Surface Modification of Polystyrene Using Nitrogen Plasma. An X-ray Photoelectron Spectroscopy Study

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Surface Modification of Polystyrene Using Nitrogen Plasma. An X-ray Photoelectron Spectroscopy Study

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A detailed X-ray photoelectron spectroscopy study of a plasma-modified polystyrene (PS) surface was carried out after N_2 plasma treatment. PS surfaces were found to be highly hydrophilic and reactive as it readily picks up oxygen giving rise to oxyfunctionalities on the surface. The plasma treatment also led to a slow chain scission with carboxyl, forming carbonate linkage.

Introduction

Surface modification methods are widely used on polymeric materials. The objective is to modify functionalities at the surface while retaining the desirable bulk properties of the polymer. One of the surface modification techniques, viz., plasma treatment, is very popular due to several advantages over other methods such as chemical oxidation, halogenation, and grafting. Plasma treatment for improving hydrophilicity of polymer surfaces is also an attractive technique from a commercial point of view as it is rapid and solvent/chemicals free. Most of the polymers such as poly(olefin), poly(ester), poly(amide), and fluoropolymers can be modified by exposing them to plasma for a few minutes without destroying their bulk properties. These plasma-treated polymers provide a good surface for adhesion and printing in addition to creating a diffusion barrier or to minimize the degradation of the polymer surface during metalization. Poly(styrene) is a popular substrate for disposable ware used in medical diagnostics, primarily, due to its optical transparency, durability, low cost, and good mouldability. These surfaces are usually modified by either plasma or corona discharge treatments (CDT) in order to obtain a hydrophilic or wettable surface while retaining its bulk properties intact.[1,2]

Many reports are available on glow discharge treatments which offer improved poly(styrene) surfaces for cell adhesion.[3,4] Several studies describe surface modification of poly(styrene) using oxygen plasma,[5] corona discharge treatments,[6] gamma irradiation,[7,8] electron beam modification,[9] argon plasma,[10,11] and Ar/H_2 plasma.[12] During plasma irradiation of the surface of polymer, a number of very stable polymer surface bonds have to be broken and linked with different functional groups.

It is well-known that plasma irradiation using an inert gas effectively creates stable free radicals on a polymer surface.[13] Most of the earlier work in the field of surface modification of polymers concerns the incorporation of oxygen on to polymer surface and its role in determining properties such as wettability, adhesion, printability, etc.[14] It is generally accepted that plasma irradiation results in the generation of polar groups on the outer few atomic layers of polymer substrate. However, surfaces modified by oxygen plasma have been shown to be most unstable with respect to both washing and aging.[15] On the contrary, far less is known about the nature of surface modification of poly(styrene) using nitrogen plasma. In this report we describe the detailed characterization of nitrogen plasma surface modified poly(styrene) surfaces using X-ray photoelectron spectroscopy [XPS].

Experimental Section

Materials. Poly(styrene) (PS) films were made by a solvent casting method using chloroform as solvent. Doubly distilled water was used for contact angle measurement. High-purity nitrogen gas was used for plasma treatment experiments. Contact angle measurements were made using an NRL contact angle goniometer, model 100-00-230, made by Rame Hart Inc. (USA) (2 μL size sessile drop method). The measurements were repeated several times at different places of the film after placing 2 μL of water, and an average of all the readings was obtained. For each contact angle measurement, duplicate films were used. All plasma-modified and unmodified films were also characterized by scanning electron microscope (Leica stereoscan, 440 model) using 10 kV EHT at various magnifications ranging from 1K to 5K.

Plasma Discharge. The plasma discharge treatment of films was carried out using a glow discharge reactor, bell type reaction cell jar model no. MARSH-MPS-300 chamber P M 600. Plasma conditions were as follows: pressure −170 mTorr; power 100 W; N_2 gas flow of 5 mL/min. The samples were kept at the center in a glass Petri dishes for plasma exposure and necessary precautions were taken to ensure homogeneous plasma treatment. After the plasma treatment for a prefixed time they were exposed to atmospheric conditions before keeping them in a desiccator. Contact angle measurement was carried out within 2 h of the plasma treatment.

