

Activated Gas Plasma Surface Treatment of Polymers for Adhesive Bonding

J. RICHARD HALL, CAROLYN A. L. WESTERDAHL,
ANDREW T. DEVINE, and MICHAEL J. BODNAR, *Adhesives
and Coatings Branch, Picatinny Arsenal, Dover, New Jersey 07801*

Synopsis

Polyethylene, polypropylene, poly(vinyl fluoride) (Tedlar), polystyrene, nylon 6, poly(ethylene terephthalate) (Mylar), polycarbonate, cellulose acetate butyrate, and a poly(oxymethylene) copolymer were treated with activated helium and with activated oxygen. Mechanical strengths of adhesive-bonded specimens prepared from treated and from untreated coupons were compared. Polyethylene (PE) and polypropylene (PP) showed the greatest increases in bond strength. Oxygen and helium were both effective with polyethylene, but polypropylene showed no improvement when treated with activated helium. The results with excited helium parallel the effects of ionizing radiation on these two polymers, as does the appearance of unsaturation bands in the infrared (965 cm^{-1} in PE, and 887 and 910 cm^{-1} in PP). Active nitrogen produced excellent bond strength with polyethylene but not with polypropylene. Of the remaining polymers examined, Tedlar, polystyrene, and nylon 6 showed the greatest improvement in bondability after treatment, and Mylar showed moderate improvement. Polycarbonate, cellulose acetate butyrate, and the poly(oxymethylene) copolymer gave approximately two-fold increases in lap-shear bond strength. In several cases, significant differences in response to time of treatment and type of excited gas were found.

INTRODUCTION

Adhesive bonding, with its many advantages, cannot be applied to many common plastics unless a special surface treatment is employed first. Thus, a solvent-type contact cement can be used for poly(methyl methacrylate) without surface treatment, but polyethylene must be flame-treated or treated with chromic-sulfuric acid for successful bonding. A review of bonding of plastics has been published by Bodnar.¹

Recently it has been reported that treatment of polyethylene surfaces with excited inert gases greatly improves the bond strength of adhesive joints prepared from polyethylene and epoxy adhesive.^{2,3} In this technique, a low-pressure gas is activated by an electrodeless radiofrequency discharge or microwave excitation to produce metastable excited species which are allowed to impinge on a polymer surface over a period of a few seconds to a few hours. Hydrogen atoms, or in the case of fluorocarbon polymers, fluorine atoms are expelled from this polymer to produce a crosslinked, partially unsaturated skin. Thus, any mechanically weak low molecular

weight or amorphous material present on a polymer surface may be converted into a strong crosslinked surface layer suitable for bonding with adhesives. This article describes some of the preliminary results obtained with a variety of polymers treated by excited gases.

Nature of Activated Gases

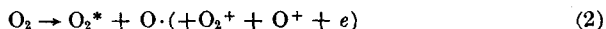
Many gases can be excited by electrodeless radiofrequency or microwave discharges to produce "active" species. Useful applications of such active atoms or molecules include chemical reactions, e.g., reduction of metal oxide powders to metal powders, low temperature ashing of biological or other sensitive materials, and surface treatment of polymers to render them wettable or bondable with adhesives.^{3,4} Synthesis of polymers by means of activated plasmas has been reported.⁵

The terms "activated gas," "excited gas," or "activated plasma" have all been used rather interchangeably. It may be worthwhile, therefore, to consider the nature of species produced in electrodeless discharges. Active molecules or atoms, e.g., active nitrogen, are un-ionized molecules or atoms which have absorbed additional energy to become spectroscopically excited species. For example, triplet ground state $O_2(^3\Sigma_g)$ is excited to the first singlet state ($^1\Delta_g$).⁴ The chemical reactions of active nitrogen have been studied extensively in recent years; the principal reactive species is believed to be ground state atomic nitrogen (4S), although excited nitrogen molecules ($A^3\Sigma$) are believed to be important for some reactions.⁶ Thus, active or activated gases would contain excited, but un-ionized atoms or molecules, and in the case of diatomic gases, reactive atoms produced by dissociation.

