after heating the polymer to temperatures of the order of 400 °C suggests that by this temperature larger delocalized fragments that may produce fluorescence have formed. Although there is some double-bond character associated with the B-amine bridge bond,[22,38] the room-temperature polymer should be considered as delocalized only to the extent of the individual borazine rings. Of course, one cannot draw the conclusion that fused borazine rings have been produced only on the basis of the fluorescence evidence, but the existence of the fluorescence as well as the higher temperature resonance-enhanced Raman activity suggests that pyrolysis leads to the development of larger delocalized fragments. The development and growth of such fragments is, of course, a necessary step in the development of h-BN.

The line broadening and peak shifts observed by Nemanich and co-workers[36] for Raman spectra of a variety of crystalline h-BN samples as a function of particle size apparently results from a different range of particle sizes than that obtained in our work. Although they do observe line broadening with decreasing particle size, all spectra display the intralayer Raman band at ≈1365 cm^{-1} characteristic of h-BN. Further, apparently no major changes in intensity were observed comparable to those reported here. Nemanich and co-workers[36] also report luminescence from their samples, but this disappears after several hours of laser irradiation. In contrast, the fluorescence observed in the present Raman spectra, which does not disappear with extended irradiation, appears prior to crystallization and increases in intensity as the polymer is converted to amorphous BN and finally crystalline BN. It is tempting to speculate that the large line broadening and frequency shift that we observe at high temperature (≈1200 °C) may reflect the extremely small particle limit of the trends observed by Nemanich.[36]

One point clear from the present study is that the Raman spectra are very sensitive to changes in the material over the entire temperature range of pyrolysis. X-ray diffraction, for example, does not give information until some crystallinity has been established at temperatures above 900 °C. Thus, Raman spectroscopy promises to be a sensitive probe of the chemical and/or physical changes that occur during pyrolysis, and we have experiments planned to investigate the effect of different starting materials.

Summary

A combination of thermal decomposition mass spectrometry, thermogravimetric analysis, Raman spectroscopy, and X-ray photoelectron spectroscopy has been used to investigate the pyrolysis of polyborazinyl amine polymers with the following conclusions:

Two important temperature regimes exist for the pyrolysis chemistry: below 400 and 400–1200 °C.

With the exception of ≈50% of the initial hydrogen all gaseous products form below 400 °C.

Decomposition products below 400 °C are NH_3, N_2, and HCl. NH_3 and N_2 are from decomposition of the polymer and HCl is from byproducts or from incompletely reacted starting material.

Isotope labeling shows that complete exchange occurs between the ring and bridging amine nitrogens at temperatures below 400 °C.

Conversion of the poly(borazinylamine) polymer to h-BN in the low-temperature regime involves deamination and ring-opening reactions, and in a high-temperature regime, diffusion-controlled N–H dehydrogenation and volume reduction steps. Diffusion is the most likely thermal limiting step.

Raman spectra give evidence for the formation of larger delocalized fragments during pyrolysis of the type necessary for h-BN formation.

Acknowledgment. This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-76p00789, the National Science Foundation (CHE-8503550), and the UNM/NSF Center for Microengineered Ceramics, which is supported by the National Science Foundation (Contract No. COR-8803512), the Los Alamos and Sandia National Laboratories, the New Mexico Research and Development Institute, and the Ceramics Industry.

Characterization of Polyester Films Modified with N_2O/Ar Plasmas

G. M. Porta, J. D. Rancourt, and L. T. Taylor*

Virginia Polytechnic Institute and State University, Department of Chemistry, Blacksburg, Virginia 24061-0212

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Poly(ethylene terephthalate) film that has undergone plasma pretreatment with a mixture of argon and nitrous oxide exhibits the effects of surface cleansing and surface functionalization at low-to-moderate plasma exposure. X-ray photoelectron spectroscopy has detected a new oxygen species resulting from the plasma/polymer interaction. The new oxygen species has been identified as primarily aldehydic, although small amounts of surface carboxylic acid may also be present. Decreasing amounts of ester oxygen and carbonyl carbon have also been detected, which suggests that dissociation of the ester functionality has occurred. With longer plasma exposure, significant amounts of oxygen are lost from the surface with a concomitant increase in surface carbon concentration.

