

Surface Characterization of Plasma-Treated Poly-*p*-Xylylene Films

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Synopsis

Plasma-treated poly-*p*-xylylene films have been characterized by neutron activation oxygen analyses, internal reflection (IRS) and transmission infrared spectroscopy, transmission electron microscopy (TEM), and surface contact angle measurements. The results indicate that an oxygen plasma roughens the surface and that oxygen is incorporated into the surface. Oxygen is not detected in the bulk of the sample. The infrared transmission spectra exhibited no carbonyl band, but the relative band intensities changed, indicating a change in ring substitution by a loss of chlorine in the chlorinated poly-*p*-xylylenes. The IRS spectra of the surface of films treated with oxygen plasma did contain carbonyl bands at 1730 and 1640 cm^{-1} . Argon and helium plasmas generally decreased the water contact angle measured on plasma-treated poly-*p*-xylylene surfaces more than oxygen or nitrogen plasma treatments. Regardless of the plasma utilized, the water contact angles increased with time after the treatment but did not recover to the original level. IRS spectra of the surface of films treated with argon plasma contained carbonyl bands at 1730 and 1695 cm^{-1} . The adhesion of a polyurethane thermosetting material to a poly-*p*-xylylene surface is greatly improved if a plasma treatment is used prior to the application of the polyurethane. The degree of improvement in adhesion was dependent on the type of plasma and the treatment time.

INTRODUCTION

The synthesis of poly-*p*-xylylene films is based on the vacuum pyrolysis of cyclic di-*p*-xylylene near 600°C followed by vapor deposition polymerization of the reactive *p*-xylylene moiety on surfaces near ambient temperature.¹ A recent review article by Szwarc summarizes the chemistry and applications of poly-*p*-xylylene in the coatings industry.² The structure and nomenclature of these polymers are shown in Table I.

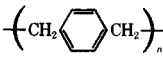
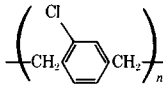
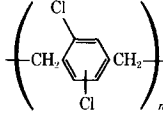
This article discusses the interaction of various plasmas with poly-*p*-xylylene films. Oxygen, nitrogen, argon, and helium plasmas were studied. Plasma-treated films were characterized by neutron activation oxygen analyses, internal reflection (IRS) and transmission infrared spectroscopy, transmission electron microscopy (TEM), and surface contact angle measurements. In addition, removal rates of polymers I, II, and III by the interaction with an oxygen plasma were measured and are discussed.

EXPERIMENTAL

General

A TEGAL Plasmaline model 211 was used to treat the samples in all plasma experiments. The rf power supply operated at 13.56 MHz with an input power variable from 0 to 300 W. Cylinder-grade oxygen, nitrogen, argon, and helium

TABLE I
 Poly-*p*-xylylenes

Structure	Nomenclature
	poly- <i>p</i> -xylylene (I)
	poly(monochloro- <i>p</i> -xylylene) (II)
	poly(dichloro- <i>p</i> -xylylene) (III)

were used in all experiments with a flow rate adjusted to give an operating pressure of 1.0 torr.

The infrared spectra were collected on a Digilab FTS-15 Fourier transform spectrometer by averaging 1000 scans at 2 cm^{-1} resolution. IRS spectra were obtained utilizing a variable angle internal reflection accessory (Harrick Scientific Corp.) equipped with KRS-5 (45° endfaces) and germanium (60° endfaces) reflection crystals. In order to obtain uniform contact, polymer films were pressed against the crystals at a uniform torque (4 in.-lb). IRS spectra were collected in the single-beam mode and ratioed against the stored spectra of a reference crystal. The depth of penetration (d_p) of the infrared radiation into the samples at 1700 cm^{-1} was $2.10\text{ }\mu\text{m}$ for KRS-5 (at 45°) and $0.31\text{ }\mu\text{m}$ for germanium (at 60°).

Neutron activation oxygen analyses were performed by Union Carbide Corporation Nuclear Products and Services Laboratory, Sterling Forest, New York.

Contact angle measurements were made with an instrument designed and built on site. Drops were $4\text{ }\mu\text{l}$ and solvents were reagent grade. The contact angle (θ) was calculated as follows (see Fig. 3):

$$\tan \alpha = h/r$$

$$\theta = 2\alpha$$

Adhesion Materials and Equipment

The polyurethane used was Conap CE-1155. It remained for 30 min under ambient conditions and then was cured for 3 hr at 60°C . The rivets were 5-lb steel with a head surface area of 0.122 in.^2 and were sanded, cleaned, and vapor degreased in trichloroethylene to ensure good adhesion to the polyurethane. An Instron (table model) was used to pull the rivets.

