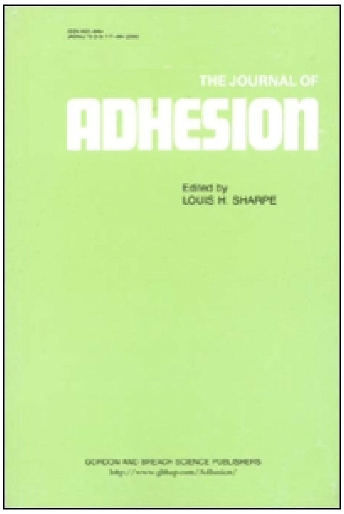

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Adhesion to Plasma-Modified LaRC-TPI II. Effect of Plasma Treatment on Peel Strength*

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LaRC-TPI, an aromatic thermoplastic polyimide, was exposed to oxygen, argon and ammonia plasmas as pretreatments for adhesive bonding. A 180° peel test with an acrylate-based pressure sensitive adhesive tape as an adherend was utilized to study the interactions of the plasma-treated polyimide surface with another polymeric material. The peel strengths of the pressure sensitive adhesive tape on the plasma-treated LaRC-TPI fell below the level of the non-treated controls, regardless of the plasma treatment used. Failure surface analysis by XPS revealed the presence of polyimide on the pressure sensitive adhesive failure surface, indicating failure in the plane of a weak boundary layer created by plasma treatment. The removal of the weak boundary layer by a solvent rinse restored the peel strength to the level of the control. Comparison with tape adhesion peel strengths of oxygen plasma-treated high density polyethylene showed that the physical condition of a polymer surface following plasma treatment plays an important role in determining the level of adhesion which can be achieved.

KEY WORDS plasma treatment; LaRC-TPI; peel test; weak boundary layer; failure surface analysis; pressure sensitive adhesive; high density polyethylene.

INTRODUCTION

The modification of low energy polymer surfaces with gaseous plasmas has been widely used to improve adhesion of other polymers, coatings and inks. It is well-known that plasmas are capable of inducing significant changes in surface chemistry and wettability without detectable changes in material bulk properties.[1,2] Part I of this study has presented the results of oxygen, argon and ammonia plasma treatment of LaRC-TPI, a commercially important thermoplastic polyimide.[3]

It was shown in Part I that after treatments with oxygen, argon and ammonia plasmas, the LaRC-TPI surface showed an increase in wettability as observed by water contact angle analysis, as well as an increase in the concentration of surface polar groups, as revealed by X-ray photoelectron spectroscopy (XPS) and infrared reflection-absorption spectroscopy (IR-RAS). It was also observed that ablation and etching of the surface was occurring, particularly in the cases of oxygen and argon plasmas. Ammonia plasma also etched away the LaRC-TPI film, but at a

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M*.

much slower rate. It was postulated that the plasma treatment had created an oxidized layer which was composed of low molecular weight polyimide fragments, resulting from chain scission.

In this study, the interactions of the oxygen, argon and ammonia plasma-treated LaRC-TPI surface with another polymer were investigated through peel testing with a pressure sensitive adhesive (PSA) tape. It is obvious that bonding with a PSA does not represent a realistic application of polyimide materials; however, it was proposed that the use of a PSA would induce the least damage to the plasma-treated surface layer, in contrast to adhesives applied from solution or in hot melt form. Thus, it becomes possible to probe the actual physical nature of the modified surface with the least possible disturbance. This form of peel testing has also been utilized by other researchers to study polymer surface dynamics.[4,5]

Although the experimental difficulties associated with peel testing have been well-documented,[6,7,8,9] it was hoped that it could serve as a test of practical adhesion and differentiate between the various plasma treatments. It was expected that increases in peel strength would be observed, due to the increases in surface wettability and polarity brought about by the plasma treatment.

EXPERIMENTAL

Materials

The development of LaRC-TPI as an aromatic, thermoplastic polyimide suitable for use in composites, adhesives and films was pioneered by researchers at NASA-Langley Research Center; its structure is shown in Figure 1. The LaRC-TPI used in this study was produced by the Mitsui Toatsu Chemical Company (New York, New York, U.S.A.) and supplied by researchers at NASA-Langley Research Center (Hampton, Virginia, U.S.A.) as a 30% w/w poly(amic-acid) solution in diglyme (2-methoxyethylether). Reagent grade diglyme used for diluting the LaRC-TPI solution was obtained from Fisher Scientific.