Introduction

The performance of metalized plastic film or articles occasionally suffers due to poor metal-to-polymer adhesion. Over the years researchers have studied and developed numerous procedures to enhance the adhesion between the polymeric substrate and the deposited metal. Two distinct methodologies have been commercially applied to improve metal/polymer adhesion. The first method is to apply a

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thin metallic or polymeric coating that acts as an adhesion promoter between the film and metal. This coating is usually applied as a separate process prior to metallization. Application of a thin layer (50 Å) of nickel between sputtered copper metal and poly(vinyl alcohol), for example, has resulted in enhanced adhesion.[1] The second method used to increase metal-to-polymer adhesion is to chemically modify or clean the surface of the substrate by the application of a gaseous plasma[2] prior to metal deposition. Jackson has used argon plasma treatment to cleanse and thereby improve the adhesion between the laminates[3] of epoxy printed circuit boards.

A limited number of authors have described the effects of plasma processing on poly(ethylene terephthalate) (PET).[2-8] Yasuda et al. exposed PET to both argon and nitrogen plasmas.[5] Following treatment with either plasma, similar types of surface change were induced. In a study by Westerdahl et al., a number of polymeric materials, including PET, were treated with oxygen and helium plasmas.[6] The adhesive bond strength of PET was found to increase at the same rate with either pretreatment. However, the rates of improved adhesion for PET were less than those of the hydrocarbon-based polymers (e.g., LD/HD polyethylene and poly(2-methylpentene)) under the same conditions. For the polar polymers (e.g., PET, Delrin, Nylon), chain degradation was probably more important than surface functionalization, and hence the rate of improvement in bond strength was lower. Dunn et al. have studied the effects of oxygen and argon plasmas on the surface properties of PET by both photoelectron[7] and infrared[8] spectroscopic techniques. Surface IR analysis indicated that oxygen plasma treatment created an additional carbonyl functionality; however, argon plasma treatment resulted in a decrease in intensity of both the C=O and the C–O infrared bands indicative of surface carbonization. XPS analysis, in agreement with these findings, showed a decrease in the surface C–C signal for oxygen plasma treatment and an increase for argon plasma treatment, particularly at high power.

It is the object of this report to document the effects of N_2O/Ar plasma treatment on the surface properties of commercial PET film prior to metalization with titanium metal in order to account for the surface chemistry leading to improved adhesion.

Experimental Section

The poly(ethylene terephthalate) film used as a substrate was Melinex type S obtained from ICI Ltd. Technical grade nitrous oxide (99.0%) and ultrapure carrier grade argon (99.999%) used to sustain an rf plasma were purchased from Air Products, Inc.

An rf plasma was generated by a 0.30-kW automatically controlled and tuned supply. The apparatus was evacuated to 2×10^{-5} Torr followed by introduction of the N_2O/Ar (1/1) pretreatment gas through a variable leak valve to attain a system pressure of $(3–15) \times 10^{-3}$ Torr. Following plasma initiation the PET substrate was exposed to the plasma for up to 1 min.

Surface Fourier transform infrared spectra were recorded on a Nicolet Model 6000 infrared spectrometer with an in-line (Wilks Scientific Corp. Model 9000) attenuated total reflectance infrared cell with a KRS-5 internal reflection element at a nominal 45° angle of incidence. For each sample, a spectral average of 1024 scans was recorded with a resolution of 4 cm^{-1} and an average intensity of approximately 1.5 V/scan (gain = 8). A background spectrum was obtained by recording the spectrum of the empty ATR cell. The Nicolet IR-Decon routine was used to deconvolute infrared peaks of interest.

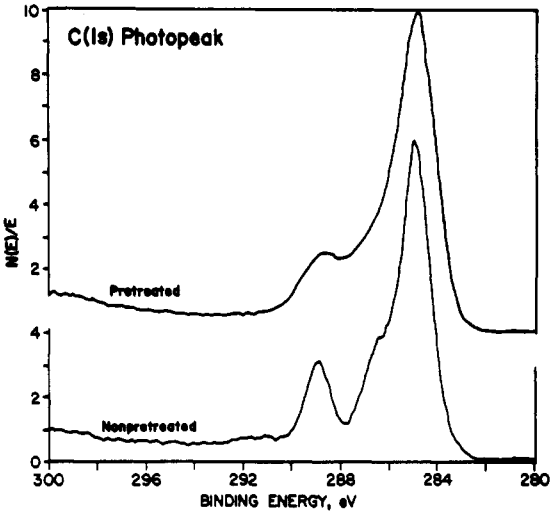

Figure 1. XPS C(1s) spectrum of both plasma-pretreated and nontreated ICI-442 polyester film.