Adhesion Testing

The samples were prepared as follows: Epoxy-fiberglass G-10 material ($4 \times 4\text{ cm}$) was coated with 0.7 mil of polymer II. The coated samples (except controls) were plasma treated. About 0.1 cm^3 of uncured polyurethane was used to bond a rivet head to each sample. This was sufficient material to completely

cover the rivet head/polymer II interface when the rivet was placed on the sample. The samples were cured and the adhesion was measured on the table model Instron at a pull rate of 0.2 in./min.

Humidity/Temperature Testing

Humidity and temperature cycling was carried out according to MIL-I-46058 which requires ten 24-hr temperature cycles at 90% relative humidity. In some cases the samples were immersed in boiling water for 1/2 hr and the adhesion tested.

RESULTS AND DISCUSSION

Neutron Activation Analyses

In order to determine if any bulk oxidation occurred during the oxygen plasma treatment of poly-*p*-xylylene films, neutron activation oxygen analyses were carried out on control (no plasma treatment) and plasma-oxidized samples. The results are summarized in Table II.

The oxygen levels measured in control films in this study show approximately one oxygen atom per one-hundred monomer units. It is assumed that residual oxygen in the deposition chamber is incorporated into the film during the polymerization process. The functionality of this oxygen is unknown.

The results indicate that the oxygen content of these films is essentially unaffected by the oxygen plasma. Consequently, the plasma oxidation must be a surface effect and little, if any, oxidation in the bulk of the sample occurs.

Topography

Transmission electron micrographs (TEM) of a poly(dichloro-*p*-xylylene) film both before and after an oxygen plasma treatment clearly indicated that the surface is roughened by the oxygen plasma treatment. Generally, the interaction of a polymeric material with a plasma which was generated with an oxygen-containing gas (CO₂, air, O₂) does induce a roughening effect. Plasmas generated with non-oxygen-containing gases (H₂, He, Ar, N₂) cause less of a roughening effect.

TABLE II
Neutron Activation Oxygen Analyses

Polymer	Treatment, ^a W	Oxygen, ^b ppm
II	control	990
II	20	800
II	100	800
I	control	1090
I	20	1360
I	100	1120

^a Oxygen plasma; 1.0 torr; 10 min.

^b Average of at least two separate determinations, values ± 200 ppm.

TABLE III
Poly(monochloro-*p*-Xylylene) Removal Rates Versus Operating Pressure

Oxygen pressure, torr	Removal rate, Å/min
0.2	220
0.3	350
0.5	800
1.0	1500
2.0	1500

Oxygen Plasma Removal Rates

Poly(monochloro-*p*-xylylene) removal rates were measured at a chamber pressure of 0.2, 0.3, 0.5, 1.0, and 2.0 torr. The operating pressure was increased by increasing the oxygen flow rate. Removal rates at 100-W power level at various operating pressures are shown in Table III.

These results indicate that the concentration of active oxygen species increases with oxygen flow up to an operating pressure ≤ 1.0 torr. Above this pressure, oxygen flow rate is no longer rate controlling. Therefore, in order to compare removal rates of I, II, and III, all experiments were carried out at an operating pressure of ~ 1.0 torr.

Figure 1 and Table IV summarize the removal rates at 20, 50, 100, and 150 W.

At 20-W input power, polymer I shows a removal rate of only 48 Å/min while II and III etch at a rate of 370 and 305 Å/min, respectively. The chamber temperature operating at 20 W and 1.0 torr was about 50°C. It is known that rates of oxidation are proportional to the ability of oxygen to penetrate into the polymer mass.³ Hence, the morphology of a polymer is important in determining polymer reactivity with molecular oxygen. Consequently, it is expected that the relative crystallinities and T_m and T_g relationships will quite markedly affect

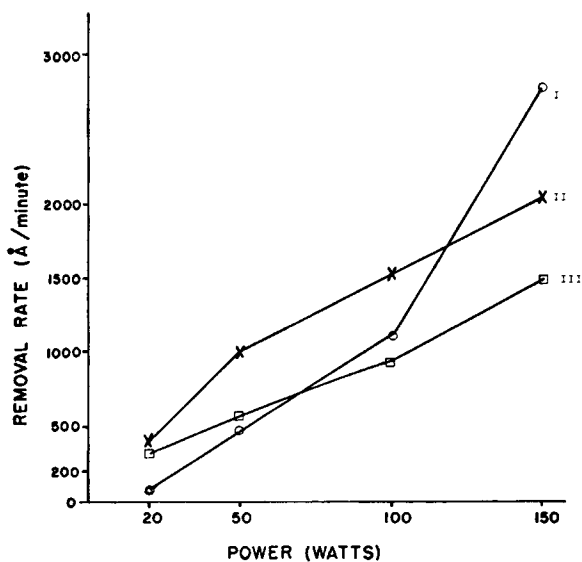


Fig. 1. Etching rates for I, II, and III with an oxygen plasma.

