Surface Modification of Polyester Films by RF Plasma

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ABSTRACT: Plasma treatment of PET films was carried out under argon, followed by exposure to an oxygen atmosphere. The films underwent considerable changes in surface composition and morphology, as demonstrated by contact angle measurements, FTIR-ATR, AFM, and XPS. It was found that the surface acquired oxygen containing polar functional groups such as —C=O, —OH, and —OOH, which increased in number as the plasma treatment time increased. During storage, the treated films underwent significant surface reorganization, and both the time and temperature contributed to the increase in the contact angle. As revealed by AFM measurements, these changes were accompanied by an increase in roughness in the form of ridges. The ridges were observed to grow in height with increasing treatment time, although their spacing showed little evolution. A correlation among the observations obtained from various techniques was established, giving a comprehensive picture of the structure and dynamics of plasma-treated PET surfaces. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1083–1091, 2000

Key words: polyester; plasma; surface modification; AFM; XPS; ATR

INTRODUCTION

Tissue engineering using polymeric materials has recently become an emerging domain of biomedical engineering. A great deal of effort has gone into developing novel polymeric materials that may be used for reconstructive surgery involving tissue replacement, tissue reinforcement, and organ transplants.[1] One of the applications of these polymeric biomaterials is in the form of support structures, which may be utilized for tissue growth. This opens up the route to the *in vitro* development of an organ and its subsequent implantation into the human body. However, it requires a specially designed macromolecular structure, where cell immobilization and growth to a full-fledged tissue can be accomplished.

The primary interaction between a biomaterial and living tissue occurs in a very narrow interfacial zone. This interaction is strongly influenced by the chemical composition, surface morphology, wettability, and physical structure of the biomaterial.[2] There are a number of polymeric materials that have excellent physical properties but do not have an active surface for the immobilization of biomolecules. Such polymers need selective modification so that specific functional groups may be imparted to the surface for the binding of biomolecules and culturing of cells.

Plasma treatment has been found to be an extremely attractive way to modify the surface chemistry and morphology of polymeric materials.[3] The plasma modification may be carried out in the presence of specific gases, such as oxygen, argon, nitrogen, and hydrogen. This results in the generation of active species, which can activate and modify the material depending on the nature of the gaseous medium. An interesting aspect of plasma treatment is that the changes are confined to a depth of a few nanometers at the surface because of the low level of penetration. This opens up possibilities for producing a wide spectrum of surface chemistries with desired compositions. The most attractive feature of the plasma processing is that by exerting proper control over the exposure conditions, a tailored surface with desired chemical functionality and morphology may be produced.

Poly(ethyleneterephthalate) (PET) has excellent mechanical strength, good stability against body fluids, and high radiation resistance for sterilization, but its surface is not favorable for the immobilization of biomolecules. Plasma modification of PET has been studied by some workers, and changes in the physical behavior and surface morphology have been reported.[4–12] These studies involve the treatment of PET surface under different gaseous environments such as oxygen, nitrogen, argon, and fluorinated gases for applications in adhesion improvement and in composites. One of the criteria for the evaluation of the surface behavior has been contact angle measurements on the surface of the exposed samples, and most of the work reported up to now deals with wettability studies on PET films. In one such study, Hsieh et al.[7] carried out the plasma treatment of PET films under argon and observed that the wettability of films was considerably enhanced. The exposed films were found to undergo a reduction in wettability, which could be arrested by treating the exposed films with interacting solvents. The nature of the chemical groups at the surface of the plasma-treated PET under various environments has been studied by Clark et al.,[8] as well as Le et al.[12] Using XPS, they demonstrated that the functionality gradient is confined to the top few nanometers of the surface.

Plasma treatment has also been carried out on PET fibers by Yasuda et al.,[13] and the wettability and morphological changes in different atmospheres have been evaluated. At the same time, Wrobel et al.[5] found that the wettability of PET is considerably influenced by the surface polarity and morphology that develops as a result of the plasma treatment. A number of studies[14–16] have been aimed at using plasma processing as a tool to modify the polymer surface for biomedical applications. For example, Piglowski et al.[14] have reported that PET can be modified into a biomaterial by plasma treatment under argon (which makes the surface hydrophilic) or with perfluorohexane (leading to a more hydrophobic surface). Both types of surfaces were found to show very good biocompatibility under both *in vivo* and *in vitro* evaluation. However, these studies have only provided information on specific aspects of the plasma-induced changes, based on contact angle, XPS, or AFM, and none of them provides an overview of the structure and characteristics of the PET surface. A comprehensive study of the plasma treatment of PET films and their physico-chemico-morphological transformation is needed as a basis for the rational use of plasma treated films as biomaterials. This is why we have attempted to investigate the surface behavior of PET films by various techniques and correlate the information in order to provide a clear picture of the modified surface.

