFL adhesive allowed a better contact between the cord and the rubber. Nevertheless, only an increase of $\sim 56\%$ was obtained. At the end of the adhesion tests, a visual appreciation with an ordinary optical microscope showed the PET cord slid out of the elastomeric matrix without extracting any fragments or particles of rubber. On the contrary, the PET cord partially lost the RFL-coated layer. So, the adhesion strength between the PET cord and the RFL adhesive was not efficient enough. Next, the cords were plasma-treated before immersing them in the RFL adhesive. The composite system with the rubber matrix was prepared in the same way. Therefore, the peel strength was significantly higher and the adhesion largely improved whatever plasma treatment had been used. If we consider the nature of the plasma treatment, the best result was obtained for a 75 W, 30/30 min, argon then oxygen plasma treatment for which the peel strength was increased from 25 N/cord to 70 N/cord, $\sim 280\%$ of the reference peel strength value. It seems that in this last treatment the different effects of the argon plasma followed by the oxygen plasma on the roughness and the hydrophilicity were accumulated.

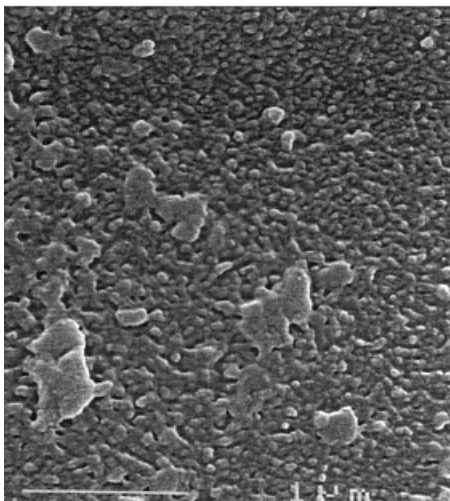
Many authors^{4,19} agree with the explanation of the origin of the oxygen grafted onto the polymer surface with argon plasma treatment, which leads to increased polarity. It is a product of interactions between radicals remaining on the treated surface and oxygen from the air when the samples are taken from the reaction vessel. This hypothesis implies a long lifetime for the radicals. Moreover, the oxygen grafting can occur during plasma treatment by the reaction of gaseous oxygen and



(a)



(b)



(c)

water, which could be present in the reactor vessel, with activated species such as radicals produced, from argon glow discharge onto the PET fiber surface.

The increase in wettability and the decrease of the polar component of the surface energy with storage time can generally be explained by a restructuring of the surface²⁰⁻²² in order to minimize the interfacial energy with air and attain a new stable thermodynamic equilibrium. This adaptability of the polymer surface to the environment was observed in the case of argon plasma, oxygen plasma, and argon/oxygen plasma in our experiments. The plasma treatment issue is an oxidation of macromolecules by oxygenated groups ($-\text{COOR}$, $-\text{COOH}$, $-\text{CO}-$, $-\text{OH}$) grafting and a probable formation of low molecular chains.^{11,15} The resulting effect is more and more marked when the treatment time increases. The consequence is a slight alteration and an etching of the surface. The short macromolecular chains produced may be compared to plasticizer molecules inducing a decrease in the glass transition temperature of the surface layer. The high number of conformations of the short macromolecular chains and their resulting mobility can facilitate the reorientation of polar groups toward the polymer bulk.

Comparison of the results of the peel tests, which were carried out using plasma-treated and RFL-coated fiber cords before introducing them in the elastomeric matrix, showed that the adhesion was not solely dependent on the γ_s^p value. Indeed, the greatest γ_s^p value (22.5 mN/m) for the argon/oxygen 15/15 plasma did not lead to an increased peel strength. The best result was obtained with argon/oxygen 30/30 corresponding to a γ_s^p value ~ 16.5 mN/m.

It seems evident that the increase in the overall treatment time from 30 to 60 min allowed a more effective degradation of the fiber and, at the same time, a decrease of γ_s^p .

The shorter treatment times would favor adhesion by the increase in the surface polarity, whereas the longer treatment times would allow a better mechanical anchorage and an easier diffusion of the low molecular weights from the fiber surface to the RFL coating to complete the adhesion.

The contact angle measurement concerns only

Figure 5 Scanning electron micrographs of plasma-treated PET fiber. (a) Argon 5 min; (b) Oxygen 5 min; (c) Argon/oxygen 5/5 min.