XPS Measurement

XPS is an ideal technique for studying plasma-induced chemistry at the modified polymer surface because of its surface sensitivity (1−10 nm), its quantification of the

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Table 1. BE Values [In EV] of C(1s), O(1s), and N(1s) Species

time (s)	C I	C II	C III	C IV	O I	O II	O III	N I	N II	N III
0	285.0									
5	285.0	287.6	289.3		532.1	534.1	534.7	399.0	400.6	402.3
20	285.0	287.6	289.6		5532.	533.9	535.3		400.5	402.2
25	285.0	287.2	289.3		532.3	533.6	534.9		400.5	402.3
30	285.0	287.4	289.5	291.8	532.4	533.6	534.9		400.6	402.5
60	285.0	287.1	289.2	291.8	532.4	533.5	535.2		400.4	402.2
120	285.0	287.2	289.2	290.9	532.5	533.8	535.5		400.5	402.3
180	285.0	287.3	289.5	291.4	532.8	534.0	535.8		400.6	402.1
300	285.0	287.1	289.2	290.8	532.7	533.1	534.9		400.6	402.1

Table 2. Percentage Composition of Carbon, Oxygen, and Nitrogen

time (s)	C I	C II	C III	C IV	O I	O II	O III	N I	N II	N III
0	98.0				2.0					
5	63.6	12.1	2.9		6.2	11.2	3.3	0.2	0.4	0.2
20	61.2	11.4	4.3		6.8	12.5	3.1		0.4	0.2
25	57.7	11.7	5.4		10.8	11.2	1.8		0.4	0.2
30	57.6	9.7	6.2	1.3	9.2	11.9	3.5		0.4	0.2
60	55.9	9.6	6.4	1.8	12.9	11.1	1.6		0.5	0.3
120	59.7	9.3	5.3	2.6	9.3	11.9	0.4		0.7	0.7
180	59.1	9.0	5.1	2.1	10.1	12.8	0.6		0.3	0.6
300	59.2	8.7	4.8	1.5	8.5	14.6	1.9		0.4	0.4

results, and the information obtained about the nature of chemical bonding from the binding energy (BE) values. XPS studies were carried out using a VG Scientific ESCA-3-MK-II electron spectrometer fitted with a Mg Kα (1253.6 eV) X-ray source (nonmonochromatic). The anode was operated at 120 W (12 kV, 10 mA) and the analyzer was operated at a constant pass energy of 50 eV. All spectra were recorded with similar spectrometric parameters. The binding energy (BE) scale was calibrated by determining the BE of Au (4f$_{7/2}$) (84.0 eV) and Cu (2p$_{3/2}$) (932.4 eV) levels using spectroscopically pure metals obtained from Johnson-Matthey, London. The binding energy values (measured to an accuracy of ±0.2 eV) are in good agreement with the literature values.[16] The resolution in terms of full width at half-maximum (fwhm) of the Au(4f$_{7/2}$) level is 1.6 eV. The films were mounted on a stainless steel holder with double-sided tape. The peak shift due to surface charging was corrected using C(1s) levels at 285 eV as an internal standard. In all the cases C(1s), O(1s), and N(1s) levels were recorded. Elemental concentrations were calculated using the XPS peak area and corresponding photoelectron cross section.[17] The C(1s), O(1s), and N(1s) levels are very broad indicating the presence of multiple carbon and oxygen species. The XPS peaks were assumed to have Gaussian line shape and were resolved into individual components after proper subtraction of baseline using the Shirley background subtraction method.[18] The downhill-simplex method was used to minimize the fitting errors. The line width was allowed to vary in the range 2.0−2.4 eV to obtain a good fit.

Results and Discussion

Contact angle measurement showed a decrease from 88 ± 2° for unmodified film to 10 ± 2° with increasing exposure to nitrogen plasma from 5 to 300 s (Figure 1). This implies that a substantial concentration of polar functionalities is introduced at the surface after nitrogen plasma treatment. The XPS spectra of unmodified PS film show the presence of C(1s) core level at 285 eV having fwhm characteristic of aromatic ring with its shakeup

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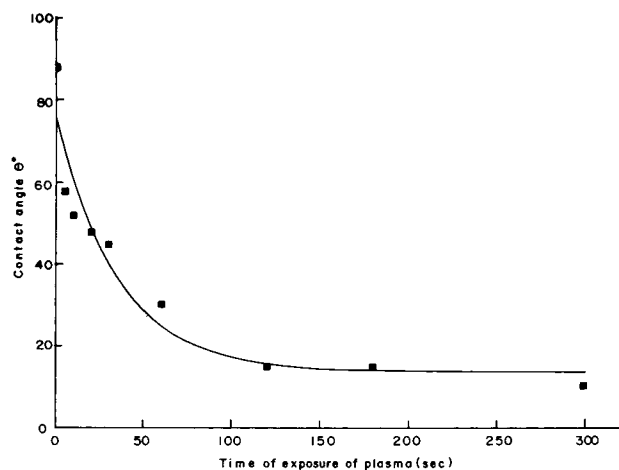
Figure 1. Dependence of contact angle on time of plasma exposure of PS film.

