X-ray Photoelectron Spectroscopy Study of Sulfonated Polyethylene†

4 AUTHORS, INCLUDING:

Susheela Idage
CSIR - National Chemical Laboratory, Pune
29 PUBLICATIONS **189** CITATIONS

SEE PROFILE

Swaminathan Sivaram
CSIR - National Chemical Laboratory, Pune
227 PUBLICATIONS **3,316** CITATIONS

SEE PROFILE

X-ray Photoelectron Spectroscopy Study of Sulfonated Polyethylene[†]

S. B. Idage, S. Badrinarayanan, S. P. Vernekar, and S. Sivaram*

Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

Received May 19, 1995. In Final Form: August 28, 1995[⊗]

Detailed X-ray photoelectron spectroscopy analysis of sulfonated high-density polyethylene (HDPE) prepared by using a gaseous mixture of $SO_3 + N_2$ was carried out. It was shown that the surface contains, apart from sulfonic acid groups, sulfate, keto, and polyene linkages. The evolution of the different surface groups depends upon the conditions of sulfonation.

Introduction

The modification of organic polymer surfaces is a subject of theoretical and practical importance.[1−3] The chemistry of polymer surfaces is important to such diverse phenomena as polymer degradation and fabrication of biocompatible devices. Interfacial chemistry of polymers is relevant to many applications of polymer materials, such as adhesion, wetting, compatibility, and gas/liquid permeability.

Modification of polyethylene surfaces has attracted increased attention in recent years.[4] Polyethylene is a relatively inert hydrocarbon, wherein there is considerable incentive for introducing polar functional groups on the polymer surface. One such reaction of interest is sulfonation, which introduces SO_3H groups on the polymer surface. Sulfonation of polyethylene can be carried out in several ways. One method involves the use of fuming sulfuric acid.[5−7] In this reaction, there can be substantial polymer degradation. A more controlled method of surface sulfonation involves the use of gaseous SO_3, suitably diluted with nitrogen to moderate the reactivity of the sulfonating agent.[8,9] Gas phase sulfonation of polyethylene is industrially practiced to impart superior hydrocarbon barrier properties to high-density polyethylene (HDPE).[10] Sulfonation with SO_3 also improves the gas barrier properties of polyethylene.[11]

In spite of widespread interest, there has been no attempt in the literature to identify the nature of surface functionalities in sulfonated polyethylenes. Ihata,[8] on the basis of IR, UV, and Raman spectral evidence, concluded that sulfonation of polyethylene is accompanied by formation of long polyene sequences. However, the conditions of sulfonation were such that substantial reaction in the bulk is anticipated.

We, therefore, undertook a detailed examination of sulfonated polyethylene surfaces with a view to speciate the nature of functional groups formed upon sulfonation using X-ray photoelectron spectroscopy.[12] This paper reports the results of this study.

Experimental Section

Materials. HDPE films (Hostalen grade GK 7740, MFI (190/5) = 1 g/10 min, $d = 0.945$ g/cm³, 100 μm thick) obtained from Polyolefin Industries Ltd., Bombay, India, were used for sulfonation without any pretreatment. The films were exposed to a gas mixture of $SO_3 + N_2$ at a constant flow rate (250 mL/min). Two different sets of experimental conditions were used, namely, (1) the volume percent (3.75%) of SO_3 gas in the mixture was kept constant and the film was exposed at various intervals of time between 2 and 15 min and (2) the time of exposure was kept constant at 5 min and the percentage of SO_3 gas in the mixture was varied from 3 to 10 vol %. After sulfonation the films were repeatedly washed with distilled water to remove any traces of sulfuric acid and dried at 28 °C. These films are designated as PE-[SO_3H]. Typical properties of sulfonated films used in the present study are given in Table 1.[13]

Analyses. FTIR-ATR spectra were recorded (32 scans) using a Nicolet 60SXB Fourier transform infrared spectrometer using an ATR attachment with a KRS5 crystal at 45°. UV−Vis spectra were recorded using a Hewlett Packard 8452A diode array spectrophotometer. Contact angles were measured using a Rame Hart Inc. NRL-CA goniometer Model 100-00-230 with triply distilled water (2 μL = typical drop size used in this work) and the sessile drop technique.

