

Effect of Activated Gas Plasma Treatment Time on Adhesive Bondability of Polymers

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Synopsis

The bondability of the following polymers as a function of length of exposure to excited helium or oxygen was investigated: low-density polyethylene, high-density polyethylene (two types), poly(4-methyl-1-pentene), poly(vinyl fluoride), poly(vinylidene fluoride), FEP Teflon, poly(oxyethylene) copolymer, nylon 6, nylon 66, poly(ethylene terephthalate), and polystyrene. Generally, the bond strength increases rapidly initially and then remains nearly constant, perhaps decreasing in some cases at long exposure times. A method is presented for calculating bond strength-versus-exposure time curves. The calculated curves generally fit the data reasonably well. Polypropylene showed a rapid increase in bondability with exposure to excited oxygen. Helium was ineffective toward this polymer under normal conditions, but could produce good bond strength at higher temperatures.

INTRODUCTION

Polymer surfaces can be usefully modified by exposure to activated gas plasma. Of particular practical interest is the improved bondability of treated surfaces with adhesives. In previous work, we found that some polymers showed a rapid increase in bond strength after treatment, but in other instances long treatment time was required. We here report the results of a more detailed investigation of the variations of adhesive bond strength with the time of exposure to excited gases.

EXPERIMENTAL

The polymers used were all commercial materials that typically would be used in engineering applications; no effort was made to extract plasticizers or antioxidants. The polymers are identified in Table I.

The polymers were cut into 3 $\frac{1}{2}$ in. by $\frac{3}{4}$ in. strips and wiped with solvent and then air dried. The "untreated" samples were bonded after the solvent wipe, and those to receive plasma treatment were placed in the plasma reactor and degassed under vacuum for 10-15 min.

The apparatus used was a Tracerlab* PRS-600 plasma reactor, previously described.¹ For these studies, 50-W power was used except where

* Name changed to Trapelo Div., LFE Corp.

TABLE I
Commercial Polymers Used

Polymer	Manufacturer and description
Low-density polyethylene	Picatinny Arsenal standard stock, 30-mil film
High-density polyethylene, Plaskon	Plaskon, PP 60-002 (Allied Chemical Corp.), 9.2-mil film
High-density polyethylene, Marlex	Marlex 6002 (Phillips Petroleum Co.), green pigment, $1/16$ -in.-thick sheet
Poly(4-methyl-1-pentene)	TPX poly(4-methyl-1-pentene) copolymer (ICI America Inc.), 10-mil film
Poly(vinyl fluoride)	Tedlar (E. I. du Pont de Nemours & Co.), 200-SG40-TR, 2-mil film
Poly(vinylidene fluoride)	Kynar (Pennsalt Chem. Corp.), $1/16$ -in.-thick (Adam Spence Corp.)
Fluorinated ethylene-propylene copolymer	FEP Teflon (E. I. du Pont de Nemours & Co.), 5-mil film
Poly(oxymethylene) copolymer	Celcon, M90-01 (Celanese Corp.), injection-molding grade (MIL-A-50424), 1-mil film
Nylon 6	Capran 77C (Allied Chemical Corp.), 3-mil film
Nylon 66	Nylon 66 (Almac Plastics), $1/16$ -in. sheet
Poly(ethylene terephthalate)	Mylar D, cartography grade (E. I. du Pont de Nemours & Co.), 10-mil film
Polystyrene, modified	Styron rubber-modified polystyrene, pigmented white (Dow Chemical Co.), 10 mil

noted; the reflected power was less than 0.1 W for excited helium and up to 0.4 W for excited oxygen. The gas flow was 20 cc/min for O₂ and 50 cc/min for He, at pressures of 0.35 to 0.45 mm Hg, except where higher pressures were required to produce a high temperature. The edge of the activator plate assembly was positioned 2½ in. from the chamber. The gases were used without further purification; helium was Matheson high purity, 99.995% minimum, oxygen was Matheson extra dry grade, 99.6% minimum. The flow rates were measured by a ball-type flowmeter calibrated for either oxygen or air and were controlled by a needle valve downstream from the flowmeter.

