

Investigation of Plasma-Induced Photochemical Reaction on a Polypropylene Surface

N. V. Bhat,^{*,†} D. J. Upadhyay,[†] R. R. Deshmukh,[‡] and S. K. Gupta[§]

Bombay Textile Research Association (BTRA), LBS Marg, Ghatkopar, Mumbai-400 086, India, Physics Division, University Department of Chemical Technology, Matunga, Mumbai-400 019, India, and Thin Film Division, BARC, Trombay, Mumbai, India

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The surface of a polypropylene (PP) film was modified using acetone and acetone/oxygen. Significant improvement in surface energy was observed due to plasma treatment. The chemical nature and stability of the surface modification was studied by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The relative change in intensity was calculated for C–H stretch vibrations of a modified PP film to understand the reactive site for surface modification. Studies were carried out to mask the reactive site of PP by pretreatment in nitrogen plasma followed by treatment in acetone/oxygen. The peel strength and effect of aging were studied on acetone and acetone/oxygen plasma modified films.

Introduction

Good bonding strength and printability are essential qualities required for packaging material. Polyolefins have a significant role in packaging industries; however, problems with adhesive and decorative properties persist. One such commercially important polymer is polypropylene (PP) having good chemical resistance and permeability in its oriented form, but it lacks bonding strength and printing strength.¹ Therefore, modifying the surface property of a PP film is essential from a packaging point of view. The bonding strength and printability of such a film can be improved by various techniques such as laminating, chemical etching, treating with glow discharge/corona discharge,^{2–4} etc.

It is the general observation that plasma modification in various gases improves the adhesion of a polymeric substrate.^{5–19} Gaseous plasma not only etches the surface, making it rough, but also incorporates hydrophilic functionalities such as –OH, –CO, –NH₂, –NO₂, etc.^{17–19} depending upon the gas used. This modified surface shows good wettability and bondability due to surface roughening and hydrophilic modification.^{20,21} However, modification of the substrate, with gases such as air, nitrogen, oxygen, ammonia, etc., fails miserably when it is required to retain properties over a long period of time. The reason for such an observation is because of the orientation of interacting hydrophilic groups with storage time.²²

Earlier, Suhr et al.²³ reported decarbonylation of fluorenone. When fluorenone is subjected to a discharge, the decarbonylation product biphenylene is obtained in a yield of 99%. A similar study was carried out by Field et al.^{24,25} showing fragmentation of phthalic anhydride to eliminate CO and CO₂ with formation of dehydrobenzene, which can easily polymerize in glow discharge to give 60% biphenylene, 20% triphenylene, and 10% polymer. All these earlier works showed that plasma could initiate decarbonylation reaction (known as a Norrish type I photochemical reaction²⁶) of a molecule containing the carbonyl

group. However, little has been done to characterize the deposited material. These reactions carried out on the polymeric surface can increase the surface energy of a hydrophobic substrate, and at the same time improve the bonding strength and printing strength.

In the present investigation efforts were taken to carry out the decarbonylation reaction of a simple ketone such as acetone. Also this photochemical reaction was carried further with the help of oxygen acting as an initiator on the PP surface. The modified film was characterized by surface energy measurement, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM).

Experimental Section

A PP film of commercial variety was obtained from Reliance Industries Ltd., India. The thickness of the film was 85 μm , and the film was of isotactic variety. Films were washed in an ultrasonic bath with acetone for 9 min and then dried in air. All chemicals used were of AR grade purchased from S. D. Fine Chemicals, India. Oxygen and nitrogen used for the experiments were of commercial variety (purity 96%). The plasma processing chamber used for surface modification was inductively coupled to a 13.56 MHz radio frequency power generator. The detailed design of the plasma chamber is described elsewhere.²⁷ For surface modification, the PP films were placed on the top of the electrode in the reactor. Before plasma treatment, the chamber was purged four times with gas or organic vapor and evacuated to a pressure of 5.06 Pa. The working pressure was adjusted to 10.13 Pa, when the flow of the gas or organic vapor was 10 sccm. For simultaneous acetone/oxygen plasma treatment the working pressure was adjusted to 10.13 Pa with a 5 sccm flow rate for acetone and oxygen. The treatment time of the sample was varied from 1 to 15 min.

The surface energy was measured by measuring the angle of contact using the sessile drop method. The liquids used for calculating surface energy are water, glycerol, and formamide of known γ^p (polar coordinate) and γ^d (disperse coordinate). The surface energy of the solid has two components, namely, a polar component (γ_s^p) and a disperse component (γ_s^d). Both

* To whom correspondence should be addressed. E-mail: bhatnarendra@hotmail.com.

[†] BTRA.

[‡] University Department of Chemical Technology.

[§] BARC.

components contribute to the total surface energy. The polar component is important to understand the hydrophilic surface modification, whereas the disperse component indicates the changes in hydrophobic modification or formation of a cross-linked network.

$$\gamma_s = \gamma_s^p + \gamma_s^d \text{ (mJ/m}^2\text{)}$$

A small drop of doubly distilled liquid was placed on the polymeric surface with a microsyringe and observed through a microscope. The height (h) and radius (r) of the spherical segment were measured, and the angle was calculated by the following equation:²⁸

$$\text{contact angle } (\theta) = \sin^{-1} \left[\frac{2hr}{r^2 + h^2} \right]$$

At least 10 readings were taken at different places, and an average value of θ was determined. The surface energy of the polymeric film was calculated using Fowkes approximation²⁹ using the equation

$$\left[\frac{1 + \cos \theta}{2} \right] \left[\frac{\gamma_l}{(\gamma_l^d)^{1/2}} \right] = (\gamma_s^p)^{1/2} \left(\frac{\gamma_l^p}{\gamma_l^d} \right)^{1/2} + (\gamma_s^d)^{1/2}$$

From the values of the slope and intercept of a plot of the left-hand side vs the right-hand side, the total surface energy of the treated film was determined. The error in the measurement of the angle is $\pm 0.5^\circ$. Additional errors can also arise because of evaporation of the liquid, dust particles, etc. On the basis of these considerations, the cumulative error in the surface energy works out to be $\pm 1.8 \text{ mJ/m}^2$.

The ATR-FTIR spectra of the film were obtained by using a Perkin-Elmer Paragon 500 FTIR spectrometer. A KRS-5 crystal with an angle of incidence of 45° with a penetration depth of $5\text{--}20 \mu\text{m}$ was used for recording the ATR spectra. To minimize possible shift of the IR band and also to obtain the relative change in absorbance with respect to the control, for every plasma treatment, an ATR spectrum of the control film was taken and also care was taken to align the film in the same direction as used for the control. ATR spectra were recorded immediately after plasma treatment. For every ATR spectrum 350 scans were taken with a resolution of 4 cm^{-1} .