XPS Measurement. X-ray photoelectron spectroscopy (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 (non-monochromatic). 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 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. 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 adhesive tape. The peak shift due to surface charging was corrected using the C(1s) level at 285 eV as an internal standard. In all the cases C(1s), O(1s), and S(2p) levels were recorded. Elemental concentrations were calculated using the XPS peak areas and the corresponding photoelectron cross sections.[14] The O(1s), C(1s), and S(2p) levels are very broad and possess multiple peaks. The XPS peaks were assumed to have Gaussian line shape and were resolved into individual components after proper subtraction of base line using the Shirley background subtraction

[†] NCL Communication No. 6281.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Feast, W. J., Munro, H. S., Eds. *Polymer Surfaces*; John Wiley and Sons: Chichester, 1987.

(2) Clark, D. T., Feast, W. J., Eds. *Polymer Surfaces*; Wiley: Chichester, 1978.

(3) Bergbreiter, D. E. In *Chemically Modified Surfaces*; Mottola, H. A., Steinmetz, J. R., Eds.; Elsevier: Amsterdam, 1992, p 133.

(4) Bergbreiter, D. E. *Prog. Polym. Sci.* **1994**, *19*, 529.

(5) Olsen, D. A.; Osteraas, A. *J. Polym. Sci., Part A*: *Polym. Chem.* **1969**, *7*, 1913.

(6) Bergbreiter, D. E.; Kabza, K. *J. Am. Chem. Soc.* **1991**, *113*, 1447.

(7) Fischer, D.; Eysel, H. H. *J. Appl. Polym. Sci.* **1994**, *52*, 545.

(8) Ihata, J. *J. Polym. Sci., Part A*: *Polym. Chem.* **1988**, *26*, 167.

(9) Gibson, H. W.; Bailey, F. C. *Macromolecules* **1980**, *13*, 34.

(10) *Plastic Technol.* **1989**, January, 27.

(11) Sabne, M. B.; Thombre, S. M.; Patil, A. S.; Patil, S. D.; Idage, S. B.; Vernekar, S. P. *J. Appl. Polym. Sci.* **1995**, *58*, 1275.

(12) Briggs, D., Seah, M. P., Eds. *Practical Surface Analysis*; John Wiley and Sons: New York, 1990; Vol. II, p 462.

(13) Patil, S. D.; Idage, S. B.; Sabne, M. B.; Patil, A. S.; Vernekar, S. P. To be submitted for publication.

(14) Scofield, J. H. *J. Electron. Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

Table 1. Properties of Films Used for XPS Analysis

time of sulfonation (min)	absorbance[a] ratio (A_{1040}/A_{2900})	integrated area[a] ν_s SO$_3^-$ at 1040 cm^{-1}	SO$_3$H[b] content ($\times 10^8$mol/cm^2)	contact angle[c] θ (deg)
0				98
2	0.53	1.7	0.25	70
5	0.92	5.2	5.50	50
7	1.23	7.5	11.00	37
10	1.76	12.8	18.00	32
15	2.55	22.6	31.75	22

[a] Determined by FT-IR-ATR at 45° with the KRS5 crystal. [b] Determined according to ref 9. [c] H$_2$O (triply distilled, 2 μL, using the sessile drop technique).