When the treatment was completed and the RF power turned off, the chamber was flushed for a minute or two with the gas and then pumped down to about 0.05 mm Hg. After a few minutes at this pressure, pumping was discontinued and the flow of gas restored. If helium was being used, the chamber was allowed to come to atmospheric pressure and the coupons were left in the chamber until required. In the case of oxygen, the chamber was partially filled with oxygen. The specimens were kept in the chamber until required, in order to prevent contact with airborne contaminants. The coupons were handled with tweezers and exposed to the open air for the shortest possible time.

The bonded specimens were single-lap shear sandwich specimens, 1 in. wide with a ½-in. overlap, consisting of aluminum/adhesive/polymer/adhesive/aluminum. Alclad 2024-T3 coupons (4 in. × 1 in. × 1/8 in.)

were used and prepared as follows. Coupons were wiped with acetone, placed in an etching bath (30 pbw water, 10 pbw concentrated sulfuric acid, and 1 pbw sodium dichromate) at 60–70°C for 10 min, washed in a tap-water bath (40°C), rinsed with deionized water, and dried at 60°C.

Specimens with 1/2-in. overlap were assembled in jigs, using an adhesive consisting of 70 pbw Epon 828 epoxy resin (Shell Chemical) and 30 pbw Versamid 140 polyamide curing agent (General Mills, Inc.). The adhesive contained no filler and had a pot life of 45 min. The specimens were lightly weighted (5 psi), allowed to cure at room temperature for at least 16 hr, and postcured for 3–4 hr at 60°C in a circulating air oven. The specimens were conditioned for 1 hr in the test environment and loaded to failure at room temperature on a Baldwin test apparatus with a Tate-Emery load indicator (5000 lb maximum) at a loading rate of 1000 lb/min, using a grip separation of 2 in. Three or more specimens were generally tested for each condition.

Contact angles were measured with a contact angle goniometer (Ramé-Hart), with a telescope and a stage mounted on an optical bench. In order to obtain consistent results, the following procedure was followed. The polymer film or sheet was soaked in acetone, washed with soap and warm water, rinsed several times with deionized water, and dried several hours at 0.01 mm Hg.

Contact angles were taken immediately after drying under vacuum in the case of untreated polymer. Plasma-treated polymer was allowed to stand several hours under helium prior to contact angle measurement. A drop of deionized water (conductivity less than 0.3 micromhos; surface tension 71.8 dynes/cm at 25°C) was placed on the polymer surface and allowed to stand for about 1 min. The contact angle was read on both sides of the drop. The procedure was repeated twice by adding a drop of water each time. Measurements were made at three to five spots on each piece of film, and all values were averaged. The reproducibility of the readings was about ± 1 –2 degrees.

Results and Discussion

Data Treatment

An examination of curves of lap shear bond strength versus duration of activated gas treatment obtained in this as well as in earlier work² suggested that the curves generally show some features in common when allowance is made for the experimental scatter. Almost invariably, these curves appear to rise quite steeply at the shorter times of plasma treatment, and then they seem to level off. In some cases they may show a downturn at the longer times, although measurements have not been made over times that are long enough to establish this conclusively.

Based on the assumption that the strength–plasma treatment time curves are similar, a method for calculating such curves has been developed. By subtracting the zero treatment time strength from that obtained at time t and dividing by t , the quantity R representing the strength change per unit

time of plasma treatment is obtained. R is found to be a function of t according to the relation

$$\frac{1}{R} = a + bt \quad (1)$$

where a and b are constants. Equation (1) indicates that a $1/R$ -versus- t plot should be linear. Least-squares analysis of the present and earlier² data gave the correlation coefficients shown in Table II.

TABLE II
Correlation Coefficients for Various Systems

Polymer	Correlation coefficient	
	Helium	Oxygen
Delrin	0.888	0.569 (0.793) ^a
Celcon	0.953	0.994
Celcon sheet	0.964	0.915
Low-density PE	0.992	0.984
Poly(4-methyl-1-pentene) copolymer	0.983	0.805 (0.987) ^a
Poly(vinyl fluoride)	0.990	0.994
HDPE-Marlex 6002	0.976	0.993
HDPE-Plaskon	0.977	0.985
FEP Teflon	0.989	0.979
Kynar	0.985	0.998
Mylar	0.934	0.997
Styron	0.950	0.959
Nylon 66	0.703 (0.992) ^a	0.873
Nylon 6	0.931	0.941

^a Excluding one very wild point.

