

Adhesion Improvement of Tire Cord Induced by Gas Plasma

ERNEST L. LAWTON,
*Monsanto Company, Chemstrand Research Center, Inc.,
Durham, North Carolina 27702*

Synopsis

The adhesion of poly(ethylene terephthalate) (PET) to rubber in tire composites was significantly improved by exposure of the PET to "low-temperature" gas plasmas. Rubber composites built using a single-dip resorcinol-formaldehyde-latex (RFL) adhesive and plasma-treated PET reinforcement were studied. The effects of treatment conditions on this adhesion improvement were examined. The improvement was insensitive to nature of the gas, exposure time, power level, and pressure within the operating limits of the plasma generator. Fiber finish on filaments being treated was detrimental to the adhesion improvement; however, an overcoating of treated filaments with finish was not detrimental. The effects of tire building operations on this adhesion improvement of treated PET were examined. The improvement was found over a wide range of adhesives, adhesive-curing conditions, rubber compositions, and bonding testing conditions.

INTRODUCTION

The introduction of poly(ethylene terephthalate) (PET) as a tire cord required the development of methods for bonding PET to rubber. Adhesion levels achieved by coating PET cord with standard resorcinol-formaldehyde-latex (RFL) adhesive used extensively to bond rayon and nylon 6.6 cords to rubber were very poor.¹ Practical solutions to this bonding problem were achieved by developing double-dip systems,¹ isocyanate-epoxide coating followed by RFL coating,^{1,2} and by modification of the standard RFL^{2,3} dip system to provide commercially acceptable adhesion between PET cord and rubber. The necessity for higher curing temperatures to achieve acceptable bonding of these adhesives to PET than those for bonding RFL to nylon 6.6 and the more complex and expensive dipping processes have stimulated interest in alternate bonding processes. Many approaches¹ have been investigated as means to alter the surface properties of PET to render it more susceptible to durable bonding to rubber with RFL and other adhesives.

The effectiveness of surface modification of PET tire cord by exposure to low-pressure gas plasmas in enhancing bondability was evaluated in this study. Exposure of polymeric objects to low-pressure gas plasmas generated by electrodeless radio-frequency excitation has been shown to

saliently increase the bonding of these objects to a number of substrates.^{4,5,6} The plasma is an ionized gas in which the number of negative and positive charges are approximately equal; perhaps one part per million of the gas is ionized at any instant.⁷ The electron is the agent which transfers energy from an electrical power supply to the gas resulting in ion production and excitation of atoms or molecules to form free radicals. At low pressures, the plasma is at a highly unequilibrated steady-state condition. The translational "temperatures" of species other than electrons are near that corresponding to room temperature while the electron "temperatures" are tens of thousands of degrees Kelvin. The high-energy electrons may also excite atoms or molecules to high-lying states of internal energy not sufficient for ionization to occur. Such excitation is responsible for the generation of ultraviolet radiation by electronically excited species and the generation of chemically active neutral species from vibrational excitation such as radicals.

The effect of plasmas on polymeric surfaces which appears common to most polymers is surface degradation, as evidenced by weight loss, while crosslinking in the surface has also been observed for many polymers.⁸ Energy transfers to the surface by free-radical attack,^{5,9} ion attack,^{5,9} absorption of ultraviolet light generated by electronically excited species,¹⁰ attack by electronically excited species,^{11,12} attack by electrons with kinetic energies greater than 3 electron volts,¹³ and by surface recombination of ions and electrons releasing 10 to 20 electron volts¹³ have been postulated. The effect of a given plasma upon a polymer surface should depend upon the steady state established by the experimental conditions such as power supply, mode of power coupling, sample position, gas flow, pressure, reaction vessel (wall effects), etc. The effect of the low-pressure plasma treatment has been found to be confined to the surface regions and not to alter bulk properties of the polymer.^{5,8,10}

EXPERIMENTAL

Fiber

A poly(ethylene terephthalate) (PET) filament bundle of 200 filaments with total denier of 1000 was utilized in this study. Filaments were spun with the application of a typical spin finish for tire cord and also without the application of the spin finish.

The filament bundle was twisted into a 2-ply (1000 denier per ply) tire cord with 12 turns per inch Z-twist in singles and 12 turns per inch S-twist in the ply.

Plasma Exposure

Fiber bundles and cords were exposed to gases which were excited by an electrodeless radio-frequency discharge. A Tracerlab LTA-600 plasma generator was modified so that a threadline could be continuously passed

through the plasma chamber. An evacuated chamber containing the feed and take-up mechanism for the threadline was attached with a gasket seal to the plasma chamber. The LTA-600 consists of a 300-watt 13.56-MHz radio-frequency generator, a capacitatively coupled plasma activator consisting of impedance-matching circuitry and a pair of activator plates, a Pyrex glass chamber with five activator tubes, a vacuum system, and a gas-metering system. Temperatures at sample surface were measured remotely by means of an infrared radiation pyrometer (Applied Systems Model 3131-02).