Table 2. Elemental Concentration of Sulfonated Films

time (min)	S/C	O/C	Br/C
0		<0.03	
2	0.029	0.101	
5	0.051	0.182	0.025
7	0.064	0.246	
10	0.085	0.266	0.098
15	0.096	0.273	0.116

method.[15] 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. In the case of the S(2p) level, both the line width and S(2p$_{1/2}$)−S(2p$_{3/2}$) separation were allowed to vary. Though the S(2p$_{1/2}$)−S(2p$_{3/2}$) separation was allowed to vary in the curve fitting program, we always obtained a value in the range 1.2−1.3 eV, which is very close to the theoretically expected value of 1.19 eV.
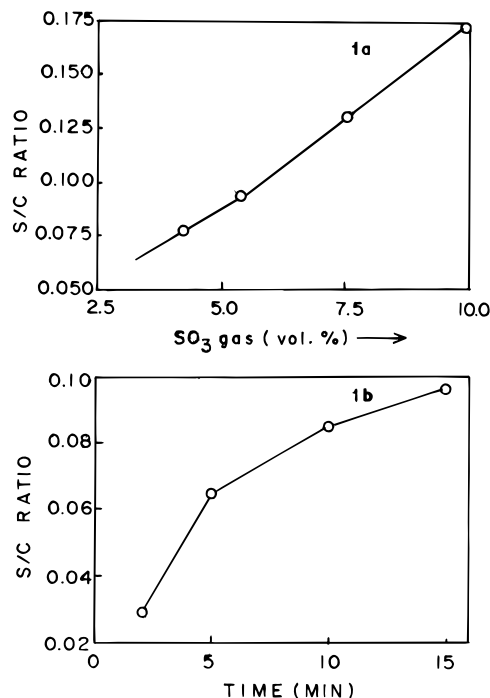
Sulfonated HDPE films may degrade upon exposure to X-rays. Hence, all spectra were recorded using a low X-ray power and a pass energy of 50 eV (to obtain a high count rate). The recording time for each spectrum was also kept to a minimum to avoid radiation-induced damage. In addition, the C(1s) spectra were recorded twice for each sample, once at the beginning and again at the end of the recording to monitor the changes, if any, taking place under exposure to X-ray radiation. No change in the spectral features of the C(1s) level was observed indicating that the surface composition remains unchanged during the time interval of recording the spectra.

Derivatization of PE-[SO$_3$H]. (a) Bromination. The sulfonated films were kept in a solution of 0.2 M Br$_2$ in CCl$_4$ (15 mL) for 12 h at 28 °C in the dark. The films were repeatedly washed with an excess of CCl$_4$ and cleaned ultrasonically in methanol at 45 °C to ensure that they were free from adsorbed bromine.

(b) Reaction with 2,4-Dinitrophenylhydrazine (DNPH). The sulfonated films were allowed to react with 2,4-dinitrophenylhydrazine in acidic ethanol at 28 °C for 1 h.[16] After the reaction, the films were Soxhlet extracted with ethanol to remove any adhering DNPH species and dried at 28 °C in an N$_2$ atmosphere for 24 h. The absence of free DNPH was confirmed by UV−Vis spectroscopy.

Results and Discussion

C(1s) Spectra. For all the samples under study, the XPS spectra of C(1s), O(1s), and S(1s) levels were recorded. The virgin HDPE film showed the presence of an Si(2p) level in addition to C(1s) and O(1s) levels. The presence of both O(1s) and Si(2p) levels is not surprising because polyethylene is known to be susceptible to slow environmental oxidation[17] and silicon contamination is frequently observed at the surface of HDPE films.[18] Since Si is insensitive to the experimental reactions, no attention was paid to its presence on the surface of the films.

(15) Shirley, D. A. *Phys. Rev.* **1972**, *B5*, 4707.
(16) Kato, K. *J. Appl. Polym. Sci.* **1977**, *21*, 2735.
(17) McKeller, J. F.; Allen, N. S. *Photochemistry of man made polymer*; Applied Science Publishers: London, 1979.
(18) Ratner, B. D. *Treatise on clean surface technology*; K. L., Mittal, Ed., Plenum Press: New York, 1987; p 247.

Figure 1. Effect of SO$_3$ gas concentration vs S/C ratio for 5 min. Effect of exposure time of sulfonation vs S/C ratio.