We have previously studied the development of PET films with controlled surface functionality by chemical means, leading to successful immobilization of cells and cell culturing.[17] Our current interest is to develop a PET surface rich in carboxyl groups by plasma-induced graft polymerization of acrylic acid. These carboxyl groups may be used as sites for the immobilization of biomolecules. In the present investigation, we have carried out the plasma exposure of PET films under argon, with subsequent contact with oxygen and the influence of the plasma conditions on the physico-chemical changes occuring at the film surface has been evaluated. Studies of the grafting of acrylic acid on plasma exposed PET films have been communicated elsewhere.[18]

EXPERIMENTAL

Materials

The poly(ethylene terephthalate) (PET) films used in this study were supplied by Goodfellow, England. The films were biaxially oriented, and had a thickness of 23 microns. They were cut into 10×10 cm^2 squares and soxhlet extracted with ethanol for 24 h. The films were then dried under
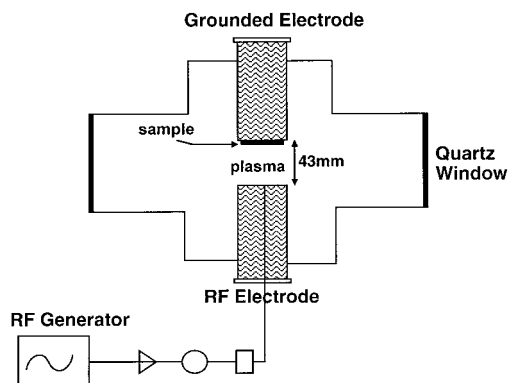
Figure 1 Schematic representation of the RF plasma reactor.

vacuum at ambient temperature (22°C), and stored in a desiccator over dried alumina before use.

Plasma Treatment

A schematic representation of the plasma treatment system is shown in Figure 1. Plasma treatment of PET films was carried out in a capacitively coupled RF reactor operating at 13.6 MHz. The reactor consisted of two cylindrical electrodes of 13 cm diameter and 4.3 cm apart in a cubic vacuum vessel. The upper electrode and the reactor walls were grounded.

The film was placed on the grounded electrode and the system was evacuated to 5 μbar. Argon was introduced into the chamber at a flow rate of 50 sccm, and the chamber pressure was subsequently maintained at 0.4 mbar. The plasma was then generated at the specified electric power (40 and 80 W) for a desired period. After plasma treatment, the chamber was evacuated to 5 μbar, and oxygen was introduced into the chamber and maintained at one atmosphere for a period of 60 min. The film was subsequently taken out and analyzed by various surface characterization techniques.

The storage of films was studied at two different temperatures of 22 and -20°C. The films (4 $\times$ 4 cm^2) were placed in a 8 $\times$ 5.5 $\times$ 1.5-cm^3 plastic box and wrapped in a polyethylene bag for storage in a desiccator under ambient conditions at 22°C as well as in a refrigerator maintained at -20°C.

Contact Angle Measurements

The contact angle of PET films was measured according to the method reported by Dahlgren

and Sunqvist.[19] All measurements were performed at 22°C using deionised water. A water droplet of 10 μL was placed on the film surface and the diameter was noted 20 s after the application of the droplet. Six measurements were recorded at different places at the film surface and averaged. The measurements on modified films were carried out within 20 min after the plasma treatment was completed.

ATR Measurements

ATR measurements on samples were carried out on Nicolet, Magna IR-560. The samples were analyzed in the reflectance mode in the range of $400-4000$ cm^{-1}.

XPS Studies

XPS measurements were recorded on a PHI 5500 system equipped with hemispherical analyzer and a nonchromatized Mg Kα X-ray source having a pass energy of 1253.6 eV. The analysis was carried out under UHV conditions (10^{-9} Torr) on an area of 0.12 mm^2. Spectra were taken at 45°.

