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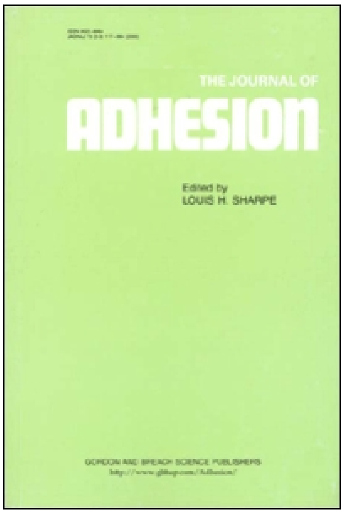

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Adhesion to Plasma-Modified LaRC-TPI
I. Surface Characterization*

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LaRC-TPI, an aromatic thermoplastic polyimide, was exposed to oxygen, argon and ammonia plasmas as pretreatments for adhesive bonding. Chemical changes which occurred in the surface as a result of the plasma treatments were investigated using x-ray photoelectron spectroscopy (XPS) and infrared reflection-absorption spectroscopy (IR-RAS). Water contact angle analysis was utilized to characterize the changes in surface wettability, and the ablative effects of the plasmas were monitored using ellipsometry. Both XPS and IR-RAS results indicated the formation of polar functional groups at the surface. Contact angle analysis showed enhanced water wettability of the plasma-treated surface. Oxygen and argon plasmas were highly ablative, whereas ammonia plasma was only moderately so. Oxygen and argon plasmas appear to react with the LaRC-TPI *via* a fragmentation/oxidation mechanism; the effect of ammonia plasma is postulated to be imide ring-opening resulting in the formation of amide functional groups.

KEY WORDS Plasma treatment; LaRC-TPI; polyimides; surface analysis; x-ray photoelectron spectroscopy; infrared reflection-absorption spectroscopy.

INTRODUCTION

Treatment of polymeric surfaces with low temperature gaseous plasmas has found widespread utility in the area of adhesion. It has been well-documented that such treatments are capable of inducing significant changes in surface chemistry and wettability without detectable changes in material bulk properties.[1] Plasma pretreatments are used in many diverse applications, including cleaning and activation of organic polymer surfaces,[2,3] microelectronics,[4] biocompatible materials[5] and carbon fibers.[6]

In this area of surface pretreatment pertaining directly to adhesion, it is important to understand more completely the nature of the modified surface. It is known that polar functional groups are incorporated into surfaces as a result of plasma treatment; however, what is not so well-known is the specific identity of those functional groups and in what way they have been incorporated into the original polymer

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structure. Such knowledge could lead to the ability to "tailor" treat a polymer surface to give optimum interaction with a given adhesive or coating.

It is the objective of this work to study the chemical changes in the surface of LaRC-TPI, a commercially important thermoplastic polyimide, after treatment with oxygen, ammonia and argon plasmas. LaRC-TPI finds application in the area of fibers, films, moldings, composites and structural adhesives.[7] Since plasma treatments are often performed to optimize performance of polymers used in these applications, the study of plasma pretreatments on LaRC-TPI can be directly related to future uses.

X-ray photoelectron spectroscopy (XPS), infrared reflection-absorption spectroscopy (IR-RAS), ellipsometry and sessile drop contact angle analysis were utilized to characterize the surface of the polymer before and after exposure to the plasmas. Through the use of these surface-sensitive techniques, both the chemical and physical characterization of the plasma-modified surfaces were carried out. The complementary use of XPS with infrared analysis of thin films was intended to give more specific information about the identity of surface functional groups than has been previously reported for plasma-treated surfaces.

Since it is known that the vast majority of plasma reactions with surfaces are free radical in nature, it is possible to correlate the observed reaction products with postulated products based on known mechanisms.[8] This served as an additional tool in this investigation.

EXPERIMENTAL

Materials

LaRC-TPI is classified as a thermoplastic polyimide, which can be fully imidized and then further thermally processed. The poly(amic-acid) precursor is prepared from the reaction of 3,3′,4,4′ benzophenone tetracarboxylic dianhydride and 3,3′ diaminobenzophenone in diglyme (2-methoxyethylether). Further heating at temperatures in excess of 200°C initiates cyclization of the imide ring. The structure of LaRC-TPI is shown in Figure 1. The Tg of the fully imidized polymer ranges from 240–260°C. The LaRC-TPI utilized in this study was produced by the Mitsui Toatsu Chemical Company (New York, New York) and supplied by researchers at NASA-Langley Research Center (Hampton, Virginia) as a 30% w/w solution in diglyme. Reagent grade diglyme used for diluting the LaRC-TPI solution was obtained from Fisher Scientific.

