Polymer surfaces treated by argon rf plasma

I. A. RUSU, G. BORCIA[*], S. O. SAYED[a], J. L. SULLIVAN[a]
Plasma Physics Department, Al.I. Cuza University, Iasi, Romania
[a]*Surface Science, EEAP, Aston University, Birmingham B4 7ET, UK*

This study aimed to investigate on a method to improve the adhesion properties of polymer surfaces. In this respect, the chemical modification induced under different plasma treatment conditions and the efficiency of plasma treatment using the rf discharge are explored. XPS, contact angle measurement and AFM were employed to characterise polymer surface modifications. Results show that the incorporation of oxygen-related functional groups on the active sites created onto the surface is favoured for mild treatment conditions, in terms of rf power, gas pressure and treatment duration, whereas extended treatment is eventually leading to reversal of the surface oxidation, due to etching under energetic ions bombardment. The surface equilibrates, under specified treatment conditions, by a combination of surface oxidation and/or loss of carbon by conversion to low weight volatile fragments.

1. Introduction

Plasma-surface interaction involves processes which can be used for polymer surface treatment in order to modify their surface energy, optical reflection, permeability, surface conductivity, biocompatibility, adhesion to other materials, etc. Recently, plasma techniques have also been used for adhesion improvement of biomolecules to polymer membranes for biotechnological applications. The most important feature of the plasma technique is that the surface properties of the treated material can be modified without changing their intrinsic bulk properties [1,2].

Plasma treatments can improve the adhesion in the polymer-coating interfaces by a combination of the following mechanisms: cleaning by ablation of low molecular weight species, dehydrogenation, chain-scission combined with cross-linking, generation or incorporation of radicals and reactive species and structural modifications of the surface topography. A good macroscopic adhesion between the polymer and a coating material depends not only on the characteristics of the interface, but rather on the whole interphase region, namely on the successive layers joining the bulk phase of the overcoat. Therefore, a good plasma treatment has to ensure suitable conditions for adhesion without involving degradation of the near surface region, i.e. the optimal adhesion strength is limited by the smallest intrinsic cohesion strength of the bulk and the surface region of the polymer [3].

Plasmas can be characterized by their electron and ion densities, radiation intensities, flux and kinetic energy of the ions interacting with the surface. In plasma, a polymer surface is exposed to a broad energetic spectrum of ions, electrons, neutrals, and electromagnetic radiation and each of them may have their own influence on the chemical type and the depth of the modification on the exposed material.

Many investigations have shown that ions are the most efficient species in the plasma to modify the polymer surface. Since the penetration depth of low energy ions in a solid is extremely small, ions seem to be very important for the modifications in the first few nanometres of the polymer surface during plasma treatment. The kinetic energy of the ions hitting the sample surface is given by their energy in plasma and by the energy obtained within the ion sheath which supports the difference between the plasma potential and the floating potential of the sample.

In this respect, the aim of these studies was to find the most effective method to improve the adhesion between thin silicon films and polymer surfaces. In this paper we report on the chemical modification induced under different plasma treatment conditions and the efficiency of plasma treatment using the rf discharge.

2. Experimental

Low pressure plasma used for surface modification was produced in an asymmetric industrial OPT (Oxford Plasma Technology) Plasmalab 100 capacitively coupled system with the grounded electrode (including the chamber walls) area much larger than the driven electrode [4]. A matching network was used to match the impedance in order to maximise the energy transfer from the rf power supply to the plasma. The pressure was kept constant automatically by measuring the pressure via a capacitive manometer (CM) gauge and a pumping throttle valve.

The sample considered in our investigations was PET (polyethylene terephthalate), provided by Goodfellow Company. The polymer samples, 200 μm thickness foils, were cut into 8×8 mm pieces, ultrasonically cleaned in alcohol to remove organic material and dried with hot air before the treatment.

Argon (99.095%) was used without further purification. The reactor was flooded with argon to a pressure of 1 Torr, for 5 min prior to plasma treatment. Typical treatment parameters were: Ar gas pressure 10 mTorr to 90 mTorr, rf power 10 to 200 W, gas flow rate 10 sccm, treatment times 10 min to 30 min.

XPS, contact angle measurement and AFM were employed to characterise polymer surface modifications.

XPS was performed in a VG ESCALAB 200D spectrometer with MgKα X-ray radiation. The XPS peaks were analysed by means of a computer program incorporated in the VG Eclipse data system. The XPS investigations were performed at 70° take-off angle measured with respect to the sample normal, yielding about 14 Å sampling depth. Spectra were fitted based on standard measurement [5].

The contact angle in sessile drop method was measured by a contact angle meter. Each value of the contact angles was taken as an average value measured from five different samples fabricated under the same experimental conditions. Surface free energy, obtained using the sum of the polar component and the dispersive component, was calculated by measuring the contact angles of two different polar liquids (water and formamide) on polymer surface. From the measured contact angles, the polar and the dispersive energy components were calculated using the Owen method [6].

