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ACTIVATED GAS PLASMA SURFACE TREATMENT OF POLYMERS FOR ADHESIVE BONDING: PART II

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ACTIVATED GAS PLASMA SURFACE TREATMENT OF POLYMERS FOR ADHESIVE BONDING: PART II

by

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OBJECT

To investigate the manner in which activated gas treatment improves the bondability of polymer surfaces.

SUMMARY

Activated gas treatment of polyethylene and nylon 6 adherend surfaces greatly improves their bondability; after such treatment, bond failure often occurs in the polymer rather than at the adhesive/polymer interface. Similar treatment of many other polymers results in increased bondability. The effect of the treatment depends on such parameters as length of treatment, chemical species present in the activated gas, and temperature of the polymer surface during treatment. Each polymer was treated with excited oxygen and excited helium; each was treated for several different periods of time. The treatment was followed by tensile testing of lap-shear sandwich specimens bonded with an epoxy adhesive. Plots of bond strength vs treatment time showed maxima for high density polyethylene (HDPE) treated with helium, cellophane treated with both oxygen and helium, and fluorinated ethylene-propylene copolymer (FEP) treated with helium and oxygen. The plots for most polymers showed an initial rapid increase in bond strength followed by a slower increase. Bond strengths of a poly-(oxymethylene) copolymer (Celcon) treated with helium reached a fairly constant value after about ten minutes. Polypropylene was treated with helium at several temperatures. Low temperature treatment gave very poor results while treatment near the softening point of polypropylene gave an eightfold increase in bond strength.

INTRODUCTION

An "activated" or "excited" gas is one in which the individual molecules or atoms are in a higher electronic or vibrational energy state than that most probable at room temperature. These gases interact with the surfaces of many polymers to make them more bondable, but leave the bulk polymer properties unchanged (Ref 1,2). The activated gas treatment is nondestructive and easy to handle, unlike acid etch treatments (Ref 3,4). The Materials Engineering Laboratory is engaged in a twofold program (Ref 5) (1) to investigate how activated gases interact with polymer surfaces, and (2) to investigate the range of applicability of the treatment.

The apparatus used in these investigations is a PRS-600 plasma reactor system (Tracerlab) which excites gases flowing through it by means of a resonance frequency field coupled capacitively to the flow tubes. The excited gases pass from the flow tubes into a chamber where the samples are located. Oxygen and helium are used for most of the work but on occasion argon, neon, nitrogen, chlorine, ammonia, and air have been used.

The polymers used in this study were films or sheets which had been treated on both sides with the plasma. The polymer film or sheet was bonded between two aluminum coupons to form a lap shear tensile specimen which was tested to failure in tension.

Many factors are involved in the formation of a new surface by activated gas or plasma treatment. This paper deals with three of them: (1) the species present in the gas, (2) the length of treatment, and (3) the chemical reactivity of the polymer surface layer during treatment, as influenced by morphology.

ACTIVE SPECIES IN EXCITED GASES

The terms "activated gas", "excited gas", and "low -temperature plasma" are used interchangeably in much of the literature. There are, however, differences in connotation. As has been mentioned above, and "activated" or "excited" gas is one in which the individual molecules or atoms are in a higher electronic or vibrational energy state than that most probable at room temperature. Plasma is a state of matter in which a large percentage of the atoms are ionized. A low-temperature plasma is one in which the kinetic temperature of the atoms is fairly low, around 100°C, while the kinetic temperature of the electrons is high, around 1000°C. Although the temperature of the atoms and molecules is relatively low, a substantial percentage of them are ionized and, of those remaining, many are in excited electronic states.

Our instrument produces both ionized and excited molecular and atomic species. The gases impinging on the polymer surfaces in the reactor are in the afterglow region, downstream from the exciter plates. Therefore the shortest -lived species of excited gases, mainly ionic, disappear before they reach the polymer. It would be helpful in predicting results of treatment to know what species are present in the plasma at a given power and pressure, and at a given location in the apparatus. Helium in a plasma can exist as a ground-state atom, as a neutral atom in various electronic states of excitation, or as an ion, also in various states of excitation. Oxygen can exist as a ground state molecule; as a rotationally, vibrationally, or electronically excited molecule; as an ionized molecule in various states of excitation; as ground-state atoms; or as excited atoms.

The ground state of a helium atom is ^1S and the first excited state is ^3S (Ref 6). This is a metastable state since the transition to the ground state is strongly forbidden. The next state lies near the first in energy. Its transition to ground is also forbidden but not so strongly. Because the lowest excited states are metastable, excited helium has a long half-life and decays mainly through collisions.

The nitrogen ground state atom, ^4S, is by far the largest atomic component in the nitrogen afterglow (Ref 7). The ^2D atom (2.38 eV above the ^4S) and the ^2P atom (3.75 eV) are present in about 1/500 the concentration of ^4S in low pressure afterglow. The predominant excited molecular species, N_2 ($^3\Sigma_u{}^+$), is 6.17 eV above the $^1\Sigma_g{}^+$ ground state. The radiative transition to the ground state occurs but is strongly forbidden. There seems to be som justification for describing the gound state as a triple bond and the triplet state as a double bond. Several people have set a lower limit of 10^{-2} sec for the triplet state's radiative lifetime and Young (Ref 8) has inferred a radiative lifetime between 50 and 0.24 sec. Many of the reactions of afterglow nitrogen imply a lifetime of 10^{-2} sec. Other low-lying molecular species such as $^3\Pi_g$ (7.35 eV above ground) and $^3\Sigma_u$ (8.76 eV) have lifetimes too short to be present in significant concentrations in the afterglow.

Ground state nitrogen molecules may exist in vibrational levels as high as the 27th with energy of 6.6 eV. Relaxation measurements have shown that vibrationally excited nitrogen (N_2^+) may have a rather long lifetime but these measurements refer to the lower vibrational levels rather than the high levels that would be necessary for participation in chemical reactions.

The ground state of molecular oxygen (Ref 9) is O_2 ($^3\Sigma_g-$). Both O_2 ($^1\Sigma_g+$) and O_2 ($^1\Sigma_g$) exist in the atmosphere. Much of the O_2 ($^1\Sigma_g+$) is formed by an "Energy-pooling" process of first excited oxygen.

$$2O_2(^1\Delta_g) \rightarrow O_2(^1\Sigma_g^+) + O_2\ (^3\Sigma_g^-)$$

It may also be formed by the vacuum ultraviolet photolysis of ground state O_2.

$$O_2(^3\Sigma_g^-)+h\nu \rightarrow O(^1D)+O(^3P);\quad O(^1D)+O_2(^3\Sigma_g^-) \rightarrow O_2(^1\Sigma_g^+)+O(^3P)$$

Since the plasma reactor is a source of strong UV radiation, this reaction is possible.