TABLE IV
Poly-*p*-Xylylene Removal Rates in an Oxygen Plasma^a

Power, W	Removal rate, Å/min			Approximate maximum temp., °C ^b
	I	II	III	
20	48	370	305	50
50	470	990	570	80
100	1080	1500	900	110
150	3000	2000	1500	150

^a Conditions: oxygen flow adjusted to give an operating pressure of 1.0 torr; films were unsupported (6.0 × 7.0 cm).

^b Measured by placing a thermometer inside the chamber.

the oxidation rates. These results indicate that at 50°C the poly-*p*-xylylene with the greatest degree of crystallinity and highest melting point (polymer I) etches the slowest.

Table V shows the correlation between polymer etch rate and melting temperature under the mild plasma conditions of 20 W of power and a chamber temperature of 50°C.

As the power level is increased, thermal effects become more important and the relative removal rates change. At 50 W of input power, the chamber temperature was about 80°C, and the removal rates for I, III, and II were 470, 570, and 990 Å/min, respectively. At 100 W of input power, the chamber temperature increases to 110°C, and the removal rates for I, III, and II are 1080, 900, and 1500 Å/min, respectively. Under these conditions, I is etched faster than III. Finally, at 150 W, I clearly etches faster than II and III.

Critical Surface Tension (γ_c) of Untreated Poly-*p*-Xylylene Films

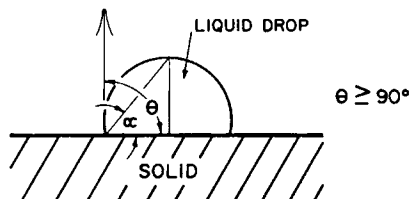
In most cases, a liquid placed on a solid will not wet it but remains as a drop having a definite angle of contact between the liquid and solid phases.⁴ Two examples are illustrated in Figures 2 and 3. For practical purposes, if the contact angle is greater than 90°, the liquid is said not to wet the solid—in such a case drops of liquid tend to move about easily on the surface and not to enter capillary pores. This case is shown in Figure 2. On the other hand, liquid is considered to wet a solid only if the contact angle is zero. The wettability increases as the contact angle approaches zero. The case is shown in Figure 3.

In practice, a measurement is made by placing a drop (in our experiments a 4- μ l drop was used) of distilled water on the substrate and a photograph is taken

TABLE V
Correlation between Oxidation Rate and Melting Temperature of the Poly-*p*-Xylylenes

Polymer	Removal rate at 20 W, ^a Å/min	Melting temp., °C
I	48	405
III	305	350
II	370	280

^a Substrate temperature approximately 50°C.



NON-WETTING CASE

Fig. 2. Nonwetting case.

from a right angle. The distances h and r are measured (see Fig. 3) and the contact angle (θ) can be calculated from $\tan \alpha = h/r$ and $\theta = 2\alpha$.

The surface tension (γ_c) of a polymer can be found by measuring the contact angles of various liquids on the polymeric surface. Plotting the cosines of the contact angles versus the surface tensions of the respective liquids and extrapolating the resulting curve to $\cos \theta = 1$ gives the surface tension (dyn/cm) of the polymer.⁵

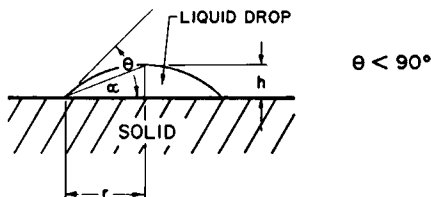
The cosine of the contact angles versus the surface tension of the various liquids is plotted in Figure 4. A critical surface tension of approximately 45 dyn/cm can be estimated from Figure 4. It should be noted that liquids with a γ_c less than γ_c for poly-*p*-xylylene (45 dyn/cm) gave a contact angle of essentially zero ($\cos \theta = 1$).

Another method for measuring the surface energy of polymers and for resolving the surface energy into contributions from dispersion (γ_s^d) and dipole-hydrogen bonding (γ_s^h) forces was developed by Owens and Wendt.⁶ This method is based on the measurement of contact angles with water and methylene iodide.

The results for this test method are summarized in Table VI. The agreement between γ_s found using the Owens method and γ_c found from the plot of $\cos \theta$ vs. γ_c of various liquids is excellent. The values obtained for the poly-*p*-xylylenes are consistent with other polymeric materials with a similar chemical composition.