If eq. (1) is rewritten

$$R = \frac{1}{a + bt} \quad (2)$$

R may be plotted against t and the curve may be calculated using values of a and b obtained from the least-squares treatment of eq. (1). When this was done, the calculated curves fitted the experimental points satisfactorily except at the shortest times of plasma pretreatment. The reason for this variation was that the reciprocal R values at short times were not weighted heavily enough when the least-squares straight line was calculated. Since the major change in properties occurs after short plasma treatment, it seemed advisable to correct this situation. The method of least squares was used to fit the best curve to the R -versus- t plot. The least-squares method involved calculation of a and b by

$$a = \frac{\Sigma R \Sigma R^2 t^2 - \Sigma R t \Sigma R^2 t}{\Sigma R^2 \Sigma R^2 t^2 - (\Sigma R^2 t)^2} \quad (3)$$

$$b = \frac{\Sigma R - a \Sigma R^2}{\Sigma R^2 t}$$

Values of a and b obtained in this way were used to calculate the curves given in Figures 1-5. The experimental points are also shown in these figures.

This treatment of the data gives a consistent method of drawing the curves despite the rather large scatter in the data. The generally rather high correlation coefficients also indicate that probably the same types of processes are occurring in the initial stages of plasma treatment for the various polymers (see Discussion).

Polyethylene

Figure 1 shows that for both low- and high-density polyethylene, the shear strength of the joints showed a substantial increase after a few seconds of exposure to either excited helium or oxygen. High-density polyethylene may show a slight decrease in bond strength at long helium

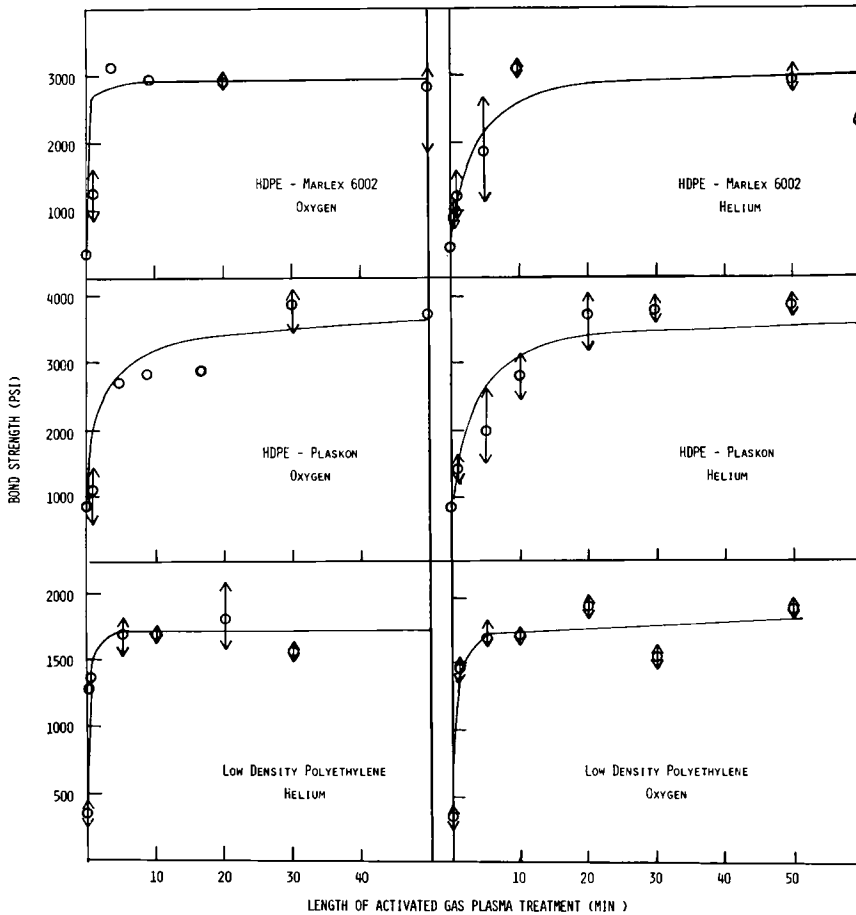


Fig. 1. Bond strength of polyethylene vs. length of exposure to activated gases.