Ground state atomic oxygen is ^3P and the first excited state is ^1D. Oxygen plasmas produced by RF discharges have been found to contain 10-20% atomic oxygen and about an equivalent acount of molecularly excited O_2. Molecular oxygen may also be vibrationally and rotationally excited.

Several different methods are available for detecting active species (Ref 10). Among these are calorimetric, barometric, chemical, and spectroscopic techniques. The calorimetric method is usually used to detect the heat released by the recombination of the neutral atoms to form diatomic molecules. Under some circumstances the heat of de-excitation of the excited molecules is also measured (Ref 11). In this case, it is necessary to find the concentration of the atoms in another way. The barometric method relies on the detection of the change in pressure caused by molecules dissociating into atoms or smaller fragments. In an early chemical technique, alkyl radicals were detected by their removal of metal mirrors deposited in reaction tubes. The rate of removal of the mirror at different locations in the tubes was used to measure the lifetimes of the radicals. Another chemical method is titration of the excited gas with a gaseous reactant. It is important that this reaction be specific and fast. An example is the titration for nitrogen atoms:

$$N + NO \rightarrow N_2 + O$$

$$O + N \rightarrow NO^*$$ (which decays with a pinkish blue glow)

At the endpoint, the afterglow due to excited nitrogen molecules and the NO* glow are extinguished. Excess NO gives:

$$O + NO \rightarrow NO_2^*$$ (which decays with a yellow green glow).

Mass spectrometry is very specific since individual components of a gas may be identified by the mass of the parent ion or fragmentation product. For instrumental reasons, it is not useful for very short-lived radicals but it is extremely sensitive to longer lived species. Electron spin resonance spectroscopy is used extensively in the study of radicals in solids and liquids but only rarely in the study of gases. The spectrum gives information about the chemical environment of the unpaired electron. E.s.r. spectroscopy is a method of high sensitivity. Emission spectroscopy can give information about excited molecules atoms and radicals, but it is not always applicable since not all excited species decay with light emission. Absorption spectroscopy can also be used to detect the presence of radicals. The spectra of the species of interest must be well known to be of use.

An effort was made to determine the concentration of oxygen atoms produced in our reactor by adding NO_2 downstream from the activator plates. This reaction (Ref 10) may be expressed as follows:

$$O + NO_2 \rightarrow O_2 + NO \qquad \text{(fast)}$$

$$NO + O \rightarrow NO_2^* \qquad \text{(slow)}$$

$$NO_2^* \rightarrow NO_2 + h\nu \qquad \text{(yellow green)}$$

The endpoint of the titration is indicated by the disappearence of the green glow. When a power of 150 w and an oxygen flow rate of 10 cc/min were used, it was found that the glow was extinguished at a NO_2 flow rate of 10 cc/min. This would imply that the oxygen was completely decomposed, which seems improbable. There were many experimental difficulties, however. On possibility is that some NO_2 was directly excited by the field and this caused the glow to persist.

LENGTH OF TREATMENT

Radicals formed by an excited gas impinging on a polymer surface can react with species in the surface or environs to form other radicals, unsaturated bonds, crosslinks, or polar functional groups. The unsaturated bonds and other functional groups increase the polarity of the surface layer and improve the wetting of the polymer surface by an adhesive. They may thereby increase the bond strength of the adhesive joint. The crosslinking strengthens the surface layer, thus eliminating failure due to a weak boundary layer. The bondability of a surface increases sharply as it is crosslinked and made more wettable, but the rate of improvement decreases as the wettability reaches a maximum value and the weak surface layer becomes densely crosslinked. The bondability may even decrease after longer periods of treatment as reactions which weaken the surface by chain scission and by destruction of crystallinity become important. For example, oxygen can be added to a radical to form a hydroperoxide which then may decompose to break a polymer chain.

With both strengthening and weakening influences at work, the bond strength may vary with time in different ways. It may increase until the cohesive strength of the polymer is reached or it may reach a plateau. There may also be an optimum treatment time, after which the bond strength decreases. If there is an optimum time, its value would depend on the power used for treatment and probably on the gas pressure. For a given polymer the effects of different gases would usually be different; plots of bond strength versus time would be the same only if the modes of interaction of different excited gases with the polymer were identical.

DISCUSSION OF EXPFRIMENTAL RESULTS

Bond strengths were obtained by tensile tests of lap -shear specimens. The specimens were sandwich-type joints consisting of an aluminum coupon, a layer of epoxy adhesive, a polymer film, another layer of epoxy adhesive, and a second aluminum coupon. In the case of high density polyethylene treated with helium, the bond strength increased by a factor of two in the first half minute of treatment and by a factor of about four in ten minutes. After thirty to forty minutes of treatment, the bond strengths obtained exceeded the ultimate tensile strength of the polymer. When high density polyethylene is treated with excited oxygen, the bond strength increases by a factor of three in the first half minute and reaches a maximum value after twenty minutes of treatment.

The plot of bond strength versus treatment time for oxygen-treated high density polyethylene shows that degradation may be important for long treatment times. Thus, the bond strength after 30 minutes of treatment is less than after 20 minutes. It exhibits a more rapid initial rise than the plot of helium-treated material, a behavior which may be attributed to the presence of polar groups in the surface. Although the helium curve rises more slowly than the oxygen curve it reaches a higher value. The bond strength reached after treatment for one hour with excited nitrogen is higher than that reached after one hour with excited helium.

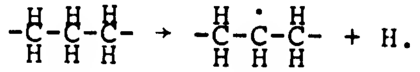
After twenty minutes of treatment with helium, oxygen, or nitrogen the locus of failure in the bond was found to be not at the polythylene surface, but in the bulk of the polyethylene, or occasionally, within the Alclad surface of the aluminum coupon. This appears to be a ductile failure of the aluminum. The bond strength produced by excited chlorine treatment is comparable to that produced by oxygen treatment.

When nylon 6 is treated with excited helium, the bond strength increases linearly for about thirty minutes or until the cohesive strength of the nylon has been reached. Excited oxygen treatment of nylon 6 causes the bond strengths to increase by a factor of three in five minutes and thereafter to increase more slowly, though not to the polymer's ultimate tensile strength.