The XPS spectra of the films exposed to SO$_3$ showed the presence of C(1s), O(1s), and S(2p) levels. The relative intensities of S(2p) and O(1s) species show good reproducibility (0.5%) when the experiments were repeated under identical conditions. The degree of sulfonation depends upon the time of exposure as well as the percent SO$_3$ in the gas (SO$_3$ + nitrogen) mixture.

A steady increase in the sulfur species on the surface of the film is observed with both the time of sulfonation and increasing volume percent SO$_3$ in N$_2$ (Figure 1a and b). The C(1s) spectra showed a distinct tailing at the high-BE side which is attributed to the appearance of oxy functionalization after sulfonation. It is known that sulfonation is generally accompanied by some degree of oxidation and/or the formation of some conjugated double bonds.

The C(1s) spectra of the sulfonated HDPE film was very broad. This was resolved into two components CI and CII. The BE values of CI and CII are 285 and 287.5 eV, respectively. The sulfonated HDPE films are expected to have four carbon peaks due to CH$_2$-CH$_2$, C-S (covalently bonded), C-O-S, and C=O bonds. The CI peak is assigned to the presence of CH$_2$−CH$_2$ and C−S bonds. Since the difference in the BE values between the C(1s) levels due to CH$_2$−CH$_2$ and C−S species is very small (0.4 eV), it is not possible to differentiate them under the present conditions of instrumental resolution. Similarly, the C(1s) peaks due to the presence of C−O−S and C=O are also expected to give a peak around 287.5 eV and hence the CII peak is assigned to these two species. The presence of the CII component on the surface is found to increase with the time of exposure to SO$_3$ gas and also with higher volume percent SO$_3$ gas in the mixture. The CII component is mainly due to keto functionalities, and hence an increase in CII intensity is an indication of the increase in the percentage of keto groups. The presence of carboxyl species on the surface will give rise to a C(1s) level at 289 eV. In the present study no C(1s) level at 289 eV was observed, clearly ruling out the possibility of the presence of this species on the surface.

The CII component can also arise due to C−O−SO$_3$H species. To confirm the BE of the C(1s) peak of the carbon
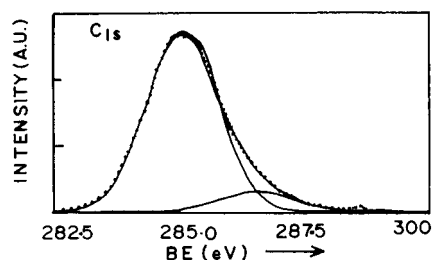
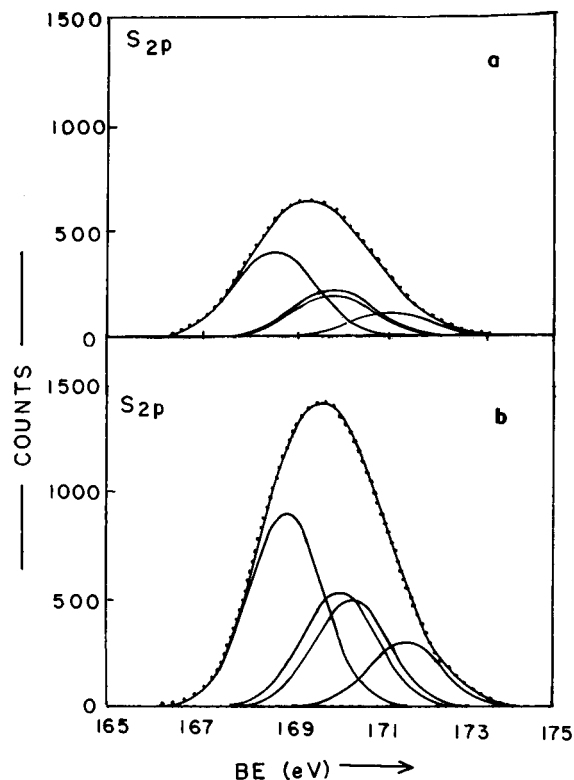**Figure 2.** C(1s) spectrum of sodium lauryl sulfate.