Ferrotype photographic plates (chromium-plated steel) used as substrates for the LaRC-TPI coating were obtained from Apollo Metals (Bethlehem, Pennsylvania, U.S.A.). 1.9 cm (¾ in) wide Scotch® Magic® Tape, having a pressure sensitive adhesive composed of poly(acrylate-co-acrylic acid), was obtained from the 3M Company (St. Paul, Minnesota, U.S.A.). 0.16 cm (1/16 in) thick high density polyethylene (HDPE) was obtained from the Atlantic Plastics Company (Roanoke, Virginia, U.S.A.).

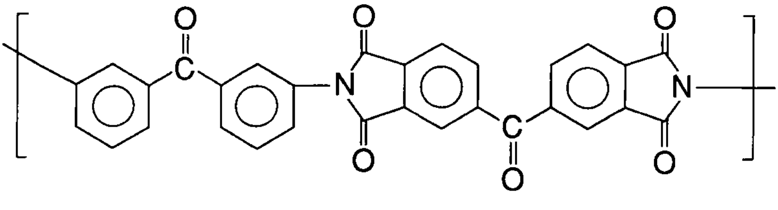

FIGURE 1 Structure of LaRC-TPI.

Oxygen and argon gases used for the plasma treatments were obtained from Airco, Inc. (Radford, Virginia, U.S.A.). Semi-conductor grade ammonia gas was obtained from Matheson Gas Products (East Rutherford, New Jersey, U.S.A.).

Sample Preparation

LaRC-TPI solution was diluted to a 24% w/w solution with diglyme and spin-coated onto a 3.8 cm × 3.8 cm (1.5 in × 1.5 in) Ferrotype plate which had been pre-cleaned with methanol and acetone. Stepwise imidization was carried out in a circulating air oven at 100°C, 200°C and 300°C, holding for 30 minutes at each temperature setting. When the imidization cycle was complete, the oven was turned off and the samples were cooled to room temperature over a period of 18 hours. Coating thicknesses as measured by a digital micrometer ranged from 5–8 μm. For tape adhesion testing, the coated Ferrotype plate was sheared into 3.8 cm × 1.9 cm (1.5 in × .75 in) coupons.

Plasma Treatments

Plasma treatments were carried out in a March Instruments Plasmod® unit (Concord, California, U.S.A.), at 13.56 MHz and 50 watts. Gas lines were purged with the gas of interest for 30–60 seconds before use. The pressure inside the unit during its operation was approximately 1 torr. Care was taken to pump down and purge the treatment chamber for at least 10 minutes prior to activating the RF field. All bonding operations were performed within 1–2 minutes of plasma treatment, to minimize the possibility of surface molecular rearrangement and/or contamination by the atmosphere.

Preparation of Adhesive Joints

LaRC-TPI-coated Ferrotype plate was cleaned with acetone and methanol, blown dry with nitrogen and treated in the plasma chamber for 1 minute and 20 minutes in each plasma. Magic® Tape was placed on the surfaces with firm pressure within seconds of removal from the plasma chamber. Samples were stored for a minimum of 24 hours and a maximum of 72 hours in a desiccator prior to peel testing.

A substrate heating effect was observed for the samples which were plasma-treated for prolonged times. When the samples were taken out of the plasma chamber after 20 minutes, the sample temperature was at least 80–90°C. This substrate heating was eliminated as a variable by removing the hot samples from the plasma chamber after a 20-minute treatment and placing them onto a block of aluminum which acted as a heat sink.

In a separate experiment, plasma-treated samples were rinsed with methanol, scrubbed with a Kimwipe® tissue soaked in methanol, then rinsed again with methanol and blown dry with nitrogen. Tape was then applied as described above after the drying step.

High density polyethylene samples were cut into 2.5 cm × 5.0 cm (1.0 in × 2.0 in) strips, treated in an oxygen plasma and bonded with Magic® Tape as a comparison with the polyimide materials. Contact angle and XPS analyses were also carried out on the oxygen plasma-treated polyethylene samples.