XPS spectra were recorded on a Perkin-Elmer-Physical Electronics 5600 spectrometer with Mg K α excitation (10 KV, 100 W) at a takeoff angle of 30° from the substrate normal (which corresponds to a sampling depth of $\sim 2 \text{ nm}$ in the polymer³⁰). A computer was used for component peak analysis based on a Marquardt minimization algorithm which assumed Gaussian peak shapes with a fixed relative full width at half-maximum.³¹ All binding energies are referred to the hydrocarbon component, 285.0 eV.³² Atomic concentration data were determined using sensitivity factors obtained from samples of known composition: C1s, 0.314; O1s, 0.733; N1s, 0.499.

The adhesion test was performed using an Instron tensile tester 1026. The standard T-peel test (ASTM-D 1976) was used with an adhesive tape. An area of $2.5 \times 4.5 \text{ cm}^2$ was used for the test. For every treatment, three specimens were prepared for the peel strength measurement and the mean value was taken.

The morphological studies were carried out using a Philips scanning electron microscope (model XL-30) at the Central Institute for Research in Cotton Technology (CIRCOT), Matunga, Mumbai, India. The samples were first mounted onto a stub using doubly coated adhesive tapes and coated with a thin

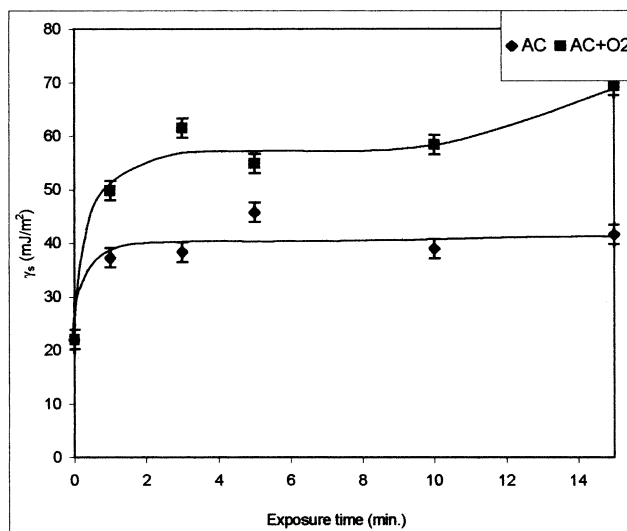


Figure 1. Surface energies of AC and AC/O₂ plasma modified PP films.

TABLE 1: Polar and Disperse Fractions of AC and AC/O₂ Plasma Modified PP Films

exposure time (min)	AC		AC/O ₂	
	polar fraction (γ_s^p)	disperse fraction (γ_s^d)	polar fraction (γ_s^p)	disperse fraction (γ_s^d)
0	0.19	0.81	0.19	0.81
1	0.77	0.23	0.76	0.24
3	0.63	0.37	0.86	0.24
5	0.51	0.49	0.77	0.23
10	0.38	0.62	0.87	0.13
15	0.34	0.66	0.91	0.09

layer (approximately 200 \AA) of gold. Coating of the samples was performed using a Polaron Equipment Ltd. SEM coating unit (model E5100). Additionally, a copper adhesive tape was stuck from the end of the sample to the stub to provide a conducting path. Several magnifications were viewed from different sample areas and overall morphological features recorded.

Results

Surface Energy Measurement. PP films were modified in acetone (AC) and acetone with oxygen (AC/O₂) plasma. The extent of hydrophilic modification achieved by AC and AC/O₂ plasma on the PP film was investigated by surface energy measurements. It can be seen from Figure 1 that the surface energy of AC plasma increased to an equilibrium value of 40 mJ/m^2 , and that of the AC/O₂ plasma modified film showed a rapid increase to achieve an equilibrium value of about 55 mJ/m^2 with a rising trend for longer time.

The chemical nature of the modified surface was investigated by splitting the total surface energy into its polar (γ_s^p) and disperse (γ_s^d) components. Table 1 shows the polar and disperse fractions for AC and AC/O₂ plasma modification. It can be seen that the value of γ_s^p is 0.77 for 1 min in AC plasma; thereafter, it decreases to 0.34 for 15 min. As modification continues the surface becomes less and less hydrophilic. In the case of AC/O₂ plasma the γ_s^p fraction increases steadily from 0.19 for the control to 0.76 for 1 min and then to 0.91 for 15 min. Overall, it seems that the PP surface becomes steadily more and more hydrophilic. This is in contrast to modification observed only with AC plasma.

ATR-FTIR Analysis. To understand the type of hydrophilic modifications achieved by AC and AC/O₂ plasma, and the

differences therein, the modified film was subjected to ATR-FTIR analysis. The possible position of attachment of a hydrophilic group on the polymer surface was predicted using the change in relative intensity of the C–H stretching vibration. The intensity of the spectroscopic band is directly proportional to the concentration of the corresponding species; hence, a decrease in relative intensity reflects the loss/conversion of that species. Due to plasma modification the following changes in the intensity of C–H stretch bands could be expected:

(1) chemical interaction of the reactive plasma with the PP surface, leading to a decrease in the intensity of the C–H stretch band;

(2) broadening, shifting, and an increase in the C–H stretch vibration due to formation of a new organic deposit;

(3) weakening and a decrease in the intensity of C–H stretch bands due to masking of the original C–H stretch of the PP surface;

(4) multiple scattering of the IR beam if the surface is nonuniform, leading to diminishing intensity at the far end.

Cumulative results of these possible consequences are reflected in the decrease in the overall relative intensity of the C–H stretch vibration. Changes in the relative intensity are mainly attributed to surface hydrophilic modification for shorter duration (i.e., reason 1). However, when a film is exposed for longer duration, simultaneous sputtering and deposition take place (i.e., reasons 2–4). Therefore, calculation of the relative intensity of the C–H stretch band could possibly reflect the site of chemical interaction on the PP surface for shorter exposure time. Therefore, the relative intensity was calculated for the PP film modified for shorter duration. The experiment was repeated three times to check the reproducibility of the method and was found to be sensitive enough to project the surface chemical changes.

The following IR C–H stretching vibrations^{33–35} of polypropylene were analyzed to understand the surface chemical reactions:

2950 cm^{-1} corresponding to ν_{as} of the $-\text{CH}_3$ (primary) group,

2917 cm^{-1} corresponding to ν_{anti} of the $-\text{CH}_2$ (secondary) group,

2906 cm^{-1} corresponding to ν of the $-\text{CH}$ (tertiary) group, which appears as a shoulder peak,

2875 and 2868 cm^{-1} corresponding to ν_{s} of the $-\text{CH}_3$ (primary) group, and

2837 cm^{-1} corresponding to ν_{s} of the $-\text{CH}_2$ (secondary) group.