Figure 3. S(2p) core level spectra of PE-[SO$_3$H] for (a) 2 min and (b) 15 min.

Table 3. BE of Sulfur (S(2p)), Carbon (C(1s), CI, and (CII) species), and Bromine (Br(3d)) Levels

time of exposure (min)	SI (eV)	SII (eV)	CI (eV)	CII (eV)	Br(3d) (eV)
0			285		
2	168.7	170.0	285	287.7	70.39
5	168.3	169.4	285	287.5	70.77
7	168.7	169.8	285	287.4	
10	168.9	170.5	285	287.5	70.44
15	169.1	170.6	285	287.3	70.49

attached to O$-$SO$_3$H, we recorded the XPS of a model compound, namely, sodium lauryl sulfate (CH$_3$(CH$_2$)$_{10}-$CH$_2-$OSO$_3$Na). The XPS spectra is shown in Figure 2. Two C(1s) levels are observed as expected with BE values of 285 and 287.5 eV. The high-BE peak is assigned to CH$_2-$O$-$S bonding. The ratio of C(285)/C(287.5) eV is nearly 11 as expected.

S(2p) Spectra. In general the S(2p) levels show similar changes when HDPE films are either subjected to a higher concentration of SO$_3$ in the gas mixture or exposed to a longer duration of time. The BE value of the sulfur species present on the surface indicates that they are present in the highest oxidized state. The S(2p) level was very broad and further developed asymmetry upon increasing the time of exposure to SO$_3$ gas or a change in the percent SO$_3$ gas concentration. The fwhm in the S(2p) level is a clear
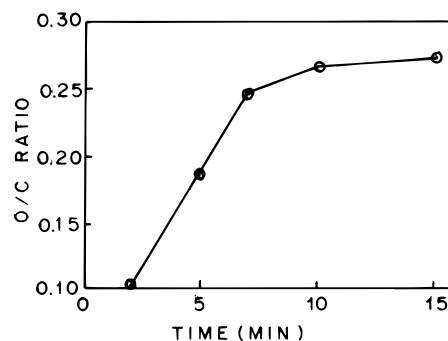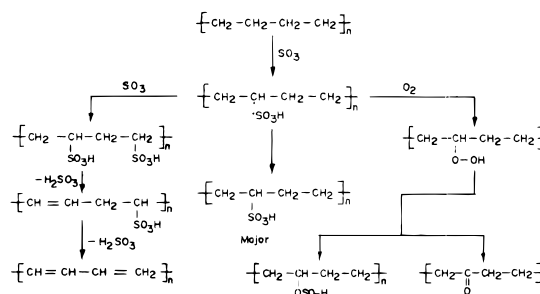

Figure 4. Effect of exposure time of sulfonation vs O/C ratio at 3.75% SO$_3$ gas.

Scheme 1

indication of sulfur species in two different chemical environments. The S(2p) level was resolved into two pairs of Gaussian components. The spin$-$orbit splitting separation was allowed to vary during the fitting. The BE values of the two S(2p$_{3/2}$) components are 168.9 and 170 eV, designated SI and SII, respectively (Table 3 and Figure 4). These are assigned to alkanesulfonic acid (C$-$SO$_3$H) (SI) and alkyl hydrogen sulfate (C$-$O$-$SO$_3$H) (SII). A study of sulfonated PE films by IR spectroscopy by Fonseca et al. clearly showed the presence of two similar species.[19] It is clear from Figure 1a that with increasing percent SO$_3$ (exposure for 5 min), the ratio of S/C shows a steady increase. Similarly, the ratio of S/C showed a steady increase when the time of exposure was changed from 2 to 15 min under constant percent SO$_3$ (3.7%) (Figure 1b, Table 2). These two species can arise from the corresponding sulfonic acid by free radical mechanism as well as from the reaction of peroxy radical with SO$_3$ radical giving rise to a keto group and alkyl hydrogen sulfate.