The treatment of Celcon with excited helium produces an increase in bond strength of a factor of almost three in one half minute. Further treatment produces little improvement. The bond strength of excited oxygen-treated Celcon rises almost linearly to a maximum of three times the bond strength of the untreated bond after ten minutes. When subjected to oxygen treatment for time periods greater than ten minutes, the thin film used in this work becomes badly weakened and very fragile.

CHEMICAL REACTIVITY OF POLYMER SURFACES

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 radical



$$-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- \rightarrow -\overset{H}{\underset{H}{C}}-\overset{\cdot}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}- + H.$$

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

$$RH^+ + RH \rightarrow RH_2^+ + R.;\quad RH_2^+ \rightarrow R. + H_2^+$$

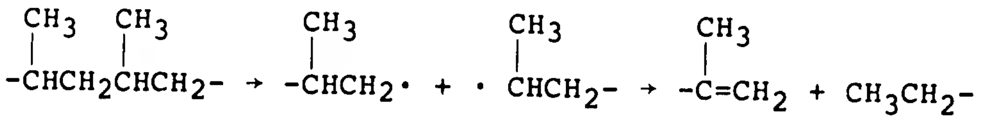
Timm and Willard (Ref 12) find no hydrogen atoms trapped during the radiolysis of solid hydrocarbons (except CH_4). This result supports the second mechanism in polyolefins. A radical can decay in several ways: by ejecting another radical to form a double bond or a crosslink; by adding a molecule to form a different radical (i.e., 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.

Results obtained with polypropylene irradiated with high energy photons and electrons (Ref 13) can be extrapolated to the case of surface treatment by active gases. Geymer (Ref 14) and Lawton (Ref 15) found that the amount of crosslinking in polypropylene depends on the temperature at which the samples are irradiated and/or aged. For example, there was much more crosslinking when the irradiated polymer was aged above its glass transition temperature than when it was aged below it. 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 (Ref 16). When polypropylene was warmed to 20° after irradiation at -196°, or when it was irradiated at 20°, the EPR and NMR spectra showed a higher concentration of radicals in the crystalline than in the amorphous phase, although the absolute concentrations were lower than at -196°. 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 the radical pairs 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. Maximum crosslinking takes place at a temperature near the crystalline melting point.

Sirota et al (Ref 17) conclude that the irradiation of polyolefins 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 in vacuum, these radicals recombine and crosslink.

Veselovskii, et al (Ref 18) 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 polypropylene are formed by recombination of free radicals."



$$-\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2- \rightarrow -\overset{CH_3}{\overset{|}{C}}HCH_2\cdot + \cdot\ \overset{CH_3}{\overset{|}{C}}HCH_2- \rightarrow -\overset{CH_3}{\overset{|}{C}}=CH_2 + CH_3CH_2-$$

Lawton et al (Ref 19) have found evidence that in linear polythylene, radicals on adjacent chains are formed in pairs. They state that there are two populations of paired alkyl radicals, one which has a ten-second half-life at room temperature and a second which persists for about five days at room temperature. The first they attribute to radicals formed directly opposite each other, the second to radicals offset by one monomer unit. Iwasaki et al (Ref 20) cite a number of ESR workers who have reported the pairwise trapping of radicals in irradiated organic solids. They present evidence that these radical pairs constitute a triplet state, i.e., the spins of the unpaired electrons are in the same direction, and are 5 - 10 Å from each other. This, they believe, implies a specific mechanism of formation which may be the charge neutralization reaction of an anion and a cation. Another possibility is that the radicals formed nearer to each other than 5 Å or in a singlet state (i.e., electron spins paired) decay so rapidly that they are not detected while those formed more than 10 Å apart influence each other very little.

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 (Table 6). An attempt to duplicate these good results some months later was unsuccessful, but when the reactor was cleaned with HF excellent bond strengths were once more obtained. It is quite possible that traces of copper and zinc on the walls of the reactor and flow tubes were catalyzing the recombination and de-activation of the oxygen and that therefore the original experimental conditions were not being obtained.

Recently, treatment of polypropylene with helium plasma at higher pressures and temperatures than usual (6mm as against 0.4mm of Hg and 130°C instead of 40°C) has produced bond strengths nearly as high as were obtained in the initial oxygen treatment. This result is probably due to increased crosslinking at the softening point of the polypropylene. Using a power of 150 watts at a temperature of about 40°C gave a very poor bond while using the same power (150 watts) at more than 130°C gave an excellent bond. In the latter case the Shell film softened and began to melt; while the Dow film was not deformed by the heat. Two effects are in competition. One is crosslinking, the other is degradation caused by rupture of the polymer chain. At the correct temperature, crosslinking predominates.

Plots of bond strength vs length of treatment for cellophane treated with excited helium, and for the same polymer treated with excited oxygen are identical within experimental error, implying that both gases affect cellophane in the same way. One possibility is that they both act in the manner expected for helium, i.e., they form radicals to which the oxygen does not add. It is also possible that the congruence is fortuitous. The strength increased by a factor of four in thirty seconds, peaked in five minutes at a factor of five, and then slowly declined to a factor of four in thirty minutes.

When FEP Teflon is treated with excited helium, there is a sharp increase in bond strength in the first half minute. The bond strength reaches a maximum at about five minutes of treatment, then slowly declines. Excited oxygen treatment of FEP Teflon causes the bond strength to increase by a factor of two in the first half minute and by a factor of four in ten minutes; the bond strength declines slowly with longer treatment times. After thirty minutes of treatment excited nitrogen produces the same bond strenght in FEP Teflon as excited helium and excited oxygen.

EXPERIMENTAL PROCEDURES

Equipment

A Tracerlab PRS-600 plasma research system was used for treatment of plastic coupons. The PRS-600 consists of an intermediate-power 13.56-mc RF generator; a capacitatively coupled plasma activator using 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 inches in ID and 10 inches high and is equipped with a Teflon bushing holding a precision-ground stirrer shaft with a ₷ 7/12 male joint at the end. A variety of glass jigs for holding specimens can be placed on the end of the shaft. The shaft is slowly rotated by means of a small motor and a gear train.

The inlet flow rate is controlled by a pressure regulator and a needle valve. It is metered continuously by a tapered-tube flowmeter. The gas flows through a glass 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.

The electronic system establishes the RF electric field in the glass exciter tubes. Included in this system are the RF generator, consisting of an oscillator and a 300-watt power amplifier; a power meter; AC and DC power supplies; and tuning circuitry.

In operation, the reaction chamber is pumped down to 0.1 torr pressure or less, and a suitable gas flow (e.g., 10-20 cc/min) is established. The pressure usually rises to 0.35mm; the pumping rate is adjusted to obtain the desired pressure. The traps protecting the pump are cooled with dry ice or liquid nitrogen. The RF generator is turned on and the RF power knob is turned up until a glow is established.

