Energy Transfer from an Argon Plasma to a Polystyrene Surface

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Abstract

Polystyrene (PS) surfaces have been modified with an RF argon plasma and the surface chemistry investigated with X-ray photoelectron spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF SIMS). These surfaces show a high selectivity to carbon singly bonded to oxygen and are stable to methanol rinsing up to an O/C ratio of 0.20. There is evidence to suggest some of the hydroxyl groups are present at ring sites on the PS. Mass spectrometry of the plasma shows a significant amount of protonation is occurring in the plasma.

Introduction

Surface treatments are widely used on polymeric materials, to overcome such problems as poor wettability and biocompatability. The primary requirement for any treatment is to modify the surface without affecting the bulk properties. One method which is receiving much attention is that of plasma treatment, particularly as the treatment is limited to the outermost 1-3nm (1). In order to assess changes in surface chemistry a number of surface analytical techniques have been used; these include XPS (1), SIMS (2) and infrared spectroscopy (3).

Oxygen plasmas have received the most attention. However, in previous studies, the modifications effected have been non-selective (usually due to over treatment) producing a wide range of new functionalities in the polymer surface. Plasma oxidised polymer surfaces have been shown to be unstable (4) with respect to both washing and ageing. The reactive species in a plasma, result from ionisation, fragmentation and excitation processes (caused by electron impact and to a lesser extent, photon absorption). These species include positive and negative ions, neutral species, atoms, metastables and free radicals (in ground and excited states). This means that the plasma chemistry, even of a monatomic gas, is extremely complex. When a plasma is brought into contact with a polymeric material, the number of possible reactions that may occur is very large. This is particularly the case with an oxygen plasma, where oxygen atoms play a dominant role in the mechanism, causing ablation and the formation of small volatile degradation products (5). To specifically study

plasma-polymer interactions (with so many possible reaction pathways available), it is wise to reduce the complexity of the system in order to reduce the number of variables. One way of achieving this is by the use of inert gas plasmas, where energy transfer is the only process occurring; i.e. there is no possibility of chemical reaction between the plasma gas and the polymer surface. Energy transfer occurs through direct energy transfer from ions and metastables, and radiative energy transfer from UV radiation (6). Whilst an inert gas cannot react with the polymer surface, unless the reactor is directly interfaced to the spectrometer, the effects of post treatment storage must be taken into consideration.

In a previous study (7), we showed the importance of storage conditions after treatment. We also considered the stability of Ar plasma treated surfaces with respect to washing and ageing. Enhanced selectivity of certain functionalities was achieved with argon treatments. The objectives of the present study are :

(1) Re-investigate the effects of plasma treatment time (the pressure in the plasma chamber in this study being 10^{-2}mbar, a decade lower than the previous study).

(2) Examine the molecular structure of these treated surfaces, using ToF SIMS.

(3) Carry out a preliminary investigation of plasma chemistry, utilising a quadrupole mass spectrometer interfaced to the plasma chamber.

Experimental

PS was supplied by Aldrich Chemical Co., UK, and had a molecular weight of 280 000. Free standing films were solution cast from toluene. All glassware was rigorously cleaned and soaked in Nitric acid prior to being rinsed in Aristar grade Methanol. Samples were treated in an inductively coupled RF plasma reactor. Argon was obtained from BOC, UK, and was of industrial grade. No effort was made to dry the gas. Prior to treatment, the reactor was flooded with argon. XPS analyses were carried out using a VG CLAM 200 photoelectron spectrometer employing Mg Kα X-rays. Wide-scan spectra (0-1000eV) and narrow-scan spectra of the C 1s and O 1s regions were acquired for each sample. Data were processed on the Scienta software system. ToF SIMS analyses were performed on a VG Ionex 23LS ToF SIMS fitted with a pulsed gallium ion source. Mass spectra were acquired using a total ion dose well within the static regime of 10^{13} ions cm^{-2}(8). Mass spectrometry of the plasma was carried out using a HAL EQP 300 quadrupole mass spectrometer supplied by Hiden Analytical. The base pressure in the plasma reactor was better than 10^{-3}mbar, while that of the spectrometer was 10^{-8}mbar.