Commercial Ferrotype photographic plates were used as substrates for the LaRC-TPI coating. Plates were obtained from Apollo Metals (Bethlehem, Pennsylvania) and consisted of a steel base plated with nickel and an approximately 80 nm thick outer layer of chromium oxide.

Oxygen and argon gases used for the plasma treatments were obtained from Airco, Inc. (Radford, Virginia). Semi-conductor grade ammonia gas was obtained from Matheson Gas Products (East Rutherford, New Jersey). Purities of the gases are listed as follows: Oxygen—99.95%, Argon—99.995%, Ammonia—99.999%.

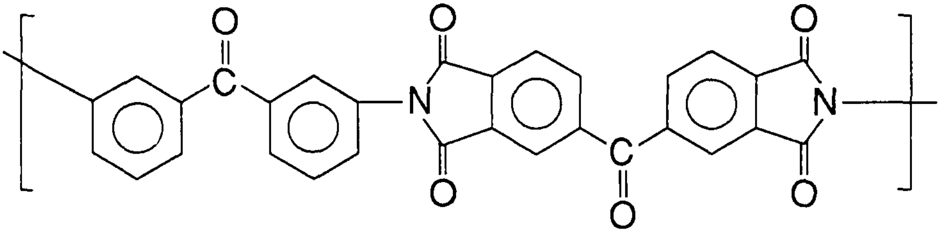

FIGURE 1 Structure of LaRC-TPI

Sample Preparation

For XPS characterization and contact angle analysis, LaRC-TPI solution was diluted to a 24% w/w solution with additional diglyme. The solution was spin-coated onto a 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. The samples were cooled to room temperature before removal from the oven. Coating thickness as measured by a digital micrometer ranged from 5–8 microns.

IR-RAS and ellipsometric analysis required thinner coatings in the 25–50 nm range. In a thin coating, the plasma-modified region represents a larger percentage of the total coating thickness, thus greatly enhancing the sensitivity of the IR technique. Thin coatings were obtained by further diluting the LaRC-TPI solution with diglyme to 2.5% w/w. Both the LaRC-TPI solution and the diglyme were cooled in an ice bath to prevent the resin from precipitating out of solution. Spin-coating and subsequent imidization were carried out as described above.

Plasma Treatments

Plasma treatments were carried out on 0.5 cm. diameter discs which were punched from the original spin-coated samples in an Tegal Plasmod® unit, at 13.56 Mhz and 50 watts. The pressure inside the unit is approximately 1 torr. Care was taken to pump down the treatment chamber for at least 10 minutes prior to activating the RF field.

Surface Analysis

XPS analysis was performed on a Perkin-Elmer PHI 5300 spectrometer with a Mg K_α achromatic X-ray source (1253.6 eV), operating at 15 keV with an emission current of 30 mA. Pressure inside the analysis chamber was held below 5×10^{-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 45°. Atomic concentration calculations and curve-fitting were carried out by use of the PHI software, version 2.0. Photopeaks of interest were fitted with Gaussian curves, varying both the peak intensity and position while holding the full width at half maximum (FWHM) at 1.7 ± 0.1 eV. Binding energies for all observed photopeaks were referenced to the value for hydrocarbon species at 284.6 eV. Between 3–5 analyses and curve fits were independently performed for each plasma treatment to assure reproducibility and obtain a statistical sampling of peak binding energies.

IR-RAS experiments were performed on a Nicolet 510 Fourier transform infrared spectrometer, utilizing a Harrick retro-mirror reflection accessory and p-polarized radiation at an incident grazing angle of 85° measured from the surface normal. The spectrometer bench was purged with dry nitrogen prior to analysis. 1000 scans were collected and averaged at a resolution of 4 cm^{-1}. A clean, uncoated Ferrotype plate served as a suitable background. Difference spectra were obtained by subtracting the spectra of the untreated LaRC-TPI from the spectra of the plasma-treated sample.

Contact angle analysis was carried out using 4 μL drops of distilled water, using a Rame-Hart 100-00 115 NRL contact angle goniometer. Both the left and right sides of at least three drops were measured and averaged.

Plasma etch rates were studied by monitoring the LaRC-TPI thickness on a Ferrotype plate by ellipsometry as a function of plasma exposure time. Ellipsometric measurements were performed by using a Gaertner L116A dual mode automatic ellipsometer. Measurements were made using a helium-neon laser as a light source at an incident angle of 70°. A value of 1.70 was used for the refractive index of the polyimide film, which is in the range of literature values given for imide-containing polymers.[9] The refractive index and absorption coefficient of the chromium oxide substrate was measured to be 3.6 and -4.1, respectively.