Peel Testing

An Instrumentors Inc. Slip-Peel Tester model SP-102B-3M90 was used for the peel testing of the LaRC-TPI/Magic® Tape joints, utilizing the Magic® Tape as the flexible adherend. The load cell was calibrated electronically prior to peel testing. Substrates were clamped to the instrument and the adherends peeled off at a 180° angle by a hook attached to a load cell as shown in Figure 2. A peel rate of 25 cm/min (10 in/min) was utilized; this rate ensured that cohesive failure within the pressure sensitive adhesive would not occur. The peel strength is calculated as the average force divided by the width of the specimen peeled. All peel strengths are reported in newtons/meter. At least 3 peel specimens were tested for each plasma treatment condition; the reproducibility of the peel strength values ranged from ±11% to ±16%.

Analysis of Failure Surfaces

Failure surfaces of the peeled specimens were analyzed utilizing X-ray photoelectron spectroscopy (XPS). Analyses were performed on a Perkin-Elmer PHI 5300 spectrometer with a Mg K_α achromatic X-ray source (1253.6 eV), operating at 15 kV and 400 watts with an emission current of 30 mA. Pressure inside the analysis chamber was held below 2×10^{-7} torr during analysis. Samples were mounted onto the spectrometer probe with double-sided tape. All analyses were of a 1×3 mm rectangular area and were carried out at a take-off angle of 15°. XPS analyses of the high density polyethylene was carried out as described above, but at a 45° take-off angle.

Atomic concentration calculations and curve-fitting were carried out by use of the PHI software, version 2.0. All binding energies are normalized to the value for hydrocarbon species at 284.6 eV. Both sides of the peeled samples were analyzed in order to make a determination of the average failure plane. Since Magic® Tape is composed primarily of carbon and oxygen and does not contain nitrogen, nitrogen was conveniently used as a tag element in the failure surface analysis.

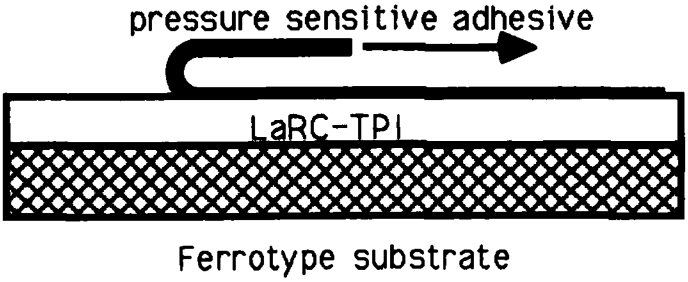

FIGURE 2 180° peel testing configuration.

RESULTS AND DISCUSSION

Bonding with Scotch® Magic® Tape

Scotch Magic® Tape was selected for these studies over other available pressure sensitive materials because of its polar character. The XPS C1s photopeak of Magic® Tape is shown in Figure 3 and is seen to contain two high binding energy shoulders at 286.2 and 288.6 eV, representative of C—O and O═C—O species. The atomic composition of the tape surface was found by XPS to be 84%C and 16%O, indicating a significant percentage of surface polar groups. It was expected that the polar groups in this PSA would be capable of interacting with the polar groups on the surface of the plasma-treated LaRC-TPI.

When a peel rate of 10 inches per minute is used, no cohesive failure within the PSA is observed. This observation was arrived at by auto-adhering two sections of the PSA together and peeling them apart in a 180° degree peel test at 10 inches per minute. Failure always occurred at the interface between the PSA and one of the backing materials, but not within the body of the adhesive.

Peel test results for the plasma-treated LaRC-TPI surfaces are shown in Figure 4. For each plasma, two sets of samples were made. One set was plasma-treated for 1 minute, the second set for 20 minutes, in order to determine the effect of treatment time. It is evident that in all instances, the peel strengths for the plasma-treated surfaces are lower than the peel strength of the control untreated surface. It is also noted that the 20-minute treatment samples show higher peel strengths than the 1-minute plasma-treated samples for all three plasmas. This may be explained by analysis of the surface topography of the polyimides after 20 minutes of plasma treatment by high resolution scanning electron microscopy (HR-SEM). Samples treated for twenty minutes in the oxygen and argon plasmas show an increase in roughness, relative to the untreated control.