TABLE III
Contact Angles of Polyethylene

	Untreated, deg	He (5 sec), deg
High-density (Plaskon)	96.5	85
Low-density film	97	76
Marlex 5003	92.5	81

exposure time. However, the data do not appear sufficient to be conclusive on this point.

Table III shows contact angles of water on untreated and treated high-density and low-density polyethylene. Marlex 5003 film (4.8 mils), containing no antioxidants or other additives, had been molded against FEP Teflon for 5 min at 350°F in a press. Similar contact angle results were observed for commercial high- and low-density polyethylenes, although values for the untreated commercial samples were somewhat higher, presumably due to greater roughness of the commercial films, which were not specularly smooth.

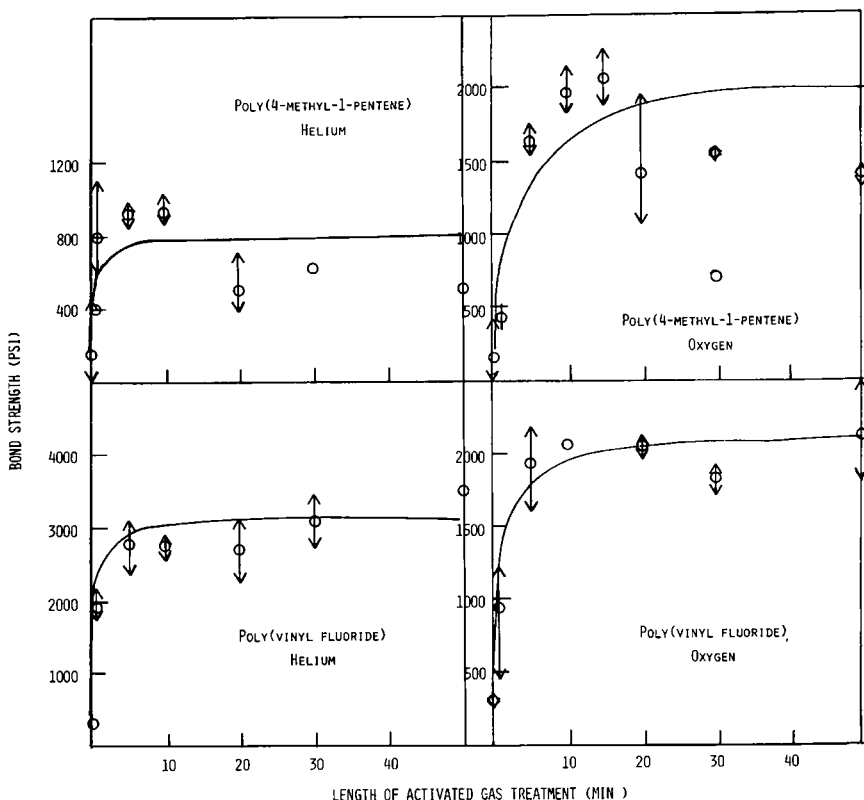


Fig. 2. Bond strength of poly(4-methyl-1-pentene) and of poly(vinyl fluoride) vs. length of exposure.

Poly(4-methyl-1-pentene) Copolymer

Figure 2 shows the results for this copolymer. Although the shape of the calculated curve at the lower times appears to be reasonable, a rather poor fit was obtained at the longest treatment times. This appears to be due to a drop off in strength at the longer times that is not predicted by the method of calculation. As mentioned above, the calculation is somewhat weighted toward the lower end of the curves where the major changes occur. ATR infrared spectra of helium-treated samples showed bands at 970 cm^{-1} (*trans*-vinylene) and 890 cm^{-1} (vinylidene). Similar bands were obtained with active nitrogen.

Poly(vinyl Fluoride)

Figure 2 shows the results for poly(vinyl fluoride). Exposure to activated oxygen is somewhat less effective in increasing bond strength than corresponding exposure to activated helium.