RESULTS AND DISCUSSION

Plasma Overview

The environment and constituents of various plasmas have been investigated by other researchers. Oxygen plasma has been found to contain a complex mixture of atomic ions, molecular ions, ozone, metastable and atomic (radical) species.[10] The important species in an argon plasma are Ar^+ and the relatively long-lived metastable species Ar^*. It has been observed that argon plasma-modified fluoropolymers are strikingly similar to samples bombarded by low-energy Ar ions at low currents. This suggests that the outermost surface reactions are dominated by direct energy transfer from Ar^+ and Ar^* species.[11] The situation in an ammonia plasma has not been well-characterized, but it is postulated that the active species are the radical and ionic forms of N, H, NH and NH_2[12].

Plasmas are also sources of vacuum ultraviolet (VUV) radiation which is extremely energetic and has the capability of inducing photochemical reactions. Because LaRC-TPI contains aromatic ketone (benzophenone) groups, which are known to be excellent chromophores, the possibility of photochemical cleavage at the benzophenone linkages exists.[13]

Although the situation within a plasma may seem exceedingly complex, all of the particle species and the VUV flux are extremely energetic and possess more than sufficient energy to break organic bonds.[14] In particular, the radical species in plasmas are capable of carrying out free radical abstractions and insertions similar to those encountered in "conventional" organic chemistry. The end result on a polymer surface is almost always some type of molecular weight change—crosslinking, scission and/or branching. Reactive sites can also be created which are capable of reacting either with activated gas species or the atmosphere to which they become exposed.

Comparison of the Three Plasmas

Table I summarizes the XPS curve-fitted results for the plasma-treated samples. The curve-fitted C_{1s} photopeaks are shown in Figure 2. As compared with the untreated LaRC-TPI, the oxygen, ammonia and argon plasmas all caused increases in the surface concentration of polar groups. It can be noted from the XPS atomic concentrations and curve-fitted photopeaks that three very different surface chemistries result from the various treatments.

The atomic concentrations of the various species in the untreated LaRC-TPI are in good agreement with the bulk theoretical values of 78.9% C, 15.8% O and 5.3% N. The peaks resolved from the C_{1s} envelope are assigned as follows:

284.6 eV	C—C
286.5	C—N, residual C—O from amic-acid
288.0	C=O, imide and benzophenone
290.5	C—C shake-up satellite

The main O_{1s} photopeak at 531.6 eV is assigned to imide oxygen and the main N_{1s} photopeak at 400.1 eV is assigned to nitrogen in the imide ring. It can be noted from the curve-fitted data that there is a stoichiometric deficiency of carbonyl functionality; this has also been observed in XPS studies of other polyimides.[15]

The increase in surface oxygen concentration is greatest in the case of oxygen plasma, followed by argon plasma. No change in oxygen concentration is observed with ammonia plasma. In contrast, treatment of LaRC-TPI with ammonia plasma produced an increased nitrogen surface concentration; no increases in nitrogen concentration are observed with either the oxygen or argon plasma. In all three cases, only minute changes in the binding energy of the N_{1s} peak are observed; hence, no oxidized nitrogen-containing species are produced by either of the three plasma treatments, evidenced by the absence of high binding energy species in the N_{1s} photopeak.

Figure 3 shows IR-RAS difference spectra, obtained by subtracting the spectra of the non-treated LaRC-TPI surface from the spectra of the treated surface; the resultant spectra reflect changes in the surface created by the plasma treatments. All three plasma treatments show new bands in the regions of the spectrum associated with C=O stretching, C—O or C—N stretching, and O—H or N—H stretching, albeit at different wave-numbers and intensities. Infrared bands and possible assignments are listed in Table II.