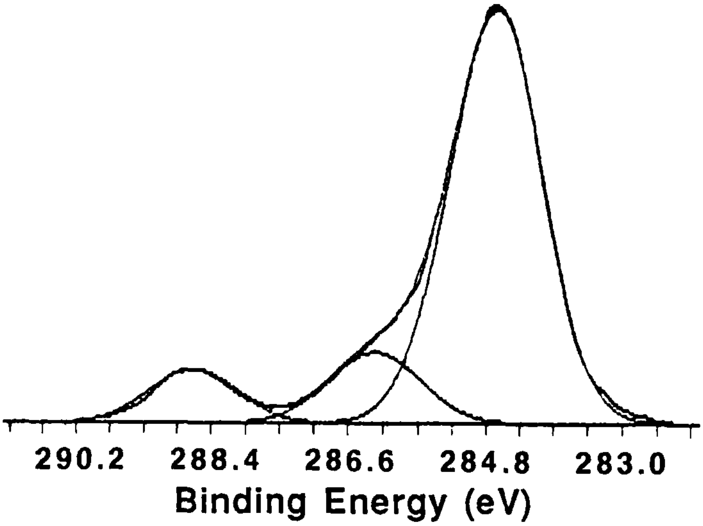

FIGURE 3 XPS C1s photopeak of Scotch® Magic® Tape.

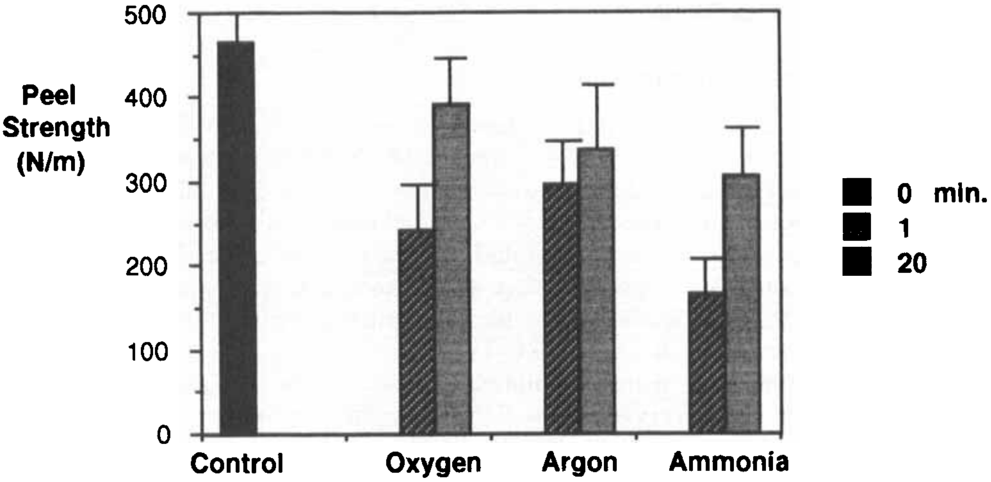

FIGURE 4 Peel test results for plasma-treated LaRC-TPI/Magic® Tape.

These observed increases in surface roughness may lead to a greater degree of mechanical interlocking and hence increased peel strength. However, this does not explain the greater peel strength of the 20-minute samples in the case of ammonia plasma, since no changes in surface topography were observed even after 20 minutes of treatment. One other possibility is that the additional *in-situ* heating which the 20-minute samples undergo could affect the nature of the modified layer. Another possibility is that although the 20-minute samples are cooled before the application of the PSA, even a slight increase in surface temperature relative to the 1-minute samples could cause better wetting of the PSA to occur on the LaRC-TPI surface.

The decreased peel strengths for the plasma-treated samples are puzzling in light of the changes in polyimide surface chemistry after plasma treatment. Increases in wettability and surface polarity are usually indicative of higher surface free energy, a situation generally favorable toward improved practical adhesion. Other studies of plasma-modified polyimides have shown increased adhesion toward chromium or copper deposited layers, due to what is generally accepted as increases in surface active sites.[10,11,12]