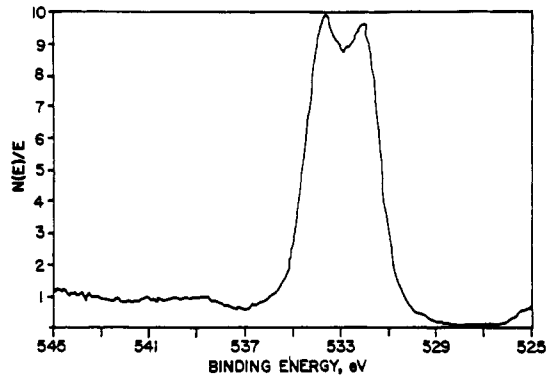

Figure 2. XPS O(1s) spectrum of ICI-442 polyester film.

X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 5300 ESCA system using a magnesium anode ($K\alpha$ = 1253.6 eV) at 250 W (14 keV, 18 mA). Operating pressures were in the range $(0.5–5.0) \times 10^{-7}$ Torr. Samples were attached onto aluminum mounts with double-sided transparent tape. The binding energies were referenced to the aromatic carbon (C(1s)) photopeak maximum at 284.6 eV.

Residual gas mass spectra, before and after glow discharge initiation, were recorded on a Inficon Model IQ-200 residual gas analyzer (RGA). A Faraday cup detector was utilized to detect molecular and atomic ions having masses between 0 and 200 amu.

Results and Discussion

X-ray photoelectron spectroscopy (XPS) was applied to obtain reference spectra of nontreated polyester film taken at normal incidence (90°) and grazing angles (15°). The carbon (C(1s)) photoelectron spectrum exhibited the pattern displayed in Figure 1. This signal may be curve resolved into the three separate carbon environments that would be expected based on the chemical structure of PET and in accord with previous measurements.[9] The calculated carbon ratios for PET are 2:2:6, corresponding to the carbonyl, ester, and aromatic carbons, respectively. Experimental ratios obtained from the area below each peak

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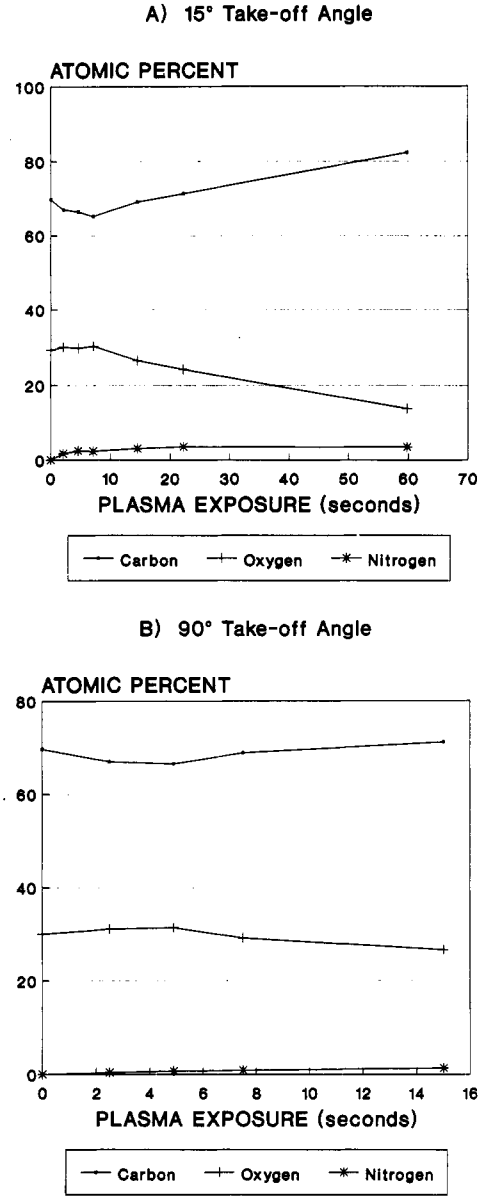