The variable inductor and variable capacitor in the tuning circuit are tuned to give the minimum reflected power, as indicated by the power meter. The power is adjusted to the desired level and the tuning knobs readjusted if necessary. Much of this work was done at 50 watts; higher power levels, 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 1/2 hour or more, although no particular change in bondability was noted with longer periods.

Titration

At the end point of a gaseous titration, a luminous species is produced, or quenched if one already exists. The indicating reaction must be fast since the titrations take place in flow systems with relatively short-lived species. In order to be quantitative, it must be complete and have a readily discernible end point (Ref 10). The titration of active oxygen by NO_2 is an excellent example of a titration

$$O + NO_2 \longrightarrow O_2 + NO \qquad \text{(fast)}$$

$$NO + O \longrightarrow NO_2^* \qquad \text{(slow)}$$

$$NO_2^* \longrightarrow NO_2 + h\nu \qquad \text{(yellow - green)}$$

system, since the active oxygen has a blue glow from which the yellow-green NO_2^* glow is easily distinguished. To perform a titration in our reactor system, the glass stirring rod on which the sample-holding jigs are placed was replaced by a glass tube (sealed at its upper end) extending well up into the reactor. Four small holes were made in it and were positioned opposite the exits of the excitor tubes. The titrating gas, NO_2 was introduced through these tubes. First, a discharge was established in the oxygen; then, the flow rate of NO_2 was increased until the oxygen glow in the exit tube disappeared. The flow rates of the two gases at the extinction point were then compared.

Assembly and Bonding of Specimens

The bonded specimens employed were single-lap shear sandwich specimens 1 inch wide by 7 1/2 inches long with a 1/2 inch overlap. The construction of the bonded assembly was as follows: aluminum (2024 bare or Alclad)/adhesive/polymer/adhesive/aluminum. Prior to bonding, the aluminum received a surface treatment consisting of an acetone wipe, FPL acid etch, tap water rinse and distilled water rinse. The distilled water rinse aluminum was then oven-dried for 15 minutes at 140°F. This treatment was necessary to assure good adhesion to the aluminum so that the specimen would preferentially fail at the expectedly weaker adhesive/polymer interface. The polymers were solvent-wiped before plasma treatment.

The adhesive used throughout the program 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. The ration of Epon 828 to Versamid 140 was 70/30 pbw. No filler material was used.

The specimens were assembled with the aid of a jig which provided for a 1/2-inch overlap. The faying surfaces of the aluminum coupons were coated with adhesive and assembled as described above. The specimens were lightly weighted (5 psi) and allowed to cure 16 hours at room temperature. This was followed by a post cure of 140°F for 3 hours in a circulating-air oven. All specimens were conditioned for one hour in the test environment before they were tested.

The bonded specimens were loaded to failure on a Baldwin test apparatus with a Tate-Emery load indicator (5000 lb max). The loading rate used was 1000 lb/min.

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TABLE 1

Tensile bond strength data[a] for high density polyethylene

Treatment	Conditions[b]	Type of Polyethylene[c]	Bond Strength[d], psi		
			Average[e]	Low	High
Control[f]		green	320	260	370
		Plaskon	880	810	920
Helium	5 sec	Plaskon	1000[g]	670	1400
	30 sec	green	920	720	1160
	1 min	green	1210[gh]	840	1620
	5 min	Plaskon	2400	2050	2650
		Plaskon	1840[i]	1500	2160
	10 min	Plaskon	2770	2420	3040
	30 min	green	3130	3050	3230
		Plaskon	3770	3600	4000
	60 min	green	2280	2180	2460
		Plaskon	3140	3050	3230
Oxygen	30 sec	green	1990	1850	2100
		Plaskon	1740	1720	1890
	1 min	green	1190[j]	820	1490
		Plaskon	1190[g]	580	1480
	5 min	Plaskon	2810	2700	2870
	10 min	Plaskon	3000	2930	3060
	20 min	green	2520	2460	2610
	20 min	Plaskon	3165	3030	3374
	30 min	green	2400[h]	2340	2470
	30 min	green	2440	2360	2500
Chlorine	10 min	Marlex 6008[c]	2510	2400	2650
Nitrogen	60 min	Plaskon	3500	3400	3560

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[a] Lap-shear sandwich specimens: Al/adhesive/polymer/adhesive/Al. Adhesive: 70/30 Epon 828 Versamid 140.

[b] 50 w power, 0.4± 0.1mm Hg pressure.

[c] Green=Marlex 6002, green pigment, 1/16" sheet.
Plaskon=PP 60-002 (Allied Chemical), 9.2 mils film.

[d] 4"x1"x1/8" 2024 Al or 2024 Alclad coupons, 1/2 inch overlap.

[e] Average of 3 specimens.

[f] Solvent wiped with acetone or ethanol, air space dried.

[g] Average of 6 specimens.

[h] 4"x1"x1/16" 2024 T-3 Al coupon, 1/2 inch overlap.

[i] 150 w power.

[j] Average of 12 specimens.

[k] Marlex 6008, 1.2 mils, 70 w power.

TABLE 2

Nylon 6
Tensile Bond Strengths[a]

Treatment	Conditions[b]	Type of Nylon 6[c]	Bond Strengths,[d] psi		
			Average[e]	Low	High
Control[f]		Capran	740[gh]	470	1000
			1060	800	1480
		Sheet	800	640	1020
Helium	30 sec	Capran	1220	1100	1520
	1 min	Capran	1230[i]	1080	1390
	5 min	Capran	1850	1710	1960
	10 min	Capran	2020	1780	2300
	30 min	Capran	3960	3700	4250
		Sheet	2180	1400	2600
	60 min	Capran	3320	2640	4020
		Sheet	2760	2390	3460
Oxygen	30 sec	Capran	1620	1420	1910
	1 min	Capran	1520[gh]	1380	1720
	5 min	Capran	2460[g]	2170	2750
	10 min	Capran	2650	2220	2950
	30 min	Capran	3490	3140	3780

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[a] Lap shear sandwich specimens: Al/adhesive/nylon/adhesive/Al. Adhesive: 70/30 Epon 828/Versamid 140.

[b] 50 w power; 0.4± 0.1mm Hg pressure.

[c] Capran 77C, 3mil film Allied Chem. Co. or nylon 6 sheet, 1/16", Almac Plastics Co.