Poly(vinylidene Fluoride)

The bond strength of Kynar exposed to activated helium or oxygen is shown in Figure 3. The results seem to be in disagreement with those pre-

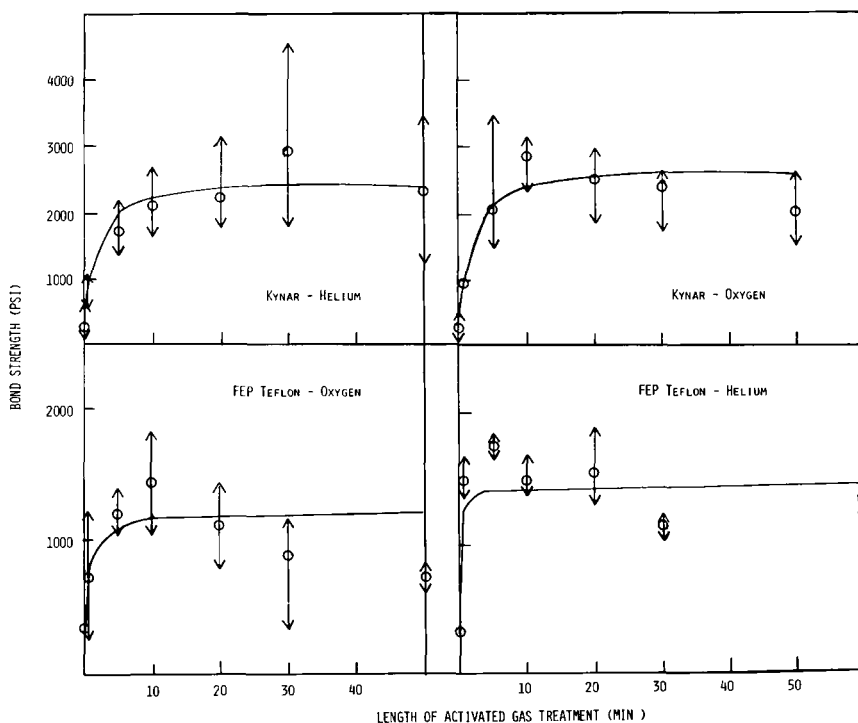


Fig. 3. Bond strength of Kynar and of FEP Teflon vs. length of exposure to activated gases.

viously published,³ which indicated that exposure of Kynar to activated helium does not result in improved adhesive joint strength. However, our value for untreated Kynar is substantially lower than that reported. The highest bond strength observed in the treatment of Kynar, 4590 psi, was reached in one sample exposed to helium for 30 min. When the specimen, prepared from 2024-T3 Alclad coupons, was broken under tensile shear stress, portions of the aluminum cladding were observed on the adhesive surface. Examination by electron microscopy showed the failure to be ductile and entirely within the cladding and not due to failure of the cladding to adhere to the base alloy.

FEP Teflon

Figure 3 shows that the bond strength obtainable with FEP Teflon increases sharply during the first 5 min of exposure to activated helium,⁴ while exposure to activated oxygen plasma results in a slower increase in bond strength. The oxygen-treated material appears to decrease noticeably in strength at the longest times, while the same tendency in the helium-treated material is less pronounced. Once more the method of calculation makes no provision for a change in mechanism leading to such a drop.

Poly(oxyethylene) Copolymer

The Celcon results are given in Figure 4. Exposure for 50 min to excited oxygen caused the thin film used in this experiment to decompose.

Poly(ethylene Terephthalate)

Figure 4 shows that the two activated gases give similar results for Mylar.

Polystyrene

The results for helium and oxygen-treated polystyrene are similar (Fig. 4).

Nylon 6 and 66

Figure 5 shows results for nylon 6 and 66.

Polypropylene

In our initial attempts to treat polypropylene with activated gases, oxygen, nitrogen, and helium were used. Nitrogen and helium gave very poor results while the bond strengths of the oxygen-treated specimens were about eight times those of the untreated specimens (see, e.g., Table IV).