Results and Discussion

Samples were treated in the plasma reactor at a pressure of 2.5 x10^{-2} mbar and a power of 10W. The effect of plasma treatment time was investigated, the results are shown in Fig. 1. On exposure to laboratory atmosphere after plasma treatment, PS picks up exclusively oxygen. The O/C ratio for the "as treated" surfaces approaches saturation after 5 minutes plasma treatment time, and the surfaces remain stable (to MeOH rinsing) up to a limiting O/C ratio of approximately 0.20. At O/C ratios greater than 0.20, low molecular weight material (LMWM) can be removed through rinsing the surfaces with methanol(7). The error bars expressed in the graph are 95% confidence intervals and were calculated using the data obtained from five treatments performed (two minutes plasma treatment time).

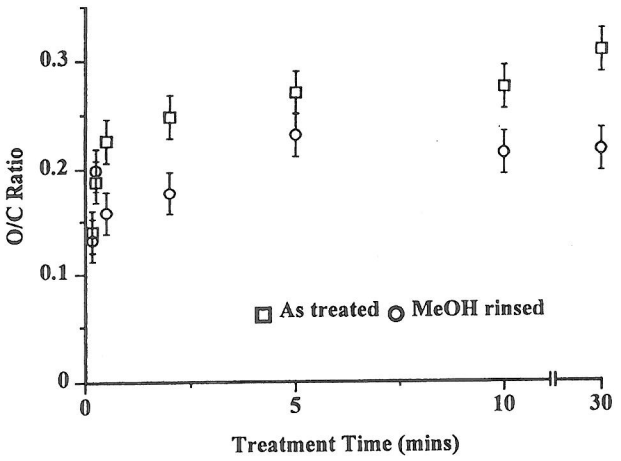

Fig. 1 O/C ratio vs plasma treatment time.

Table 1 Curve fitting results of C 1s core line (O/C ratio = 0.19).

Peak Position (eV).	Shift(eV)	Environment	Area(%)
285.0	0	C-C, C-H	83.3
285.7	0.7	C-CO_2H/R	0.5
286.5	1.5	C-O	11.8
288.0	3.0	C=O	2.7
289.0	4.0	CO_2H/R	0.5
290.0	5.0	CO_3^{2-}	0.5
291.6	6.6	$\pi \Rightarrow \pi^*$	0.9

For the 15s treatment (O/C ratio = 0.19), the C 1s core level was fitted for several carbon oxygen environments, the results are shown in Table 1 and Fig. 2. These highlight the selectivity of argon plasma treatments that produce stable surfaces to carbon singly bonded to oxygen functionalities. LMWM manifests itself in the C 1s spectrum as carboxylic acids and carbonate functionalities, which are removed from the C 1s core level upon rinsing with methanol (7).

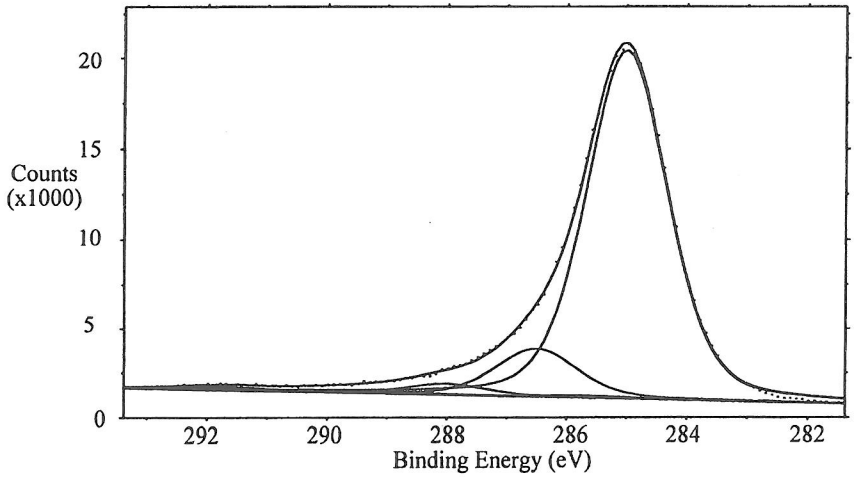

Fig. 2 Curve fit of C 1s region of Ar plasma treated PS (O/C ratio = 0.19)