[d] 4"x1"x1/8"2024 T-3 bare or 2024 Alclad coupons, 1/2 inch overlap.

[e] Average of 3 specimens.

[f] Solvent-wiped with acetone or ethanol, air-dried.

[g] Average of 6 specimens.

[h] 4"x1"x1/16" 2024 T-3 Al coupons, 1/2 inch overlap.

[i] Average of 5 specimens.

TABLE 3

Celcon[a]
Tensile Bond Strength[b]

Treatment	Conditions[c]	Bond Strengths,[d] psi		
		Average[e]	Low	High
Solvent wiped		420	370	480
Helium	30 sec	1050	820	1370
	5 min	1150[f]	940	1400
	10 min	1020[f]	780	1270
	30 min	1220[g]	920	1450
Oxygen	30 sec	500	270	840
	1 min	640	510	780
	5 min	990	840	1100
	10 min	1260	1110	1390
	20 min	1180[h]	1110	1240
	30 min	1160[h]	1040	1290

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[a] Celcon poly(oxymethylene) copolymer, Celanese Plastics Co. M90-01, injection molding grade, 1 mil film.

[b] Lap shear sandwich specimens: Al/adhesive/Celcon/adhesive/Al. Adhesive: 70/30 Epon 828/Versamid 140.

[c] 50w power, 0.4±0.1mm Hg pressure.

[d] 4"x1"x1/8" 2024 Al or 2024 Alclad coupons, 1/2" overlap.

[e] Average of 3 specimens.

[f] Average of 6 specimens.

[g] Average of 4 specimens.

[h] 2 specimens. Celcon was oxidized to fragile film.

TABLE 4

Cellophane[a]
Tensile Bond Strength[b]

Treatment	Conditions[c]	Bond Strengths[d], psi		
		Average[e]	Low	High
Solvent Wiped		280	280	280
Helium	30 sec	1290	1250	1350
	5 min	1430	1370	1520
	10 min	1330	1280	1420
	30 min	1200	1040	1300
Oxygen	30 sec	1190[f]	700	1480
	5 min	1400	1230	1510
	10 min	1340	1300	1430
	30 min	1280	1220	1390

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[a] 0.6 mil film.

[b] Lap shear sandwich specimens: Al/adhesive/PVF/adhesive/Al. Adhesive: 70/30 Epon 828/Versamid 140.

[c] 50w power, 0.4±0.1mm Hg pressure.

[d] 4"x1"x1/8" 2024 Al or 2024 Alclad coupons 1/2" overlap.

[e] Average of 3 specimens.

[f] Average of 6 specimens.

TABLE 5

FEP Teflon[a]
Tensile Bond Strengths[b]

Treatment	Conditions[c]	Bond Strengths,[d] psi		
		Average[e]	Low	High
Solvent Wiped		330	320	370
Helium	30 sec	1490	1340	1680
	5 min	1730	1650	1850
	10 min	1490	1380	1680
	30 min	1160	1020	1250
Oxygen	30 sec	770[f]	240	1210
	5 min	1300	1140	1410
	10 min	1440[f]	1020	1820
	15 min	990	840	1060
	20 min	1380	1280	1440
	30 min	1080	940	1200
	30 min	2260[g]	2000	2520
Nitrogen	30 min	1080	930	1200

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[a] Fluorinated ethylene propylene co-polymer, 5 mil, FEP Type A, Franklin Fibre-Lamitex Corp. Wilmington, Delaware.

[b] Lap shear sandwich specimens. Al/FEP/adhesive/Al. Adhesive: 70/30 Epon 828/Versamid 140.

[c] 50 w power, 0.4±0.1mm Hg pressure.

[d] 4"x1"x1/8" 2024 Al or 2024 Alclad coupons, 1/2 inch overlap.

[e] Average of 3 specimens.

[f] Average of 5 specimens.

[g] Average of 2 specimens.

TABLE 6

Lap shear bond strength[a] of polypropylene

Activated gas	Conditions				Bond strength,[c] psi
	Time	Power	Temperature	Pressure	
None					370 (6)
Helium	10 min	50 w	40°	0.30 mm	400 (5)
Helium	5 min	150 w	130°	6.0 mm	2600 (2)
Oxygen	15 min	50 w	60°	0.35 mm	800 (6)
Oxygen	30 min	50 w	130°	0.50 mm	2630 (3)
Oxygen	10 min	50 w	130°	0.40 mm	3080 (2)
Oxygen	30 sec	50 w	130°	0.35 mm	1870 (3)

---

[a] Lap shear sandwich specimens: Al/adhesive/PP/adhesive/Al. Adhesive: 70/30 Epon 828/Versamid 140.

[b] Dow 201 film, 4.8 mils.

[c] Number of specimens in parenthesis.

[d] Film softened.

[e] Film melted.