satellite at 292.5 eV. The presence of O(1s) level can be attributed to adsorbed oxygen on the surface (BE 532 eV), its concentration being very negligible. In addition its intensity is reduced further by abrading the surface. The XPS spectra of modified PS films showed a very weak but broad N(1s) peak. After the nitrogen plasma modification both the O(1s) and C(1s) levels broadened indicating a change in the surface composition. The resolved components of C(1s) and O(1s) and N(1s) with their BE values are given in Table 1. The C(1s) spectra had four components designated as CI, CII, CIII, and CIV (three components for plasma treatments up to 25 s and the fourth component appearing at higher exposure time—Table 1, Figure 2) whereas, the O(1s) level had three components designated as, OI, OII, and OIII (Table 1) and the N(1s) had three components NI, NII, and NIII for the 5 s plasma treatment and two components NII an NIII for rest of the treatments (Table 1, Figure 3). The incorporation of oxygen in polymeric surface after plasma treatment even with a non-oxygen-containing plasma is a common phenomenon.[19] It is well-known that during plasma treatment free radical intermediates play an important role. Free radicals thus formed react very fast

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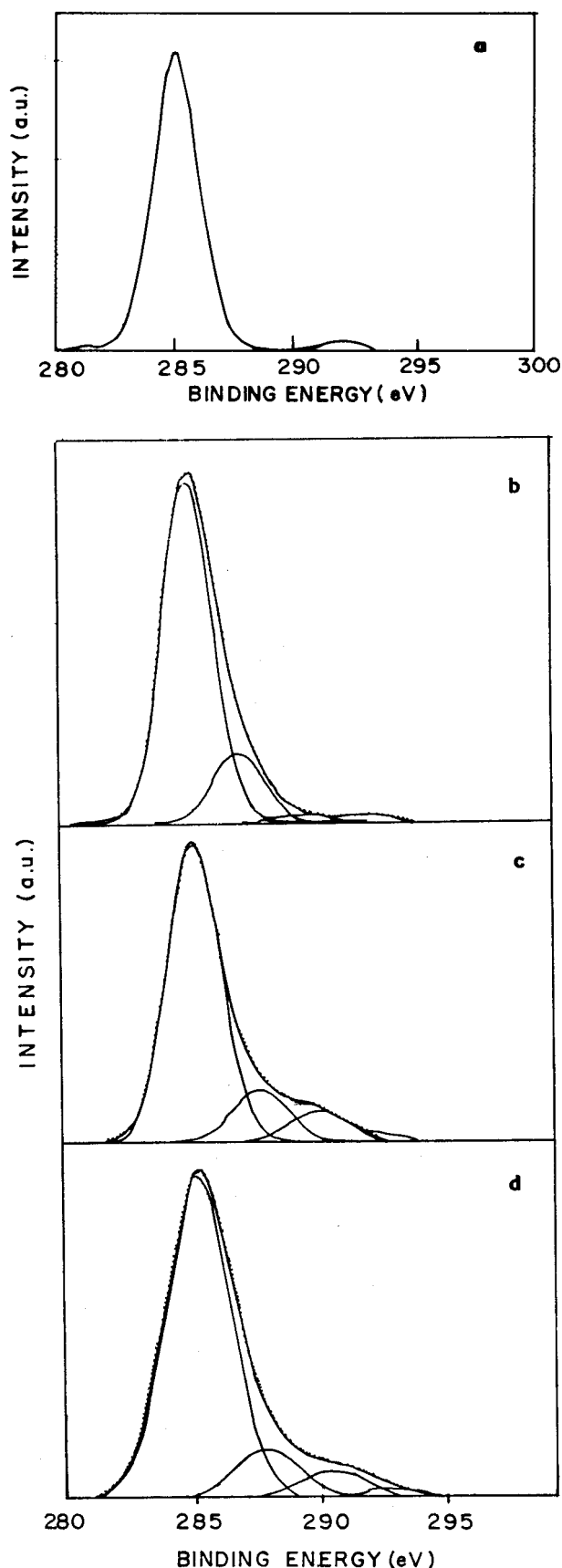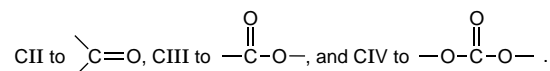
Figure 2. (a) C(1s) XPS spectrum of untreated PS film C(1s) XPS spectra of PS film after plasma treatment: (b) 5 s; (c) 30 s; (d) 300 s.