Figure 3. (A) Plot of the change in elemental composition versus plasma exposure for ICI-442 polyester film at a 15° takeoff angle. (B) Plot of the change in elemental composition versus plasma exposure for ICI-442 polyester film at a 90° takeoff angle.

gave a ratio of 2:2:7, which is in good agreement with the calculated ratio. The slight increase in the lowest binding energy peak (284.6 eV) area is probably due to surface carbon contamination, which would appear at this binding energy. The oxygen (O(1s)) photopeak, as expected, exhibits two types of oxygen species (carbonyl and ester, Figure 2). Theoretically, one would expect a 1:1 ratio between these oxygen species. Experiment yields a 1:1 ratio, which shows excellent agreement.

Changes in surface composition relative to the nontreated film were noticeable for all plasma-treated films regardless of the extent of plasma exposure and the XPS takeoff angle. Figure 3 shows the changes in elemental (C, N, O) composition versus plasma exposure for both the 15° and the 90° takeoff angles. Nitrogen may be incorporated through the interaction of plasma-activated N_2O (metastable) or N_2O decomposition products such as nitrogen radicals or ions with the polyester surface. Both Hellund[10]

(10) Hellund, E. J. *The Plasma State*; Reinhold: New York, 1961; pp 65–101.

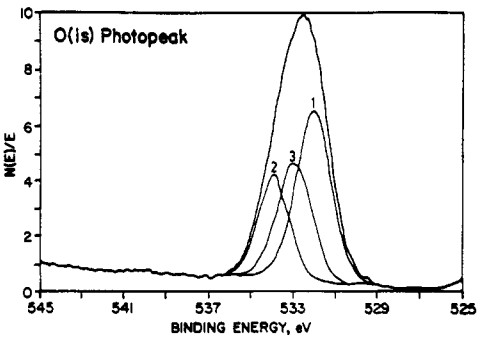

Figure 4. Curve resolved XPS O(1s) spectrum of plasma-pretreated ICI-442 polyester film.

and Swartz[11] have proposed and observed N^+ (cation), N (atomic), N* (metastable), and N_2* (metastable) species among others in plasma environments. Aluminum also appears and is probably a contaminant originating from the inner surface and/or the electrodes of the plasma pretreatment chamber. Significant surface coverage by aluminum occurs at longer exposure (~6 atom % at 60 s). XPS analysis suggested that the aluminum was in the form of Al_2O_3.

The duration of plasma exposure has an effect on the carbon and oxygen surface composition. There are two noticeable trends in the data that are dependent upon the length of exposure. First, with less than 10 s of exposure, comparison to the untreated polyester indicated that while the total carbon concentration decreased slightly upon plasma treatment, the oxygen concentration was constant. Second, at pretreatment exposures exceeding 10 s, there was substantial loss of surface oxygen that intensified with increasing exposure.

Surprisingly, the oxygen (O(1s)) photopeak revealed that at less than 10 s there was a change in functionality due to the application of the plasma treatment. Figure 4 displays a typical curve resolved oxygen (O(1s)) photopeak for a plasma treated polyester film. The photopeak binding energies and full width at half-maximum (fwhm) obtained from the functional groups of the nontreated film were used as a reference. Upon close inspection, one notices that there are actually three types of oxygen present on the surface. Oxygens 1 and 2 corresponded to the carbonyl and ester oxygens, respectively. Oxygen 3, which exhibited an intermediate binding energy (~532.4 eV), was a new functionality induced by the plasma pretreatment. Typically, aldehydes or ketones appear at this binding energy; however, XPS is not able to resolve these functional groups by analysis of the oxygen (O(1s)) signal alone.