The term "plasma," properly speaking, refers to a mixture of positive ions and electrons produced by ionization (e.g., in an arc or by very high temperatures). An RF discharge will produce a glow region in the vicinity of the activator plates or coil; this glow region is a "cold" plasma which consists of ionized species, free electrons (approximately 1×10^{11} electrons/cm³), free radicals (or atoms from dissociation of molecules), excited molecules or atoms, as well as unchanged gas. The ions rapidly recombine with the free electrons as they move out of the glow region. The glow seen, for example with oxygen, is primarily due to this recombination reaction.

Oxygen plasmas produced by RF discharges have been found to contain 10–20% atomic oxygen and about an equivalent amount of molecularly excited O_2 .⁴ In the absence of oxidizable material, a faint pink glow due to the 7920 cm⁻¹ line is visible; in the presence of organic compounds, a blue color of greater intensity due to de-excitation of CO_2 is seen.

In summary, the principal reactions leading to the formation of the plasmas used in most of this work are:

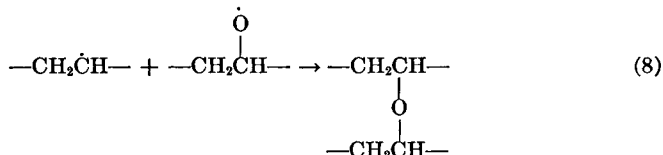
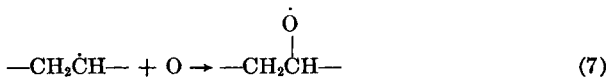
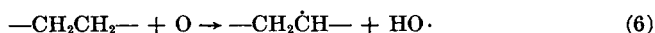
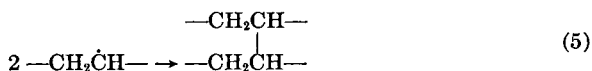
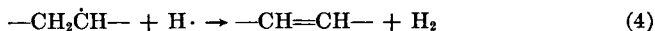
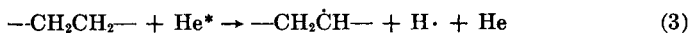


In some experiments silicone rubber was treated with ammonia plasma. Although the reaction has not been studied in detail, a portion of the ammonia is decomposed to hydrogen and nitrogen. Presumably, intermediate species such as $\text{NH}_2\cdot$ are formed. However, no $-\text{NH}$ was detectable by multiple internal reflectance (MIR) infrared spectroscopy on the surface of the silicone after treatment.

Effect of Activated Gases

The effect of activated gases on polymer surfaces may be divided into several categories: removal of a weak surface layer by oxidation; cleaning of a surface by removal of adsorbed materials through kinetic action and de-excitation of a plasma; crosslinking of polymer surface; chemical reaction or grafting, e.g., production of unsaturation or addition of ether linkages. Obviously, these categories are not independent of one another. Thus it has been shown by Hansen and Schonhorn^{2,3} that treatment of polyethylene with helium produces an insoluble crosslinked surface film; the presence of *trans*-ethylenic unsaturation is shown by MIR infrared spectroscopy.^{2,3,8} Treatment of polyethylene with activated oxygen produces a surface which is presumably also crosslinked and which gives the same bond strengths as helium-treated polyethylene. A strong C-O band at 1101 cm^{-1} and a weak band at 1664 cm^{-1} were reported to be present by Hollahan,⁵ but no carbonyl or hydroxyl absorptions were found. We were unable to observe these changes by MIR infrared spectroscopy however.

These observations may be rationalized by the steps shown in eqs. (3)–(8).



Hansen et al. found that incorporation of varying amounts of a good thermal antioxidant had no effect on the oxidation rate of polypropylene.⁹ It may be concluded that chain processes are unimportant in oxidation of polypropylene by activated oxygen.

Experimental

A Tracerlab PRS-600 plasma research system was used for treatment of plastic coupons. The PRS-600 is comprised of a 300-W 13.56 Mc RF generator, a capacitatively coupled plasma activator consisting of impedance matching circuitry and a pair of activator plates, a glass reactor chamber with four activator tubes, a vacuum system, and a gas metering system.

The reactor chamber is approximately 4 in. in internal diameter and 10 in. high and has provision for rotating specimens in the activated gas stream. The inlet flow rate is controlled by the pressure regulator and a needle valve. The gas flows through a brass manifold and then through glass capillary tubing sealed to the ends of activator tubes. Operating pressure of the system is metered by a thermocouple type pressure transducer and its associated electronic circuitry, or by a tilting McLeod gauge.