XPS spectra were also recorded at different grazing angles (30° and 75°) of electron ejection, which effectively reduces the escape depth and provides information regarding the nature of the surface species. However, the S(2p) component does not vary appreciably at different grazing angles, indicating that sulfonic acid species may be uniformly distributed, within XPS depth, in the HDPE film.

In all cases the major peak is at BE 169 eV indicating that most of the sulfur species are in the form of sulfonic acid (C$-$SO$_3$H) (Scheme 1).

O(1s) Spectra. In general the intensity of the O(1s) level was found to increase with the time of exposure to SO$_3$ as evidenced by the increase in the O/C ratio as shown in Table 2 (Figure 3). This trend indicates an increase in the oxygen functionalities introduced after sulfonation. This is clearly due to the formation of two oxygen-containing species C$-$OSO$_3$H and C$-$SO$_3$H, along with some contribution from the ketone functionality. The O(1s) level, in general, was resolved into three peaks with

(19) Fonseca, C.; Perena, J. M.; Fatou, J. G.; Bello, A. *J. Mater. Sci.* **1985**, *20*, 3283.
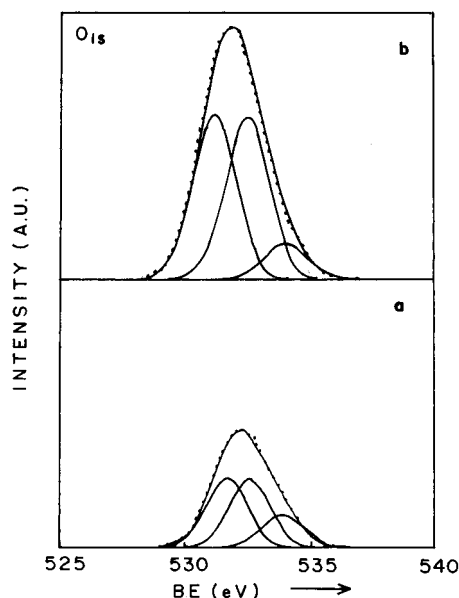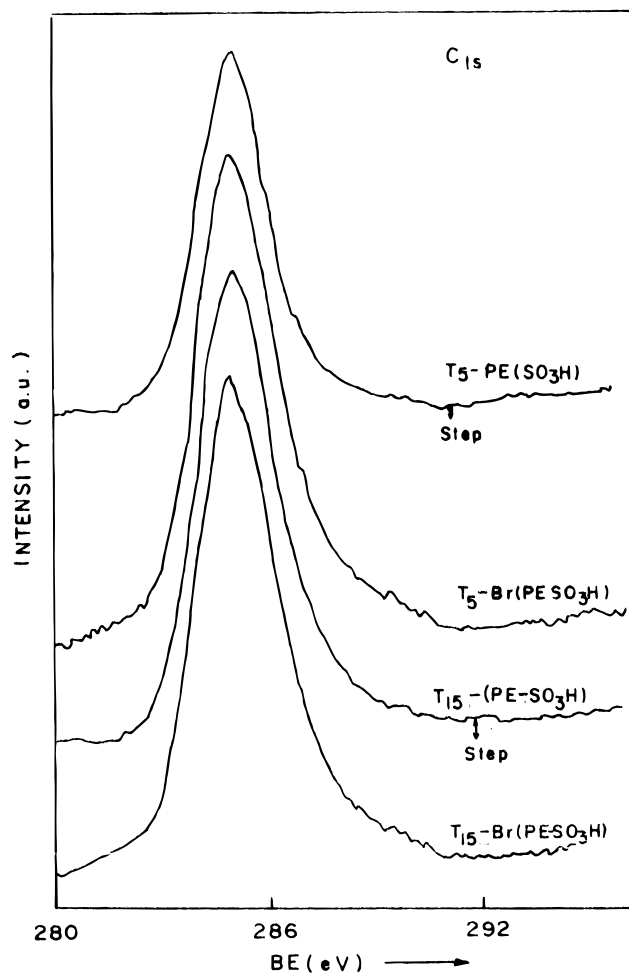
Figure 5. O(1s) core level spectra of PE-[SO$_3$H] for (a) 2 min and (b) 15 min.
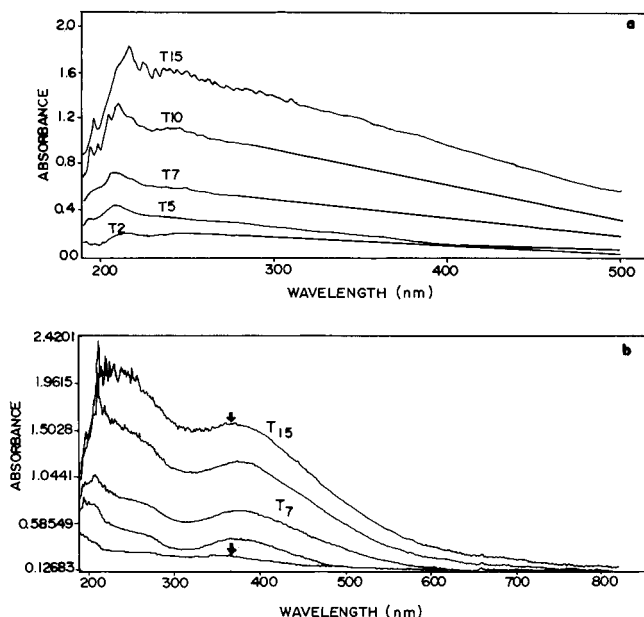
Figure 6. UV spectra of PE-[SO$_3$H] films (a) before and (b) after hydrazone derivative formation.