Since the total surface oxygen concentration is relatively constant during the 10-s exposure, the new oxygen species produced must arise at the cost of another species rather than through incorporation of additional oxygen from the plasma or through atmospheric exposure. Figure 5 displays the changes in oxygen functionality with plasma exposure. The carbonyl oxygen concentration remained steady for the films produced at short and moderate exposures, yet a significant decrease in the ester oxygen followed by an increase in the new species concentration is noted with increasing plasma exposure. At high exposure, surface carbonyl oxygen is lost along with additional amounts of ester oxygen. It is therefore, probable that some energetic species ($h\nu$, electrons, ions, metastables) produced in the plasma pretreatment process impart sufficient energy to the ester functionality to cause its dissociation. The new

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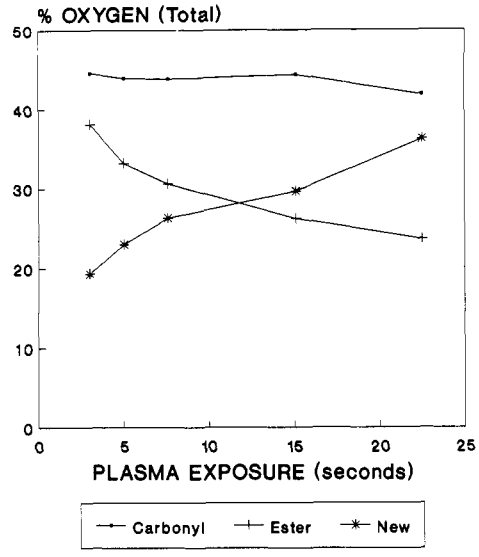
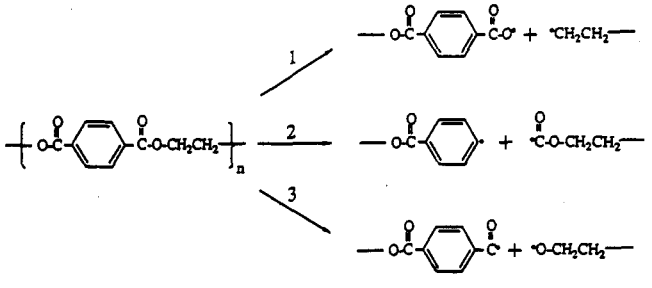


Figure 5. Plot of the change in concentration of oxygen species versus plasma exposure for ICI-442 polyester film at a 15° takeoff angle.

Scheme I. Commonly Reported Thermal and Photolytic Decomposition Mechanisms of Poly(ethylene terephthalate)



oxygen functionality most likely results from the relaxation of radical species. This is considered very probable since the samples were analyzed more than 24 h after production. Curve resolution of the carbon (C(1s)) photopeak of a plasma-treated film was attempted, but the numerous combinations of possible fits due to both oxygen–carbon and nitrogen–carbon functionalities precluded unambiguous results. However, one does notice a decrease in carbonyl carbon (288.8 eV) and an increase in the intermediate carbon binding energies (indicative of aldehyde and ketone) following plasma treatment (Figure 1).

Insight into probable functional changes in the PET backbone may be gained by studying both thermal and photochemical decomposition routes, each of which have been shown to center around dissociation of the ester functionality. It is generally agreed that thermal dissociation of the ester functionality occurs between the ester oxygen and the primary methylene group in the backbone.[12] The major products of thermooxidative degradation, therefore, are carboxylic acids and vinyl groups. Photolysis of PET, on the other hand, is more complex than thermal degradation and the possible mechanisms are more contested. Typically two photolytic decomposition routes are reported. Scheme I provides a compendium of the more probable mechanisms. On energetic grounds, reactions 1 and 3 (84 and 88 kcal/mol) seem more probable than reaction 2, with an estimated bond dissociation energy of 102 kcal/mol. Reactions 1 and 3 are normally termed Norrish type II and type I decompositions, respectively.[13] The major products of photolytic decomposition would therefore be carboxylic acid and vinyl groups for reaction 1 (Norrish type II) and aldehydes for reaction 3 (Norrish type I).

In our work we believe either a carboxylic acid or aldehyde functional group is responsible for the appearance of the new oxygen functionality. Among these two choices, the aldehyde functionality agrees more closely with the observed changes in binding energy than the presence of a carboxylic acid. Furthermore, a carboxylic acid C(1s) photopeak would most likely appear in the vicinity of the ester carbonyl carbon and, therefore, would not result in loss of signal intensity in this region.

To further define the nature of the new surface species as well as to support one of the dissociative mechanisms described in the previous section, attenuated total reflectance Fourier transform infrared spectrometry (ATR-IR) was used to study the effects of plasma pretreatment on the polyester film. Day and Wiles[14] and Blais et al.[15] have used ATR-IR with success to study the effects on PET of ultraviolet radiation.