It is hypothesized that the ablative action of the plasma has created a loosely-attached, highly-oxidized layer on the surface of the bulk LaRC-TPI. This overlayer acts as a weak boundary layer, preventing strong adhesion to the substrate below. Figure 5 shows a schematic representation of this weak boundary layer concept. The region denoted as "plasma zone" is the weakened polyimide which lies between the PSA and the bulk polyimide. During peel testing, the polar weak boundary layer does adhere strongly to the PSA; however, the cohesive strength of this layer as well as its adhesion to the underlying polyimide is weak. This results in a lower force to initiate peeling, and failure occurs either within the weak boundary layer or at the interface between the layer and the polyimide substrate. This hypothesis is consistent with results from etch rate experiments, XPS curve-fitted data and HR-SEM analysis which clearly showed that ablation resulting from chain scission was occurring.[3]

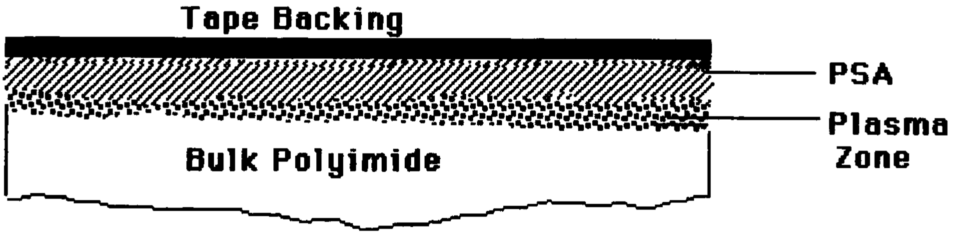

FIGURE 5 Proposed structure of weak boundary layer on LaRC-TPI, created by plasma exposure.

XPS analysis of the failure surfaces also provides additional evidence for this hypothesis. Table I lists the XPS analysis results for the tape sides and polyimide sides of the peel joint for the LaRC-TPI/Magic® Tape system. Because the PSA does not contain nitrogen, any nitrogen which is detected on the tape must originate from the surface of the polyimide. For the non-treated LaRC-TPI samples, no traces of nitrogen were found on the tape peel surface. However, for all of the plasma-treated samples, small quantities of nitrogen are detected on the tape side, indicating that the average plane of failure is cohesive within the plasma-treated polyimide surface. Only loosely attached material on the surface could be lifted off by the peeling action of the PSA. The fact that no nitrogen was detected on the tape sides of the control samples shows that the polyimide surface is not inherently weak.

Lazare and Srinivasan[13] also found that an oxidized layer was formed on polyimide after exposure to high energy vacuum ultraviolet radiation; they also observed that this layer was removed by contact with polar liquids. The formation of low molecular weight material after corona discharge treatment of polypropylene was studied by Strobel *et al.*[14] This low molecular weight material was also removed by washing with polar solvents, but was found to be completely insoluble in nonpolar

TABLE I
XPS analysis of LaRC-TPI/Magic® Tape peel surfaces

		Atomic concentration (%)		
Sample		C	O	N
Non-treated	Tape Side	86	14	0
	LaRC-TPI Side	82	15	3
1 min. Oxygen		85	13	2
		85	13	2
1 min. Argon		86	13	1
		85	13	2
1 min. Ammonia		84	15	1
		84	15	1
20 min. Oxygen		85	14	1
		71	26	3
20 min. Argon		84	15	1
		85	13	2
20 min. Ammonia		87	12	1
		82	16	2

solvents such as hexane. Onyiriuka *et al.* have reported on the solubilization of polystyrene surface moieties following treatment with corona discharge or plasma.[15] Other researchers have also found reduced levels of adhesion thought to be a consequence of low molecular weight oxidized materials on the surface of corona or plasma-treated polymers.[16,17]

Methanol Washing of Plasma-treated Surfaces

In light of the evidence presented above and references from the literature, solvent rinsing of the plasma-treated surfaces was carried out in an attempt to remove the weakly bound plasma-treated layer. Figure 6 shows peel test results for plasma-treated LaRC-TPI, compared with the non-treated control and samples which were rinsed in methanol immediately after plasma treatment. In all cases, samples which were washed with methanol following plasma treatment exhibited improved peel strengths over the plasma-treated samples, comparable with the peel strength of the control. This clearly shows that removal of the weak boundary layer created by plasma restores the original peel strengths by eliminating this weak point in the interphase region.