In use, the reaction chamber is pumped down to 0.1 mm pressure or less and a suitable gas flow (e.g., 20 cc/min.) established. The pressure usually rises to 0.35 mm; the pumping rate is adjusted to obtain the desired pressure and a discharge is established. Much of this work was done at 50 W; higher powers, particularly with oxygen, often caused melting of thermoplastics. Temperatures were monitored if necessary with Thermotubes (Paper Thermometer Co., Natick, Mass.), or sealed melting point tubes containing a suitable compound.

After exposure of the plastic coupons or film for the appropriate time, the RF power was turned off, the residual gas pumped out, and the chamber returned to atmospheric pressure, usually with helium. The treated samples were generally kept under a stream of helium for $\frac{1}{2}$ hr or more, although no particular change in bondability was noted with longer periods.

Infrared spectra were determined with a Beckman IR-9 spectrophotometer by using a Wilks multiple internal reflectance attachment. The internal reflectance element used was either a 45° or 60° $2 \times 20 \times 50$ mm KRS-5 (TlBr-TII) plate.

The gum silicone was a catalyst-free dimethylsiloxane polymer supplied by General Electric, DC-400, lot 7150. The silicone elastomer was a pigmented dimethylsiloxane (Dow-Corning customer formulation #157); $\frac{1}{2}$ -in. wide strips of $\frac{1}{16}$ -in. sheet were bonded to $\frac{1}{16}$ -in. strips of Lexan (G.E.) with Uralane 8089 urethane adhesive, supplied by Furane Plastics, Inc. Silicone strips were treated with excited ammonia for 30 min at 20 cc/min and 50 W.

Assembly and Bonding of Specimens

The bonded specimens employed were single-lap shear sandwich specimens, 1 in. wide \times 7.5 in. long with a 0.5 in. overlap. The construction of the bonded assembly was as follows: 2024-T3 bare aluminum/adhesive/polymer/adhesive/2024-T3 bare aluminum. Prior to bonding, the aluminum coupons received a surface treatment consisting of an acetone wipe,

FPL acid etch, and tap water rinse, followed by oven drying at 120°F for 15 min. The polymer coupons were solvent-wiped before plasma treatment.

The adhesive was a two-component, polyamide-modified epoxy system consisting of Shell Chemical's Epon 828 epoxy, and Versamid 140 polyamide curing agent manufactured by General Mills, Inc., in a ratio of 70/-30 pbw. No filler material was used.

The specimens were lightly weighted (5 psi) and allowed to cure 16 hr at room temperature (ca. 75°F), followed by a postcure of 120°F for 3 hr in a circulating air oven. All specimens were conditioned for 1 hr in the test environment before testing. The bonded specimens were loaded to failure on a Baldwin test apparatus with a Tate-Emery load indicator (5000 lb maximum) at a loading rate of 1000 lb/min.

Results and Discussion

In previous work the relative effectiveness of flame treatment, sanding, and several sulfuric acid-dichromate treatments on the joint strength of adhesive-bonded polyethylene using various types of adhesives was investigated.¹⁰ The polyethylene was a pigmented, high-density material, Marlex 6002 (Phillips Petroleum Co.), in the form of $4 \times 1 \times 1/16$ -in. coupons, bonded with a 0.5 in. overlap. Initial investigation of the activated plasma treatment utilized the same polyethylene in order to compare the new treatment with previous methods, except that 3.5-in. coupons were used instead of 4-in. coupons in order to permit rotation of the coupons in the reactor chamber.

Since trial specimens with $1/2$ -in. overlaps gave failure in the adherend, smaller overlaps, i.e., $1/4$ and $1/8$ in., were also investigated in an attempt to

TABLE I
Joint Strength, High-Density Polyethylene, Lap Shear^a

Treatment ^c	Load to failure, lb ^b		
	$1/2$ in. overlap	$1/4$ in. overlap	$1/8$ in. overlap
O ₂ plasma, 30 min	222 ± 6	208 ± 10	170 ± 4
O ₂ plasma, 1 min	233 ± 12	216 ± 15	172 ± 8
He plasma, 1 min	232 ± 4	198 ± 11	168 ± 8
Control, solvent wiped ^d	23 ± 6 (46 ± 11 psi) ^e	—	—

^a Marlex 6002 (Phillips Petroleum), green pigment, $3 \times 1 \times 1/16$ in.; 4 specimens each overlap, bonded with Epon 828 epoxy/Versamid 140, no filler.