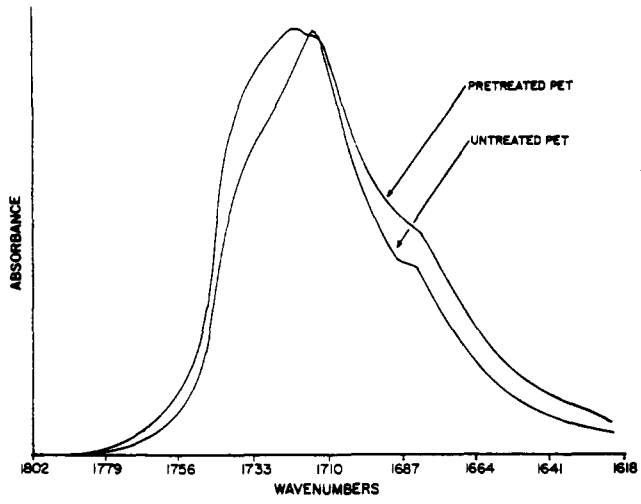


Figure 6. Carbonyl region of both plasma-pretreated and nontreated ICI-442 polyester film obtained by ATR-IR.

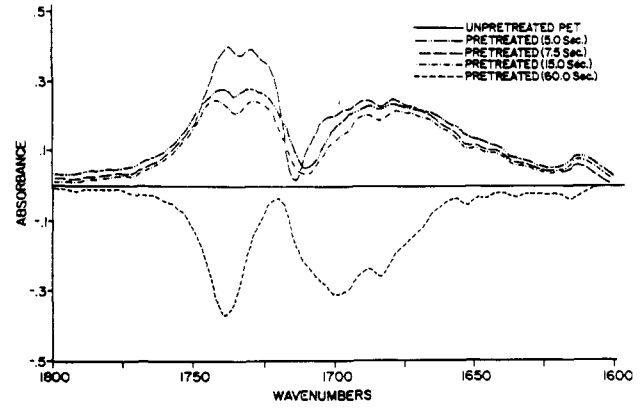


Figure 7. Effect of plasma exposure on the carbonyl region of ICI-442 polyester film obtained by ATR-IR. The difference spectra are shown (plasma-treated spectrum – nontreated spectrum).

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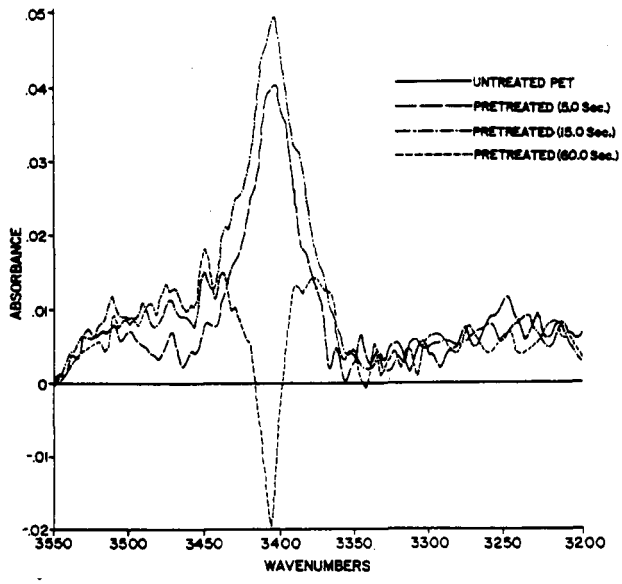

Figure 8. Effect of plasma exposure on the –OH stretching region of ICI-442 polyester film obtained by ATR-IR. The difference spectra are shown (plasma-treated spectrum – nontreated spectrum).