Figure 7 shows a comparison of the XPS C1s photopeak for untreated, oxygen plasma-treated and oxygen plasma-treated/methanol-rinsed LaRC-TPI surfaces. A high-intensity, high-binding-energy shoulder at 288.3 eV is seen to appear in the C1s photopeak of the oxygen plasma-treated surface, as previously reported in Part I.[3] This high binding energy material is apparently removed by the methanol rinse, as the resulting C1s photopeak (see Figure 7c) is essentially identical to the original surface. This experiment showed that the methanol rinse did not drastically change the surface chemistry of the LaRC-TPI, but simply removed an overlayer of loosely-attached, oxidized material.

An attempt was made to collect the methanol rinse residues in order to characterize chemically the weak boundary layer material. UV-visible spectroscopy was

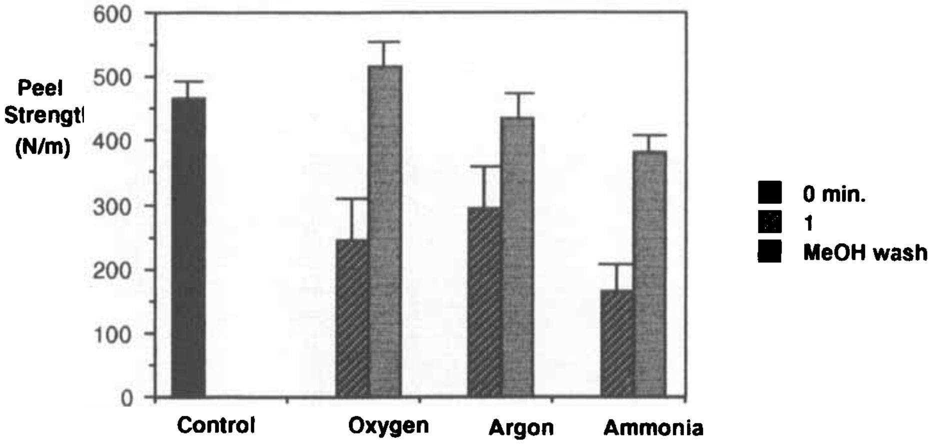

FIGURE 6 Peel test results for LaRC-TPI/Magic® Tape, following plasma treatment and plasma treatment/methanol wash.

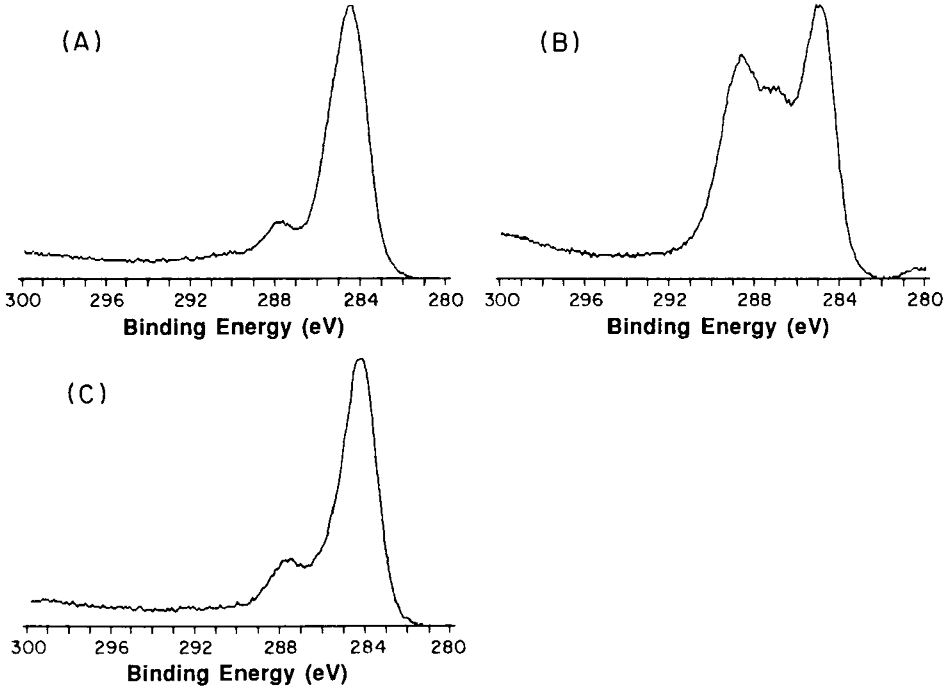

FIGURE 7 Cls photopeaks for (A) non-treated LaRC-TPI (B) oxygen plasma-treated LaRC-TPI (C) oxygen plasma-treated LaRC-TPI followed by methanol wash.

used to analyze the rinse solutions. However, due to the very small amount of material which was collected in the solvent, no signal was detected above the baseline.