^b Average deviation, calculated by averaging the absolute values of the differences between individual readings and the average.

^c 50 W RF power, 20 ml gas/min, 0.35 mm pressure for O₂, 0.30 mm for He.

^d Value taken from Devine et al.¹⁰ for 70/30/5 Epon 828/Versamid 140/Cab-o-sil specimens.

^e Adhesive failure. All other specimens failed in adherend; values are given as load to failure (lb).

cause failure in the bonded overlap. The purpose was to provide a means of comparing the relative effectiveness of plasma treatment with flame treatment and other surface preparation techniques. However, adherend failure also occurred in specimens with the shorter overlaps; lower failing loads were observed because of the greater bending moments produced.

Adhesive specimens prepared from polyethylene coupons treated with excited oxygen for 30 min and 1 min show essentially no difference in the strengths obtained with the two treatment times for equal overlaps (Table I). A $\frac{1}{2}$ -in. overlap, for example, resulted in an average breaking load of 222 lb and 233 lb for treatment times of 30 min and 1 min, respectively.

The polyethylene specimens treated with helium for 1 min gave results of the same order of magnitude as those treated with oxygen for 30 min and 1 min. Likewise, all failures occurred in the polyethylene, and the longer overlapped specimens resulted in higher breaking loads.

TABLE II
Bond Strength of Lap Shear Sandwich Specimens*

Polymer	Treatment conditions ^b	Bond strength, psi	Type of failure ^c
Polyethylene, high-density ^d	Control ^e	315 ± 38 ^f	Adh. from polyethylene
	O ₂ plasma, 30 min	2436 ± 52 ^g	Adh. from aluminum, 2/3 Adh. from polyethylene, 1/3 Trace of polyethylene failure
	O ₂ plasma, 1 min	1160 ± 136 ^f	Adh. from aluminum, 2/3 Adh. from polyethylene, 1/3
	O ₂ plasma, 1 min	1220 ± 213 ^f	Adh. from aluminum, 2/3 Adh. from polyethylene, 1/3
	O ₂ plasma, 30 sec	1984 ± 89 ^g	Adh. from polyethylene with slight deformation of surface
	He plasma, 30 min	3125 ± 68 ^g	Coh. in polyethylene
	He plasma, 1 min	1212 ± 242 ^f	Adh. from polyethylene with slight deformation of surface
	He plasma, 30 sec	924 ± 158 ^g	Adh. from polyethylene
	N ₂ plasma, 60 min. ^h	3500 ± 68 ^g	Coh. in polyethylene
	Polyethylene, low-density ⁱ	Control ^e	372 ± 52 ^f
O ₂ plasma, 30 min		1466 ± 106 ^g	Coh. in polyethylene
O ₂ plasma, 1 min		1446 ± 36 ^f	Coh. in polyethylene
He plasma, 30 min		1324 ± 38 ^g	Coh. in polyethylene
He plasma, 1 min		1382 ± 17 ^f	Coh. in polyethylene
He plasma, 30 sec		1250 ± 33 ^g	Coh. in polyethylene
N ₂ plasma, 60 min		1401 ± 50 ^g	Coh. in polyethylene

* $4 \times 1 \times \frac{1}{8}$ in. aluminum coupons were used.

^b 50 Watts net power, 20 ml/min gas flow, 0.30–0.35 mm pressure.

^c Adh. = adhesive, Coh. = cohesive.

^d Marlex 6002, green pigment, $\frac{1}{16}$ in. thick.

^e Solvent-wiped with acetone or ethanol, air-dried.

^f Average of 6 specimens, 1 in. wide, $\frac{1}{2}$ in. overlap.

^g Average of 3 specimens, 1 in. wide, $\frac{1}{2}$ in. overlap.

^h Plaskon PP60-002 (Allied Chemical), 9.2 mils thick.

ⁱ 30 mils thick, Picatinny Arsenal stock.

Because of the problems encountered in testing $3.5 \times 1 \times 1/8$ in. polyethylene coupons bonded to each other directly and the more general availability of different polymers as films, lap shear sandwich specimens were used for most of this work. The effect of treatment time on bond strength for some polymers, in the form of sandwich specimens, is shown in Table II. For example, high-density polyethylene (HDPE) showed nearly an eight-fold increase in bond strength (2400 psi) after treatment for 30 min with excited oxygen. Oxygen plasma treatment times of 30 sec and 1 min duration yielded strengths of approximately 2000 and 1200 psi, respectively.