Study of the carbonyl region (1650–1800 cm^{-1}) indicated significant changes in carbonyl peak shape following plasma pretreatment at low-to-moderate exposure (Figure 6). Growth of IR bands in this region suggested the formation of new carbonyl species. However, at high plasma exposure reduction in carbonyl band intensity was observed, indicating loss of this functionality. It had been shown by XPS that plasma exposure had significantly affected surface composition. With short exposure, surface functionalization was evident. Long exposure revealed that extensive surface deoxygenation had occurred. Thus changes in carbonyl functionality determined by FT-IR follow the behavior previously observed by XPS. Figure 7 displays ATR-IR difference spectra of the carbonyl region of PET films, which vary widely in plasma exposure. Initially, there was an increase in band intensity at 1720–1745 and 1705–1670 cm^{-1}. The observed increases reached a maximum at a plasma exposure of approximately 7.5 s. Figure 8 displays difference spectra for the IR region between 3200 and 3550 cm^{-1} for the same PET samples. Besides the first overtone of the carbonyl region (3440 cm^{-1}), which changes in the expected manner with exposure, no other IR absorption is present in this region, suggesting that carboxylic acid formation is very minor if occurring at all during plasma pretreatment. It appears then that surface aldehydes account for the primary growth of carbonyl species in the pretreated films. In accord with the changes observed by XPS, plasma exposure beyond 10 s resulted in loss of carbonyl structure.

Dissociation of the ester functionality in PET through any of the possible mechanisms would also result in reduced C–O–C IR band intensity.[16,17] Figure 9 displays the C–O–C IR stretching region (1200–1300 cm^{-1}) for both plasma-pretreated and nontreated ICI-442 polyester film. Indeed, in all cases, pretreatment leads to a reduction in the C–O–C stretching mode intensities at approximately 1275 and 1250 cm^{-1}. Systematic changes in C–O band intensity are also produced by varying the pretreatment time. The intensity of the bands at both 1275 and 1250

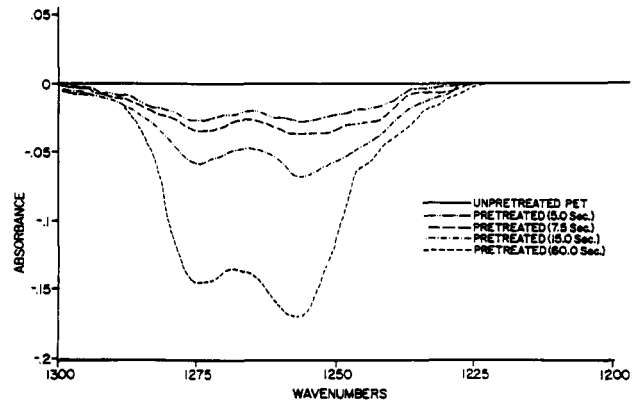

Figure 9. Effect of plasma exposure on the C–O region of ICI-442 polyester film obtained by ATR-IR. The difference spectra are shown (plasma treated spectrum – nontreated spectrum).

Table I. RGA Mass Spectral Data of the Glow Discharge[a]

	rel abundance	
m/z	before initiation	after initiation
18	6.4	5.8
20	20.9	19.8
28	0.9	6.6
40	100.0	100.0
44	0.0	0.2

[a] Pet film exposed to plasma for 60 s (average); 100% argon used as pretreatment gas.

cm^{-1} decrease at the same rate as more energy is input into the PET surface.

As noted previously, with long plasma exposure, a prevalent effect of the pretreatment process may be chain scission followed by loss of carbon monoxide. RGA was used to monitor the gas composition before and after plasma initiation. A comparison of the abundance of CO relative to argon should indicate whether loss of CO subsequent to chain cleavage is a viable decomposition route. Table I compares RGA data obtained in the pretreatment chamber before and after glow discharge initiation employing 100% argon and 60-s exposure. The mass spectrum is simple, allowing one to normalize all peaks to the singly ionized argon state at m/z 40. The use of N_2O rather than Ar resulted in more complex mass spectra arising from the decomposition of N_2O following plasma initiation. The mass spectra yielded both singly (m/z 40) and doubly (m/z 20) ionized argon before plasma initiation in the anticipated 5:1 ratio.[18] There is also a rather large amount of water (m/z 18) and a small amount of carbon monoxide or possibly N_2 (m/z 28) detected. The water is most likely a result of the film off-gassing because there is no change in the relative abundance of H_2O before versus after plasma initiation. Increases in both CO and CO_2 concentrations were observed in the RGA mass spectrum following plasma induction. CO generation alone, we feel, accounts for the growth of the peak at m/z 28, since there is no possible source of increased N_2 concentration in the plasma treatment chamber. The increase in carbon monoxide abundance can occur only through chain decomposition following a Norrish type I mechanism. Indeed, significant amounts of CO have resulted from the photolytic degradation of PET.[19-21] For example, both

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mass spectrometric and gas chromatographic analyses have indicated that CO and CO_2 account for over 95% of the total volatiles. CO production, in most cases, was reported to be 2–4 times as great as CO_2 production and was dependent upon the duration of UV exposure. Thermal decomposition on the other hand yielded CO_2 as the major volatile product. The minor amount of carbon dioxide detected following plasma initiation here also supports the Norrish type I decomposition pathway.