Oxygen Plasma Treatment of High Density Polyethylene

Oxygen plasma treatment, contact angle analysis and peel testing of high density polyethylene (HDPE) was carried out as a comparison with LaRC-TPI. As noted above, polyimide chain scission was the primary result of plasma treatment. In contrast, polyethylene is known to undergo surface crosslinking as a consequence of irradiation with ionizing radiation.[18,19,20,21,22] It was expected that such differences in the physical state of the surface after crosslinking would cause differences in the level of adhesion.

Figure 8 shows the results of contact angle analysis for HDPE. HDPE, like the polyimides, also exhibits a high contact angle prior to plasma treatment and is not easily wetted by water. Wiping the surface with solvents actually causes the water contact angle to increase. After oxygen plasma treatment, the contact angle is seen to decrease by more than 50%, again indicating that a higher energy, more wettable surface has been created.

Changes in the Cls photopeak following oxygen plasma treatment of HDPE are shown in Figure 9. The oxygen atomic concentration on the surface increased from essentially zero before the plasma treatment to 26% after 5 minutes of treatment.

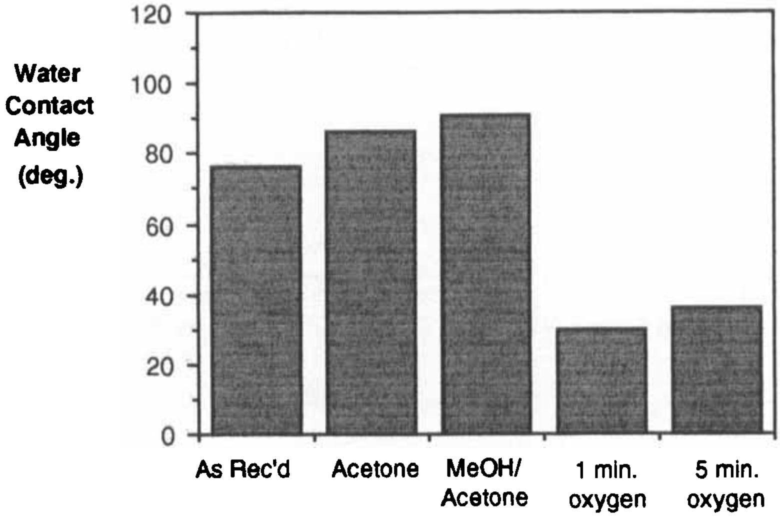

FIGURE 8 Water contact angles on as-received, solvent cleaned and oxygen plasma-treated high density polyethylene.

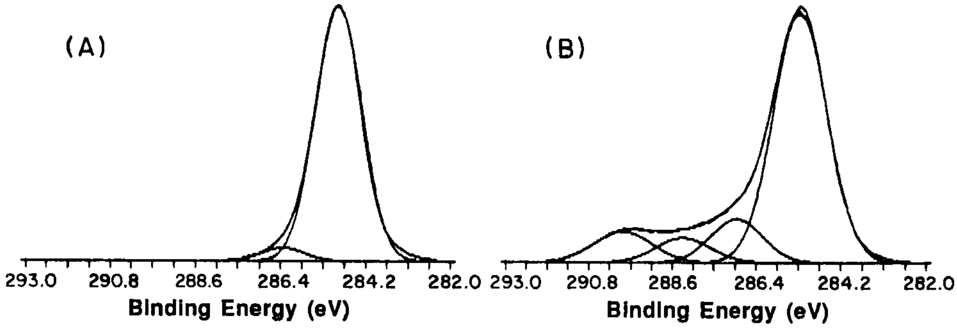

FIGURE 9 XPS C1s photopeaks for (A) as-received and (B) oxygen plasma-treated high density polyethylene.

Several new peaks are seen in the high binding energy region at 286.3, 287.7 and 289.3 eV, corresponding to the formation of C—O, C=O and O=C—O species.