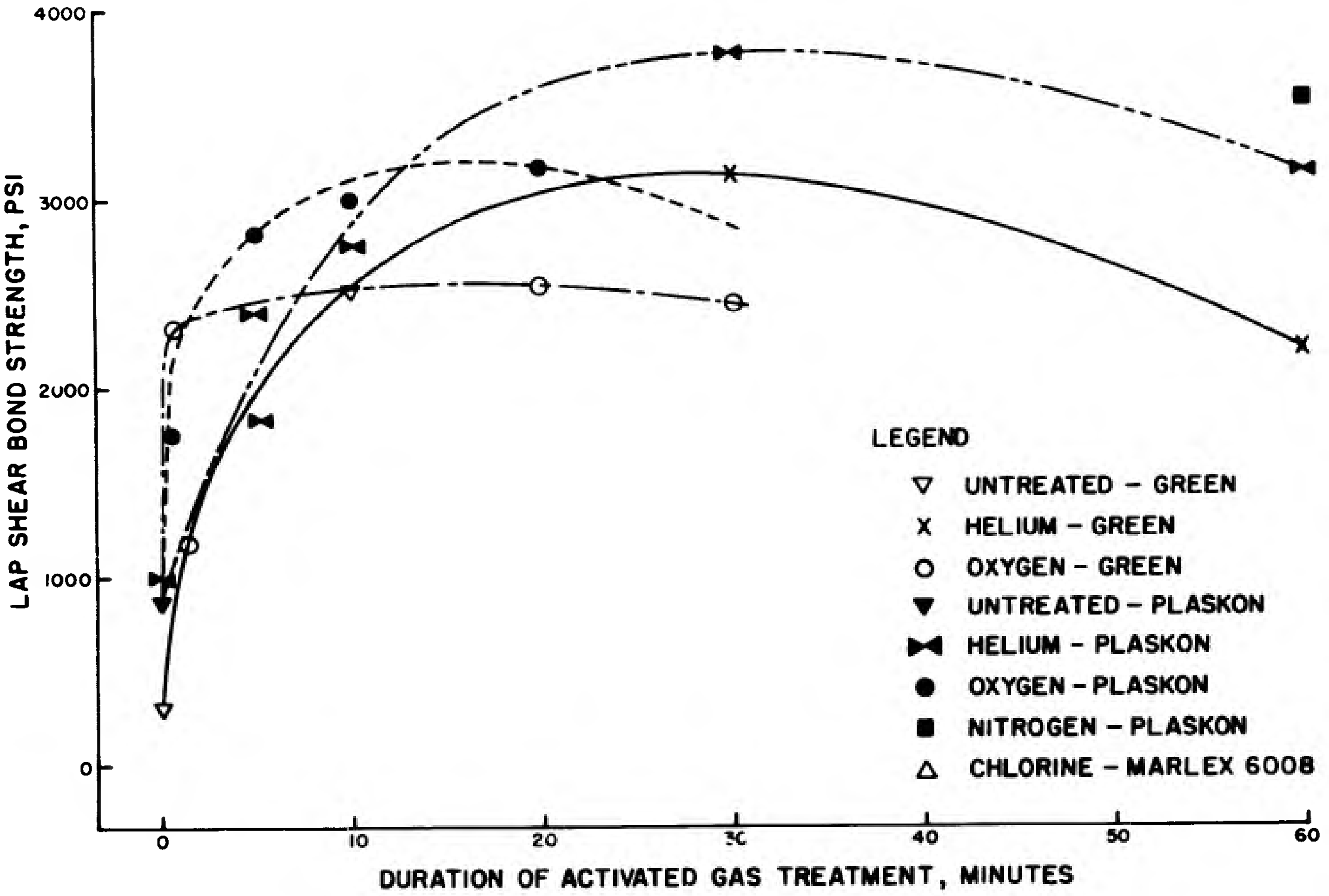

Fig 1 High density polyethylene: Tensile bond strength of lap shear sandwich specimens vs. duration of activated gas treatment with helium, oxygen, nitrogen or chlorine
(Table 1)

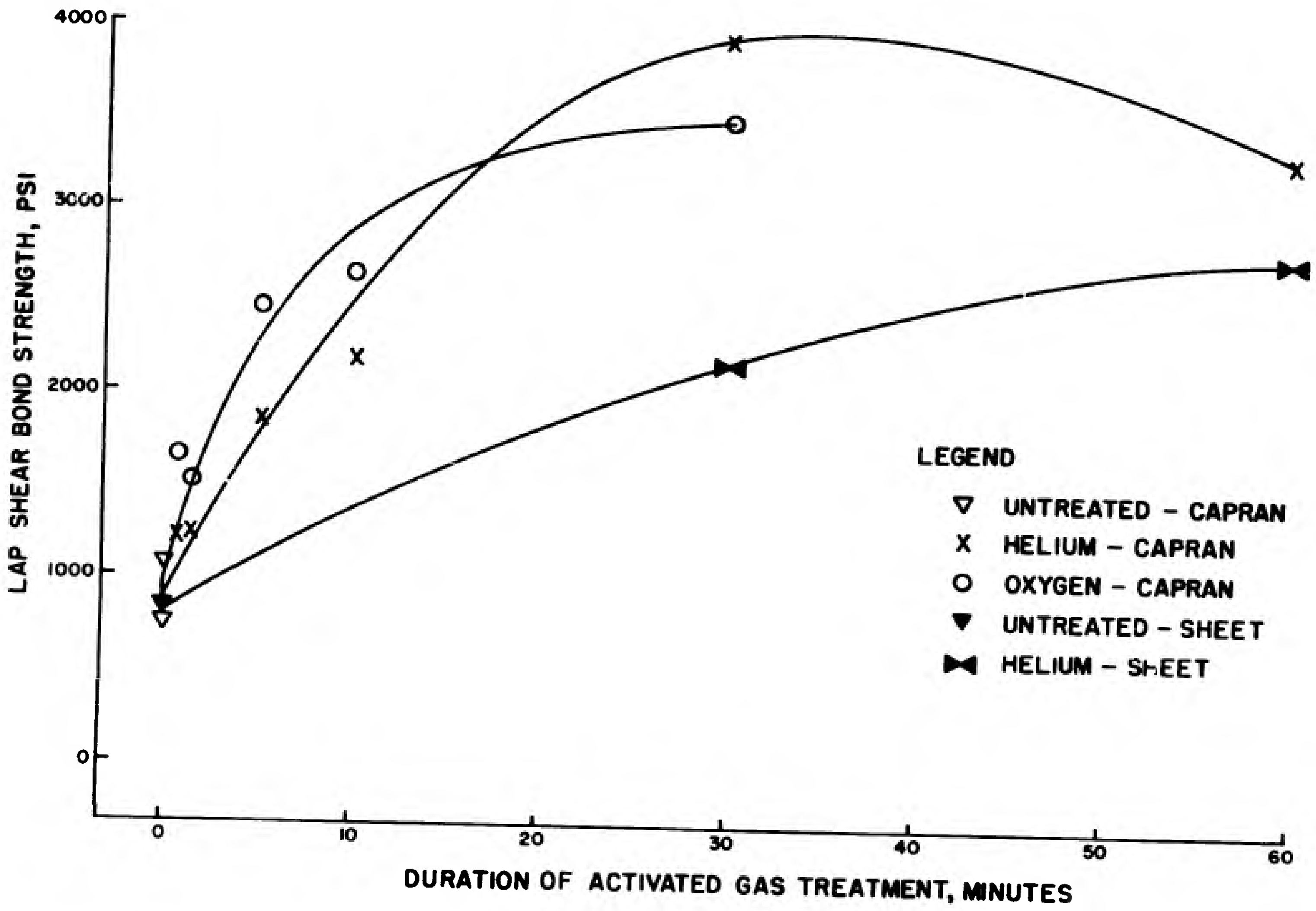

Fig 2 Nylon 6: Tensile bond strength of lap shear sandwich specimens vs. duration of activated gas treatment with helium or oxygen (Table 2)