Water Contact Angles of Plasma-Treated Poly-*p*-Xylylene Films

In this study, it was shown that the interaction of an oxygen, nitrogen, helium, or argon plasma with polymer I, II, or III caused significant changes in wettability. As previously discussed, the water contact angle of untreated I, II, or III is approximately 90°, and the critical surface tension of wetting is 45 dyn/cm. After



WETTING CASE

Fig. 3. Wetting case.

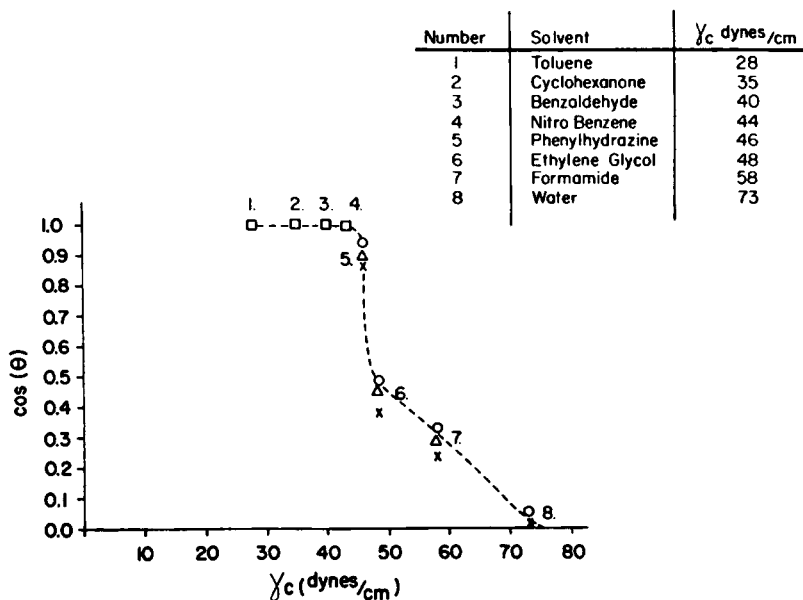


Fig. 4. $\cos \theta$ (water contact angle) for various liquids on I, II, and III. (×) I; (O) II; (Δ) III; (□) I, II, and III.

the plasma treatment, the water contact angle decreases to $<40^\circ$. The actual contact angle measured has been shown to depend on the type of plasma, treatment time, and the polymer used. However, regardless of the plasma and conditions employed, the contact angle changes with time after the plasma treatment and usually stabilizes in about 24 hr. A typical example is illustrated in Table VII.

An examination of Table VII shows that the changes in θ are more pronounced

TABLE VI
Components of Surface Energy for I, II, and III Determined using the Owens Method

Polymer	Contact angle, deg		erg/cm ²		
	H ₂ O	CH ₂ I ₂	γ_s^d	γ_s^h	γ_s
I	89	25	45.7	0.6	46.3
II	87	23	46.2	0.9	47.1
III	90	25	45.9	0.4	46.3

TABLE VII
Post-Plasma-Treatment Water Contact Angles for Poly(monochloro-*p*-Xylylene)

Water contact angle θ , ^a deg	Time after treatment, ^b hr
28	0.3
31	2.0
38	4.0
43	6.0
49	24.0
48	6 days

^a 4- μ l drop; initial value 90° .

^b Oxygen plasma, 1.0 torr, 100 W for 3 min.

TABLE VIII
Water Contact Angles after Treatment with Various Plasmas^a

Gas	Contact angle θ , deg		
	I	II	III
Helium	SPR (0)	22	27
Argon	SPR (0)	18	20
Oxygen	32	18	25
Nitrogen	12	21	23

^a SPR(O) = water spreads spontaneously over the surface. Conditions: 100 W; 1.0 torr for 6 min. θ measured 0.3 hr after treatment.

immediately after the plasma treatment. Consequently, the critical surface tension of wetting is greater immediately after the treatment and decreases with time but does not recover to the original value.

The utilization of different gases under similar plasma conditions gave interesting results. The values of water contact angles measured 0.3 hr after a plasma treatment with various gases are summarized in Table VIII. Argon, helium, nitrogen, and oxygen were evaluated.

The results shown in Table VIII indicate that under these particular plasma conditions, the water contact angles for all four plasma gases are comparable for II and III. However, the inert gas plasmas (helium and argon) did increase the surface energy of I more than oxygen or nitrogen plasma treatments. In addition, the contact angle measured after the oxygen plasma treatment was independent with treatment time. This was not the case with the inert gas plasmas.