Figure 7. C(1s) core level spectra of PE-[SO$_3$H] (a) 5 and 15 min before PE-[SO$_3$H] bromination and (b) 5 and 15 min after bromination, Br(PE-[SO$_3$H]) and Br(PE-[SO$_3$H]).

BE values of 531.7, 532.2, and 533.7 eV. The 531.7 eV peak was assigned to O(1s) from sulfonic acid. The 532.2 eV peak is assigned to a keto functionality and the peak at 533.7 eV to the formation of the hydronium salt of the sulfonic acid, along with a contribution from C−OSO$_3$H species (Figure 5).

We have made an attempt to quantify the XPS data using the peak area and the photoelectron cross section values. The C(1s) level designated CII (287.5 eV) has contributions from C=O and C−OSO$_3$H. Their relative concentration on the surface is difficult to estimate. Further, the starting HDPE film showed the presence of both O(1s) and Si(2p) levels. Si is expected to be present in the form of SiO$_2$, and the corresponding O(1s) level is expected to have a BE value around 531−532 eV. In addition, slow environmental oxidation can give rise to an O(1s) level around 531−532 eV. All these factors lead to uncertainty in making a quantitative analysis. However, an attempt was made to quantify the data using the sulfur species. The ratio CI(285 eV)/SI(169 eV) decreases

from a value of 50 at $t = 2$ min to 16 at $t = 15$ min, indicating that the film is increasingly sulfonated. However, the ratio of SI/SII remained unchanged (SI/SII is nearly 2) indicating that these species are formed in the same ratio. The ratio of OII/OIII shows an increase from 2 to 4.5. This could imply either an increase in the C=O component or a reduced concentration of the hydronium salt at a higher degree of sulfonation, or both. However, the fact that the ratio of OIII/SII decreased from 1.8 at $t = 2$ min to nearly 1 at $t = 15$ min favors the latter hypothesis.