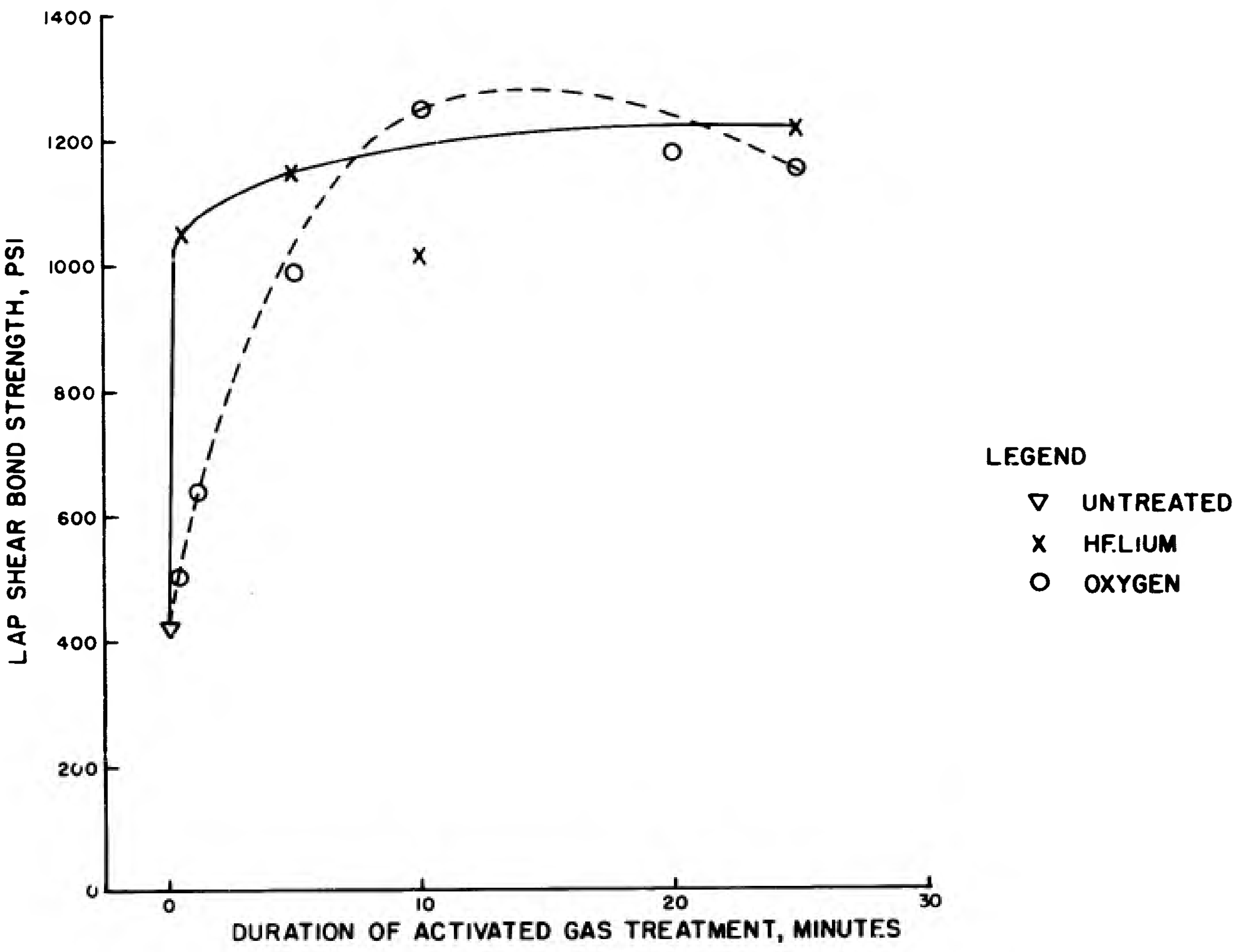

Fig 3 Celcon: Tensile bond strength of lap shear sandwich specimens vs. duration of activated gas treatment with helium or oxygen (Table 3)