Positive ion ToF SIM spectra were acquired for untreated PS and Ar plasma treated PS (O/C ratio = 0.11) and these are shown in Fig. 3. The SIM spectrum for untreated PS (Fig. 3a), shows ions diagnostic of PS at *m/z* 77, 91, 103, 115, and 128 (9). After treatment, a number of new ions are introduced into the spectrum (Fig. 3b) and a number of the diagnostic ions are reduced in intensity (particularly ions at *m/z* 91, 103). Of particular note are the new ions present at *m/z* 107, 109, and 119-121. These are observed in the SIM spectrum of poly(*p*-hydroxystyrene) (10), and suggest that some of the hydroxyl groups present in the modified surfaces are situated at ring sites on the PS.

Positive ion mass spectra of the argon plasma were acquired under the same plasma conditions as used for treatment. The spectrometer allows tuning of various analyser voltages, including the energy of ions accepted at the quadrupole. These voltages were tuned to Ar^+ (*m/z* 40), to produce the spectrum shown in Fig. 4. Immediately apparent from this spectrum is the level of protonation in the plasma as shown by the presence of ArH^+ (*m/z* 41). Also visible is Ar_2^+ (*m/z* 80). The protonation is thought to be due to the reactions of absorbed water that is present on the walls of the reactor. If the energies of the individual ions are scanned, it is found that H_2O^+ has a distribution peak at 10.6eV as opposed to Ar^+ at 7.5eV. When the spectrum is repeated at an energy of 10.6eV, the water present in the plasma becomes more prominent in the spectrum and this is shown in Fig. 5. A complete retuning of all the analyser voltages to H_2O^+, would produce a spectrum dominated by this ion. ArH^+ is more pronounced in Fig. 5 as it's energy maximum is at 8.6eV, i.e. between that of Ar^+ and H_2O^+.

While the reaction of oxygen in the plasma with the PS surface is not ruled out, we have shown elsewhere (7) that the majority of oxygen incorporated in the surface arises from post plasma reactions.