Treatment of polypropylene with helium plasma at higher pressures and temperatures than usual (6 mm as against 0.4 mm Hg and 130°C instead of 50–60°C) has produced bond strengths nearly as high as were obtained in the oxygen treatment. This result is probably due to increased crosslinking at the softening point of the polypropylene. Using a power of 150 watts at

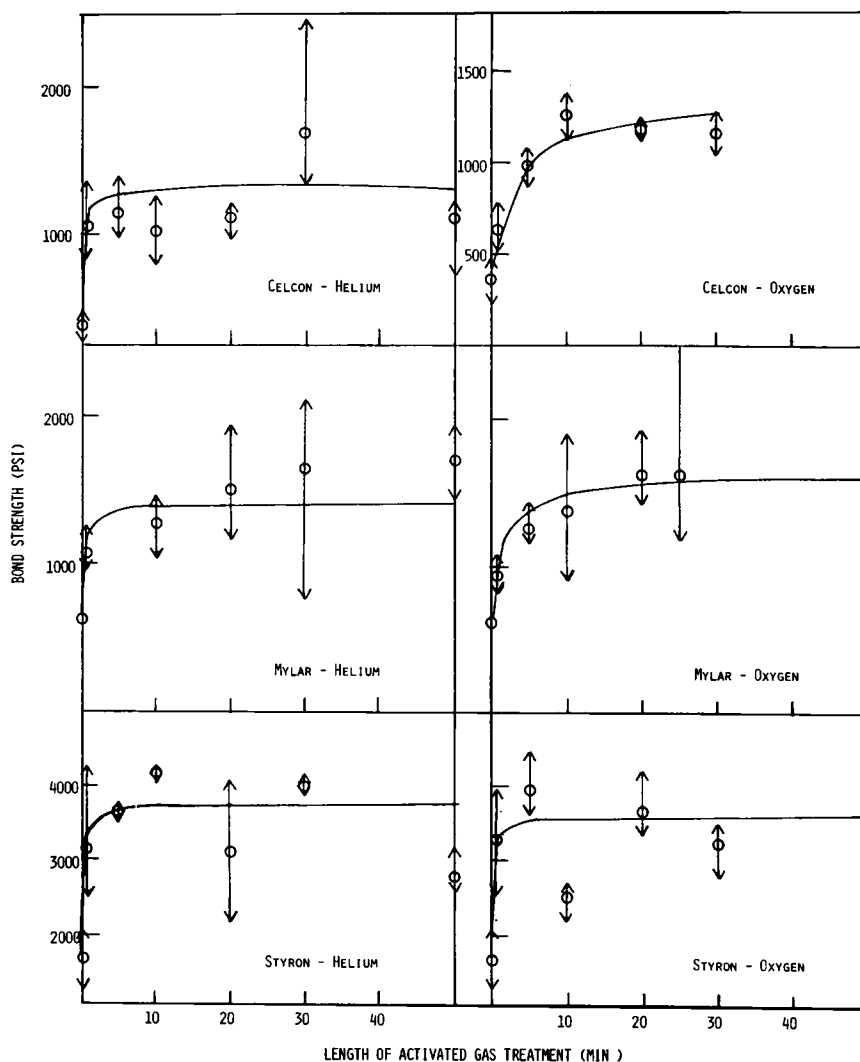


Fig. 4. Bond strength of Celcon, Mylar, and Styron vs. length of exposure to activated gases.

a temperature of about 40°C gave a very poor bond, while using the same power at more than 130°C gave an excellent bond. The increased bond strength is not very reproducible, however, probably because of the problem of controlling the temperature of the exposed film. The higher temperatures were obtained by raising the pressure to several mm Hg at higher power.

Treatment of polypropylene film with activated oxygen gave a rapid increase in bond strength, followed by a leveling off at about 3000 psi. Schonhorn et al.⁵ have also reported the use of excited oxygen for rendering polypropylene bondable.