Because the oxygen plasma treatments etch the polymer at an appreciable rate (i.e., 1500 Å/min) the resulting surface is changing rapidly, but the average composition of the surface is quite constant. However, with inert and/or other very slow etching gases, the surface exposed to the plasma interaction is not etched, and therefore the composition of the surface is now dependent on the length of time the plasma and surface interact. These effects are demonstrated by the contact angle data and will also be seen in the adhesion results to be discussed later.

Table IX summarizes the results for a helium plasma. The measured water contact angle depended on the power input and the treatment time, suggesting that longer plasma exposures yielded more surface modification. For example, at 100 W and 1 min of treatment time, the contact angle was 37°. After 6 min of plasma exposure, the contact angle was only 22°. With an oxygen plasma this was not the case.

TABLE IX
Interaction of a Helium Plasma with Poly(monochloro-*p*-Xylylene)

Time, min	Water contact angle, ^a degrees	
	20 W	100 W
1	41	37
6	32	22

^a Values measured 0.3 hr after the plasma treatment.

Infrared Characterization of Poly(monochloro-*p*-Xylylene) Treated in an Oxygen Plasma

Plasma-treated films were initially examined using infrared transmission spectroscopy. No new bands were detected; however, several changes in band intensities were observed. The most significant change was a decrease in the intensity of the 878 cm^{-1} band with respect to the 827 cm^{-1} band. Both of these bands are out-of-plane aromatic ring hydrogen wagging modes; the 878 cm^{-1} band is characteristic of an isolated hydrogen, whereas the 827 cm^{-1} band is characteristic of two adjacent hydrogens. This suggests a loss of chlorine atoms from some of the aromatic rings.

IRS surface infrared spectra were obtained with KRS-5 reflection crystals (45° effective angle). These spectra showed the same changes in band intensities which had been observed in the transmission spectra. There was also some indication of a carbonyl band near 1700 cm^{-1} , but this was extremely weak. In

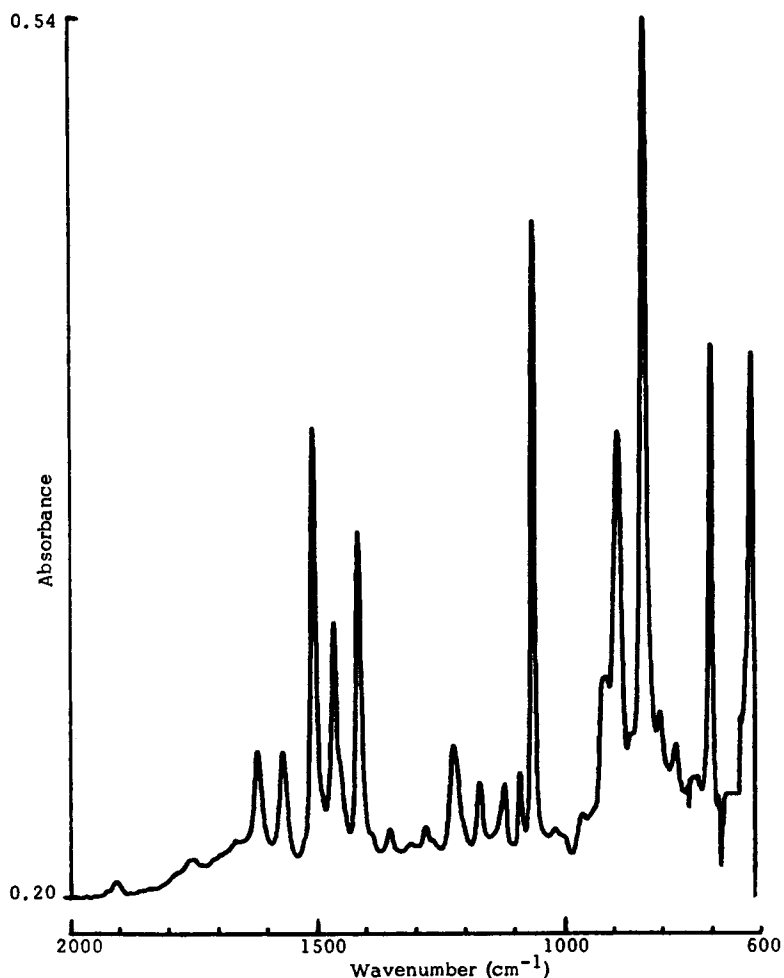


Fig. 5. Infrared IRS spectrum of II treated in an oxygen plasma for 6 min (germanium crystals at 60° effective angle).