The C–H bending vibration of the $-\text{CH}_3$ group corresponding to 1376 cm^{-1} was chosen as a standard for calculating the relative intensities. It is known that substitution of the electro-negative group affects the C–H stretching vibration,³⁶ and as a result the intensity of the band is expected to decrease due to modification in plasma. To understand the site of attachment of hydrophilic groups on PP, relative intensity changes of only symmetric bands were considered, since symmetric bands were more sensitive to chemical change than asymmetric or anti-symmetric bands. Figure 2 shows the ATR-FTIR spectra of the modified film.

In the case of an AC plasma modified PP film, broadening in the region of 3600–3700 cm^{-1} was observed due to formation of carboxylic acid.^{36,37} Absorption near 1716–1636 cm^{-1} was observed due to saturated ketone (dialkyl type).^{36,37} Weak absorption near 1557–1507 cm^{-1} was observed and may be due to C–H deformation of $-\text{CH}_2-\text{CO}-$. The changes in relative intensities of the IR absorption bands for AC and AC/O₂ plasma modified films are shown in Table 2. It may be seen

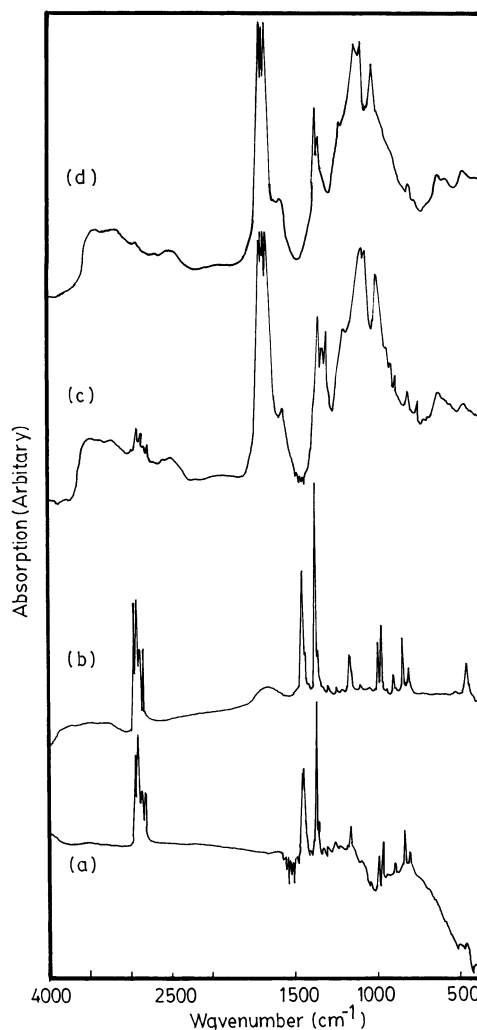


Figure 2. ATR-FTIR spectra of (A) untreated PP, (B) AC-treated PP, and (C) AC/O₂-treated PP and (D) difference spectra of the AC/O₂ deposit with respect to the control.

TABLE 2: Relative Intensities of IR Bands of AC and AC/O₂ Plasma Modified PP Films

band (cm^{-1})	untreated PP film	AC plasma modified PP film	AC/O ₂ plasma modified PP film
2950, ν_{as} of $-\text{CH}_3$ (primary)	0.66	0.32	0.66
2917, ν_{anti} of $-\text{CH}_2$ (secondary)	0.75	0.37	0.65
2906, ν_{s} of $-\text{CH}$ (tertiary)	0.55	0.20	0.55
2875, ν_{s} of $-\text{CH}_3$ (primary)	0.44	0.10	0.52
2868, ν_{s} of $-\text{CH}_3$ (primary)	0.44	0.18	0.51
2837, ν_{s} of $-\text{CH}_2$ (secondary)	0.46	0.14	0.54

that for the C–H stretching vibration of a PP film modified in AC plasma, the relative intensity for the primary carbon atom showed the lowest value, i.e., the band corresponding to 2875 cm^{-1} for ν_{s} of $-\text{CH}_3$. Similarly, the band corresponding to 2837 cm^{-1} for ν_{s} of $-\text{CH}_2$ (secondary) also showed a decrease in the relative intensity value. However, the relative intensity changes of IR bands for an AC/O₂ plasma modified surface show different trends; i.e., there is increase in intensities. The C–H stretching band showed an increase in relative intensity of absorption bands at 2875 and 2868 cm^{-1} corresponding to ν_{s} of $-\text{CH}_3$. An increase in the relative intensity of C–H stretch bands corresponding to primary and secondary carbon atoms was also observed. The visual observation of a modified film showed formation of a white deposit on the surface which makes

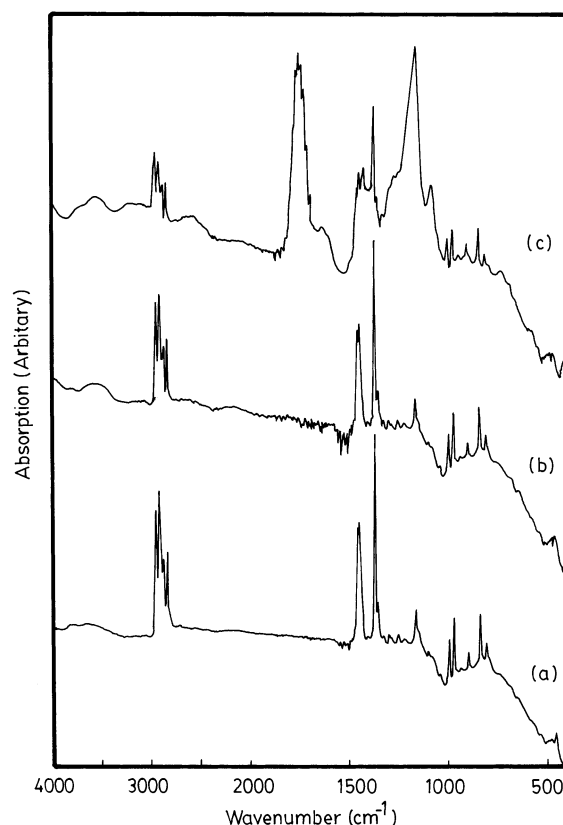
TABLE 3: New IR Bands Observed on the PP Film after AC/O₂ Plasma Modification