Atomic Force Microscopy (AFM)

The topographical studies on the film surface were carried out using a Park Scientific Instruments Autoprobe CP Scanning Probe Microscope. A 100 μm scanner was used with a 2-μm thick silicon carbide "Ultralever." Intermittent contact mode imaging in air was used throughout to prevent significant deterioration of the surface of the films. The surface roughness of samples was eval-
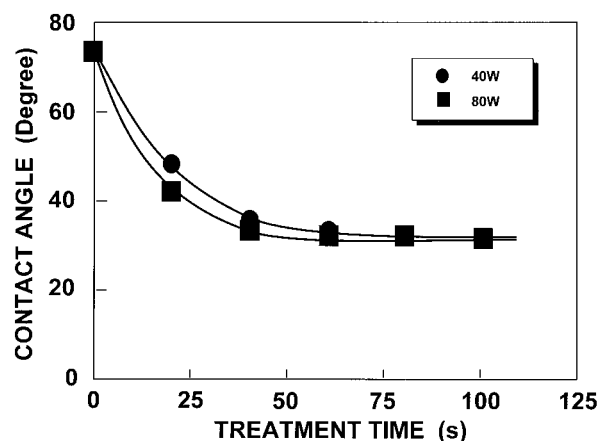

Figure 2 Variation of the contact angle with the plasma treatment time. Conditions: pressure, 0.4 mbar; Ar flow rate, 50 sccm, O$_2$ exposure time, 1 h.

uated in terms of the mean amplitude and wavelength of fluctuations in the sample height.

RESULTS AND DISCUSSION

As plasma treatment is a surface selective process, it has a significant effect on the surface energy as reflected by the contact angle measurements. The variations in the contact angle with the plasma treatment time at 40 and 80 W are presented in Figure 2. The PET film showed a contact angle of 72.9° prior to the plasma treatment. The plasma treatment initially led to a considerable reduction in the contact angle and a contact angle of 33.8° was achieved after 40 s of treatment. Moreover, it remained almost unaffected with further increases in the exposure time. The decrease in the contact angle is indicative of the magnitude of the chemical changes taking place at the film surface due to plasma treatment, which makes the surface hydrophilic relative to the virgin film. In our studies, the plasma treatment of films was immediately followed by exposure to the oxygen atmosphere. It may, therefore, be assumed that the radicals generated during the plasma treatment reacted with oxygen to produce hydrophilic groups on the surface of PET films. The contact angle results are in agreement with those of the other workers who attributed the decrease in contact angle to the formation of polar groups, such as —OH and —OOH, and —COOH at the surface of different polymer films.[20]

The significant feature of above results is that an increase in the plasma power is accompanied by a further decrease of the contact angle only for low exposure times. At a higher exposure time of 100 s, the contact angle was almost identical at 40 and 80 W. It is suggested that the buildup of the polar groups is slow at the low power of 40 W, resulting in a relatively high contact angle at small exposure times. Once a minimum polarity is achieved at the surface (100 s of treatment time) the contact angle reaches almost identical values to those at 80 W.

After plasma treatment, PET film were stored at −20°C, and at an ambient temperature of 22°C in air under darkness. The contact angle of treated films showed a gradual increase with storage times up to 10 days, as shown in Figure 3. This suggests that the hydrophilicity, and hence, the polar functionality, undergo considerable changes with the passage of time. The PET sur-
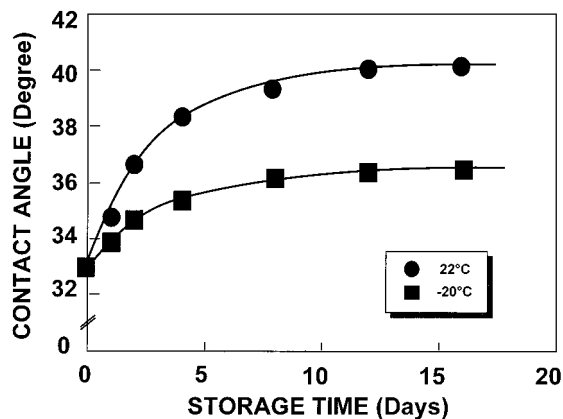

Figure 3 Variation of the contact angle with the storage period at different temperatures. Conditions: plasma power, 80 W; treatment time, 60 s; pressure, 0.4 mbar; Ar flow rate, 50 sccm.

face just after plasma treatment is, therefore, not stable, and rapid migration of the polar segments towards the bulk of the polymer takes place, reducing the interfacial tension. However, it is always possible that a fraction of the functional groups are transformed into some stable structures at the surface itself and diminish the surface hydrophilicity. Yasuda et al.,[21] Heish et al.,[22,23] and Le et al.[12] have reported similar observations for the plasma-treated PET films, and have correlated them with the reorganization of the surface, as well as surface contamination during storage.