All three spectra also exhibit negative bands at 2930 and 2860 cm^{-1}, corresponding to aliphatic C—H stretching. These bands are postulated to result from

TABLE I
Curve-fitted XPS data for plasma-treated LaRC-TPI

		Non-treated		Oxygen		Ammonia		Argon	
Photopeak	Assignment	Binding energy (eV)	Atomic concn. (%)	Binding energy	Atomic concn.	Binding energy	Atomic concn.	Binding energy	Atomic concn.
C_{1s}	—C—C	284.6	61.9	284.6	23.2	284.6	51.7	284.6	47.5
	—C—O			286.0	4.8				
	—C—N	286.5	5.6	286.8	9.2	286.1	9.9	286.4	6.4
	—C=O	288.0	9.4	288.3	15.7	287.8	11.6	288.0	13.0
	O=C—O—			289.2	4.6			289.8	2.3
	shake-up	290.5	3.4	290.4	1.2			291.8	0.9
		Total:	**80.3**		**58.7**		**73.2**		**70.1**
O_{1s}		530.4	0.7			530.1	0.5		
				531.0	2.3				
	O=C—	531.6	11.3	531.8	10.1	531.5	11.4	531.6	14.7
				532.6	11.1	532.7	2.1	532.8	5.9
	—O—C—	533.1	2.1	533.4	8.7			533.8	2.7
				534.3	3.9				
		Total:	**14.1**		**36.1**		**14.0**		**23.3**
N_{1s}						398.6	2.8		
	O=C—N—	400.1	5.6	400.2	5.2	399.7	10.0	400.0	6.6
		Total:	**5.6**		**5.2**		**12.8**		**6.6**

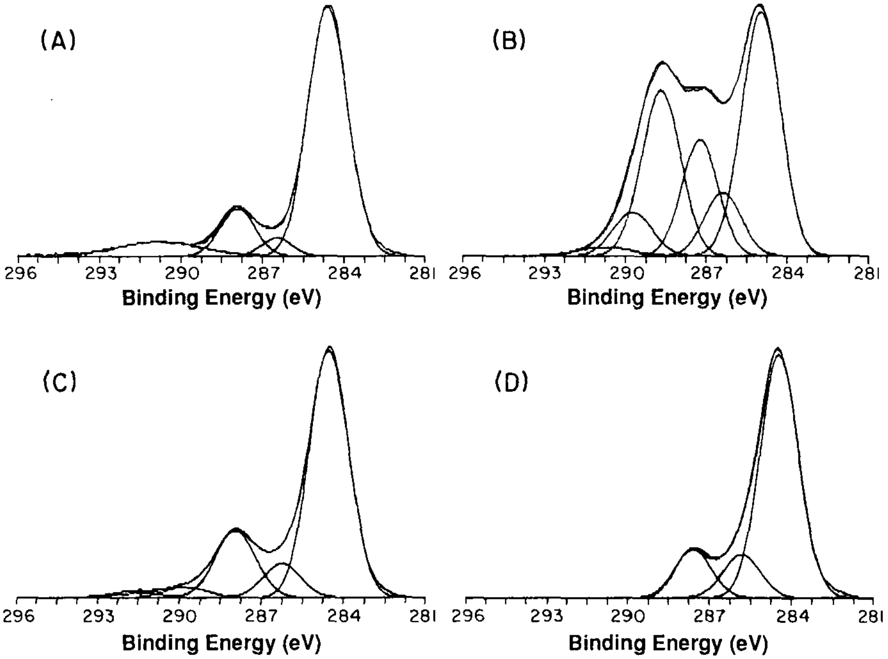

FIGURE 2 Curve-fitted Cls photopeaks (A) Untreated (B) Oxygen plasma (C) Argon plasma (D) Ammonia plasma

carbonaceous contamination picked up during the high-temperature imidization of the LaRC-TPI coatings; subsequent plasma treatment removes this thin layer of contamination, causing the peaks to be seen as negative. Negative peaks are also observed in the spectra of the ammonia plasma-treated surface at 1856 and 1780 cm^{-1}. These peaks are assigned to imide ring vibrations which are observed in the spectra of non-treated LaRC-TPI.[16] The observation of these negative peaks provides strong evidence that imide ring chemistry is altered during exposure to ammonia plasma.

Figure 4 shows the contact angle data for the plasma-treated surfaces, compared with the as-cured and acetone-wiped surfaces. It is easily seen that all three plasmas are capable of improving the water wettability of the polyimide surface. Oxygen plasma, in particular, is highly effective in decreasing the water contact angle. These greatly decreased contact angles are indicative of a higher energy surface, no doubt brought about by the increased surface polarity as characterized by XPS and IR-RAS.

The results of etch rate experiments are shown in Figure 5. Oxygen and argon plasmas etch LaRC-TPI extremely rapidly, whereas ammonia plasma is only mildly ablative in the early stages of etching. This finding suggests that significantly more chain scission is occurring in the cases of oxygen and argon plasmas, which in turn suggests differences in reaction mechanisms.