band (cm ⁻¹)	type
3500	bonded -OH intermolecular dimer, free carboxylic acid
3244	bonded -OH intermolecular polymer, peroxide -OH, free carboxylic acid
3009	C-H stretching of CH ₃ -C=O
2974	n _{as} C-H stretching of -CH ₃
2889	n _s C-H stretching of -CH ₃
2571	O-H stretching of bonded carboxylic acid
1712-1757	C=O stretch of ester, ketone, saturated carboxylic acid
1632	C=O stretch of internal H-bonded acid
1424	-CH ₂ -CO (C-H deformation), C-O stretch of carboxylic acid
1396	O-H deformation of tertiary alcohol and carboxylic acid
1273	C-O stretching of primary alcohol and carboxylic acid, O-H deformation of carboxylic acid
1176	C-O stretch of ester (propionate type)
1160	C-O stretch of tertiary alcohol
1080	O-H deformation of secondary alcohol
1028	O-H deformation of primary alcohol
898	CH ₃ bend of -(CH ₂) _n -CH ₃ type
850	alkyl peroxide
718	skeletal -(CH ₂) ₄ - or -(CH ₂) ₄ O-
564	

the transparent PP film opaque. Such organic deposits can occur due to many fragments/reaction products occurring in the plasma state.

Further analysis of the ATR-FTIR spectra of AC/O₂ plasma modified PP films showed a number of new bands. ATR-FTIR spectra of AC/O₂ plasma modified PP films, after subtraction of the untreated PP film, showed a series of new peaks listed in Table 3. From the observed new peaks it can be understood that various hydrophilic groups such as -OH, -COOH, -COOCH₃, and -COO- formed on the polymer surface or may be in the form of an organic deposit that leads to an increase in surface energy to a great extent.

Masking of the Reactive Site Using Pretreatment. It is well known that the presence of a hydrophilic group in the backbone chain or side chain affects the wettability of the substrate. The presence of a hydrophilic group in the backbone chain makes the surface more hydrophilic as compared to that on the side chain.^{38,39} From our earlier study²⁷ and as reported by other researchers,⁴⁰ it was found that oxygen preferentially attacks at the primary carbon atom, creating a peroxy radical. As a result incorporation of an ester, acid, peroxy group occurs preferentially at the primary carbon atom. It was therefore thought interesting to incorporate hydrophilic groups at the polymer backbone chain by masking the primary carbon atom. On the basis of our studies,²⁷ it is understood that treatment of a PP film in air or nitrogen plasma for a short time, i.e., from 1 to 3 min, gives rise to incorporation of groups such as -OH, -NH₂, -NO₂, etc. selectively at the primary carbon atom. Hence, pretreating the PP film either in air or in nitrogen plasma can incorporate a hydrophilic group mainly at the backbone chain. It was expected that groups such as -OH, -NH₂, -NO₂, etc. may occupy the primary carbon atom first, which may restrict the formation of a peroxy radical at the primary carbon atom when exposed subsequently in AC/O₂ plasma, and it may attack at either the secondary or tertiary carbon atom, making the surface more hydrophilic than observed without pretreatment. The extent of hydrophilicity induced in such a case was expected to be more as compared to earlier, since hydrophilic groups now occupy the position in the backbone chain. A nitrogen-pretreated PP film following AC/O₂ plasma exposure shows a

**Figure 3.** ATR-FTIR of (A) untreated, (B) 3 min N₂ pretreated, and (C) AC/O₂ plasma modified PP films.**TABLE 4: Relative Intensities of IR Bands of the Nitrogen-Pretreated PP Film Following AC/O₂ Plasma Modification**

band (cm ⁻¹)	untreated PP film	N ₂ plasma treated PP film	AC/O ₂ plasma modified PP film
2950, ν _{as} of -CH ₃ (primary)	0.66	0.54	0.49
2917, ν _{anti} of -CH ₂ (secondary)	0.75	0.57	0.47
2906, ν _s of -CH (tertiary)	0.55	0.46	0.44
2875, ν _s of -CH ₃ (primary)	0.44	0.32	0.39
2868, ν _s of -CH ₃ (primary)	0.44	0.32	0.38
2837, ν _s of -CH ₂ (secondary)	0.46	0.40	0.40

surface energy of 73 mJ/m², whereas the surface energy of an only AC/O₂ plasma modified film shows a surface energy of 58 mJ/m². This indicates that hydrophilicity induced after pretreatment is exceptionally high as compared to the one without pretreatment. The possible contribution to surface energy due to nitrogen pretreatment cannot be neglected. A PP film pretreated only in nitrogen plasma showed a surface energy of 52 mJ/m².

An ATR-FTIR spectrum of the nitrogen-pretreated PP film is shown in Figure 3. Modified films were subjected to ATR analysis followed by relative intensity measurement shown in Table 4. The PP film treated in nitrogen plasma showed maximum decreases in relative intensity of 2875 and 2868 cm⁻¹ corresponding to ν_s of the CH₃ (primary) group. Weak absorption near 3500-3700 cm⁻¹ was due to N-H stretching of the primary amide, that near 1659 cm⁻¹ was due to CO stretching of the primary amide, and that near 1599.5 cm⁻¹ was due to N-H deformation of the primary amide^{36,37} (shown in Figure 3). The IR spectrum of the nitrogen-pretreated PP film subjected to AC/O₂ plasma is shown in Figure 3. The relative intensity of the band corresponding to ν of CH (tertiary) is affected most.