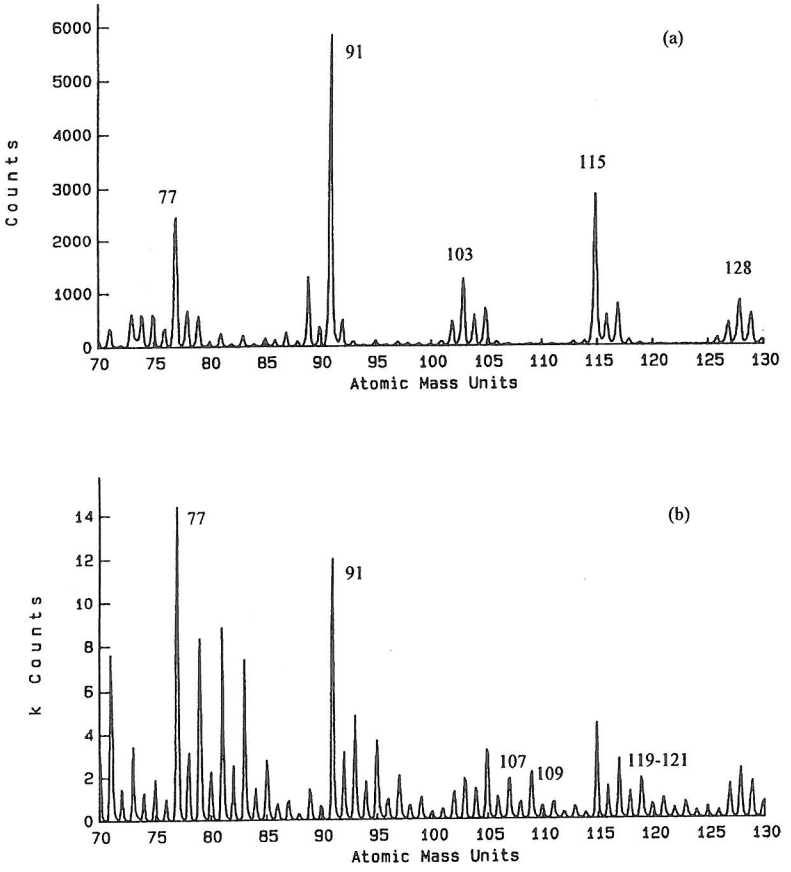

Fig. 3 Positive ion SIM spectra (a) untreated PS and (b) Ar plasma treated PS (O/C ratio = 0.11).

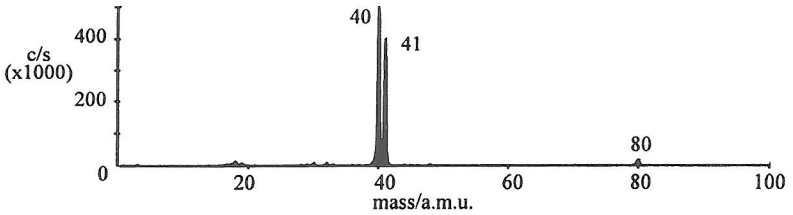

Fig. 4 Positive ion spectrum of Argon plasma. (Energy = 7.5eV)

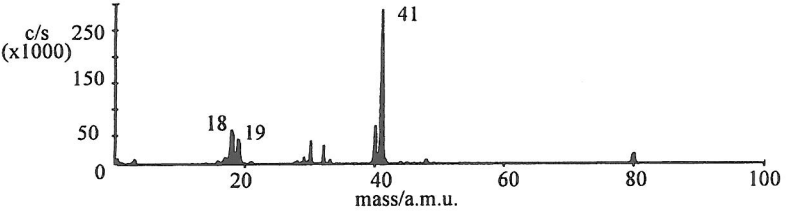

Fig. 5 Positive ion spectrum of Argon plasma (Energy = 10.6eV)

Conclusions

Upon exposure to the atmosphere, Ar plasma treated surfaces are highly reactive and readily pick up atmospheric oxygen. The treated surfaces are stable up to an O/C ratio of 0.20, and stable surfaces are characterised by a high selectivity of carbon singly bonded to oxygen functionalities. ToF SIMS data show some of these functionalities could be situated at ring sites on the polymer. The plasma is far from inert with significant protonation occurring, it does however represent a situation close to that of the industrial treatment of these materials.

References

(1) Clark, D.T. & Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.*, **16** (1978) 911.
(2) Lub, J., vanVroomhoven, F.C.M.B., vanLeyen, D. & Benninghoven, A. *Polymer* **29** (1988) 998.
(3) Hansen, R.H. & Schonhorn, H. *J. Polym. Sci., Polym. Lett.* **B4** (1966) 203.
(4) Munro, H.S. & McBriar, D.I. *J. Coatings Tech.* **60** (1988) 41.
(5) Clouet, F. & Shi, M.K. *J. Appl. Polym. Sci.* **46** (1992) 1955.
(6) Clark, D.T. & Dilks, A. *J. Polym. Sci., Polym. Chem. Ed.* **15** (1977) 2321.
(7) France, R.M. & Short, R.D. *Polym. Deg. Stab.* **45** (1994) 339.
(8) Briggs, D. & Hearn, M. *Vacuum*, **36** (1986) 1005.
(9) Briggs, D., Brown, A. & Vickerman, J.C. *Handbook of Static Secondary Ion Mass Spectrometry*, Wiley, Chichester (1989).
(10) Chilkoti, A. & Ratner, B.D. *Surface Characterization of Advanced Polymers*, VCH publishers, Inc., Germany, (1993).