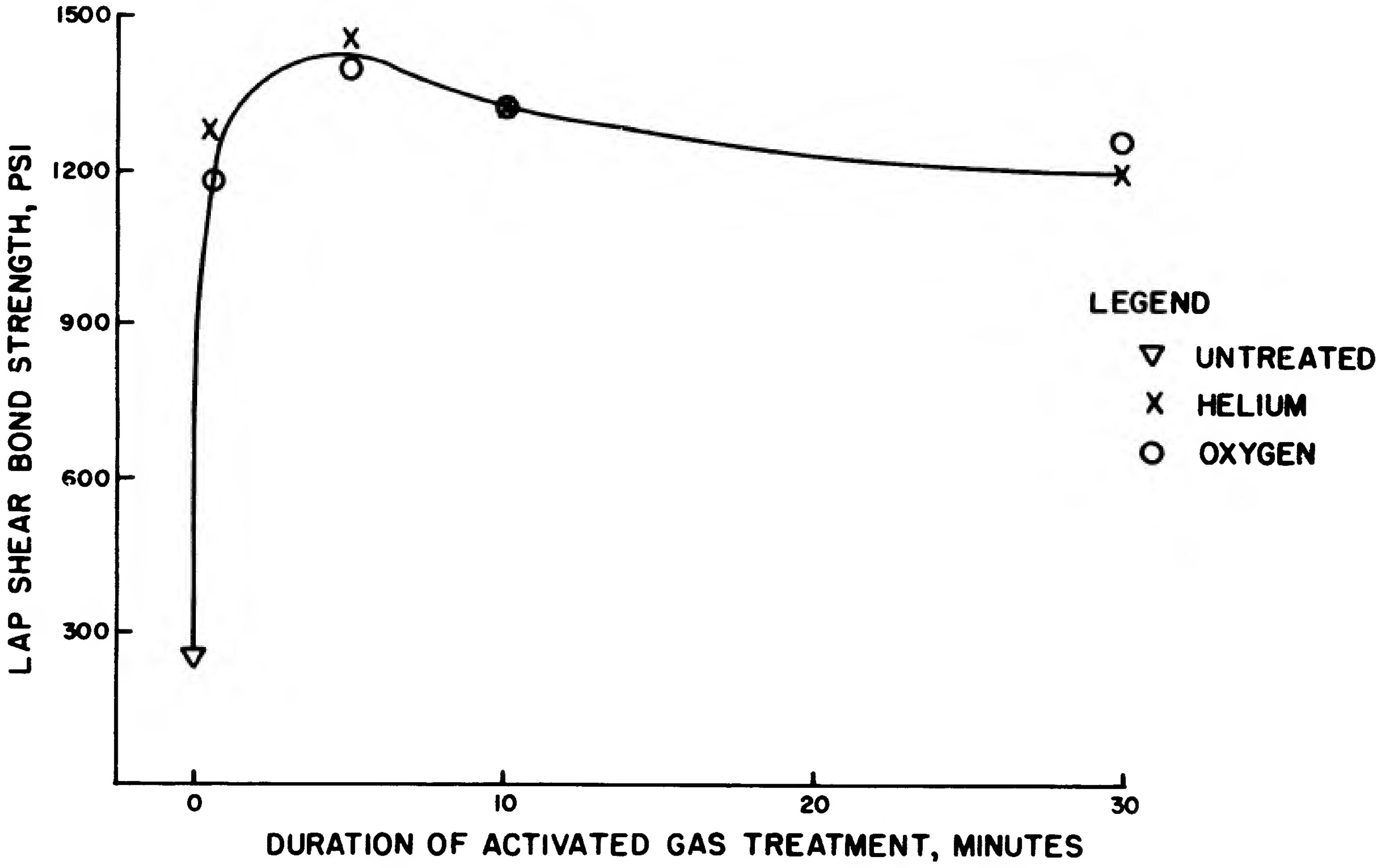

Fig 4 Cellophane: Tensile bond strength of lab shear sandwich specimens vs. duration of activated gas treatment with helium and oxygen (Table 4)

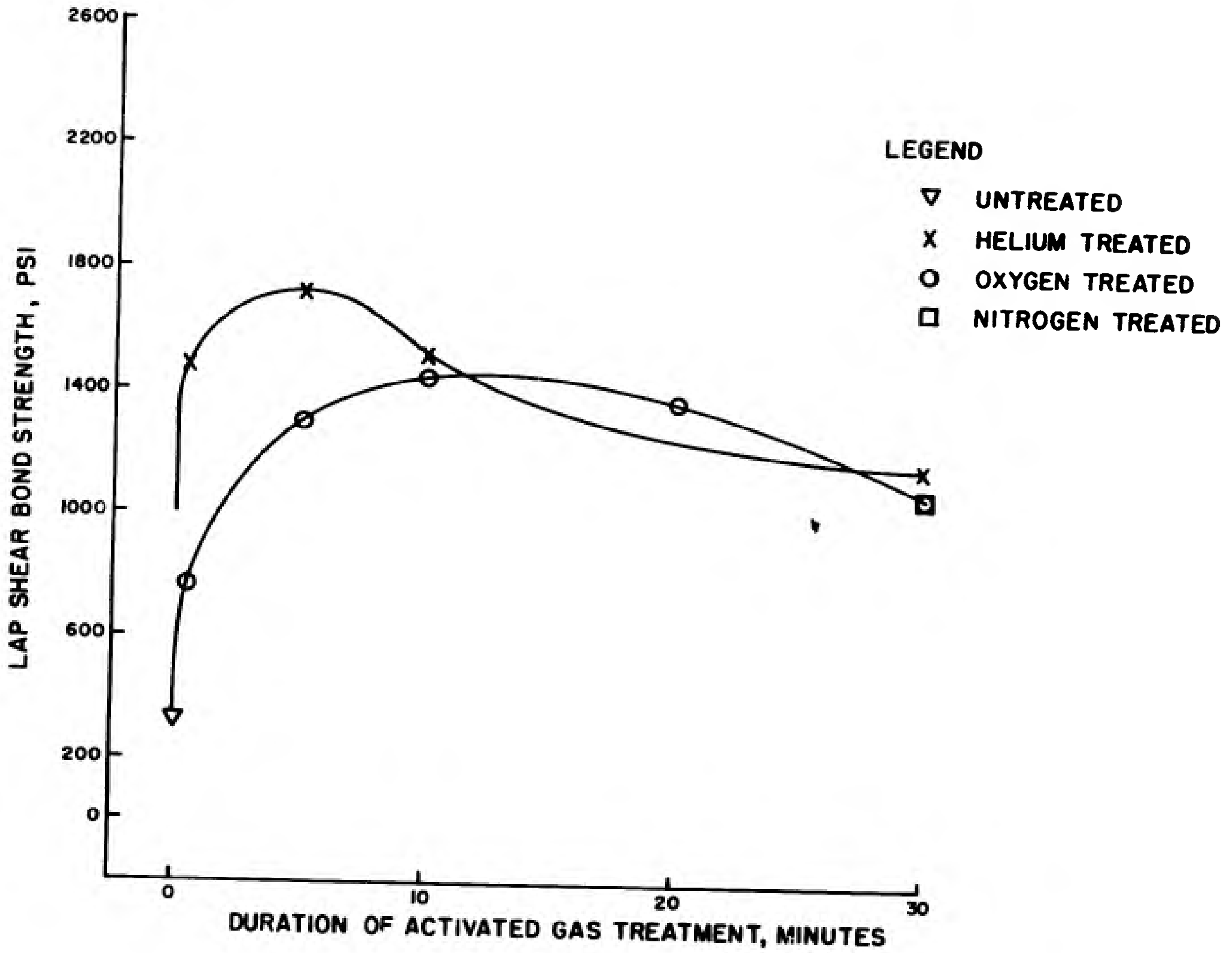

Fig 5 FEP Teflon: Tensile bond strength of lap shear sandwich specimens vs. duration of activated gas treatment with helium, oxygen and nitrogen (Table 5)

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13. ABSTRACT

Activated gas treatment of polyethylene and nylon 6 adherend surfaces greatly improves their bondability; after such treatment, bond failure often occur in the polymer rather than at the adhesive polymer interface. Similar treatment of many other polymers results in increased bondability. The effect of the treatment depends on such parameters as length of treatment, chemical species present in the activated gas, and temperature of the polymer surface during treatment. Each polymer was treated with excited oxygen and excited helium; each was treated for several different periods of time. The treatment was followed by tensile testing of lap-shear sandwich specimens bonded with an epoxy adhesive. Plots of bond strength vs treatment time showed maxima for high density polyethylene (HDPE) treated with helium, cellophane treated with both oxygen and helium, and fluorinated ethylene-propylene copolymer (FEP) treated with helium and oxygen. The plots for most polymers showed an initial rapid increase in bond strength followed by a slower increase. Bond strengths of a poly (oxymethylene) copolymer (Celcon) treated with helium reached a fairly constant value after about ten minutes. Polypropylene was treated with helium at several temperatures. Low temperature treatment gave very poor results while treatment near the softening point of polypropylene gave an eightfold increase in bond strength.

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Adhesive joint strength						
Polyethylene						
Aluminum sandwich specimens						
Tracerlab PRS-600 plasma research system						
Nylon 6						
Polypropylene						
Cellophane						
FEP Teflon						
Poly(oxymethylene) copolymer						