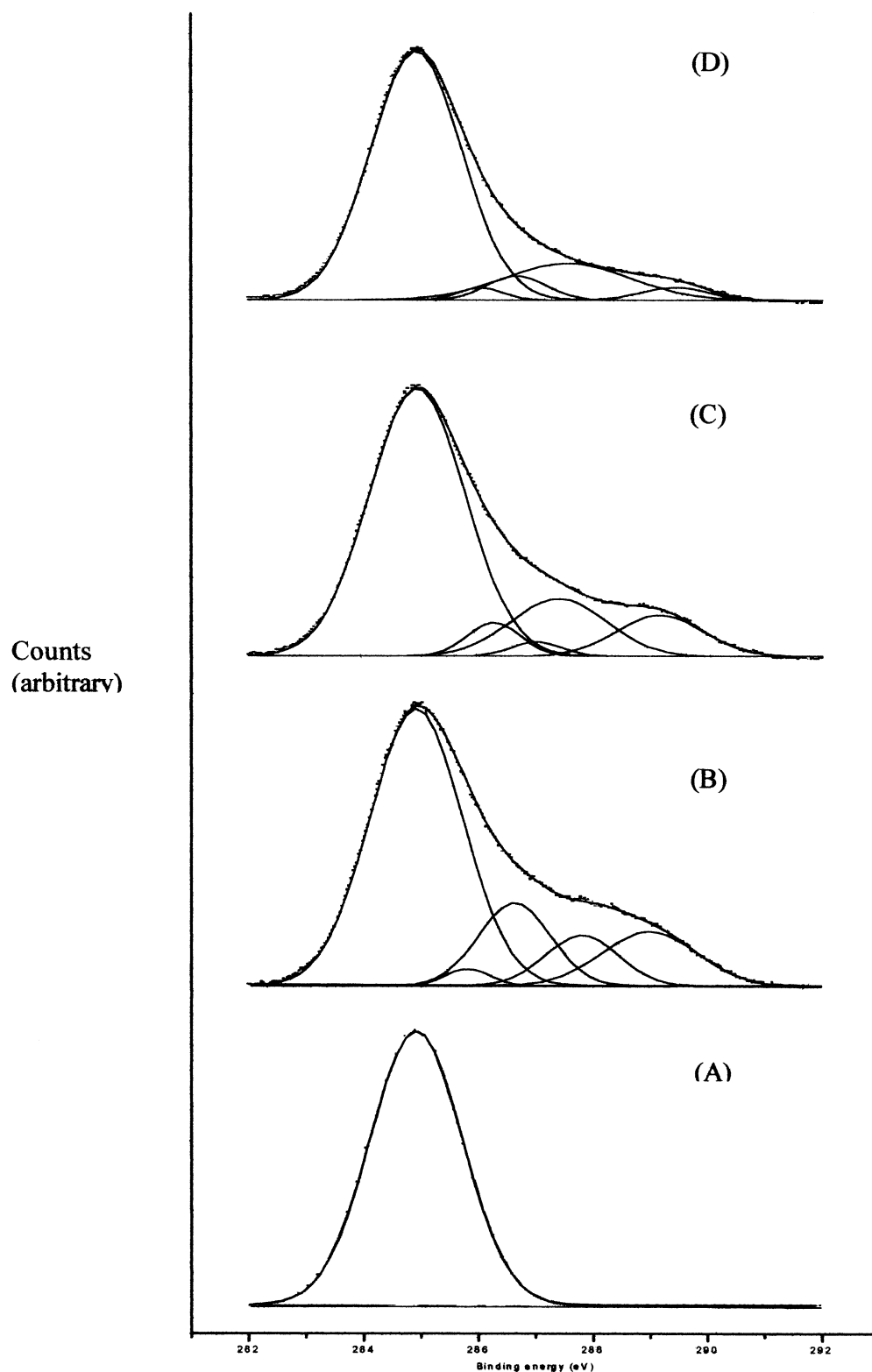


Figure 4. XPS C1s spectra of (A) the control and (B) AC-treated and (C) AC/O₂-treated PP films and (D) a PP film after nitrogen pretreatment followed by AC/O₂ plasma modification.

The band at 2837 cm^{-1} due to ν_s of $-\text{CH}_2$ also showed a decrease in relative intensity. The observed increase in relative intensity of ν_s of $-\text{CH}_3$ may be due to formation of an organic deposit having a $-\text{CH}_3$ group. The surface energy and ATR-FTIR results are indicative of successful masking of the primary carbon atom of the PP film and incorporation of a hydrophilic group at the tertiary carbon atom predominantly.

XPS Analysis. Untreated PP was examined by XPS and was found to be free from contamination. Untreated polymer exhibits a single C1s peak which corresponds to C_xH_y functionalities (i.e., $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ groups) as shown in Figure 4. The relative percentages of carbon, oxygen, and nitrogen observed due to different plasma modifications are tabulated in Table 5. Modification of the PP film in an AC plasma

TABLE 5: Percentage Composition of the Plasma Modified PP Film

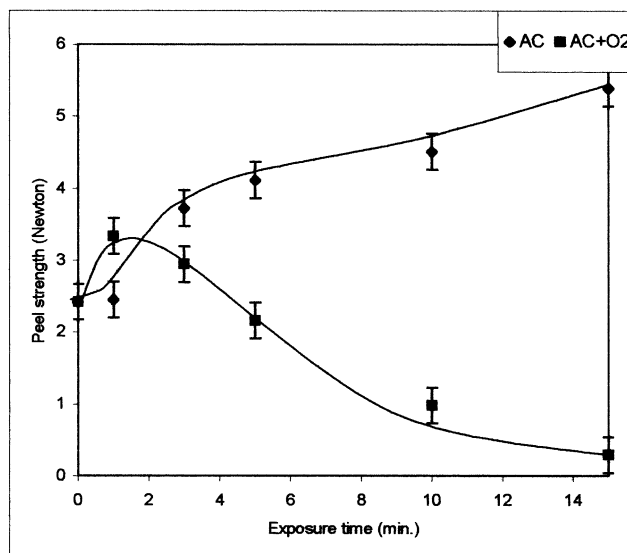
modification	% C	% O	% N
AC	72.9 ± 0.5	21.2 ± 0.3	5.9 ± 0.8
AC/O ₂	70.5 ± 0.4	27.7 ± 0.3	1.8 ± 0.7
N ₂ /AC/O ₂	80.7 ± 0.7	18.0 ± 0.5	1.3 ± 0.9

environment shows a shoulder at high binding energies, which was taken as being indicative of the buildup of an oxygenated carbon center. Binding energies distinctive of different types of oxidized carbon moieties were referenced to the hydrocarbon peak ($-C_xH_y-$) at 285.0 eV,^{41,32} the peak for carbon adjacent to a carboxylate group ($C-CO_2$) at 285.9 eV, the peak for carbon singly bonded to one oxygen atom ($C-O-$) at 286.72 eV, the peak for carbon doubly bonded to one oxygen atom ($C=O$) at 287.89 eV, and the peak for carboxylate groups ($-O-C=O$) at 289.07 eV. The relative concentrations of oxidized functionalities are given in Table 6. The ratio O:C for AC plasma treatment was measured to be 0.29 ± 0.02 , in good agreement with the theoretical value of 0.32 expected from possible formation of acetyl, carboxylate, hydroxyl, and ether groups.

The PP film treated in an AC/O₂ plasma environment showed peaks for hydrocarbon ($-C_xH_y-$) at 285.0 eV, carbon singly bonded to one oxygen atom ($C-O-$) at 286.33 eV, oxygen singly bonded to two carbon atom (cyclic) ($C-O-C$) at 287.07 eV, carbon doubly bonded to one oxygen atom ($C=O$) at 287.46 eV, and carbonate carbon ($-O-CO-C-$) at 289.23 eV. The relative concentrations of oxidized species are listed in Table 6. The ratio O:C for AC/O₂ plasma treatment was found to be 0.39 ± 0.03 . The value is in good agreement with the expected value of 0.38 due to formation of a cyclic ether linkage, acetate, ester, hydroxyl, carbonate, and carboxylate groups.