with the peroxy radicals leading to its incorporation on the polymer surface. This implies that a small amount of oxygen in plasma has great affinity to the treated surface

even though an oxygen atom need not necessarily be excited by plasma. Furthermore, after exposure, radical centers may still be on the surface, which will react with oxygen when the surface is exposed to the atmosphere.

The following BE values were assigned to the various C(1s) and O(1s) and N(1s) components: CI, 285 eV; CII, 287.4 eV; CIII, 289.4 eV; CIV, 291.3 eV; OI 532.7 eV; OII, 533.7 eV; OIII, 535.2 eV; NI, 399 eV; NII, 400.5 eV; NII, 402.3 eV (Figure 3). From the available literature values, CI is assigned to CH_2,

$$\text{CII to} \quad \overset{\diagdown}{\diagup}C{=}O, \quad \text{CIII to} \quad -\overset{\overset{\displaystyle O}{\|}}{C}-O-, \quad \text{and CIV to} \quad -O-\overset{\overset{\displaystyle O}{\|}}{C}-O- \ .$$

The corresponding O(1s) BE values were as follows. OI-532.7 eV assigned to CII bonded to oxygen, and OII will arise from oxygen bonded to CIII and CIV (Figure 2, Table 2). The O(1s) region is not very sensitive to changes in the chemical surroundings as it is observed that the experimental BE values for various oxygen species overlap over a broad region. In the present study, O(1s) from >C=O varies between 532.3 and 532.6 eV, the