The results in Figure 3 show strong influence of storage temperature on the contact angle variation with time. The surface reorientation stabilizes after a week, but the surface hydrophilicity can be maintained to a greater extent by keeping the films at a lower temperature (−20°C). It seems that the surface behavior is strongly guided by two prominent factors, namely molecular mobility and surface polar functionality.

It should be stressed that the reorganization that we are concerned with is within the functionally transformed PET layer and not the bulk PET. The modified surface layer contains a large amount of polar functional groups that would absorb moisture from the atmosphere and plasticize the fragmented polymer chains, thereby contributing to the mobility of chains. At −20°C, the molecular mobility is much lower than at ambient temperature. As a result, the PET chains at such a low temperature do not undergo significant reorganization, following which the surface characteristics are restored to a large extent. Because
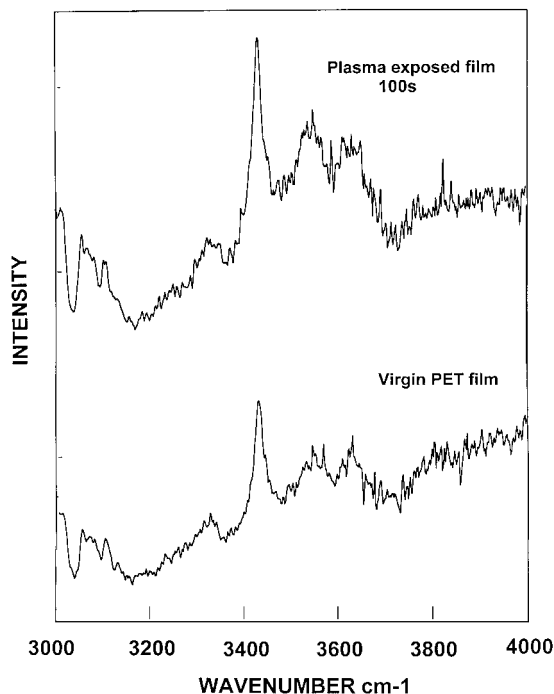
Figure 4 FTIR spectra of virgin and plasma-treated PET films. Conditions same as in Figure 3.

films are stored under air, some of the active radical species may react with the atmospheric contamination as well. This contamination partially inhibits the polarity at the surface which is reflected by an increase in the contact angle. By performing these storage experiments under identical and closed conditions, the effect of deposited contaminations should be identical. Therefore, the noted differences must be attributed to the temperature effect.

The ATR results for virgin and plasma treated PET films are presented in Figure 4. It was not possible to distinguish variations in the 1400–1800 cm^{-1} wave number range for any detectable chemical change on the film surface. However, the region between 3200–3800 cm^{-1} showed distinct changes in the spectra of exposed films. Because plasma-treated films were exposed to oxygen, the functionality was expected to be oxygen based, leading to a polar surface. Although, the most prominent functional groups were thought to be hydroxyl and hydroperoxide groups, various other groups such as ketone, aldehyde, and carboxylic groups may also have formed as a result of the subsequent reactions among polar groups. Virgin PET shows a sharp peak for —OH stretching at 3430 cm^{-1} due to the presence of terminal hydroxyl groups in the chain.[24] Following plasma

treatment, the intensity of this peak increased reflecting the increase in hydroxyl functionality in the treated sample. Similarly, the broad peaks at 3500–3600 cm^{-1} and 3600–3770 cm^{-1} also increased in the treated sample, which indicated the enhanced hydrogen bonding among hydroxyl moieties generated during the plasma treatment. The ratio of the optical density (O.D.) of the —OH peak at 3430 cm^{-1} and the C—H stretching at 2970 cm^{-1} is shown in Figure 5. There was a continuous increase in this ratio with exposure time, suggesting that the formation of functional groups is a function of the plasma treatment time. As evident from the previous discussion, the contact angle showed no significant change beyond 40 s. This suggests that there is a critical concentration of polar functionality at the PET surface necessary to achieve maximum hydrophilicity and the lowest contact angle, and that this occurred after 40 s of exposure. An increasing treatment time may lead to enhanced hydrophilicity but not the lower contact angle.