The nitrogen-pretreated PP film following AC/O₂ plasma treatment showed peaks for hydrocarbon ($-C_xH_y-$) at 285.0 eV, carbon singly bonded to one oxygen atom ($C-O-$) at 286.12 eV, oxygen singly bonded to two carbon atoms (non-cyclic) ($C-O-C$) at 286.75 eV, carbon doubly bonded to one oxygen atom ($C=O$) at 287.63 eV, and carbonate carbon ($-O-CO-C-$) at 289.51 eV. The ratio O:C for nitrogen pretreatment followed by AC/O₂ plasma treatment was found to be 0.22 ± 0.05 . The value is in good agreement with the theoretical value of 0.30 expected from possible formation of acetate, ether, carbonate, etc.

It has been observed that the percentage of $C=O$ carbon increases for three different modifications (from AC-treated to nitrogen-pretreated samples). This is also indicative of how the value of the surface energy varies for three different modifications. To understand the site of attachment of hydrophilic functional groups and to verify the masking of the primary carbon atom by pretreatment, XPS spectra were analyzed by observing the relative shift in the respective peak of the oxidized species. For AC plasma modification a β -shift was observed which is indicative of substitution of functional groups selectively at the primary carbon atom. However, this peak was not observed for subsequent plasma modification. The relative chemical shift among the respective oxidized functional groups of AC/O₂ and nitrogen-pretreated AC/O₂ was observed to be more in the latter case. On the basis of possible substitution, it is expected that in the case of the pretreated sample electrons in the core level are shielded more as compared to those in the sample with only AC/O₂ modification, and as a result the chemical shift observed in the pretreated sample is more. The chemical shift for the $C-O-C$ peak in AC/O₂ was more

**Figure 5.** Peel strength of AC and AC/O₂ plasma modified PP films.

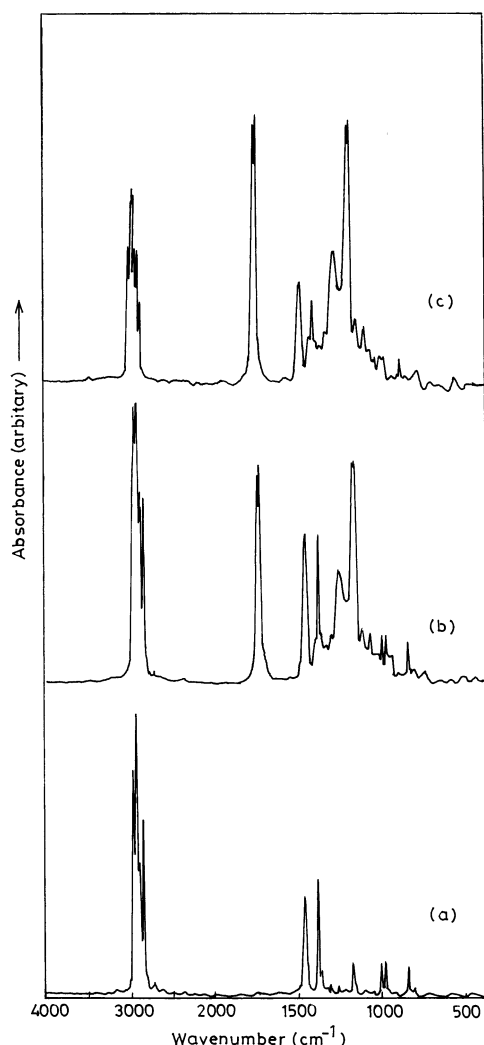
compared to that of the pretreated sample, due to the cyclic and noncyclic nature of $C-O-C$.

T-Peel Test. Modified films were subjected to peel strength measurement as a function of exposure time to understand the effect of hydrophilic groups on bonding strength. The values of peel strength are plotted versus time of exposure and shown in Figure 5. Only in the case of AC plasma did the value of the peel strength increase continuously with time. On the other hand, the AC/O₂-treated film showed a decrease in bonding strength as compared to the control film. It is worth noting that the AC plasma modified film does not show significant improvement for shorter time (i.e., for 1 min); however, for longer time the value of the peel strength increased to a great extent. On the contrary, in the case of the AC/O₂ plasma modified PP film the peel strength improved for shorter time (1 min), but for longer time the peel strength decreased drastically to such an extent that the value of the bonding strength was less than that of the untreated film. Earlier studies carried out on plasma-induced surface modification revealed that improvement in hydrophilicity gives better bonding strength.^{42,43} However, with AC/O₂ plasma modification the surface becomes hydrophilic to maximum extent due to incorporation of groups such as hydroxyl, ester, carboxylic acid, and peroxy as evident from FTIR and XPS studies, but surprisingly, the peel strength did not improve at all. Also it is evident from Table 1 that the polar and disperse fractions for 1 min of exposure time for both AC and AC/O₂ plasma are the same, whereas the bonding strengths are totally different. This observation requires further investigation of the modified substrate as well as the nature of the adhesive used in commercially available Scotch tape.

For the better bonding strength two parameters are essential; one is molecular contact between the adhesive material and the substrate, and the second is the force of attraction between interacting layers.⁴⁴ Usually, molecular contact can be improved by improvement in physical contact, compatibility, flow wicking, interpenetration, and cohesion. However, the force of attraction depends on the nature of the interacting group. Figure 6 shows the transmission FTIR spectra of Scotch tape. The Scotch tape used for the peel strength measurement is a biaxially oriented polypropylene (BOPP) film. To understand the nature of the adhesive layer on the BOPP film, the difference spectra were taken by subtracting the spectra of the BOPP film without adhesive. Adhesive material shows similarity with acrylates,

TABLE 6: XPS C1s Data of the Plasma Modified PP Film

modification	% functionality					
	$-C_xH_y-$	$C-COOR$ (β -shift)	$C-OR/H$	$C-O-C$	$C=O$	$COOR/H$
AC	45.4 ± 0.6	1.3 ± 0.4	10.6 ± 0.1		6.5 ± 0.1	9.1 ± 0.1 , carboxylate
AC/O ₂	48.6 ± 0.4		3.4 ± 0.3	1.4 ± 0.4 , cyclic	10.4 ± 0.4	6.8 ± 0.2 , carbonate
N ₂ /AC/O ₂	60.8 ± 0.5		1.5 ± 0.4	3.9 ± 0.2 , noncyclic	12.3 ± 0.1	2.3 ± 0.4 , carbonate

**Figure 6.** FTIR spectra of (A) Scotch tape without adhesive and (B) Scotch tape with adhesive and (C) difference spectra.

which are commonly used as adhesive material for Scotch tape,⁴⁵ as shown in Table 7. The material is known to be poly(vinyl propionate).⁴⁶ Similarity of the major peaks of the adhesive material poly(vinyl propionate) and the organic deposit obtained from AC/O₂ plasma could be evident by comparing Tables 3 and 6. It is quite clear from the observed similarity between the spectra of the AC/O₂ plasma modified film and adhesive layer that both contain similar characteristic functional groups. Thus, the AC/O₂ plasma modified surface severely lacks the necessary molecular contact due to lack of interpenetration and cohesion, although it is rich in interacting groups. Naturally, despite having sufficient functional groups, the peel strength does not improve.