Two mechanisms, dependent on the degree of treatment severity, are therefore most probable. Initially, at low energy input a relaxation process that forms a new carbonyl structure (Norrish type I ester cleavage) is favored. If the energy is higher, then loss of carbon monoxide is favored. The adhesive strength of metalized PET follows this trend in behavior. That is, at low plasma exposure the production of active surface species may provide reaction sites between the polymer and the metal that allows increased adhesion. High plasma exposure leads to substantial chain scission and loss of CO before metalization. A weak boundary layer, consisting of low molecular weight polymer, may be formed by this degradation and thereby decrease adhesion. The small amount of CO_2 detected suggests that chain scission between the ester oxygen and the primary methylene group is minor (Norrish type II). Further details regarding the adhesion mechanism of titanium to these plasma-treated PET films will be reported in a subsequent paper.

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Registry No. PET, 25038-59-9; N_2O, 10024-97-2; Ar, 7440-37-1.

Molecular- and Atomic-Beam Scattering from Surfaces. Dynamics of Gas–Surface Interactions and Mechanisms of Condensation of Cesium Iodide Molecules and Cesium Atoms Incident on NaCl(c,100)

T. Brown, M. Kliewer, K. Pranata, E. Heyman, and R. Schoonmaker*

Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

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Mechanisms of condensation are given for molecular beams of CsI(g) and Cs(g) that are incident on clean and beam-deposited NaCl(c,100) surfaces, and dynamics of gas–surface interactions for these systems are discussed. Reflection coefficients and angular distributions of scattered molecules have been determined at several angles from normal to near glancing incidence of the molecular beams and as a function of equivalent monolayer coverage of the surface by molecules deposited from the molecular beam. Intensities of molecules scattered at the specular angle have been measured as a function of equivalent monolayer coverage of the surface.

Introduction

Most chemical and physical processes occur at interfaces. For example, interactions of gas molecules with a surface play a crucial role in processes as diverse as heterogeneous catalysis, corrosion, lift and drag on vehicles in flight, atmospheric precipitation and fabrication of integrated circuits. In materials science, development of new processing strategies to support high technology requires knowledge about microscopic mechanisms of growth and removal of atoms or molecules from surfaces of metals, semiconductors, insulators, polymers, ceramics, and composites.[1] In recent years a great deal of effort, both theoretical and experimental, has been expended and corresponding progress made in understanding processes which occur at the gas–metal and gas–semiconductor interfaces; but there has been much less activity associated with investigation of the gas–insulator interface, which has been the subject of continuing study in this laboratory. The present work continues our series of investigations[2-5] of gas–surface interactions and condensation of gaseous alkali metal halide molecules on alkali metal halide crystal surfaces and extends it to include interaction of alkali metal atoms with alkali metal halide surfaces.

Condensation of a gas on a solid surface may be characterized by complex combinations of kinetic processes that always involve a collision at the surface that may be accompanied or followed by thermal and momentum accommodation, adsorption, surface diffusion, nucleation, reevaporation, etc. The condensation coefficient, α_C, is defined as the fraction of gas molecules striking a surface that condenses. The reflection coefficient, $\alpha_R = (1 - \alpha_C)$, is the fraction of incident molecules that is restituted to the gas phase after collision with the surface. There is a close connection between the dynamics of the gas–surface collision and the condensation (or reflection) coefficient and between α_C (or α_R) and the mechanism of condensation. At the present time it is not possible by either classical or quantum methods to make a reliable a priori calculation of the coefficient for condensation of any gas on any surface or to predict from theory the detailed mechanism and rate-controlling steps in the condensation of molecules on surfaces. In the absence of an exact, detailed and computationally tractable method for treating the dynamics of gas–surface collisions and the mechanism of condensation, our experimental program has been established to measure coefficients for condensation of gas

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