The following gases were utilized as received: argon, nitrogen (pre-purified), helium (grade A), carbon dioxide, oxygen (U.S.P.), and hydrogen, all from Air Reduction. Ammonia (anhydrous) and propene (C.P.) were from Matheson, and they were also utilized as received.

The bobbin of fiber or cord was placed on the feed roll of the modified LTA 600, and then the chamber was evacuated to approximately 0.5 torr. A suitable gas flow rate was then established to achieve the desired pressure. The discharge was then established and the movement of fiber through the plasma chamber was begun. After completion of a run, the chamber was returned to atmospheric pressure with air. Retaining the treated bobbins in the chamber without exposure to air for 30 min under a stream of nitrogen produced no change in bondability.

Testing

The modified RFL dip consisted of 82 ml H-7 adhesive (Imperial Chemical Industries Ltd.); 50 ml Gen-Tac Latex (General Tire & Rubber Company, poly(vinylpyridine)-styrene-butadiene latex, 41 wt-% solids); and 73 ml deionized water. The composition and chemistry of this adhesiv-dip has been described.^{2,3} The H-7 adhesive was not combined with RFL adhesive as suggested by the manufacturer.^{2,3}

A standard RFL dip was prepared by dissolving 5.5 g resorcinol in 116 ml water containing 0.15 g sodium hydroxide. To this solution, 81 g of 37 wt-% aqueous formaldehyde was added, and the solution was stirred for 5 min. This resin master solution was allowed to age for 6 hr at 24–26°C. The 133 g resin master was added to a dispersion of 122.0 g Gen-Tac and 30.0 g deionized water, and the resulting dispersion was mixed for 15 min. The RFL dip was used within 72 hr.

An (isocyanate and epoxide)-RFL double dip was formulated as described in references 1 and 2.

The cord was dipped through a bath of adhesive, passed through a 6-ft drying zone maintained at 165°C, and then into an electrically heated circulating hot-air oven. Cord was cured at constant length for 1 to 3 min. The dry add-on of adhesive was approximately 5% based upon the original weight of the cord.

The cured cord was tested for static adhesion at 120°C in the H-pull test as described in ASTM D-2138-67, with the exception that $\frac{3}{16}$ in. rather than $\frac{1}{4}$ in. of cord was pulled from rubber. The peeling adhesion of 1-in.

by 6-in. strips of a cord rubber composite were tested at 120°C. The two plies of cord were parallel and the strips were pulled at 12 in./min at 180° angle and the peel force averaged for 2-in. lengths of peel. This strip adhesion test was described by Brownlee.¹⁴ The sample was constructed as described in ASTM D-2630-71.

The rubber used in H-blocks and strips was a commercial skim stock. Mooney scorch time (5-point rise/135°C) was 13.5 min; a Monsanto MP-V rheometer indicated a cure time of 20 min at 153°C. The H-block and strip block mold surface was subjected to 500 lb/in.² in a Pasadena Hydraulics press Model Q-230 at 149°C for 25 min during vulcanization.

Pull loads listed in the tables are average values from eight H-blocks. Errors are stated as 95% confidence intervals. Peeling loads are average values from five strips from a single mold. The strip peeling loads exhibited a maximum average deviation from the mean of ± 1.5 lb.

Surface Characterization

Scanning electron micrographs were taken on a Stereoscan scope of Cambridge Ltd., using surface replicas from vapor deposition of platinum-gold alloy.

The solid-liquid contact angles of single fibers were measured as described by Grindstaff.¹⁵ All specimens were conditioned at 21°C and 40% relative humidity for at least 48 hr prior to testing. All measurements were made in the same conditioning room. The liquids used in these measurements were purified as described by Fox and Zisman.¹⁶

Reported values of solid-liquid contact angles are averages of at least ten readings on at least two filaments from a given fiber bundle. The mean deviation from the average was $\pm 1^\circ$.

RESULTS

Effect of Gas

Bundles of 1000-denier (200 filaments) fiber without finish were processed through the modified Tracer Laboratories LTA-600 plasma generator as described in the experimental section. The exposure to the plasma was under the following operating conditions: forward power = 100 ± 5 watts; reflected power = 0 ± 5 watts; pressure = 0.5 ± 0.1 torr; exposure time = 9.4 sec.

The flow rate of each gas was adjusted to achieve a pressure of 0.5 torr in the plasma chamber. The flow rate thus varied from 20 to 40 cm³/min, depending on the gas. Approximately 1000 yards of fibers was processed during each run lasting approximately 140 min (take-up speed = 231 in./min). The fiber was removed from the evacuated chamber after a run. The fiber was then twisted into 2-ply, 1000-denier-per-ply cord with 12 turns per inch Z-twist in singles and 12 turns per inch S-twist in the ply. Adhesives were applied and rubber-to-cord adhesion was tested as described in the experimental section.