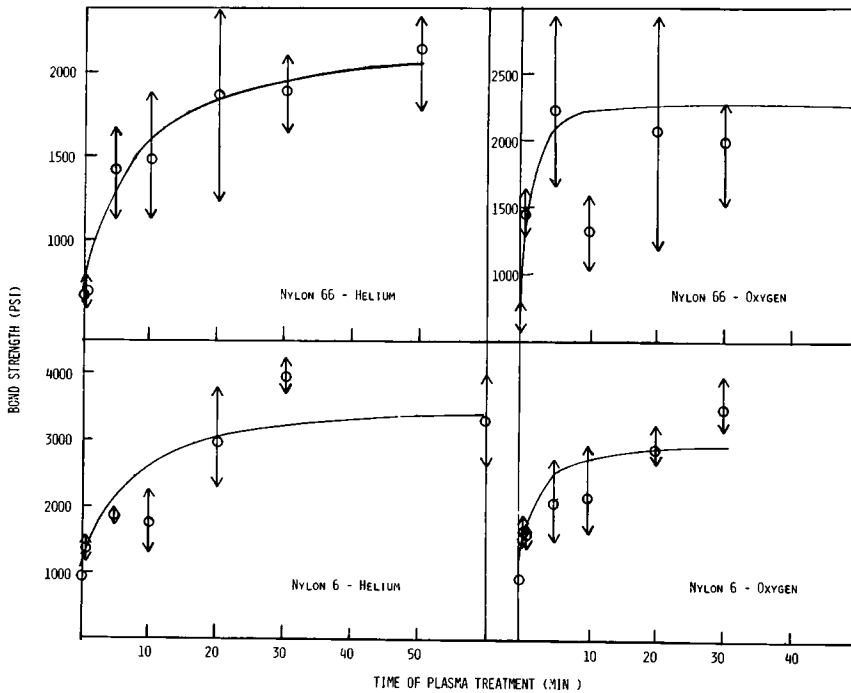


Fig. 5. Bond strength of nylon vs. length of exposure to activated gases.

TABLE IV
Tensile Bond Strength of Polypropylene^a Lap Shear Sandwich Specimens

Activated gas	Treatment conditions ^b	Bond strength, psi		
		Avg. ^c	Low	High
Control	—	370 (6)	250	410
Helium	0.30 mm Hg, ^d 10 min	300 (5)	240	340
Helium	6.0 mm Hg, ^e 5 min	2600 (2)	2190	3010
Oxygen	0.38 mm Hg, 30 sec	1870 (3)	1840	1900
Oxygen	0.40 mm Hg, 11.5 min	3080 (2) ^f	2900	3260
Oxygen	0.50 mm Hg, 30 min	2630 (3)	2320	3090

^a Dow 201 polypropylene film, 4.8 mil.

^b 50 W RF power.

^c Number of specimens in parentheses.

^d Polymer surface temperature approximately 50–60°C.

^e 150 W RF power, 50 ml/min gas flow rate.

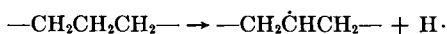
^f Oxidation of film was noticeable.

General Discussion

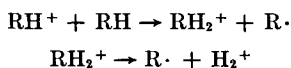
The behavior of the polymers upon exposure to activated gases varies. In some cases the bond strength rises to several times that of the untreated polymer in seconds (e.g., FEP Teflon treated with activated helium), while in other cases, bond strength rises slowly (e.g., nylon 6 treated with acti-

vated helium). Oxygen treatment causes the bond strength in some cases to rise more rapidly than with helium (e.g., nylon 66), but in other cases (FEP Teflon) the response to activated helium is more rapid. Although the data for longer treatment times is rather limited, it appears that ultimately bond strength levels off and in some cases actually decreases.

The several types of behavior seen in the polymers investigated can be explained by the interaction of the mechanisms which improve the bond strength and those which lower it. The improvement of bond strength following activated gas treatment may be attributed to two effects: (1) the formation of a strong surface layer by crosslinking and the elimination of low molecular weight fractions, and (2) the improvement in wettability of the surface caused by the introduction of polar groups and unsaturated groups which derive from radicals and radical ions formed by the activated gas. One proposed mechanism of radical formation is by direct ejection of a hydrogen radical⁶:



Another is by ejection of an electron to form RH^+ which reacts as follows:



Timm and Willard⁷ find no hydrogen atoms trapped during the radiolysis of solid hydrocarbons (except CH_4). This result supports the second mechanism in polyolefins. A radical can decay in several ways: by ejecting another radical to form a double bond; by adding a molecule to form a different radical (e.g., the addition of an oxygen molecule to form a hydroperoxide radical), by termination with another radical, generally to form a crosslink; or by migrating along the polymer chain to an unsaturated position to form a stable allyl radical.