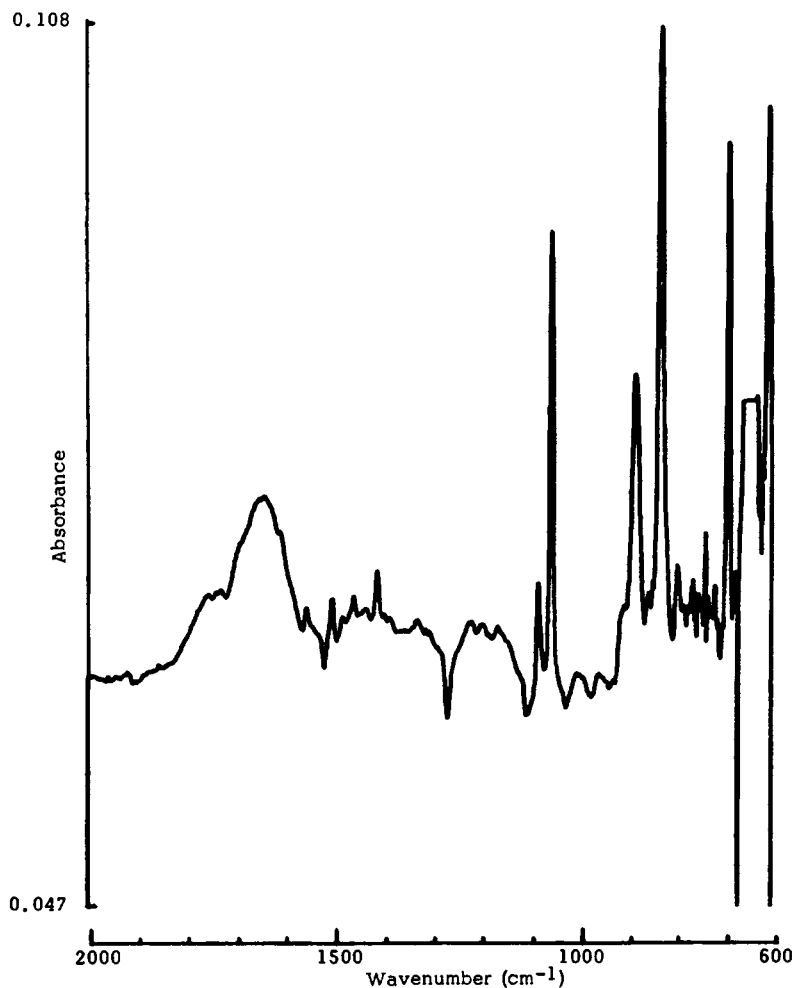


Fig. 6. Subtraction of a spectrum of control film from spectrum of II treated in oxygen plasma for 6 min (germanium crystals at 60° effective angle).

order to minimize the penetration depth, germanium (60° effective angle) IRS crystals were employed. These spectra contain weak absorption bands in the carbonyl region ($1650\text{--}1800\text{ cm}^{-1}$). Spectral subtraction techniques were used in order to isolate these carbonyl bands from the bands resulting from II. The results are shown in Figures 5 through 7.

Figure 5 is the IRS spectrum of II treated in an oxygen plasma. All the major bands are characteristic of II; a broad background absorption is observed at $\sim 1650\text{ cm}^{-1}$. Figure 6 shows the results of subtracting the spectrum of a control film. Two broad, distinct carbonyl absorption bands were detected at 1730 and 1640 cm^{-1} . Absorption bands owing to II were not completely removed; this is frequently encountered when subtracting IRS spectra. Note that the full-scale absorbance in the subtraction spectrum is 0.061. Similar results were obtained for films treated in argon plasmas. Figure 7 shows the spectral subtraction for this system. Carbonyl bands were observed at 1730 and 1695 cm^{-1} .