Table V Different Plasma Treatments and Peel Strength of PET-Treated Cord Incorporated in a Rubber Matrix

Plasma Treatments			Peel Strength (N/cord)	
Gas	Power (W)	Time (min)	RFL Uncoated Cord	RFL Coated Cord
Untreated Cord			16	25
Argon	75	5	17	48
Argon	75	30	18	61
Argon	75	60	18	65
Oxygen	75	5	18	54
Oxygen	75	30	18	54
Argon/Oxygen	75	5/5	18	57
Argon/Oxygen	75	15/15	18	63
Argon/Oxygen	75	30/5	18	55
Argon/Oxygen	75	30/30	18	70

1–2 nm depth from the extreme surface of the polymer and cannot correctly account for the phenomena of migration and interpenetration of the molecules during the formation of the adhesive layer. We can reasonably consider that the oxidized fragments produced by discharge treatment and macromolecular chain scission as represented in Figure 6^{23,24} are able to migrate from PET fiber surface to RFL coating to form an interdiffusion layer.

Many tests of elongation at break have been carried out in order to estimate the plasma treatment effects on the solidity of the cord. A risk of long plasma treatment was a potential cord fragilization.^{25–27} Figure 7 shows the plasma-treated cord lengthening according to the applied traction strength. In all treatments, the breaking strength was characterized by a value of ~ 19.2 daN, very close to the value for the untreated cord. The resistance of the treated cord was not disturbed. So, experiment confirms that only the extreme surface of the sample was modified by plasma treatment without any consequence upon the mechanical properties.

CONCLUSION

Glow discharge plasma treatment is an effective technique to enhance the adhesion between polymer surfaces. In this article, various treatments of PET fibers with argon plasma, oxygen plasma, and argon/oxygen plasma are described.

The plasma-treated fibers were coated with RFL adhesive and then they were enclosed in a rubber matrix. The goal of this article was to verify whether the various plasma treatments using selected parameters, which we have carried out, would be able to activate the fiber surface to make it more receptive to adhesive. All plasma treatments increased the wettability and surface energy of PET material; however, $\theta_{\text{H}_2\text{O}}$ and γ_s^d values were affected by storage time. Moreover, the roughness of the samples was accentuated with plasma treatment time.

The adhesion strength was measured by peel tests and showed that the best results were obtained for a 75 W, 30/30 min argon then oxygen plasma treat-

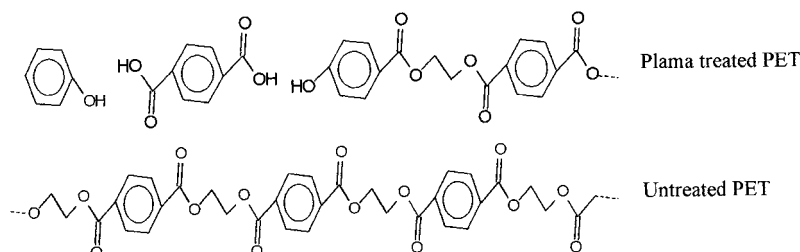


Figure 6 Possible fragments produced by plasma discharge treatment of PET samples.

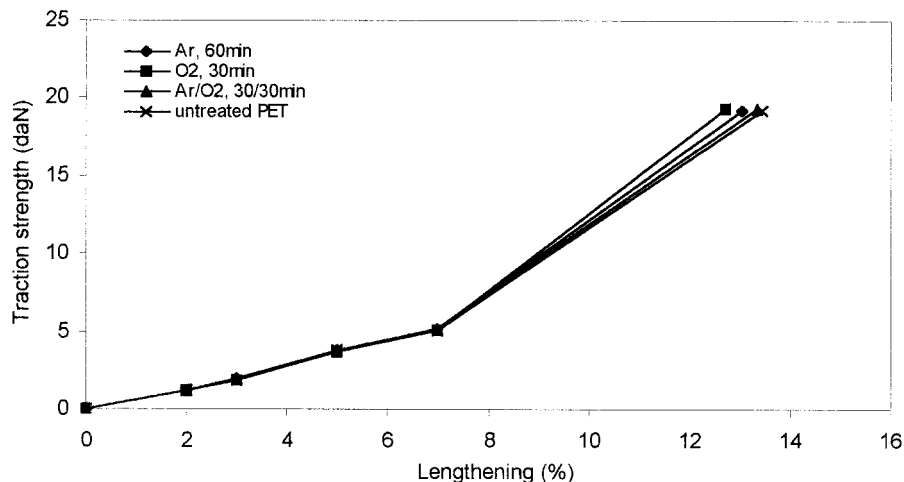


Figure 7 Traction strength (daN) of plasma treated PET cords.

ment. These successive plasma treatments allowed the adhesion to be optimized by increasing the polarity of the surface and the mechanical anchorage.

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