Helium plasma-treated specimens gave bond strengths of 3125, 1210, and 925 psi for treatment times of 30 min, 1 min, and 30 sec, respectively. The mode of failure on the 30-min helium-treated HDPE was cohesive in the polymer, that for the 1-min treatment was adhesive from polyethylene with slight deformation of the polymer surface, while failure in the 30-sec-treated sample was adhesive from polyethylene. Activated nitrogen produced excellent bond strengths (3500 psi).

Low-density 10-mil polyethylene film (Table II) was treated with oxygen plasma for 30 min and 1 min. In both instances the mode of failure was cohesive in the polymer, and failing loads were almost identical at 1465 psi for 30 min and 1445 psi for 1 min. The low-density polyethylene (LDPE) specimens treated with helium for 30 min, 1 min, and 30 sec also failed cohesively at 1325, 1380, and 1250 psi, respectively. Treatment with

TABLE III
Bond Strengths of Lap Shear Sandwich Specimens^a

Polymer	Treatment conditions ^b	Bond strength, psi ^c	Type of failure
Lexan ^d	Control ^e	410 ± 10	Adh. from Lexan
	O ₂ plasma, 30 min	928 ± 66	Adh. from Lexan with cracking
	O ₂ plasma, 30 sec	800 ± 42	Adh. from Lexan with cracking
	He plasma, 30 min	840 ± 60	Adh. from Lexan with cracking
	He plasma, 30 sec	660 ± 27	Adh. from Lexan
Polypropylene ^f	Control ^e	370 ^g	Adh. from polypropylene
	O ₂ plasma, 30 min.	3080 ± 180	Adh. from polypropylene Adh. from polypropylene with deformation of surface
	O ₂ plasma, 30 sec	1870 ± 20	Adh. from polypropylene with deformation of surface
	He plasma, 30 min	200 ^g	Adh. from polypropylene
	He plasma, 30 sec	450 ± 50	Adh. from polypropylene
	N ₂ plasma, 30 min	633 ± 158	Adh. from polypropylene

^a Aluminum coupons, $4 \times 1 \times 1/8$ in.

^b 50 W power, 20 ml/min gas flow, 0.30–0.35 mm pressure.

^c An average of 3 specimens, 1 in. wide, $1/2$ in. overlap.

^d Bisphenol A polycarbonate, General Electric Co., $1/16$ in. sheet.

^e Solvent-wiped with ethanol.

^f Dow 201, 0.0048 in. thick film.

^g Only one determination was made.

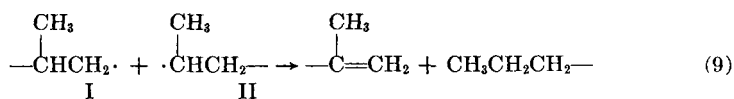
activated nitrogen produced cohesive failure at 1401 psi. These values compare favorably with the bond strength of 365 psi for the untreated control.

Polypropylene (PP) treated with helium plasma for 30 min and 30 sec showed no improvement over the untreated control sample (Table III). Bonds were so poor, in fact, that the samples failed during normal handling. Excited oxygen treatment for 30 min and 30 sec resulted in bond strengths of 3080 and 1870 psi, respectively. Activated oxygen treatment of polypropylene proves a very effective and rapid means of surface treatment for improving adhesive bonds to polypropylene. Activated nitrogen treatment was only somewhat more effective than activated helium.

The effect of activated inert gases and of ionizing radiation on polyolefins may be compared. The crosslinking and scission of polyolefins with ionizing radiation have been found to depend on crystallinity, temperature, presence of oxygen, molecular weight distribution, and vinyl endgroup content.¹¹⁻¹⁶ For example, Marans and Zapas¹⁵ found that irradiation of polypropylene with 2-MeV electrons at low doses caused a reduction in reduced specific viscosity (RSV) and bulk viscosity, whereas high-density polyethylene gave an increase in RSV. The decrease in RSV of PP was explained by the reduction in \bar{M}_w by equivalent simultaneous crosslinking and chain degradation and by a decrease in the value of the exponent in the Mark-Houwink equation, rather than by dominance of chain degradation over crosslinking. Nevertheless, the much greater tendency of linear polyethylene to crosslink rather than degrade is apparent, since the same effects should operate to reduce the RSV of polyethylene. Furthermore, Marans and Zapas annealed their samples at 175°C in order to allow trapped radicals to decay, thus causing an increase in crosslinking. The marked tendency of polypropylene to exhibit delayed crosslinking by heating above the melting temperature subsequent to irradiation has been reported, for example, by Sobue and Tozima.¹⁷