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

varies between 532.9 and 533.5 eV, and

$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$
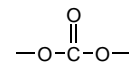
varies from 532.9 to 533.8 eV. The entire O(1s) region is spread between 532.3 and 533.9 eV. Hence it is not reliable to use the O(1s) data for any meaningful quantitative analysis. The NI component is assigned to amine, the NII to imine, and the NIII component is likely to arise from R−NHOH. The C(1s) component due to the amine is very close to 285.8 eV and that due to imine is 287 eV. Since C(1s) levels due to carbon−oxygen bond is also falls in this region and the intensity of nitrogen peak is very weak, no attempt is made to separate the C(1s) components arising out of carbon−nitrogen bonding. However, an attempt is made to quantify the percentage composition of various species on the surface by considering the peak area and the photoelectron cross section. The percentage composition is given in Table 2. It can be seen that the component CI decreases from 63.6% (5 s) to 56.4% (180 s) and then increases to 59.2% (300 s). The CII component starting with 12.1% for 5 s plasma treatment remains constant up to 25 s exposure and then decreases to 8.7%. The CIII component increases from 2.9% (5 s) to 6.4% (60 min) and then decreases to 4.8%. The CIV component starts forming after 30 min exposure increases to 2.6% at 120 min plasma treatment and finally drops to 1.5%. The decrease of CII, CIII, and CIV components with concomitant increase in the CI component clearly indicates that longer duration of plasma treatment leads to sputtering of the surface and, as a consequence, the loss of the modified surface. Up to 30 s of plasma exposure, all the three components namely, CI, CII, and CIII, are formed simultaneously. The first stage of surface modification could be the formation of CI and CII. It is very difficult to say whether the formation of CIII is due to the breakdown of CII or is an independent occurrence. The constant value of 12% for CII combined with the decrease in the value of CI can indicate that the surface is first modified to CII and then subsequently converted to CIII. The decrease in CIII combined with increase in CIV could
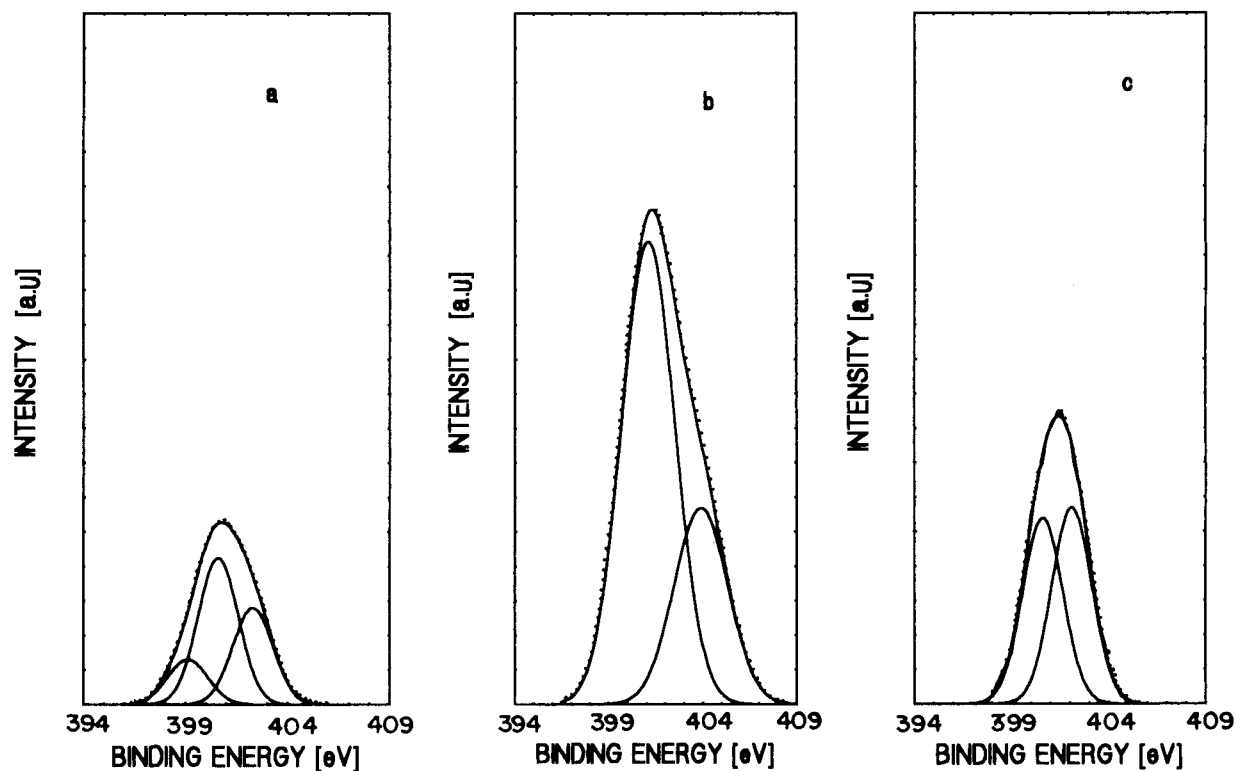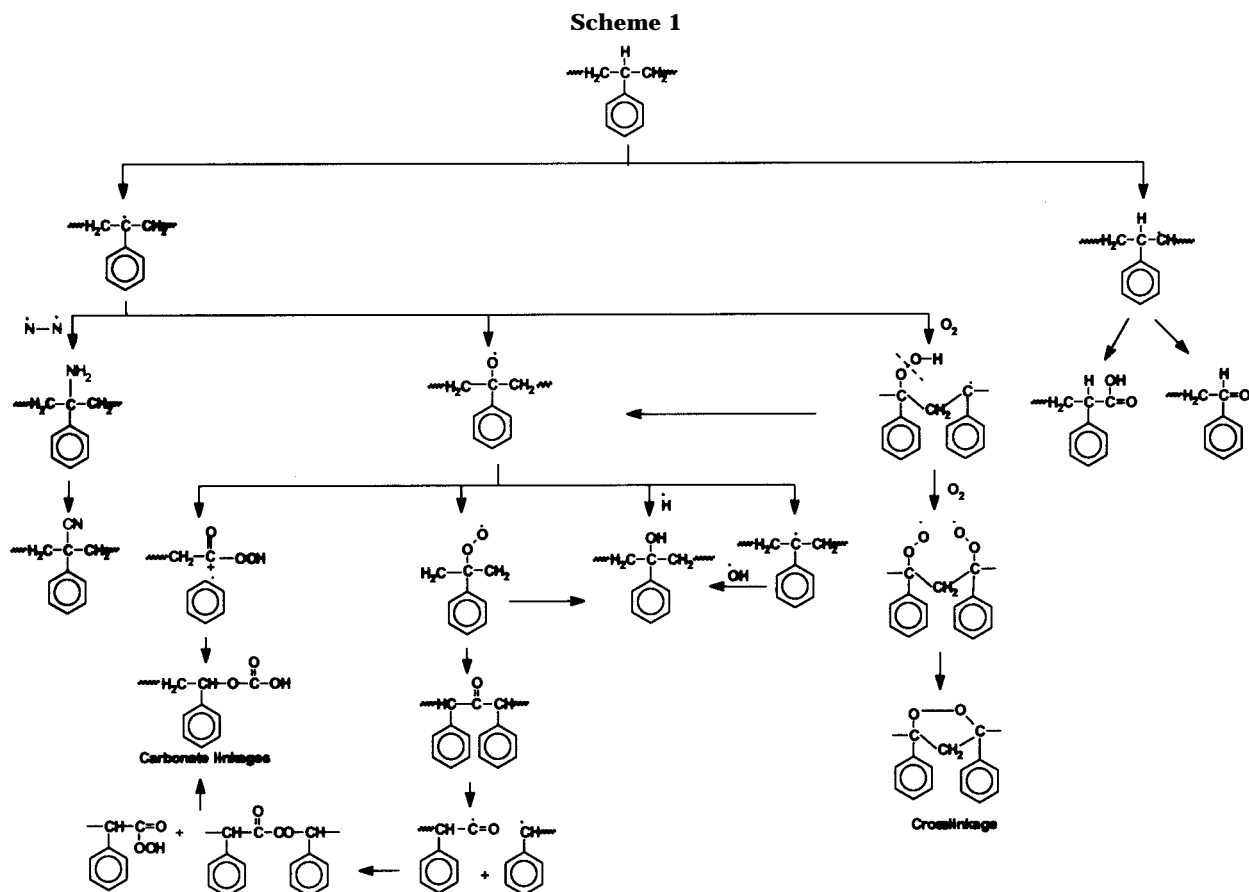
Figure 3. N(1s) XPS spectra after plasma treatment: (a) 5 s; (b) 30 s; (c) 300 s.
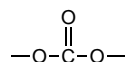
Scheme 1