The evolution of the topography of the film surfaces as observed by AFM is illustrated in Figure 6. The virgin film had a relatively smooth and uniform surface. However, the surfaces became progressively rougher with increasing treatment time. This is shown quantitatively in Figure 7. The RMS amplitude of the modules calculated from single line scans showed a linear increase with exposure time in the range of 0–100 s. The impact of plasma treatment on the surface is evident from the fact that the amplitude increases fourfold when the treatment time increases from 20 to 100 s. On the other hand, the mean wave-
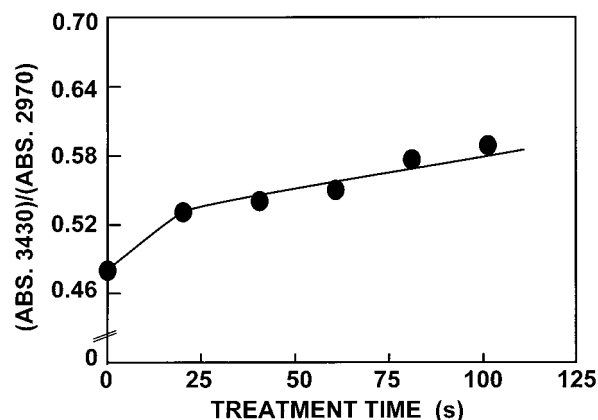

Figure 5 (Abs. 3430/Abs. 2970) vs. treatment time. Conditions same as in Figure 3 except for the treatment times.
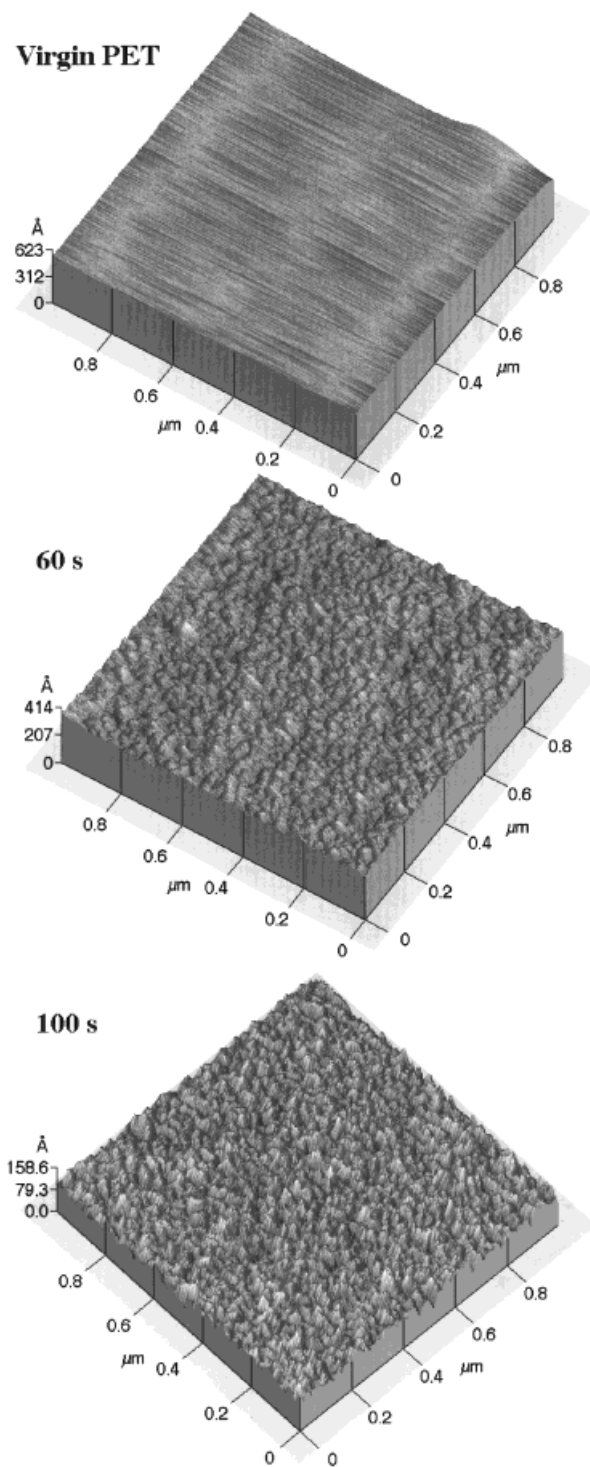
Figure 6 AFM images of original and exposed PET films. Numbers represent the time of treatment. Conditions same as in Figure 3 except for the treatment times.