For both plasma treatments, some subtraction spectra contained another broad

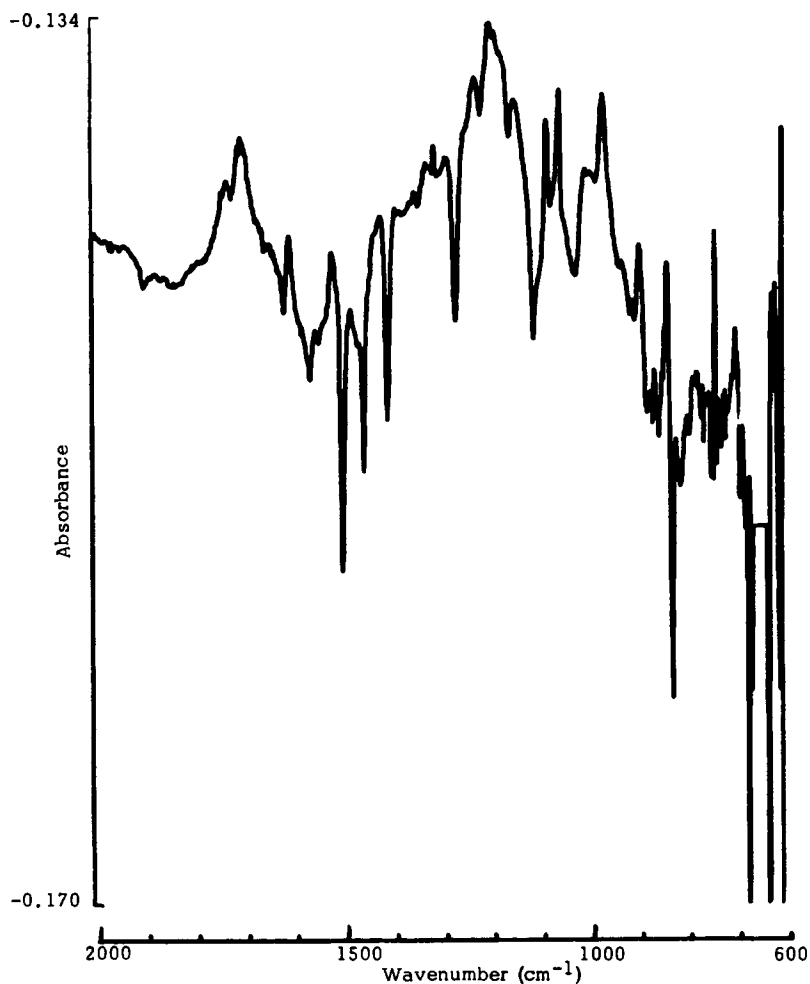


Fig. 7. Subtraction of a spectrum of control film from spectrum of II treated in an argon plasma for 6 min (germanium crystals at 60° effective angle).

feature at 1200 cm^{-1} ; this is consistent with a C-O species. However, this was not observed in all spectra and may be an artifact of the experiment.

A series of samples were treated under various conditions in order to study the effect of plasma power and treatment time on the infrared spectrum. The results are summarized in Table X. The absorbance values for the carbonyl bands were ratioed against the 1610 cm^{-1} reference band in order to obtain quantitative results. Considering the oxygen plasma, the relative amounts of carbonyl species appear to be independent of treatment time except for the 1640 cm^{-1} band at the low power (50 W). The intensity of the 1730 cm^{-1} band increases with increasing plasma power, whereas that of the 1640 cm^{-1} band does not.

Considering samples treated in an argon plasma, longer treatment times increase the intensities of both 1730 and 1695 cm^{-1} bands at 50 W of power, but have little effect at 100 W of power. Increased plasma power increases the amount of both types of carbonyl species.

TABLE X
Dependence of Carbonyl Band Intensities upon Plasma Type, Power, and Treatment Time

Conditions	$\frac{A_{1730}}{A_{1610}}$	$\frac{A_{1695}}{A_{1610}}$	$\frac{A_{1640}}{A_{1610}}$
Oxygen Plasma			
50 W, 1 min	0.080	—	0.145
50 W, 6 min	0.081	—	0.198
100 W, 1 min	0.132	—	0.136
100 W, 6 min	0.129	—	0.131
Argon Plasma			
50 W, 1 min	0.068	0.094	—
50 W, 6 min	0.095	0.128	—
100 W, 1 min	0.153	0.153	—
100 W, 6 min	0.146	0.155	—

Adhesion of Polyurethanes to Plasma-Treated Films

Various plasma treatments were examined as a pretreatment conditioning step to promote the adhesion of polyurethane thermosetting resins to poly-(monochloro-*p*-xylylene) coated substrates. The plasmas examined and the conditions utilized are shown in Table XI.

The polyurethane material was applied immediately after the plasma treatment, and the rivet was placed onto the polyurethane. The adhesion was measured as described in the Experimental section. For each condition, at least 15 separate measurements were made. In 10 measurements the samples remained under ambient conditions for up to one week before the adhesion was measured, and in five samples, temperature and humidity conditioning according to MIL-I-46058 was employed. All results are summarized in Table XI. The results indicate that the adhesion of the polyurethane to poly(monochloro-*p*-xylylene) increases approximately four- to eightfold if a plasma treatment is used prior to the application of the polyurethane. The degree of adhesion improvement was dependent on the type of plasma and the length of treatment time. With an oxygen plasma, the adhesion was comparable regardless of the treatment

TABLE XI
Adhesion of Polyurethane to Poly(monochloro-*p*-Xylylene)

Plasma (time of treatment, min) ^a	Adhesion, lb/in. ² (nonconditioned) ^b	Adhesion, lb/in. ² (temp.-humidity cycled) ^{b,c}
None ^d (0)	26 ± 6	40 ± 6
Oxygen (1)	180 ± 30	220 ± 30
Oxygen (6)	200 ± 45	230 ± 25
Argon (1)	220 ± 25	—
Argon (6)	390 ± 120	420 ± 150
Helium (1)	190 ± 50	—
Helium (6)	355 ± 55	430 ± 90

^a Plasma power 100 W; gas pressure with the chamber was 1.0 torr.