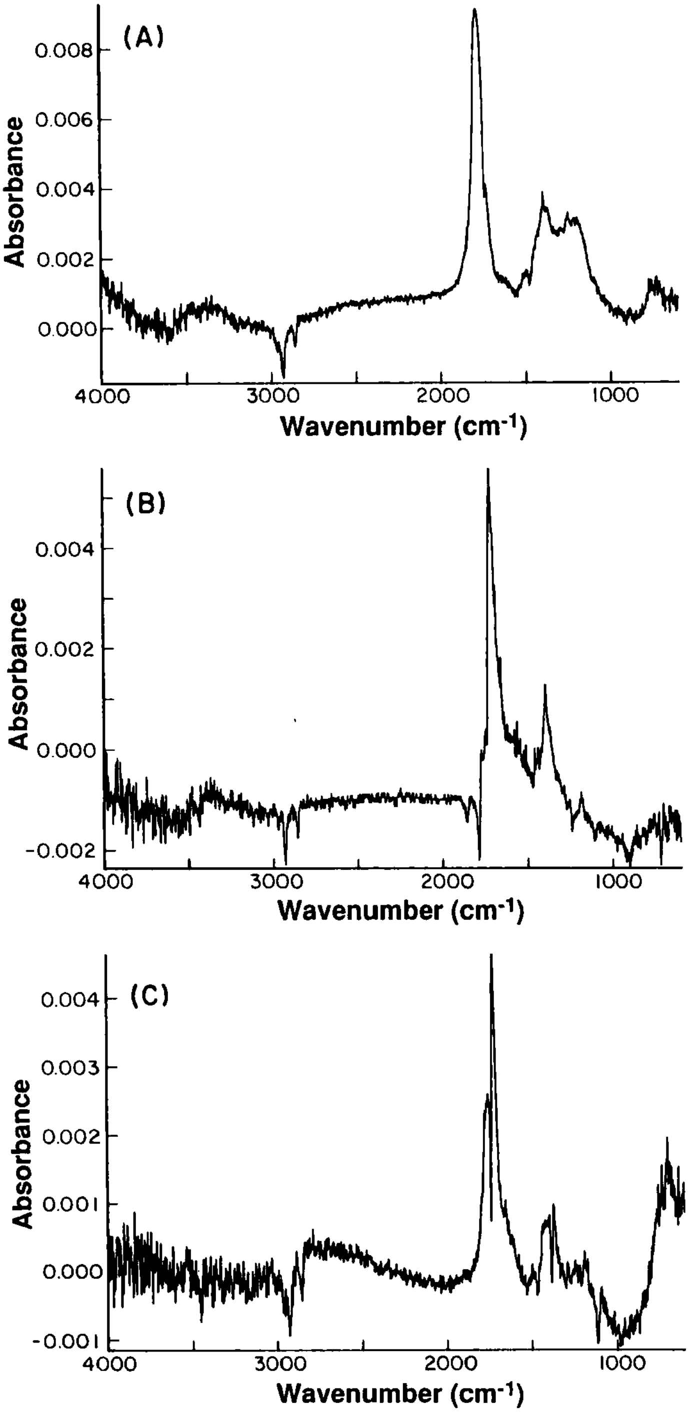

FIGURE 3 IR-RAS difference spectra (A) Oxygen plasma (B) Ammonia plasma (C) Argon plasma

TABLE II
IR-RAS Bands from difference spectrum

Plasma	Frequency (cm^{-1})	Assignment
Oxygen	3332	O—H stretch
	1770	C=O stretch (ester)
	1725 (shoulder)	C=O stretch (acid)
	1390	C—O stretch
	1205	C—O—H bend
Ammonia	3345	N—H stretch
	1716	C=O stretch (amide)
	1390	C—N stretch
	1856 (negative)	C=O stretch (imide)
	1780 (negative)	
Argon	1758	C=O stretch
	1724	C=O stretch
	1406	C—C=O bend (ketone)
	1190	C—O stretch