length saturated at about 35 nm. This suggests that the distribution of ridges is not much influenced by the plasma treatment. It is the size of

ridges, which increases as the treatment time is increased. Hopkins et al.[24] have observed similar behavior in AFM studies of plasma-treated polysulfone films. Hsieh et al.,[7] on the other hand, who studied the surface morphology of PET films by scanning electron microscopy (SEM), reported no substantial change in morphology up to 1 min of treatment, although they did find significant changes for treatment times greater than 2 min. Any change in the surface is reflected in the contact angle variation as well. As the surface morphology undergoes considerable changes, it would also influence the observed contact angle variation in films. However, it is difficult to quantify the independent contributions of hydrophilicity and roughness to the contact angle variation.

The XPS studies offered further insight into surface of the films. The spectra of virgin and treated PET films are shown in Figure 8. The deconvolution of core level C_{1s} peaks showed a striking change in the exposed samples. The virgin PET film indicated the presence of three components with binding energy of 284.7, 286.4, and 288.7 eV. The peak at 284.7 eV arises from C—C bonds, and the peak at 286.4 eV may be assigned to C—O bonds. The remaining peak at 288.7 eV is due to the presence of O=C—O groups in the chain.[18] The spectra of treated films [Fig. 8(b)–(d)] also showed peaks for C—C, C—O, and O=C—O, at the same time, additional peaks at 286.7 and 288.1 eV also arise, which may be attributed to C—OH and/or C—O—O—H, and —C=O groups.

The variation of (O_{1s}/C_{1s}) with treatment time is shown in Figure 9. The ratio increased from
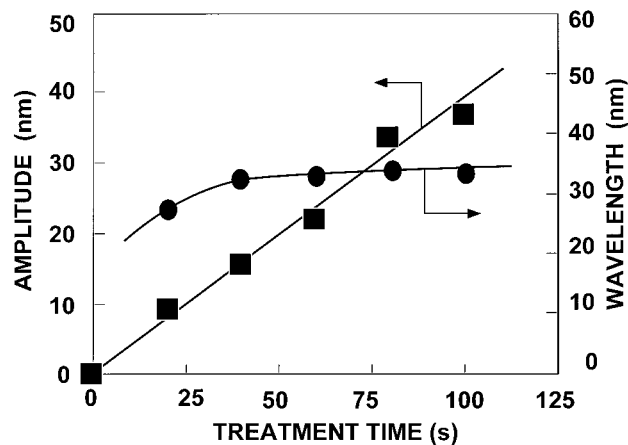

Figure 7 AFM results on the variation of the amplitude and the wavelength with the treatment time. Conditions: same as in Figure 3 except for the treatment times.
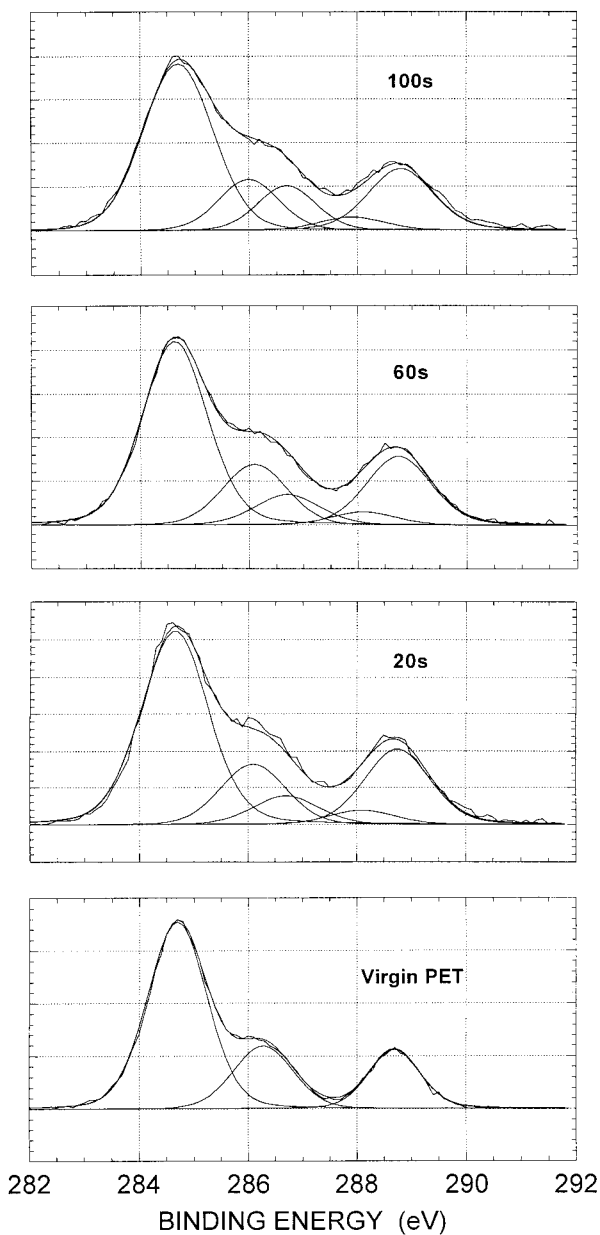
Figure 8 Deconvolution of XPS core level C_{1s} spectra of PET films. (a) Virgin and exposed for (b) 20 s, (c) 60 s (d) 100 s. Conditions: same as in Figure 3 except treatment times.