Effect of Aging. Due to plasma modification hydrophilic groups are incorporated on the polymer surface, and as a result the surface energy shows improvement for the fresh samples. However, when the modified samples are stored for longer time, oxidation and orientation of the hydrophilic group can occur, leading to an increase in the contact angle and decrease in the

TABLE 7: Band Assignments for the Adhesive Layer of Scotch Tape Used for the Peel Test and Poly(vinylpropionate)

absorbance (cm ⁻¹)		
due to adhesive layer	due to poly(vinylpropionate) ^a	peak assignment ^b
2973	2980	C-H stretching of ν_{as} of CH ₃
2944	2940	C-H stretching of ν_{as} of CH ₃
2931		C-H stretching of ν_{as} of CH ₂
2917	2920	C-H stretching of ν_{as} of CH ₂
2913		C-H stretching of ν_{as} of CH ₂
2905		C-H stretching of ν of CH
2874	2880	C-H stretching of ν_s of CH ₃
2839	2860	C-H stretching of ν_s of CH ₂
1745–1725	1740	C=O stretching of saturated ester
1468, 1452	1470, 1430	asymmetric C-H deformation
1396, 1377	1350	symmetric C-H deformation
1254	1280	C-O- stretching of acetate or propionate
1173, 1160	1190	C-O- stretching of acrylate, fumarates, maleates, etc.
1118	1130	C-C skeletal
1065	1080	-CH-O- vibration
942	1010	
739	890, 810	
653		
508	580	

^a Taken from ref 46. ^b Taken from refs 36 and 37.

surface energy value. This phenomenon of a decrease in the wettability of the modified surface is due to the phenomenon of the orientation of the surface mobile group,²² which is mainly hydrophilic in nature. This unavailability of interacting groups further hampers the bonding strength of the surface on aging. However, the mobility of the groups can also be affected due to cross-linking and other steric factors or due to the presence of a bulkier hydrophilic group.

AC and AC/O₂ plasma modified films were stored in a vacuum desiccator for two months, and the surface energy was measured again. Figure 7 shows that after aging the surface energies of AC plasma modified films show a significant decrease but are still better than that of the control PP film. On the other hand, AC/O₂ plasma modified and subsequently aged films do not show such a large decrease as is evident from Figure 7. After aging it has been observed that the contribution of the γ_s^p fraction to the total surface energy has been decreased for AC plasma (shown in Table 8). For AC/O₂ plasma modified aged films, the γ_s^p fraction does not decrease much and surface is still sufficiently hydrophilic as compared to the control film.

The peel strength of aged films showed a decrease in bonding strength due to storage. Figure 8 shows after aging the peel strength value for AC plasma modified film has decreased. Surprisingly, the film exposed for 1 min shows slight improvement after aging, and the decrease observed for 3 and 5 min is not significant. In the case of the AC/O₂ plasma modified film anomalous behavior of the peel strength was observed. Figure 8 shows an increase in peel strength in contrast to the observed negative peel strength of the freshly treated sample. This could be due to possible oxidation of the organic deposit with storage time; as a result the molecular content increases with improvement in the cohesive force.

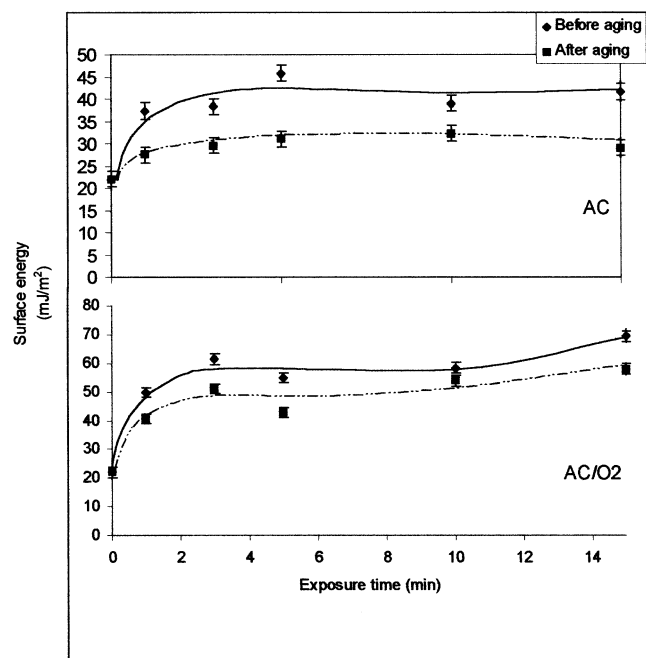


Figure 7. Surface energy of acetone and AC/O₂ plasma modified PP films before and after aging.

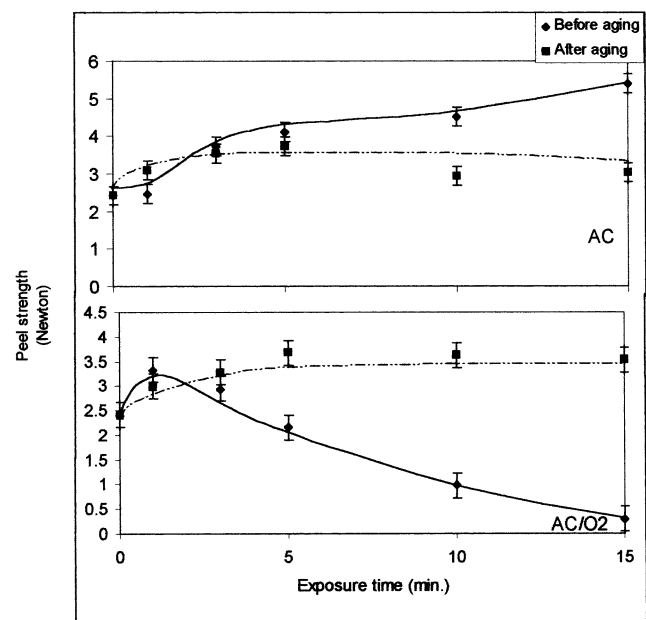
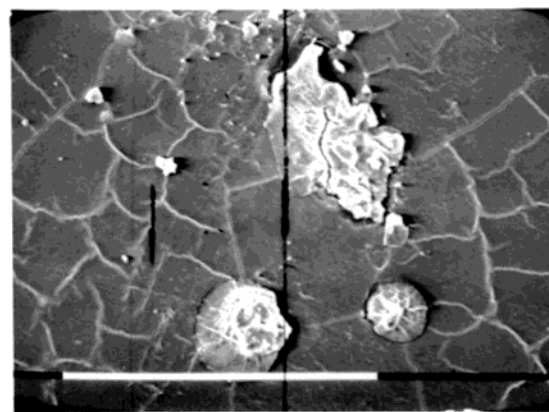


Figure 8. Peel strength of acetone and AC/O₂ plasma modified PP films before and after aging.