Table I illustrates the extremely large improvement in adhesion obtained by these treatments. The bondability of polyester tire cord to rubber using a single dip standard RFL adhesive system was greatly improved. Bondability with a single-dip system using H-7 as the adhesive and the commercial double-dip system D417 (first dip, glycidyl ether of glycerine and phenol-blocked diphenylmethane diisocyanate cured at 230°C for 1 min; second dip, standard RFL cured at 204°C for 1 min) was also improved. For comparison, the adhesion values for commercial nylon 6.6 840 denier, 2-ply tire cord processed through the same RFL dip and cured at 210°C for 3 min were 24.1 lb/in. strip peel load and 14.0 ± 3.9 lb H-block pull load.

The effectiveness of the gases tested in improving bondability with RFL followed the order $\text{NH}_3 > \text{N}_2 > \text{A} \approx \text{He} > \text{air} > \text{O}_2$. However, since many variables, i.e., exposure time, power level, pressure, adhesive, and rubber composition, may effect the adhesion improvement achieved with a given gas, this order should not be construed as being applicable to other conditions of plasma treatment.

The oxidizing plasmas, oxygen and air, which continually remove measurable quantities of material from the polymer surface,^{5,17,18} appear least effective of the gases tested. The ablation of the surface produced by the oxygen plasma may result in a weak surface layer containing partially oxidized polymer chains.

The plasma treatment as described above was applied to tire cord of 1000-denier-per-ply, 2-ply construction. These cords were from fiber spun without finish. Plasma treatment of the cords was also very effective in increasing bondability of polyester. It is not known to what extent the plasma penetrated into the interior of the cord structure during the 9-sec exposure time. Even if the surface modification is confined to those fibers on the outer surface of the cord, bonding between adhesive and cord normally involves only the outer layers of filaments in the cord with little penetration of adhesive into the cord structure.¹ Table II illustrates the improvement achieved by treating cord. Cord was passed through the various plasmas at 1.0 ± 0.1 torr of pressure for a 9.4-sec exposure time at 100 watts of forward power. With cord, the gases tested were approximately equivalent in improving adhesion.

Exposure Time

Bundles of 1000 denier/200 filaments fiber without finish were subjected to a nitrogen plasma at a pressure of 0.5 torr for varying exposure times at forward power level of 100 watts and approximately zero reflected power. The exposure time was adjusted by controlling the take-up speed of the fiber bundle passing through the 36-in. plasma chamber. The adhesion improvement appeared to be relatively insensitive to exposure time in the range of 4 to 34 sec. Results of these adhesion tests are recorded in Table III. The adhesive was RFL cured at 210°C or 232°C for 3 min with the cord held at constant length.

TABLE I
Effect of Gas on Adhesion Improvement

Adhesive	Cure conditions	Strip adhesion peeling load at 120°C, lb/in.						
		N ₂	A	He	NH ₃	Air	O ₂	Control
RFL	210°C, 3 min	16.9	14.5	11.5	21.0	—	7.5	2.5
RFL	232°C, 3 min	18.6	10.6	15.0	23.7	14.1	11.2	3.0
H-7	243°C, 3 min		19.0					16.0
D417	{ 230°C, 1 min } { 204°C, 1 min }	22.8						20.0
H-Block pull load at 120°C, lb								
Adhesive	Cure conditions	H-Block pull load at 120°C, lb						
		N ₂	A	He	NH ₃	Air	O ₂	Control
RFL	210°C, 3 min	13.9 ±1.8	15.6 ±0.7	11.7 ±1.1	9.5 ±0.9	—	10.6 ±0.7	7.5 ± 0.3
RFL	232°C, 3 min	17.0 ±1.8	13.8 ±1.2	13.9 ±0.9	10.7 ±1.7	11.4 ±1.8	12.3 ±0.6	8.6 ± 0.7
H-7	243°C, 3 min		17.7 ±0.6					13.5 ± 1.3

TABLE II
Effect of Gas on Adhesion Improvement

Adhesive	Cure conditions	Strip adhesion peeling load at 120°C, lb/in.									
		N ₂	A	He	H ₂	NH ₃	H ₂ O	CO ₂	O ₂	CH ₂ = CHCH ₃	Control
RFL	230°C, 3 min.	16.9	15.1	15.6	17.6	18.1	16.1	17.6	18.2	11.5	8.2
H-7	200°C, 3 min.	17.9	19.4	21.4	23.1	17.8	20.1	20.1	19.5	20.9	18.8

TABLE III
Effect of Exposure Time to N₂ Plasma on Adhesion Improvement

Exposure time, sec	Strip adhesion peeling load at 120°C, lb/in.		H-Block pull load at 120°C, lb	
	RFL— 210°C	RFL— 230°C	RFL—210°C	RFL—230°C
0	2.5	3.0	7.5 ± 0.3	8.6 ± 0.7
4.3	22.3	22.5	10.7 ± 1.7	15.7 ± 1.8
9.6	16.9	18.6	13.9 ± 1.8	17.0 ± 1.8
34.0	15.4	18.4	14.8 ± 0.8	10.4 ± 1.5

Hall et al.¹⁹ found that bondability of PET film to an epoxy adhesive reached a plateau value after several minutes of exposure to helium or oxygen plasmas. Bondability increased rapidly during the shorter times of exposure and leveled off before 5 min of exposure.