For polymers for which excited oxygen is the more effective treatment, the introduction of polar groups, removal of low molecular weight species by oxidation, and possibly crosslinking via ether links would be the dominant effects. Polypropylene is readily made bondable with excited oxygen, but not with helium (under the usual operating conditions) because chain scission dominates over crosslinking in the latter case.¹ In polymers where the reverse is true, crosslinking by excited helium predominates. In this latter case, it may be that the surface is not readily oxidized, or that ablation is so rapid that there can be no accumulation of a modified surface layer. In polymers where the concentration of polar groups is high, further addition of polar groups by excited oxygen would not greatly increase the polarity.

The initial steep rise in bond strength is probably caused by the elimination of the weak surface layer by oxidation, or rapid crosslinking. The slower increase which usually follows is probably caused by the slower penetration of active species to inner levels of the polymer. The diffusion of radicals into the body of the polymer is doubtless the rate-limiting step.

Schonhorn and Hansen³ found that the thickness of the skin produced by exposing polyethylene to activated helium increased with longer treatment times.

Fall-off in bond strength may occur when processes such as destruction of crystallinity become a more important effect on the bond strength than processes of crosslinking. Exposure to activated oxygen can ultimately lead to deterioration and erosion of the polymer surface.

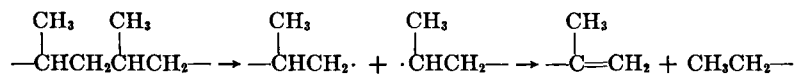
Plateaus, when further treatment neither increases or decreases the bond strength, can occur when the cohesive strength of the polymer has been reached. They can also be the result of a balance of strengthening and weakening processes.

Our observation that polypropylene may be made bondable with excited helium at high temperature, but not at the usual treatment temperature, corresponds to results reported for irradiation of polypropylene at various temperatures with ionizing radiation. Thus, Geymer⁸ and Lawton⁹ found that the amount of crosslinking in polypropylene depends on the temperature at which the samples are irradiated and/or aged. There was much more crosslinking when the irradiated polymer was aged above its glass transition temperature than when it was aged below it. These effects are attributed to temperature-dependent reactions of trapped radicals. The EPR and NMR spectra of polypropylene irradiated with gamma rays at -196°C showed that the concentration of radicals is much higher in the amorphous than in the crystalline phase.¹⁰ When the irradiated polypropylene was warmed to 20°C , the EPR and NMR spectra showed a higher relative concentration of radicals in the crystalline than in the amorphous phase, but lower absolute concentrations than at -196°C . The rate of formation of radicals during irradiation is probably the same in the two phases. In the crystalline phase, many of the radicals (which are formed in pairs) are unable to diffuse apart. Hence they recombine almost immediately. Those which do separate are then in fairly stable configurations. In the amorphous phase, the two members of a radical pair diffuse apart more easily into metastable positions, but they also recombine more easily when the temperature is raised slightly. The remaining radicals in the crystalline phase do not recombine to any great extent until movement of molecular segments is possible at temperatures above the glass transition point. Thus, maximum recombination of trapped radicals and maximum crosslinking take place at a temperature near the crystalline melting point.

Sirota et al.¹¹ conclude that the irradiation of polyolefins by electrons at temperatures considerably below the melting temperature is accompanied by crosslinking mainly in the amorphous phase. The number of radicals is higher in the crystalline regions, and upon heating under vacuum, these radicals recombine and crosslink.

Veselovskii et al.¹² state that "most of the intermolecular bonds produced by irradiation of isotactic polypropylene are evidently formed by reaction of double bonds, mainly of the vinylidene type, produced by rupture of the polymer," while "the major proportion of the crosslinkages produced in

irradiation of amorphous (atactic) polypropylene are formed by recombination of free radicals." Thus, a temperature dependence of effectiveness of helium plasma treatment of polypropylene as well as the presence of vinylidene bonds in the ATR infrared spectra of treated samples is to be expected:



Lawton, Balwit, and Powell¹³ have demonstrated the formation of long-lived trapped radicals in linear polyethylene by irradiation with high-energy electrons. ESR measurements show radical decay to be temperature dependent and very rapid at the crystalline melting point. Thus, crosslinking of polyethylene by activated plasmas would be expected to be more rapid at high temperature. However, the *G*-value for crosslinking for polyethylene is sufficiently high at or near room temperature so that a rapid increase in bondability is observed.¹

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