AFM images were obtained using a Topometrix scanning probe microscope. Contact mode topographic images were recorded at 0.5 Hz scan rate.

3. Results and discussion

3.1. XPS analysis

The monomer unit of PET contains three functional groups, marked as 1, 2 and 3 in its chemical structure in Fig. 1. Accordingly, three main types of carbon are present in the C1s spectrum: the carbon atoms in the benzenic ring (C1), those in the CH_2 group bonded to the oxygen in the terephthalate group (C2) and those in the carboxyl group (C3). In a similar way, the O1s spectrum has two peaks, due to oxygen atoms in the carboxyl group (O2), and those binding the terephthalate group and the glycol atoms (O1).
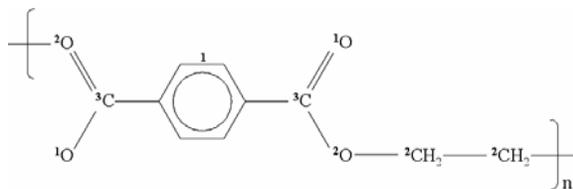

Fig. 1. PET repeat unit (superscript indices on C and O atoms correspond to C1s and O1s XPS components)

The binding energies of the carbon and oxygen atoms in PET, as determined from spectra in Figure 1, are presented in Table 3. Quantitative information on the polymer surface comes from the ratio of the areas under the peaks in the high-resolution spectra. The results of the calculations are presented in Table 3, showing good correlation, between data obtained from the C1s and O1s spectra, concerning the respective amounts of carbon-bonded-to-oxygen groups, i.e. $O1 : O2 \cong C2 : C3$.

Table 1. Binding energies and relative peak areas of the PET C_{1s} and O_{1s} fitted peaks

	C1s				O1s	
	C1	C2	C3		O1	O2
BE (eV)	285.0	286.6	288.9		532.2	533.6
Area (%)	59	21	20		51	49

O/C, C1/C and C2/C ratios, after PET surface treatment, were obtained and compared as a function of rf power, gas pressure values and treatment time. An important oxidation reaction is rendered to evidence, since the O/C ratio is higher, compared with untreated PET, for all treated samples, as presented in Table 2. Here the oxygen, present even at very low levels, due to residual air, and mainly to water adsorbed on the reactor chamber walls, activated in the plasma, represents a very surface reactive species.

Table 2. O/C ratio vs. gas pressure and rf power.

	10mtorr	30mtorr	50mtorr
0 W	0.341	0.341	0.341
10 W	0.385	0.364	0.460
50 W	0.783	0.180	0.670
100 W	0.880	0.992	0.720
150 W	0.786	0.323	0.397
200 W	0.506	1.137	0.320

The increase in the oxygen content is due to the growth in both C2 and C3 components, as shown in Fig. 2, presenting the C2/C and C3/C ratio versus rf power and pressure.

The level of surface oxidation firstly increases with increasing rf power, yet, after reaching a maximum, starts to decrease. The maximum is observed at 100 W injected power, for lower and higher pressure, i.e. 10 and 50 mTorr, whereas it shows up at 150 W for "intermediate" value of the pressure, i.e. 30 mTorr. Moreover, the same limitation in surface oxidation occurs as a function of the gas pressure, since the maximum oxygen content is being observed for 30 mTorr.
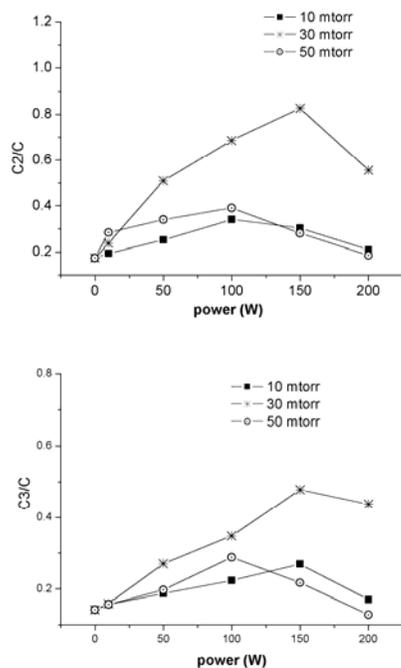
Fig. 2. C2/C and C3/C ratio vs. rf power and pressure

Fig. 3. Surface energy of treated PET vs. rf power for
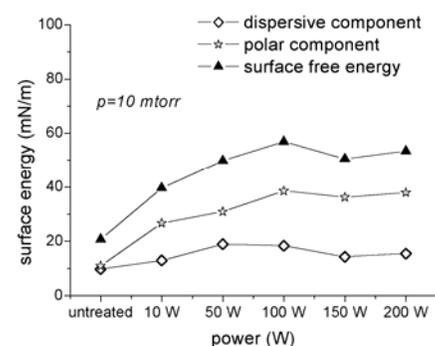*a) 10 mTorr, b) 30 mTorr, c) 90 mTorr*

Obviously, it is to be expected that all sample surfaces reach a limiting level of oxidation as the surface equilibrates, under specified discharge conditions, by a combination of surface oxidation and/or loss of carbon by conversion to low weight volatile fragments, such as CO or CO_2. Extended treatment, in terms of power, duration, or density of active species (pressure), is eventually leading to reversal of this behaviour, i.e. a diminution of the level of oxidation arises due to etching under energetic ions bombardment. This is observed here for higher rf power and gas pressures.