Power Level

No effect of power level on adhesion values obtained after plasma treatment of fiber with a nitrogen plasma at 0.5 torr of pressure for an exposure time of 9.4 sec could be detected. Experiments within the 75- to 275-watt range did not detect an effect of power input on adhesion. However, it has been shown that the rates of weight loss of polymer films exposed to plasmas exhibit marked dependence on power.^{8,18}

Pressure and Gas Flow Rate

No effect of gas pressure on adhesion values obtained after plasma treatment of fiber with a nitrogen plasma at 100 watts forward power level for an exposure time of 9.4 sec was detected. The pressure was varied from 0.2 to 1.5 torr. At pressures above 2 torr, temperatures in excess of 150°C were encountered at the filament surface as measured by infrared radiation pyrometer. By use of a bleed valve between the vacuum pump and the exhaust outlet of plasma chamber, the pressure in the chamber was held at 1.0 ± 0.1 torr while the nitrogen flow rate was varied from 20 to 40 cm³/min at a power level of 100 watts and an exposure time of 9.4 sec. The adhesion values of cord did not appear to depend on gas flow rate within this range. However, the temperature and species present in the plasmas are highly dependent upon pressure and flow rate.⁷

Fiber Finish

Since the interaction of a plasma with a polymer is a true interfacial reaction in the sense that only the first several hundred angstroms of surface are involved,^{5,6,10} it might be expected that the spin finish applied to the surface of polyester fibers before drawing would interfere with the plasma treatment. The spin finish is typically a proprietary mixture of

TABLE IV
Effect of Finish on Adhesion Improvement with RFL

Fiber	Plasma	Cure	Strip peeling load at 120°C, lb/in.	H-Block pull load at 120°C, lb
PET without finish	A	210°C, 3 min	14.5	15.6 ± 0.7
PET with finish prior to treatment	A	232°C, 3 min	10.6	13.8 ± 1.2
PET without finish	A	210°C, 3 min	6.6	8.8 ± 0.7
PET with finish applied after treatment	N ₂	232°C, 3 min	7.2	11.6 ± 2.8
	N ₂	232°C, 3 min	21.4	10.4 ± 0.9
	N ₂	232°C, 3 min	19.6	13.4 ± 1.1

lubricants and surfactant applied to the surface of filaments by the fiber producer to aid in drawing and twisting the filaments.

Bundles of filament fiber with and without a spin finish were exposed to an argon or nitrogen plasma at 0.5 torr for 9.4 sec at a 100-watt power level. Table IV illustrates that the presence of finish has a detrimental effect upon the adhesion improvement achieved by plasma treatment. After being treated, fiber without finish was coated with finish to an approximate 1% dry pickup of finish. This coating was accomplished by passing the 200-filament bundle over a finish wheel followed by drying and twisting into cord. The data of Table IV indicate that overcoating plasma-treated fiber with finish does not significantly affect the adhesion improvement. Much of the finish is washed from the surface of the fibers during the adhesive dipping.

Adhesive Curing

A large quantity of 1000-denier, 200-filament fiber spun without finish was exposed to a nitrogen plasma at 0.5 torr for 9.4 sec at 100 watts of forward power. This fiber was then plied into 2-ply tire cord. The plasma-treated sample and a control were dipped and cured at constant length under a variety of conditions. Strip adhesion samples were built and tested from these cords.

This dip was prepared as described for the standard RFL dip in the experimental section, except that in a series of dips the quantity of formaldehyde was increased or decreased while the quantity of resorcinol was held constant to achieve the stated molar ratios. The quantity of water was adjusted to obtain the same total weight of material in all cases. All sam-

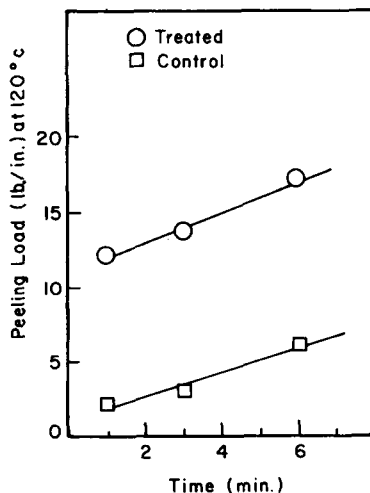


Fig. 1. Effect of curing time at 230°C on adhesion improvement with RFL after exposure to 0.5 torr nitrogen plasma at 100 watts for 9.4 sec.