To further confirm the presence of a keto group the sulfonated films (after recording XPS) were derivatized with 2,4-dinitrophenylhydrazine (DNPH) to form a hydrazine derivative. The modified films were analyzed by XPS. The presence of the hydrazone derivative was confirmed by UV−Vis spectroscopy which showed λ_{max} at 365 nm[16] (Figure 6). The intensity of this peak increases with the time of sulfonation showing that the concentration of keto group increases. The films after DNPH treatment lead to a product which exhibits two nitrogen species as expected with BE values of 400 and 407 eV which are assigned to (>C=N−NH−) and NO$_2$, respectively.

Furthermore, the presence of unsaturation in sulfonated PE was confirmed by bromination of the PE-[SO$_3$H] samples. The XPS spectra of brominated PE-[SO$_3$H] show the presence of Br(3d) levels. On the contrary, the virgin HDPE film upon treatment with bromine does not show the presence of a Br(3d) level, indicating the absence of any significant degree of unsaturation. The BE of Br(3d) (70.5 eV) (Table 3) is characteristic of bonded Br (C−
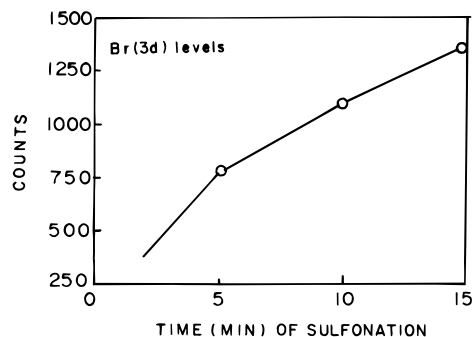
Figure 8. Bromination of PE-[SO_3H] vs Br(3d) levels (counts).

Br).[20,22] The observed BE of C—Br is within the expected range as shown in Table 3. The surface concentration of bromine increased with the time of sulfonation (Table 2). This indicates that unsaturation increases steadily as sulfonation proceeds. The increase in unsaturation upon sulfonation gives rise to both a bathochromic and a hyperchromic effect in UV reflectance spectroscopy. This is indicative of the formation of conjugated double bonds and results in step formation in the background in the C(1s) XPS spectra due to polyene formation[8] (Figure 7). Upon bromination, this step in the background disappeared completely. As the extent of bromination (unsaturation) increased, the intensity of the Br(3d) level also increased (Figure 8) and correspondingly the step in the background disappeared.

(20) Wagner, C. D. *J. Vac. Sci. Technol.* **1978**, *15*, 518.

(21) Munro, H. S.; Grunwald, H. *J. Polym. Sci. Polym. Chem.* **1985**, *23*, 479.

(22) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers*; John Wiley & Sons: New York, The Scienta ESCA300 Database; 1992; p 274.

A distinct shake up satellite in polymers such as polybutadiene and polystyrene due to the presence of unsaturation is well-known. As conjugation is increased, the number of allowed shake up transitions increases. It has been shown that the shake up component of the C(1s) spectrum broadens over a wider range of energies. As a consequence, the asymmetry of the direct photoionization peak increases and a step in the background is obtained.[21] In the sulfonated film, it is evident that there is an asymmetric tailing to higher binding energy leading to a step in the background level going from the low-BE side to the high-BE side. The presence of this step in the C(1s) level can be taken as evidence of the existence of extensive unsaturation in PE-[SO_3H]. This unsaturation appears to be predominantly of the conjugated type. The step in the background increases with the sulfonation time and vanished after bromination, confirming that this step is due to the presence of polyene (Figure 7). On the basis of surface speciation of PE-[SO_3H], a mechanism of gaseous sulfonation on HDPE films has been proposed and is shown in Scheme 1.

Conclusions

Detailed XPS analysis of sulfonated high-density polyethylene PE-[SO_3H] prepared by using a gaseous mixtures of $SO_3 + N_2$ shows the presence of a number of functional groups. These are PE-(SO_3H), PE-(OSO_3H), PE-(C=O), and polyene unsaturation sequences. The presence of ketone and unsaturation was unequivocally established by XPS characterization of derivatized surfaces. The effect of volume percent SO_3 in the $SO_3 + N_2$ mixture and reaction time on the evolution of various functional groups was established.