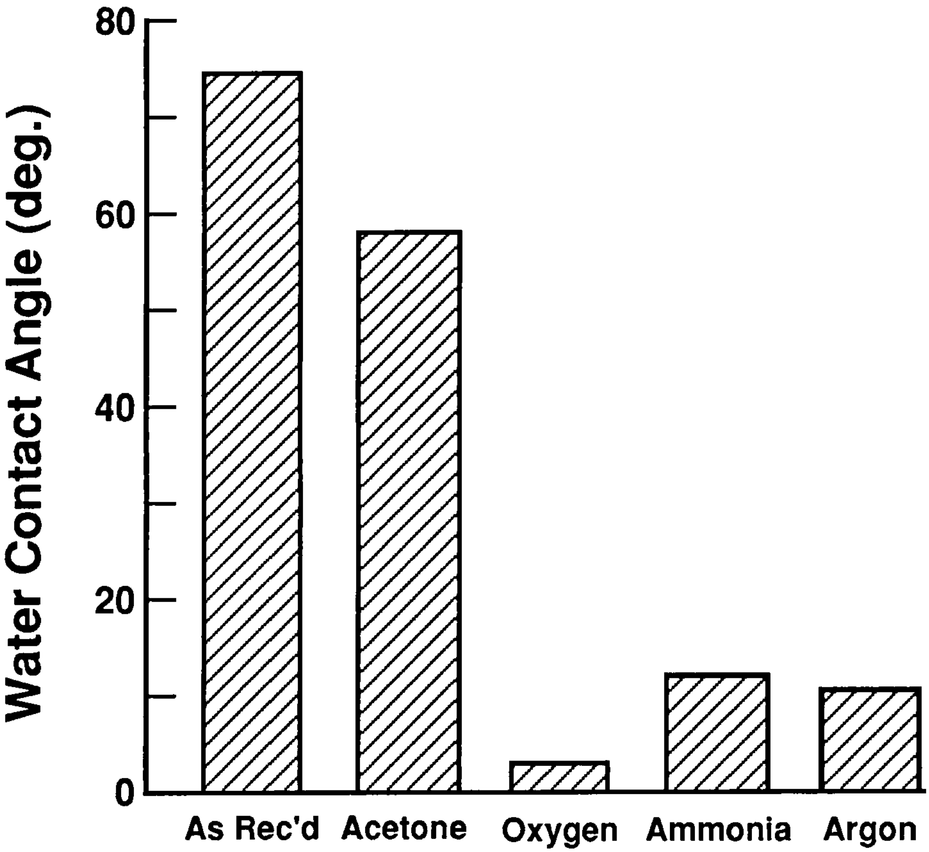

FIGURE 4 Water contact angle analysis of plasma-treated LaRC-TPI, compared to untreated and acetone-cleaned surfaces

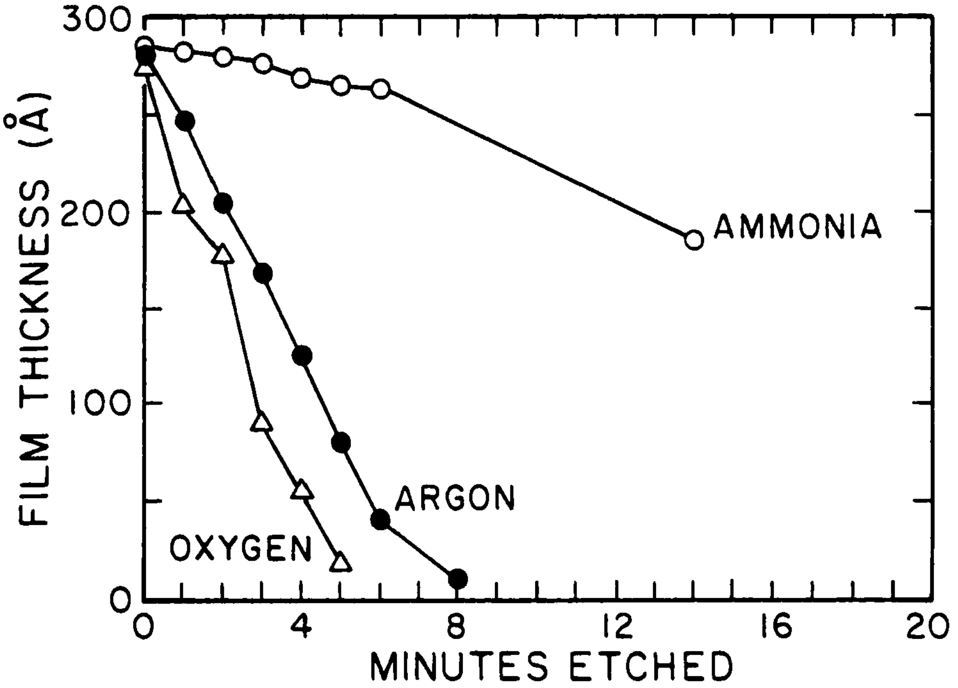

FIGURE 5 Etch rates of LaRC-TPI in oxygen, argon and ammonia plasmas

Oxygen Plasma

The C_{1s} photopeak for oxygen plasma-treated surfaces shows new peaks at 286.0, 286.8 and 289.2 eV; these are tentatively assigned to hydroxyl, carboxylic acid or ester species (See Table I). The origin of these species can be shown to result from the free radical reactions of atomic oxygen, molecular oxygen, hydroxyl radicals and other species, with organic materials.[17,18,19] The fact that a weak shake-up satellite can still be fitted into the C_{1s} envelope shows that aromatic ring structures are still present in the plasma-treated surface.