0.43 in the virgin film to 0.66 in a film exposed for 100 s, indicating a higher level of oxygen-based functional groups at the surface. Although a treatment time of 20 s increased the oxygen functionality by 32%, a further increase in exposure led to a slow and steady buildup of functional groups. These results are well in agreement with the trend observed by Clark et al.[25] on PET films.

The relative areas of the C_{1s} peaks in films are presented in Table I. The C—C component de-

creases significantly even after a short exposure of 20 s, but showed little change for further increases in the exposure time up to 100 s. The —C=O (288.1 eV) intensity did not change for the exposure times between 20–100 s, but the O=C—O (288.8 eV) peak showed an initial increase up to 20 s and then decreased with further increases in the exposure time. A much more relevant variation was associated with peaks at 286.1 and 286.7 eV. Although the —C—O— peak at 286.1 eV decreased, the —OH peak at 286.7 eV exhibited an increasing trend with exposure time. This close relationship suggests that a substantial proportion of the hydroxy and hydroperoxy functionalities may arise from the —C—O— linkages in the PET chain. Some of these —C—O— bonds may undergo fragmentation during the plasma treatment and contribute to the formation of —OH as well as —OOH groups. Incorporation of hydroxyl groups by this route would be in addition to those accumulated by the reaction of radicals produced by plasma with the molecular oxygen. The results in Table I show an increase in the carboxyl groups even for a short period of 20 s. However, there is a slight decrease in the —COOH fraction once the exposure time increases. It is always possible that some carboxyl groups are lost during the prolonged treatment with Ar plasma itself accounting for the decrease in their content. This is consistent with the observation of Terlingen et al.[26] that the degradation of carboxyl groups proceeds by a decarboxylation process during plasma treatment.

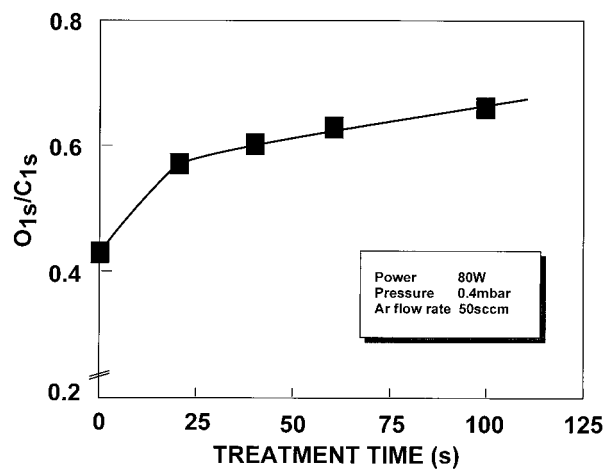It is certainly not possible to ascertain the fraction of —OH and —OOH moieties in the PET

Figure 9 Variation of O_{1s}/C_{1s} ratio with the treatment time.

Table I   Relative Intensity Data of the Deconvoluted C_{1s} Core Level Spectra of PET Films Treated for Different Periods

Exposure time (s)	—C—C— ~ 284.60[a]	—C—O— ~ 286.10[a]	—C—OH ~ 286.70[a]	—C=O ~ 288.10[a]	O=C—O ~ 288.75[a]
			Atomic Ratio (%)		
Untreated	62.06	20.66	—	—	17.28
20	53.04	15.4	7.62	3.78	20.15
40	51.8	16.08	8.47	3.36	20.33
60	51.9	16.35	8.70	3.72	19.37
100	52.2	13.75	11.59	3.8	18.65

Treatment conditions: plasma power, 80 W; Ar pressure, 0.4 mbar; Ar flow rate, 50 sccm; O_2 contact 1 h.