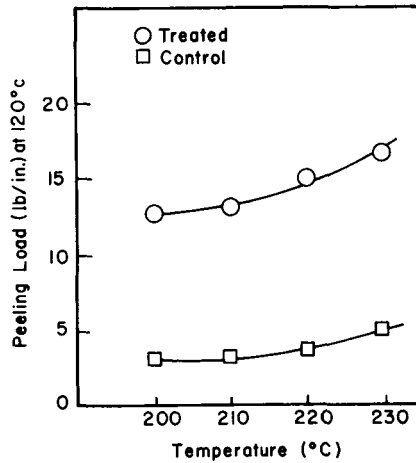


Fig. 2. Effect of curing temperature for 3 min on adhesion improvement with RFL after exposure to 0.5 torr nitrogen plasma at 100 watts for 9.4 sec.

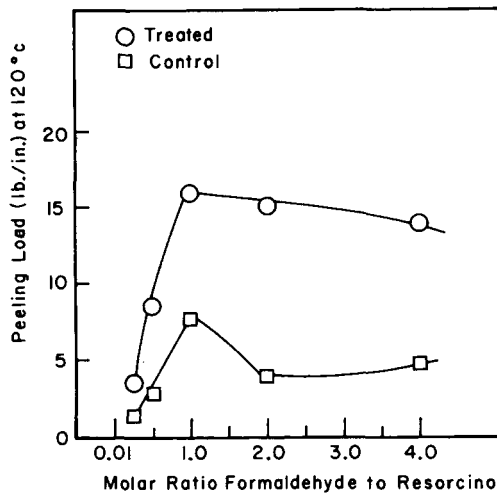


Fig. 3. Effect of formaldehyde to resorcinol ratio on adhesion improvement with RFL cured at 220°C for 3 min after exposure to 0.5 torr nitrogen plasma at 100 watts for 9.4 sec.

ples where the formaldehyde-to-resorcinol ratio was varied were cured at 220°C for 3 min.

The relations between adhesion improvement and time and temperature of cure are presented graphically in Figures 1 and 2. The RFL adhesive on plasma-treated cord shows increased adhesion at longer cure times and higher temperatures, while the control cord has very poor adhesion at all processing conditions. The increase with increased time and temperature of cure is similar to that exhibited by the commercial H-7 adhesive on control polyester. The level of adhesion achieved by curing H-7 on un-

treated polyester at 230°C (strip peeling load of 18 to 20 lb/in.) can be achieved with H-7 on plasma-treated polyester cured at 200°C.

The adhesion level achieved with RFL on plasma-treated fiber also responds to the composition of the dip. Figure 3 illustrates that there must be at least a 1:1 mole ratio of formaldehyde to resorcinol to achieve adequate bonding of plasma-treated fiber. The methylol content of the RF resin and structure of the RFL resin resulting after addition of latex and curing vary greatly with this ratio.¹ In general, a ratio of around 2:1 has been used for nylon 6.6 and rayon to achieve a resin with limited network formation but with considerable methylol functionality.^{1,2}

Rubber Composition

The bonding of plasma-treated cord to rubbers ranging in composition from pure natural rubber to pure synthetic rubber was tested in the strip peeling test. Samples of 1000-denier, 2-ply cord without finish were exposed to a 1.0-torr nitrogen plasma for 9.4 sec at 100 watts of forward power. The bonding of this cord to three typical rubbers was determined with RFL and H-7 adhesives as shown in Table V.

TABLE V
Effect of Rubber Composition on Adhesion Improvement*

Rubber	Strip peeling load at 120°C, lb/in.			
	Treated RFL	Untreated RFL	Treated-H-7	Untreated H-7
Natural	20.1	14.8	29.6	15.3
Synthetic, SBR	15.2	15.1	29.4	20.0
Natural/synthetic (50/50 wt-%)	22.6	8.3	30.7	12.1

* Cord exposed to 1.0 torr nitrogen plasma at 100 watts for 9.4 sec.

The cord was dipped in RFL and cured at 230°C for 3 min at constant length, or dipped in H-7 and cured at 200°C for 3 min at constant length. The adhesion improvement achieved by plasma treatment was effective with all three rubber compositions.

In-Tire Testing

A filament bundle was exposed to nitrogen plasma at 0.8 torr and 100 watts for 9.4 sec. This filament bundle was then coated with 1 wt-% of a typical spin finish for tire cord and plied into 1000/2 cord. The cord was dipped in RFL adhesive and cured at 232°C for 3 min at constant length. The cord was built into two 2-ply, 8.25 × 14 tires for wheel testing. Both tires passed the Motor Vehicles Safety Standard DOT-109 step-load endurance test. In contrast, the adhesion between standard PET cord dipped in RFL and skim stock rubber is so poor that the tire composite barely has sufficient integrity to allow tire construction.