Our observation that activated helium treatment of polypropylene does not produce a bondable surface, whereas treatment of polyethylene does, may be explained by the greater tendency of polypropylene to yield chain degradation, and quenching of trapped radicals by oxygen upon exposure of the treated film to the atmosphere. Williams¹⁸ has expressed the view that crosslinking in polypropylene occurs as a result of decay of unsaturation initially present or found during irradiation in contrast to polyethylene, which is postulated to crosslink by interaction of free radicals or by ion-molecular processes.

Multiple internal reflectance spectroscopy of helium-treated polypropylene revealed the presence of bands at 887 and 910 cm^{-1} , indicative of vinylidene and vinyl unsaturation, respectively. The 887 cm^{-1} absorption was reported by Black and Lyons¹⁹ and both the 887 and 910 cm^{-1} absorptions were found by Slovakhotova et al.²⁰ in irradiated polypropylene and are consistent with disproportionation of radicals formed by chain scission [eq. (9)].



Vinyl groups may arise from disproportionation of radical I and II to give a vinyl and an isopropyl endgroup, or by loss of a methyl group from I or a propyl endgroup. Krasnansky found that the gaseous products from γ -irradiation of polypropylene contained 5% methane and 95% hydrogen in contrast to linear polyethylene which gave no methane.²¹

Activated nitrogen, like activated helium, produced excellent bond strengths with polyethylene, but not with polypropylene. No vinylidene or vinyl groups were found in polypropylene as a result of treatment with activated nitrogen. Weininger²² reported gel formation in polyethylene and, to a lesser extent, in polypropylene after treatment with active nitrogen.

Silicone elastomer was treated with activated ammonia and bonded to polycarbonate strips with a urethane adhesive. Peel strength was somewhat improved, but the results were erratic. Exposure of gum silicone

TABLE IV
Bond Strengths of Lap Shear Sandwich Specimens*

Polymer	Treatment conditions ^b	Bond strength, psi ^c	Type of failure
Styron ^d	Control ^e	566 ± 17	Adh. from Styron
	O ₂ plasma, 30 min	3118 ± 278	Coh. in Styron
Mylar A ^f	He plasma, 30 min	4015 ± 85	Coh. in Styron
	Control ^e	530 ± 51	Adh. from Mylar A
Mylar D ^g	O ₂ plasma, 30 min	1215 ± 29	Adh. from Mylar A with some cracking or film failure
	He plasma, 30 min	1660 ± 40	Adh. from Mylar with cracking
	Control ^e	618 ± 25	Adh. from Mylar D
Tedlar ^h	O ₂ plasma, 30 min	1185 ± 83	Adh. from Mylar D with cracking
	He plasma, 30 min	1216 ± 522	Adh. from Mylar D with cracking
Tedlar ^h	Control ^e	278 ± 2	Adh. from Tedlar
	O ₂ plasma, 30 min	1280 ± 73	Adh. from aluminum, 1/2 Coh. in Tedlar, 1/2
	O ₂ plasma, 30 sec	1370 ± 80	Adh. from aluminum, 1/2 Coh. in Tedlar, 1/2
	He plasma, 30 min	1200 ± 80	Adh. from aluminum, 1/2 Coh. in Tedlar, 1/2
	He plasma, 30 sec	1290 ± 40	Adh. from aluminum, 1/2 Coh. in Tedlar, 1/2

* Aluminum coupons, 1/8 in. thick, 4 in. long, 1 in. wide, were used.

^b 50 W power, 20 ml/min gas flow, 0.30 to 0.35 mm pressure.

^c Average of 3 specimens, 1 in. wide, 1/2 in. overlap.

^d Dow modified polystyrene, #475 or 480, 10-mil film, smooth on one side.

^e Solvent-wiped and air-dried.

^f Poly(ethylene terephthalate), du Pont, general purpose, 10-mil film.

^g Poly(ethylene terephthalate), du Pont, cartography grade, 10-mil film.