The peak at 286.5 eV corresponding to C—N linkages in the non-treated sample is seen to disappear, and the binding energy of imide carbonyl is seen to increase from 288.0 to 288.3 eV. Phthalimide XPS standards have also been observed to show a peak at 288.3 eV. The combination of these two observations leads to the conclusion that phthalimide-like structures have been formed from the original imide rings. It has been shown by Walling that succinimidyl radical, similar in structure to phthalimide, is extremely stable due to extensive pi delocalization of the odd electron.[20]

Since imide functionality is not known to be created within the free radical environment of an RF plasma, the increase in the concentration of species at 288.3 eV as compared with the original imide concentration suggests that selective etching/fragmentation of the original LaRC-TPI structure has occurred. In other words, non-imide containing segments of the molecule have been more quickly ablated away, leading to an enrichment of imide-containing fragments at the surface. This apparent chain scission is also consistent with the physical evidence presented in the etch rate studies.

The IR-RAS difference spectrum for the oxygen plasma-treated surface shows an intense band at 1770 cm^{-1}, having a slight shoulder at 1725 cm^{-1} (see Table II). These can be assigned to carboxylic acid or ester functionality, as observed by the XPS curve-fitted data. A weak broad band at 3332 cm^{-1} could be indicative of O—H stretching from carboxylic acids and/or hydroxyl groups. Further evidence for ester or hydroxyl groups is provided by the presence of bands associated with C—O stretching observed at 1390 and 1205 cm^{-1}.

Argon Plasma

Careful observation of the curve-fitted XPS data for argon plasma-treated LaRC-TPI reveals that, overall, there is essentially very little change in the binding energies of the original curve-fitted peaks, except for a few important additions. The C_{1s} photopeak can be fitted with a new component at 289.8 eV and the O_{1s} photopeak contains two new components at 532.8 and 533.8 eV. These are assigned to the formation of an ester species, with the two O_{1s} components corresponding to the doubly and singly-bonded oxygens of the ester, respectively. The presence of a weak shake-up satellite is indicative of aromaticity in the treated surface.

As in the case of oxygen plasma, the atomic concentration of the imide group in the plasma-treated surface has also increased. This is possibly another case of fragmentation/oxidation as observed with oxygen plasma-treated LaRC-TPI. Argon, like oxygen, was also shown to be an ablative plasma in the etch rate experiments.

The IR-RAS spectrum shows new bands at 1758, 1724, 1406 and 1190 cm^{-1}. No resolvable bands are seen in the high-frequency region of the spectrum, thus precluding the presence of carboxylic or hydroxyl functional groups. Bands at 1758 and 1724 cm^{-1} appear to correspond to ester, carbonate or ketone species; bands at 1190 and 1406 cm^{-1} are assigned to C—O stretching and ketone C—C=O bend, respectively.

Because argon is an inert gas, no components of the plasma are capable of reacting with the free radicals which are generated in the surface of the LaRC-TPI. Thus, all active radicals persist until they are exposed to the outside atmosphere, at which time reaction with oxygen, carbon dioxide, moisture and other species can occur. The most likely site for fragmentation to occur in LaRC-TPI would be at the benzophenone linkages, which have the potential to be cleaved by ionizing radiation. The most probable surface structure of argon plasma-treated LaRC-TPI would be one in which imide-containing segments are terminated by ester, carbonate or ketone end groups at benzophenone linkages.

Ammonia Plasma

In contrast with oxygen and argon XPS results, no new species are observed in any photopeak; instead significant shifts in binding energies are observed. Imide carbonyl formerly located at 288.0 eV has decreased in binding energy to 287.8 eV; imide nitrogen at 400.1 eV has shifted to 399.7 eV. The binding energy of the C—N linkage has also shifted to 286.1 eV. Another significant observation is that the shake-up satellite can no longer be fitted in the high binding energy end of the C_{1s} photopeak; this could be indicative of loss of aromaticity as a result of ammonia plasma exposure.