^b Rivet pull test was used as described in the Experimental section.

^c Temperature/humidity cycled according to MIL-I-46058.

^d Control samples received no plasma treatment.

time. However, with argon or helium plasma treatments, the adhesion was better in the 6-min plasma treatment samples than in the 1-min treated samples. For example, control samples gave adhesion values in the 25–40 lb/in.² range, while oxygen 1- and 6-min, and argon 1-min and helium 1-min samples gave adhesion values between 180 and 230 lb/in.² Argon and helium 6-min samples gave measurements between 355 and 430 lb/in.² These results correlated with water contact angles ($\theta_{\text{H}_2\text{O}}$) measured on plasma-treated poly(monochloro-*p*-xylylene) surfaces. In an earlier section it was noted that $\theta_{\text{H}_2\text{O}}$ decreased with increasing plasma exposure time for helium- and argon-treated surfaces. With oxygen, $\theta_{\text{H}_2\text{O}}$ was independent of treatment time.

These observations are interpreted as follows: With an oxygen plasma the polymer surface is etched at about 1000 Å/min. Consequently, at any one instant during the plasma treatment experiment, only a finite amount of oxygen is present in the surface (a dynamic surface). However, with an argon or helium plasma, very little etching is taking place and residual oxygen in the plasma chamber can react with reactive sites on the polymer surface which are created by collisions with argon- and helium-activated species. In the argon and helium plasma treatments, the surface is static and longer exposure times will give a different surface modification than shorter exposure times. A significant amount of oxygen is incorporated into the polymer surface during argon and helium plasma treatments, presumably, from residual oxygen in the plasma chamber. Therefore, these plasma treatments modify the surface differently giving different water contact angles and offering different degrees of adhesion promotion of a polyurethane to the poly(monochloro-*p*-xylylene).

Examination of the fracture areas after the rivets were removed from the samples indicates that with the control samples and the oxygen plasma-treated samples, the failures were at the poly(monochloro-*p*-xylylene)/urethane interfaces. However, with argon- and helium-treated samples, the failures were at the polyurethane/rivet interfaces. Therefore, the rivet pull test indicates that in these samples the adhesion measured is the lower limit of the urethane to poly(monochloro-*p*-xylylene) adhesion.

Results given in a previous section indicated that the surface modification, induced by a plasma treatment, changes with time after the treatment is terminated. Water contact angles gradually increase from about 30° to 50° over a period of one week. However, the contact angles never recover to the preplasma condition of about 90°. In order to determine if the length of time between the

TABLE XII
Adhesion of a Polyurethane to Poly(monochloro-*p*-Xylylene) One Week after the Plasma Treatment

Plasma ^a	Adhesion (lb/in ²)	
	Control ^b	One Week ^c
Air	233 ± 25	322 ± 24
Oxygen	178 ± 35	268 ± 19
Argon	319 ± 6	365 ± 54
Helium	353 ± 37	408 ± 52

^a Plasma power 100 W for 6 min.

^b Polyurethane applied immediately after the plasma treatment.

^c Polyurethane applied one week after the plasma treatment.

plasma surface modification and the application of the polyurethane to the surface affects adhesion of the polyurethane to poly(monochloro-*p*-xylylene), the polyurethane was applied one week after the plasma treatment was performed. These results, shown in Table XII, show that the adhesion is comparable regardless of the length of time (up to one week) between the end of the plasma modification step and the application of the polyurethane to the substrate. Adhesion increases slightly for air and oxygen plasmas.

CONCLUSIONS

The interaction of inorganic plasmas with poly-*p*-xylylene films can be used to either completely etch the film or to promote the adhesion of a thermosetting material, such as a polyurethane, to the surface of the film. Argon and helium plasma treatments improve the adhesion more than an oxygen treatment.

Water contact angles of plasma-treated poly-*p*-xylylene surfaces were $<40^\circ$. The contact angles increased after the plasma treatment but never recovered their original values before treatment of 90° .

The IRS spectra of the surface of films treated with oxygen plasma did contain carbonyl bands at 1730 and 1640 cm^{-1} . For helium or argon plasmas, the carbonyl bands were found at 1730 and 1695 cm^{-1} .

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