When peel testing was carried out in the same manner as for the plasma-treated LaRC-TPI polyimides, the oxygen plasma-treated HDPE exhibited a 700% increase instead of a decrease in peel strength, as seen for the polyimide materials. Peel strengths at four plasma treatment times are shown in Figure 10. Since polyethylene undergoes surface crosslinking instead of chain scission, no weak boundary layer is formed. Conversely, any low molecular weight material on the surface can be crosslinked to form a stronger substrate. The resulting increase in degree of surface oxidation is not accompanied by a decrease in the cohesive strength of the surface material and, thus, an increase in the level of adhesion is observed.

Gleich *et al.*[23] carried out lap shear bonding studies on plasma-treated polypropylene and polyimide coupons before and after plasma treatment. It was found that

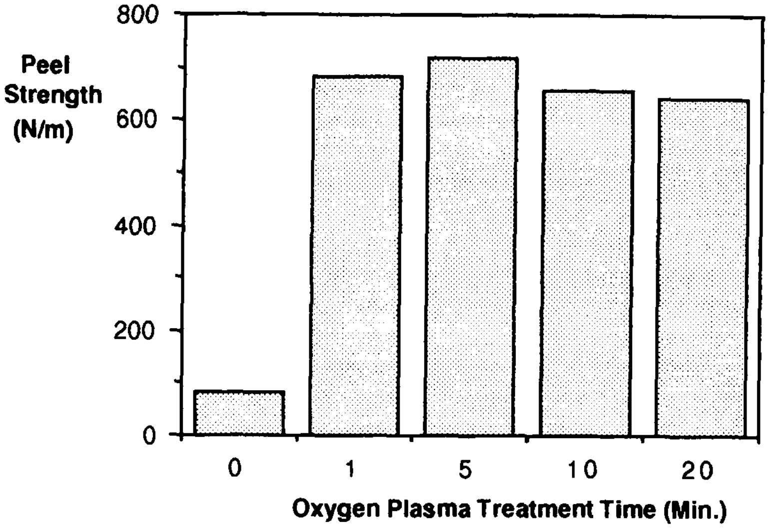

FIGURE 10 Peel test results for as-received and oxygen plasma-treated high density polyethylene.

for the polypropylene samples, increases in surface energy caused by the plasma treatment correlated with an increase in shear strength of the bonded samples. However, for the polyimide materials, no such correlation was seen. Although the surface energies of the plasma-treated polyimides increased, no increases in lap shear strength were observed. The results of the present work appear to be consistent with the findings of this study; that is, both the physical and chemical state of a surface play an important role in adhesive bonding.

SUMMARY

Tape peel testing with the use of a pressure sensitive adhesive was instrumental in showing the weak cohesive strength of the plasma-modified layer on the polyimide LaRC-TPI. The peel test results were correlated with the results of surface analysis in which the formation of a low molecular weight, oxidized layer was suggested. The PSA tape did not disturb the plasma-modified layer but was able to differentiate between the non-treated, plasma-treated and plasma-treated/methanol rinsed surfaces. In this particular instance, it was shown to be a sensitive probe of the interphase region.

The weak boundary layer which was formed as a result of plasma treatment was shown to interfere with adhesion to a pressure sensitive adhesive. Removal of this layer was accomplished by solvent treatment, and resulted in improved adhesion as well as a decrease in the concentration of surface polar groups. It is possible that in a more realistic bonding situation, this thin plasma-modified layer could be dislodged or absorbed by an adhesive applied from solution or in melt form. In such a case, no detrimental effects on adhesion should be observed. However, it is conceivable that the presence of these low molecular weight, polar molecules in the bondline could lead to plasticization or disruption of cure stoichiometry in the interphase region, creating a weakened mechanical response.

Plasma treatment was shown to improve peel strength in the case of high density polyethylene. Although surface oxidation was occurring with polyethylene, chain scission was not, since most polyolefins are known to undergo surface crosslinking when bombarded with high energy radiation. Thus, no weak boundary layer was created on the surface of high density polyethylene. This comparison of the LaRC-TPI polyimide and polyethylene illustrates the fact that the physical as well as the chemical characteristics of a plasma-treated surface play an important role in adhesion.

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