[a] Binding energy in eV.

surface by XPS. The peak at 286.7 reflects both the —OH and —OOH groups. It appears that the —OOH component is present in an appreciable amount on the film surface. This is evident from the fact that the exposed films when grafted with acrylic acid respond to the addition of $FeSO_4$ in the reaction medium.[18] The homopolymer formation was completely suppressed by the $FeSO_4$ addition while the grafts are still formed. This is possible only when Fe^{2+} ions interact with the OH^- ions formed upon the thermal decomposition of —OOH groups.

Results from different investigations provide independent information on the surface behavior under plasma treatment. Although AFM is a near-surface technique, XPS can penetrate somewhat deeper (4–6 nm) into the surface layers of the films. ATR, at the same time, could reveal information much deeper (micron range) within the film surface. A conclusive picture of the physico-chemical changes taking place at the surface can be derived from these observations, and has been shown in Figure 10. The two-step

plasma treatment, i.e., exposure to Ar plasma and contact with oxygen, leads to a surface that is hydrophilic in nature due to the formation of polar functional groups. At the same time, the roughness at the surface also appears. The magnitude of this physico-chemical change at the surface is time dependent. As the time of exposure increases, the surface becomes richer in oxygen functionality but also rougher. It is difficult to quantify the independent influence of both of these factors, but they contribute to the contact angle variation in films. The storage of treated films introduces surface reorganization and possible contamination from the atmosphere. Some of the active species on the surface may react with the atmospheric contamination instead of reacting with oxygen and is bound to change the contact angle. This is again a time-dependent process, and can be minimized at a lower temperature. Hence, the surface dynamics plays an important role in the development of the surface under pre- and postplasma treatment conditions.
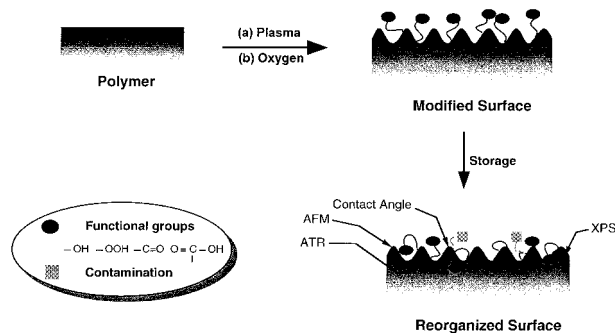
CONCLUSIONS

Plasma treatment of PET films under argon and subsequent exposure to oxygen leads to significant chemical as well as morphological changes on the surface. The surface acquires oxygen functionality in the form of hydroxyl, hydroperoxide, and carboxyl groups, which is reflected in a significant reduction in the contact angle of the film from 72.9 to 33.8° after 40 s treatment. Films treated beyond 40 s do not show any significant change in the contact angle. However, the plasma power has some influence on the contact angle

Figure 10   Schematic representation of the plasma-induced surface changes in PET films.

variation only for low treatment times. For a treatment time of 100 s, the contact angle was identical to the 40 s treatment time. This reflects that there is a threshold value for the minimum polarity that is required for the surface hydrophilization. This can be achieved faster at a higher power of 80 W. The roughness in the form of ridges at the surface, as evident from AFM measurement, also increases with the increase in the plasma treatment. A hill–valley wavy structure originates even at the early stage of plasma treatment. The number of ridges on surface does not change much, but their size increases linearly with the treatment time. The amplitude for these films varied in the range of 10–40 nm for the treatment of 20–100 s. Both the surface functionality and the surface morphology have their independent contribution to the contact angle variation. ATR measurements on films show the increase in the hydroxyl functionality at the surface. This was further confirmed by the XPS measurements, which showed that the oxygen content increases at the surface, and this is in the form of hydroxyl, hydroperoxides, carbonyl, and carboxyl groups. The modified surface is not stable with time, and undergoes rearrangement of the modified surface layers, leading to the incorporation of some of the functional groups within the surface layers. The surface reaches stability in 2 weeks time. Therefore, to characterize and use these surfaces, their time-dependent nature has to be taken into account.

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