clearly indicate that the component CIII gives rise to CIV on plasma treatment. The unmodified PS film shows a shakeup satellite at 292.5 eV which disappears after 30 s of exposure to plasma. Instead, a new peak develops at 291.3 eV after 2 min of irradiation, which could be due to the cleavage of a polymer chain giving rise to carbonate linkage. This carbonate linkage was assigned to highly oxidized groups such as peroxy acids and peroxy esters, which become more numerous during the later stages of oxidation.[20] Further prolonged exposure causes a decrease in intensity of this peak, presumably, due loss of functionalities on account of ablation or cross-linking. The

binding energy value combined with the absence of the satellite structure clearly shows that the peak is not due to an aromatic ring and the disappearance of the satellite structure is due to the splitting of the aromatic ring leading to the formation of the carbonate functionality. The C(1s) peak shows an increase in either

$$-\overset{|}{\underset{|}{C}}-O, \quad -\overset{|}{\underset{|}{C}}-OOH, \quad -\overset{|}{\underset{|}{C}}-OH, \text{ and } \quad \diagup\!\!\diagdown C=O$$
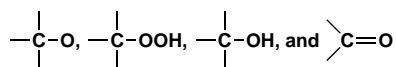
species along with

$$-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

linkages characteristic with COOH species. On the basis of surface speciation of plasma-treated PS films, a mechanism has been proposed and is shown in Scheme 1.

The loss of the N(1s) component from the modified PS surface can be explained as follows. We have used a direct plasma modification technique whereas the previous studies[21,22] used a remote plasma treatment method. In addition in the earlier studies the complete experiment was carried out in a reaction chamber which is directly attached to the XPS unit. After the plasma treatment the sample was transferred to the analyzer chamber without exposing it to the atmosphere. Further, before the experiment was started, the reaction chamber was pumped down to a pressure of 2×10^{-9} Torr. The incorporation of nitrogen on the surface of the polymer is dependent on several factors. The direct plasma method, which is a more destructive technique, may lead to sputtering of the implanted surface as compared to the remote plasma technique. The base pressure of the reaction chamber in the present study is of the order of 10^{-5} Torr. This also affects to a greater extent the incorporation of nitrogen on the surface. The minimum pressure inside the reactor before the start of the reaction should be very low, and as this pressure increases, the incorporation of nitrogen is greatly hampered. In our studies the pressure was 10^{-5} Torr as compared to the earlier studies which were performed with a starting pressure of 2×10^{-9} Torr. Another factor which can affect the incorporation of nitrogen is the recombination of nitrogen atoms at a rate faster than the reaction between the plasma and the polymer surface. To overcome this difficulty, dilution of the excited nitrogen with another gas such as argon was tried. In the present study the experiments were carried out with high-purity nitrogen without any dilution. Yet another factor is the durability of the modified polymer surface which tends to degrade as the surface is exposed to the atmosphere after the plasma treatment. In our study all of these causes could have led to the very low concentration of nitrogen observed on the surface.