Fiber Properties

There appeared to be no difference in bulk physical and chemical properties of the treated and untreated fibers. This finding agrees with all published data on plasma modification of polymers which indicate that the reactive species in the plasma penetrate only the first several hundred or thousand angstroms of the polymer surface.^{5,6,8,10}

Surface Characterization

Comparison of Figures 4 and 5 illustrates that scanning electron micrographs of the dipped and cured cords show a globular and discontinuous coating of RFL resin on the surface filaments of the untreated cord, while the treated cord has a surface which is covered by a continuous coating of RFL resin which bridges the interfilament areas on the cord surface.

Contact angles of liquid drops on polymer surfaces have been widely accepted as a measure of wettability of polymer surfaces. Changes in the contact angle of a liquid on the surface of a given polymer have been interpreted as reflecting changes in the chemical or physical properties of the polymer surface and thus a change in the environment (chemical or physical) to which the drop is exposed. In this study the contact angles of a number of liquids on the PET fiber have been measured, and these angles clearly reflect an increased wettability of the polymer surface after exposure to plasma treatment. In Table VI, the contact angles (θ) of

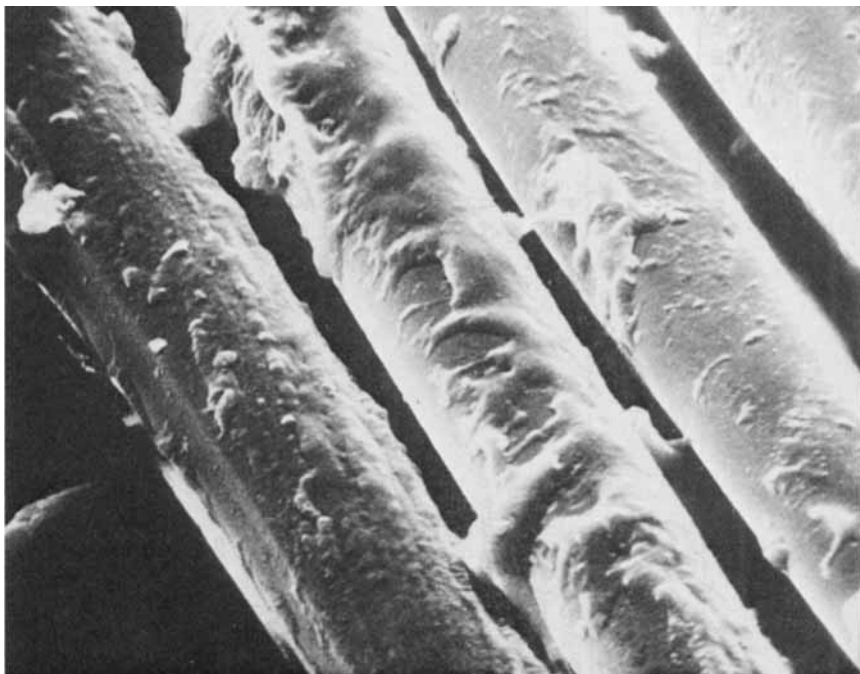


Fig. 4. Cured RFL coating on untreated filaments from cord, 1000 \times .

TABLE VI
Contact Angle and Change in Work of Adhesion of Liquids on Filaments

Liquid	Surface tension γ_L , dynes/cm	Contact angle		$\Delta W_a = \gamma_L(\cos \theta_2 - \cos \theta_1)$, dynes/cm
		Untreated θ_1	Plasma-treated ^a θ_2	
Water	72.8	83	70	16
Glycerol	63.4	79	75	4
N,N-Dimethylformamide	58.2	71	56	14
2,2'-Thiodiethano	54.0	79	67	11
Methylene iodide	50.8	78	67	10
Ethylene glycol	47.7	80	75	4
1,1,2,2-Tetrabromoethane	47.5	84	75	7
1,3-Propanediol	46.0	84	75	7
1-Bromonaphthalene	44.6	73	69	3
Diethylene glycol	44.0	77	66	8
1-Methylnaphthalene	38.7	60	50	6
1,2-Propanedio	35.8	73	57	9
Di(cyclohexane)	33.0	51	41	4
n-Hexadecane	27.7	49	41	3
RFL dip	—	70	59	—
H-7 dip	—	64	56	—

^a Filaments exposed to 0.5 torr nitrogen plasma at 100 watts for 9.4 sec.