^h Poly(vinyl fluoride) film, 1 mil thick, du Pont 100 SG 30 TR.

elastomer to activated ammonia at high power for 1 hr resulted in formation of a puckered skin; no $-\text{NH}_2$ bonds were found by MIR infrared spectroscopy. However, a thin film of low molecular weight silicone remained on the KRS-5 reflector plate after contact with vulcanized silicone elastomer. Thus, it would appear that the poor bondability of silicone is due to the presence of low molecular weight fractions which continually diffuse to the surface, and not to lack of crosslinking with activated gases. The best adhesives for silicones are the RTV moisture-curing dimethylsiloxane adhesives, which are compatible with the low molecular weight fractions and thus do not permit the formation of a weak boundary layer.

Of the remaining polymers examined, poly(vinyl fluoride) Tedlar (Table IV), polystyrene (Table IV), and nylon 6 (Table V) showed the greatest improvement in bondability after treatment and poly(ethylene terephthalate) Mylar (Table IV) showed moderate improvement. Polycarbonate (Table III), cellulose acetate butyrate (Table V), and a poly(oxyethylene)

TABLE V
Bond Strengths of Lap Shear Sandwich Specimens^a

Polymer	Treatment conditions ^b	Bond strength, psi ^c	Type of failure
Cellulose acetate butyrate (CAB) ^d	Control ^e	1090 ± 27 655 ± 70 ^{f,g}	Adh. from CAB
	O ₂ plasma, 30 min	1380 ± 60	Adh. from CAB
	O ₂ plasma, 1 min	455 ± 95 ^f	Adh. from CAB
	O ₂ plasma, 30 sec	1126 ± 141	Adh. from CAB
	He plasma, 30 min	2516 ± 22	Adh. from CAB with polymer deformation and cracking
	He plasma, 1 min	590 ± 170 ^{f,g}	Adh. from CAB
	He plasma, 30 sec	1250 ± 150	Adh. from CAB with polymer deformation and cracking
Nylon 6 ^h	Control ^e	846 ± 166 ^g	Adh. from nylon 6
	O ₂ plasma, 30 min	3490 ± 233	Adh. from aluminum with film failure
	O ₂ plasma, 1 min	1520 ± 111	Adh. from aluminum
	O ₂ plasma, 30 sec	1624 ± 191	Adh. from aluminum
	He plasma, 30 min	3956 ± 195	Adh. from aluminum with film failure
	He plasma, 1 min	1238 ± 75 ^g	Adh. from aluminum with failure in nylon 6
	He plasma, 30 sec	1220 ± 120	Adh. from aluminum

^a 1/8 in. aluminum was used.

^b 50 W power, 20 ml/min gas flow, 0.30–0.35 mm pressure.

^c An average of 3 specimens, 1 in. wide, 1/2 in. overlap.

^d Uvex, 0.60 in. thick, Eastman Chemical Prod., Inc.

^e Solvent-wiped with ethanol or acetone, air-dried.

^f 1/16 in. aluminum was used.

^g An average of 6 specimens, 1 in. wide, 1/2 in. overlap.

^h Capran 77C, 3-mil film, Allied Chemical Co.

TABLE VI
Bond Strengths of Lap Shear Sandwich Specimens

Polymer	Treatment conditions ^a	Bond strength, psi ^b	Type of failure
Butt-tensile specimens			
Celcon ^c	Control ^d	1450	Adh. from Celcon
	He plasma, 5 min	3290	Adh. from Celcon
Lap-shear specimens			
Celcon ^e	Control ^d	118 ± 4	Adh. from Celcon
	O ₂ plasma, 30 min	258 ± 16	Adh. from Celcon
	He plasma, 30 min	236 ± 22	Adh. from Celcon
	He plasma, 30 sec	186 ± 58	Adh. from Celcon

^a 50 W power, 20 ml/min gas flow, 0.30–0.35 mm pressure.

^b Butt-tensile values are for single specimens, ASTM D-897 metal-to-metal specimens, 1 in.² faying surface area. Lap-shear values are averages of 3 specimens, $\frac{3}{4} \times 3\frac{1}{2} \times \frac{1}{8}$ in. thick, $\frac{1}{2}$ in. overlap.

^c Celcon C-130, 20% chopped glass, ground, rotationally molded, pigmented brown with stabilizer, $\frac{1}{16}$ in. thick.

^d Solvent-wiped with ethanol.