XPS analysis of Kevlar®, an aromatic polyamide, and Nylon 6,6 standards reveal that there are very close matches between these standards and the ammonia plasma-treated LaRC-TPI surface, indicating the possibility of amide formation. The IR-RAS difference spectrum also shows evidence for amide formation. Bands at 1716, 1390 and 3345 cm^{-1} correspond to the Amide I carbonyl, C—N stretching and N—H stretching, respectively. The Amide I band falls into the high end of the amide range; more appropriately, it could be assigned to a lactam or cyclic amide structure. The possibility of nitrogen from the ammonia plasma being incorporated into amine groups as opposed to amide is a possibility, but a less likely one. Not only would the C—N stretch for amines be observed at lower frequencies than 1390 cm^{-1}, but amine formation would also not account for the intense C=O absorption, since the XPS atomic concentration data shows that no additional oxygen was incorporated as a result of plasma treatment.

As previously discussed, the presence of negative bands in the IR-RAS spectrum for ammonia plasma pointed to the possibility of imide ring-opening. Thus, a likely scenario for the ammonia plasma exposure is that NH or NH_2 species attack directly at the carbon of the imide ring, causing ring-opening and subsequent amide formation. These amide groups may also continue to react with imide rings on other LaRC-TPI molecules, leading to surface crosslinking. This is a likely mechanism based on the spectroscopic as well as the physical evidence which revealed that very little etching (and hence chain scission) was occurring as a result of ammonia plasma exposure.

CONCLUSIONS

The results of this study show that dramatic changes occur in the surface of LaRC-TPI upon exposure to oxygen, argon and ammonia plasmas. Increases in surface wettability as well as in the concentration of surface polar groups have been observed. Initial findings suggest that oxygen and argon plasmas cause chain scission, resulting in the formation of imide-containing fragments functionalized by oxygen-containing functional groups. Ammonia plasma is seen to attack LaRC-TPI in a non-ablative manner and convert imides to amides.

These findings were made possible by the coupling of information from two extremely surface sensitive spectroscopic techniques, XPS and IR-RAS analysis of thin films. It should also be possible to apply these complementary techniques to the analysis of surface modification of other polymer systems. The adhesion interactions of the plasma-treated LaRC-TPI surface with other polymeric materials are being investigated and will be reported at a later date.

Acknowledgements

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References

1. E. M. Liston, *J. Adhesion*, **30,** 199 (1989).
2. D. J. D. Moyer and J. P. Wightman, *Surface and Interface Analysis*, **14,** 496 (1989).
3. M. Hudis and L. E. Prescott, *J. Polym Sci.*, **10,** 179 (1972).
4. A. D. Katnani, A. Knoll and M. A. Mycek, *J. Adhe. Sci. Technol.*, **3**(6), 441 (1989).
5. T. A. Giroux and S. L. Cooper, *J. Colloid and Interface Science*, **139,** 351 (1990).
6. C. Jones and E. Samman, *Carbon*, **28**(4), 509 (1990).
7. A. K. St. Clair and T. L. St. Clair, *NASA Technical Memorandum* 84516, June 1982.
8. A. T. Bell and J. R. Hollahan, *Techniques and Applications of Plasma Chemistry* (John Wiley and Sons, New York, 1974).
9. J. Brandrup and E. H. Immergent, Eds., *The Polymer Handbook* (Wiley Interscience, New York, 1989), 3rd edition.
10. A. T. Bell and J. R. Hollahan, *Techniques and Applications of Plasma Chemistry* (John Wiley and Sons, New York, 1974).
11. D. T. Clark and A. Dilks, *J. Polym. Sci., Polym. Chem. Ed.*, **15,** 2321 (1977).
12. J. R. Hollahan and B. B. Stafford, *J. Appl. Polym. Sci.*, **13,** 807 (1969).
13. J. K. Rabek, *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers: Theory and Applications* (John Wiley and Sons, New York, 1987).
14. H. V. Boenig, *Plasma Science and Technology* (Cornell University Press, Ithaca, 1982).
15. H. J. Leary and D. S. Campbell, *Surface and Interface Analysis*, **1**(3), 75 (1979).
16. P. D. Frayer in *Polyimides: Synthesis, Characterization and Applications*, K. L. Mittal, Ed. (Plenum Press, New York, 1984).
17. G. H. Williams, *Homolytic Aromatic Substitution* (Pergamon Press, New York, 1960).
18. E. S. Huyser, *Free Radical Chain Reactions* (Wiley Interscience, New York, 1970).
19. F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry*, 2nd edition (Plenum Press, New York, 1985).
20. J. K. Kochi, Ed., *Free Radicals*, Vol. 2 (John Wiley and Sons, New York, 1973).