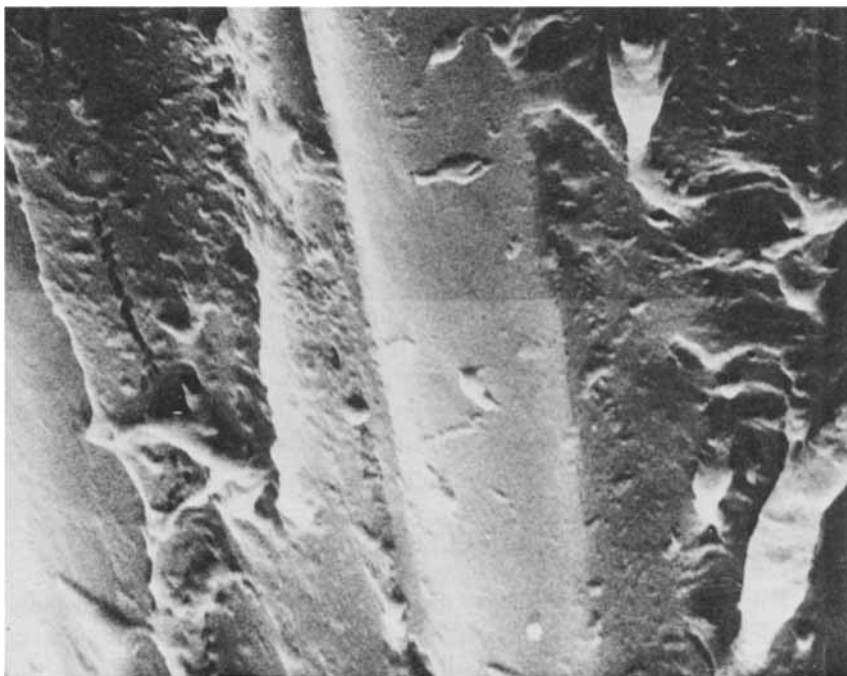


Fig. 5. Cured RFL coating on plasma-treated filaments from cord, 1000 \times .

liquids and the calculated change in work of adhesion (ΔW_a) of liquid contact with PET filaments with and without exposure to a nitrogen plasma at 100 watts and 0.5 torr for 9.4 sec are presented. The surface appears to be more wettable after the treatment and thus has a considerably higher surface free energy. After plasma treatment, the interaction efficiency of liquids with the surface appears to increase to a greater extent for the liquids with polar and/or hydrogen bonding properties than for the nonpolar liquids. It should be noted that contact angles are for uniaxially oriented fibers. Literature values of contact angles of liquids on PET generally refer to biaxially oriented films. However, Good et al.²⁰ have reported that contact angles may be anisotropic with oriented films, being higher for a liquid front advancing or retreating perpendicular to the direction of stretch than for advance or retreat in the parallel direction. This behavior was attributed to an anisotropic force field of oriented polymer molecules at the surface.

The work of Bradley and Heagney²¹ has suggested that exposure of PET to a gas discharge ion plasma results in the generation of surface free-radical sites which react with oxygen upon exposure to the atmosphere, to form surface peroxide groups. These peroxide sites were reported to disappear upon annealing the treated polymer under vacuum, but not upon annealing in air. The peroxide sites were found to be stable in air at room conditions for an indefinite period of time.

The electron paramagnetic resonance spectra of filament bundles exposed to oxygen or nitrogen plasmas were examined to determine if sufficient free radicals were generated from peroxide decomposition for detection. Samples were examined in evacuated tubes (few microns of pressure) as well as in the presence of oxygen as a function of temperature (60°C to 220°C in 20 min) with a Varian 4502-12 spectrometer equipped with a variable-temperature accessory. No signal that could be associated with an organic-free radical was detected. The surface peroxide concentrations described by Bradley and Heagney²¹ should have generated a free-radical concentration well within the detection limits of the instrument.

Since Bradley and Heagney²¹ gave no details of their method of exposure of PET to the plasma or the nature of the plasma, it may be that surface peroxide sites are formed only under certain conditions and are not a general surface feature of PET after exposure to a plasma.

DISCUSSION

The adhesion of many polymers to various materials has been markedly improved by exposure of the surfaces of these polymers to various low-pressure, radio frequency-activated gas plasmas. Explanations of the relationship between altered chemical and physical properties of the surfaces and the adhesion improvement achieved are nearly as numerous as the cases that have been examined. Schonhorn and co-workers^{5,6,22} proposed that the increased bond strength resulted from crosslinking of the surface region inducing increased cohesive strength. Others^{23,24,25} have associated changes in the wettability and increased compatibility with adhesive of polymer surfaces due to chemical changes (oxidation, etc.) induced by the plasma with the improved bonding of treated surfaces.