^e Same material as for butt-tensile tests, but reground and injection-molded.

copolymer (Celcon) (Table VI) gave approximately twofold increases in bond strength. Since the lap-shear bond strength of untreated Celcon is quite low (118 psi), doubling of this value as a result of treatment is of marginal utility.

Other polymers besides polypropylene also responded differently to excited helium and oxygen. For example, cellulose acetate butyrate showed a significant increase in bond strength only when treated with helium for a relatively long period (30 min); no improvement was found after oxygen treatment. With polystyrene, activated helium was rather more effective than activated oxygen, although both resulted in cohesive failure in the adherend. Perhaps significantly, the depth of failure in the helium-treated specimen was greater than that for the oxygen-treated specimen, suggesting a thicker crosslinked layer on the helium-treated polystyrene. One would expect that only a thin crosslinked layer could be formed with activated oxygen, since the outermost layer of polymer is continuously oxidized to CO, CO₂, and H₂O vapor.⁹ In no case examined was gel found after oxygen treatment (e.g., polycarbonate, polypropylene, polyethylene), although gel was readily formed by helium treatment of those polymers which responded to activated helium (e.g., polycarbonate, polyethylene). Changes in a very thin (e.g., 10–10² Å) crosslinked layer might well go undetected by internal reflectance infrared spectroscopy, since the depth of penetration is approximately 2–3 μ .

The authors wish to thank Dr. D. W. Levi for his helpful advice, Mr. Sandor I. Einstein for preparation of some of the adhesive specimens, and Mrs. Dorothy A. Teetsel for manuscript preparation.

References

1. M. J. Bodnar, in *Handbook of Adhesives*, I. Skeist, Ed., Reinhold, New York, 1962.
2. R. H. Hansen and H. Schonhorn, *J. Polym. Sci. B*, **4**, 203 (1966).
3. H. Schonhorn and R. H. Hansen, *J. Appl. Polym. Sci.*, **11**, 1461 (1967).
4. J. R. Hollahan, *J. Chem. Ed.*, **43**, A401 (1966).
5. J. R. Hollahan, private communication.
6. A. Tsukamoto and N. N. Lichtin, *J. Amer. Chem. Soc.*, **84**, 1601 (1962).
7. J. R. Hollahan and R. P. McKeever, paper presented at the Pacific Conference for Applied Spectroscopy, American Chemical Society and Society for Applied Spectroscopy, Anaheim, California, Oct. 30–Nov. 1, 1967.
8. J. R. Hollahan, private communication.
9. R. H. Hansen, J. V. Pascale, T. DeBenedictus, and P. M. Rentzepis, *J. Polym. Sci. A*, **3**, 2205 (1965).
10. A. Devine, W. Bodnar, E. Duda, and M. Bodnar, "Effects of Surface Treatments on Bonding to Polyethylene with Various Type Adhesives," Picatinny Arsenal Technical Memorandum 1797, October 1967.
11. M. Dole and K. Katsuura, *J. Polym. Sci. B*, **3**, 467 (1965).
12. R. Kitamaru, L. Mandelkern, and J. Fatou, *J. Polym. Sci. B*, **2**, 511 (1964).
13. R. Kitamaru and L. Mandelkern, *J. Amer. Chem. Soc.*, **86**, 3529 (1964).
14. E. J. Lawton, U.S. Pat. 2,948,666 (Aug. 6, 1960).
15. N. S. Marans and L. J. Zapas, *J. Appl. Polym. Sci.*, **11**, 705 (1967).
16. T. Okada, L. Mandelkern, and R. Glick, *J. Amer. Chem. Soc.*, **89**, 4790 (1967).
17. H. Sobue and Y. Tozima, *Nature*, **188**, 315 (1960).
18. T. F. Williams, *Nature*, **186**, 544 (1960).
19. R. M. Black and B. J. Lyons, *Proc. Roy. Soc. (London)*, **A253**, 322 (1959).
20. N. A. Slovakhotova, Z. F. Il'icheva, L. A. Vasil'ev, and V. A. Kargin, *Vysokomol. Soedin.*, **6**, 608 (1964).
21. V. J. Krasnansky, B. G. Achhammer, and M. S. Parker, *SPE Trans.*, **1**, 133 (1961).
22. J. L. Weininger, *J. Phys. Chem.*, **65**, 941 (1961).

Received December 27, 1968