Nitrogen plasma treated surface seems to retain functionalities better than oxygen-treated samples even though the depth of modification is nearly the same in both cases.[23] Nitrogen plasma-modified polymer surfaces were found to be less susceptible to surface reorganization

than oxygen plasma modified polymer surfaces.[24] Incorporation of CO along with CN functionalities can be explained by the generation of free radical sites on the polymer surface and its subsequent interaction with the atmospheric oxygen when these treated PS surfaces were removed from the plasma chamber. Only Gerenerser[25] obtained saturation level N/C ratio = 0.25 in the nitrogen plasma treated poly(ethylene) and was able to avoid oxygen uptake by carrying out all the experiments in the preparation chamber of the XPS spectrophotometer and thereby avoiding any exposure of the treated film to the atmosphere prior to surface analysis. In the present study no special precaution was taken to avoid exposure to oxygen after nitrogen plasma treatment. As shown in Table 2 the O/C ratio increased when irradiation time increased from 5 to 60 s. Beyond 60 s the O/C ratio decreases. This implies that a significant concentration of oxyfunctionalities was introduced after plasma irradiation. The $\pi-\pi^*$ shakeup satellite observed in the unmodified PS, which is indicative of aromaticity, was found to decrease rapidly in intensity even for smaller duration of irradiation to plasma (<30 s) and was undetectable at higher irradiation times (>30 s). However, its detection at longer irradiation time was difficult due to the presence of an oxygen bearing functionality observed in the binding energy region $285-292$ eV. The reduction in the intensity of the satellite structure is indicative of the pendant aromatic ring site being one of the major sites of attack by nitrogen plasma.

Multifunctional surfaces produced by plasma exposure creates a severe characterization problem because of the strong overlap of the individual components in the XPS core level spectra, where the peaks under study tend to broaden due to the presence of several elements being present on the surface in different chemical environments. It is possible to overcome this difficulty by using a specific derivatization agent which preferentially reacts with one of the functional groups and labels it with a distinctive element.[26] Previous studies employed the liquid-phase reaction which can lead to surface reorganization through solvent-induced transport effects and material loss. A gas-phase reaction is often more suitable such as functionalization of

$$-\overset{|}{\underset{|}{C}}-OH$$

groups using trifluroacetic anhydride vapors (TFA).[27] Modified PS films were exposed to TFA vapors under dry conditions for 3 h in a sealed vessel followed by flushing with nitrogen. The XPS of derivatized sample was recorded. For comparison a fresh PS sample (unmodified) was also subjected to similar treatment. Unmodified PS film did not show the presence of F(1s) levels. However, modified PS film showed the presence of a F(1s) peak at BE 689 ± 0.2 eV, characterstic of the F bonded to the polymer surface. Keto and aldehyde functionality was evidenced by DNPH derivatization as described earlier.[28] Peaks due to of N(1s) levels derived from C=N and C−NO$_2$ were observed at 400 and 407 eV, respectively.

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Conclusion

N$_2$ plasma irradiation of PS surfaces generate highly hydrophilic surfaces which are reactive, picking up atmospheric oxygen leading to the generation of oxyfunctionalities. Beyond 30 s irradiation slow chain scission is observed leading to the generation of carboxyl and carbonate linkages. This is evidenced by the absence of shakeup satellites, characteristic of the aromatic ring. In addition, an increase in the O/C ratio is observed up to 60 s irradiation followed by a decrease indicating the occurrence of ablation or cross-linking. A few seconds of plasma exposure is sufficient to cause a deep-rooted change in the surface properties of PS. The nitrogen-plasma-treated PS surface appears more stable than the corresponding oxygen-treated surface.

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