The evidence for surface crosslinking in polymers such as polyethylene is extensive.^{5,8,10} In the case of polyethylene in a hydrogen plasma, photochemical reactions resulting from absorption of ultraviolet radiation produced by the plasma apparently account for the observed crosslinking.¹⁰ Evidence for chemical modification of polymer surfaces by attachment of polar groups in certain plasmas has also been presented; for instance, HO— to poly(methylsiloxane),²⁶ H₂N— to polypropylene and polycarbonate²⁷ and HOO— to polybutadiene.¹¹ It has also been suggested that certain discharges induce long-lived heterogeneously distributed surface charges on polymers.²⁸ Thermoluminescence has been observed from poly(tetrafluoroethylene) and polycaprolactam exposed to electrodeless discharge and attributed to recombination of trapped ions and electrons in the polymer surface.²⁹

Good³⁰ has recently proposed a rather general theory to describe separation in adhering systems based upon crack analysis of fracture. The important parameters in the theory are difference in elastic moduli between phases, differences in the energy dissipation per unit crack extension be-

tween phases, thickness of the region where dissipation occurs, and the strength of interfacial bonding. Good²⁰ has proposed that plasma treatment might have three effects: (1) increase the potential for strong interfacial bonds by introducing polar groups, peroxide groups, free radicals, etc., at the polymer surface; (2) increase surface crosslinking and the contaminant energy dissipation; and (3) possibly increased elastic modulus through crosslinking.

Good speculated that any of the three effects could account for the adhesion improvement observed depending upon the nature and thickness of the layer modified by plasma treatment. Until more revealing analytical techniques are developed to examine the interfacial region of bonding and to physically and chemically characterize polymer surfaces, it is unlikely that causal relationships between adhesion improvement and surface properties will be firmly established.

References

1. T. Takeyama and J. Matsui, *Rubber Chem. Technol.*, **42**, 159 (1969).
2. D. W. Anderson, *Rubber Age*, **103**, 69 (Sept. 1971).
3. J. Mather, *Brit. Polym. J.*, **3**, 58 (1971).
4. J. R. Hall, C. A. L. Westerdahl, A. T. Devine, and M. J. Bodnar, *J. Appl. Polym. Sci.*, **13**, 2085 (1969).
5. R. H. Hansen, in *Interface Conversion*, P. Weiss and G. D. Cheevers, Eds., Elsevier, New York, 1969, p. 257.
6. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1461 (1967).
7. W. L. Fite, in *Advances in Chemistry Series, Number 80*, American Chemical Society, New York, 1969, p. 1.
8. H. Yasuda, C. E. Lamaze, and K. Sakaoku, *J. Appl. Polym. Sci.*, **17**, 137 (1973).
9. G. A. Byrne and K. C. Brown, *J. Soc. Dyers Colour.*, **88**, 113 (1972).
10. M. Hudis, *J. Appl. Polym. Sci.*, **16**, 2397 (1972).
11. M. L. Kaplan and P. G. Kelleher, *Science*, **169**, 1206 (1970).
12. M. L. Kaplan and P. G. Kelleher, *Polym. Preprints*, **12**, 319 (1971).
13. A. Bradley and J. D. Fales, *Chem. Technol.*, **1**, 232 (1971).
14. E. L. Brownlee, Modified Strip Adhesion Method, presented to ASTM Subcommittee A-9, October 17, 1962.
15. T. H. Grindstaff, *Text. Res. J.*, **39**, 958 (1969).
16. H. W. Fox and W. A. Zisman, *J. Colloid Sci.*, **5**, 514 (1950).
17. R. H. Hansen, J. V. Pascale, T. De Benedictis, and P. M. Rentzepis, *J. Polym. Sci. A.*, **3**, 2205 (1965).
18. E. L. Lawton, *J. Polym. Sci. A-1*, **10**, 1857 (1972).
19. J. R. Hall, C. A. L. Westerdahl, M. J. Bodnar, and D. W. Levi, *J. Appl. Polym. Sci.*, **16**, 1465 (1972).
20. R. J. Good, J. A. Kvikstad, and W. O. Bailey, *J. Colloid Interfac. Sci.*, **35**, 314 (1971).
21. A. Bradley and T. R. Heagney, *Anal. Chem.*, **42**, 894 (1970).
22. H. Schonhorn, F. W. Ryan, and R. H. Hansen, *J. Adhesion*, **2**, 93 (1970).
23. N. J. DeLollis, *Rubber Chem. Technol.*, **46**, 549 (1973).
24. R. R. Sowell, N. J. DeLollis, H. J. Gregory, and O. Montoya, *J. Adhesion*, **4**, 15 (1972).
25. Y. Kitazaki and T. Hata, *J. Adhesion*, **4**, 123 (1972).
26. J. R. Hollahan and G. L. Carlson, *J. Appl. Polym. Sci.*, **14**, 2499 (1970).

27. J. R. Hollahan, B. B. Stafford, R. D. Falb, and S. T. Payne, *J. Appl. Polym. Sci.*, **13**, 807 (1969).
28. C. Y. Kim, J. Evans, and D. A. I. Goring, *J. Appl. Polym. Sci.*, **15**, 1365 (1971).
29. V. A. Vonsyatskii, Ye. P. Mamunya, and Yu. S. Lipatov, *Polym. Sci. USSR*, **13**, 2436 (1971).
30. R. J. Good, *J. Adhesion*, **4**, 133 (1972).

Received June 26, 1973

Revised November 5, 1973