TABLE 8: Polar and Disperse Fractions of AC and AC/O₂ Plasma Modified PP Films after Aging

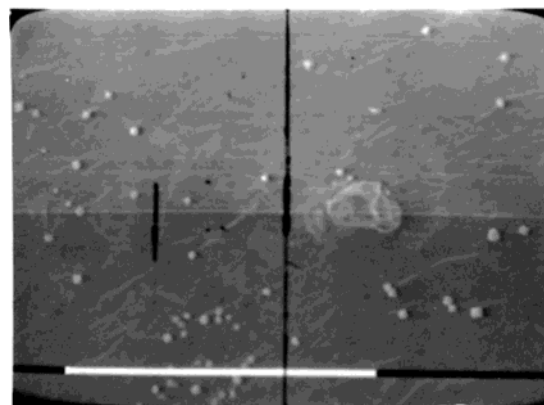
exposure time (min)	AC		AC/O ₂	
	polar fraction (γ_s^p)	disperse fraction (γ_s^d)	polar fraction (γ_s^p)	disperse fraction (γ_s^d)
0	0.19	0.81	0.19	0.81
1	0.64	0.36	0.71	0.29
3	0.46	0.54	0.72	0.28
5	0.40	0.60	0.75	0.25
10	0.37	0.63	0.80	0.20
15	0.34	0.66	0.81	0.19

Morphological Studies. The morphological features were investigated by SEM. Figures 9 and 10 show the micrographs of the control PP film showing some spherical growths



M-680X Bar length-0.1mm

Figure 9. SEM micrograph of the control PP film.



M-680X Bar length-0.1mm

Figure 10. SEM micrograph of the control PP film.

embedded on the surface with a clear demarcation periphery. They also show some crack-like lines, giving the appearance of polygons. The structure also shows some grains whose shape varies from circular to ellipsoidal to squarelike. The measurement of the large spherical structure showed that it exists in many sizes and the diameter varies from 19 to 31 μm with an average value of 25 μm . These structures can presumably be due to some crystalline growth or spherulitic growth. The polygonal structures bonded by lines are probably because of zones formed due to coalescing of several spherulites growing simultaneously. It may be recalled that PP films when drawn from the melt and quenched usually have a large number of spherulitic and partially crystalline growths (known as transcrystallization). The average area of these structures was found to be $4 \times 10^{-4} \text{ mm}^2$. The width of the zonal lines bounding the polygons was observed to be 0.9 μm . The smallest grainlike dot observed was found to have a size of about 0.2 μm with a range extending up to 2.5 μm . Some smaller grains were observed to have a definite squarelike or diamondlike shape with an average size of about 2 μm . They appear like single crystal growth, and it is quite likely that these features develop from low molecular weight fractions forming a small crystallite.

It may be seen that the surface structure is completely altered from that of the control, and now one can see small particles of uniform sizes 0.6–1 μm deposited when the PP film is modified in AC plasma (Figure 11). At some places depositions of larger sizes (1–3 μm) were observed which are due to enhanced growth of AC products. It is noteworthy that two small-sized particles are clearly distinguished from each other by small black

Surface modification of the polymer film in plasma initiates mainly with abstraction of hydrogen from the polymer followed by various secondary processes such as bond scission, cross-linking, recombination, termination of radicals, etc. Two types of interaction can occur at the plasma–polymer interface:⁴⁷ (i) direct reaction at the surface due to incident neutral species, ions, photons, and electrons and (ii) indirect processes in the subsurface region as a result of vacuum ultraviolet (VUV) radiation. As a consequence, free radical centers are created in the surface region via atom abstraction,^{48,49} ion bombardment,⁴⁹ and photoexcitation.⁵⁰ Subsequently, these radical species can either react with the adjacent plasma medium or undergo cross-linking. The former is predominant in the case of oxygen plasma treatment on the basis of thermodynamic factors,⁵¹ whereas the latter tends to be more likely for nitrogen plasma exposure as a consequence of less favorable energetics for chemical reaction.⁵²

VUV photodegradation processes occur near the surface region, leading to polymer chain scission accompanied by the formation of atomic hydrogen. Since hydrogen free radicals are likely to be short-lived within the polymer subsurface, formation of molecular hydrogen is expected. The reaction becomes more complicated when modification is carried out in an acetone plasma environment. On the basis of the known photochemistry of AC, dissociation of AC in plasma is expected to follow reaction 1. Radical sites generated due to hydrogen free radicals on the PP surface react readily with the reactive plasma environment and subsequently terminate by recombination reaction. Due to the reactive nature of plasma and possible occurrence of multiple steps simultaneously, it becomes difficult to understand the mechanism of all surface chemical processes. However, on the basis of ATR-FTIR and XPS probing the chemical nature of the reaction product discussed in an earlier paragraph could be anticipated.

Conclusions

Using AC and AC/O₂ plasma, the surface energy of a PP film can be improved to a significant extent. Incorporation of an acetyl group was observed due to AC plasma modification. The AC/O₂ plasma incorporates various hydrophilic groups such as ester, carboxylic acid, alcohol, etc. The site of attachment of hydrophilic groups is observed mainly at the primary carbon atom. The bonding strength of the AC plasma treated film showed improvement as the treatment time increased. However, AC/O₂ plasma treated films showed a negative value. The observation is due to a lack of cohesive bonding between the adhesive material and modified substrate. After aging, the film retained significant hydrophilicity. After aging, the peel strength improved from negative to positive for AC/O₂ plasma modified films. Experiments carried out to mask the reactive site of the PP film by pretreatment in nitrogen plasma followed by AC/O₂ plasma modification showed that hydrophilic groups can preferentially occupy the tertiary carbon atom.

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