It is shown that at higher ion doses (high power and long treatment time) a chain scission can appear with the elimination of the O-ArC=O groups [7]. The most active elements in the plasma system, responsible for chain scission, are ion bombardment, UV radiation and atomic Ar (excited species) bombardment.
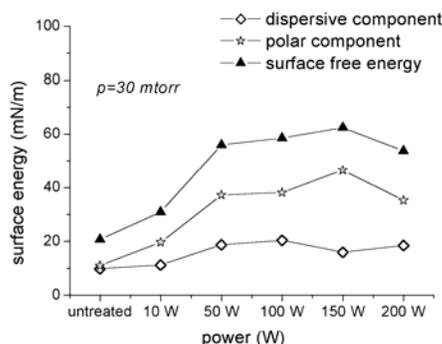
The scission of the polymer chain due to plasma ion bombardment determines the appearance of microdomains with low molecular weight, especially at the limit of the ion penetration depth. The dimension of the polymer chain which serves as primary nucleus is a critical one, since only such a nucleus is expected to be able to redissolve and reform repeatedly; shorter chains than this are redissolved.
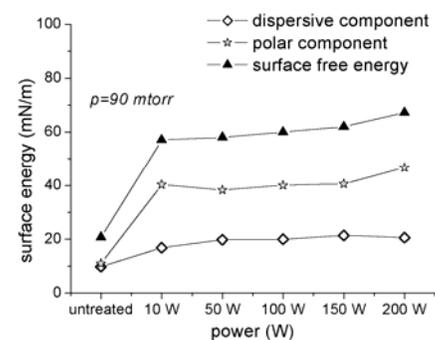
3.2. Contact angle measurement

Plasma treatment is modifying the surface energy of PET.

As shown in Fig.3, plasma treatment of PET increases the polar component of the surface energy, but not the dispersive component. In a polymer, the increase of the polar energy component is known to be mainly due to the formation of polar groups such as –(O-C)-, -(O=C)- and -O–(C=O)- [4].

These results are in good correlation with the obtained XPS data at lower pressure, 10 and 30 mTorr, where the maximum surface hydrophilization occurs at about 100-150 W injected power. At higher pressure, e.g. 90 mTorr, there is a distinct plateau for the values of the surface energy components, covering the entire investigated range of rf power.

3.3. AFM analysis

In order to examine the relation of contact angle and surface free energy to surface roughness, AFM analysis was carried out (Fig. 4). Increased surface roughness is observed with increasing rf power and treatment time.
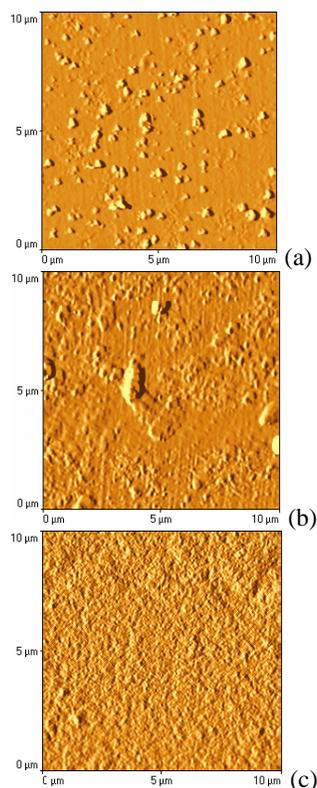

Fig. 4. AFM images for PET surface at 30 mTorr:
a) untreated, b) 100W, b) 200 W

The AFM images are showing to evidence an etching plasma effect for higher rf power. The observed effect could be initiated by a cleaning mechanism, by preferential physical sputtering of amorphous polymer regions. The polymer surface layer, having low cohesion and high chemical inertness, is thus removed, triggering the surface functionalization by creation of unsaturated moieties and polar groups. The plasma exposure may thus produce such effects as removal of contaminants, oligomers and amorphous layers existing on the surface, allowing the chemical activation of the material. The next stage would be then the incorporation of oxygen-related functional groups on the active sites created onto the surface, this mechanism being obviously favoured for "mild" treatment conditions, in terms of rf power, gas pressure and treatment duration. Then, the same as shown by XPS analysis, extended treatment, in terms of either power or duration, is eventually leading to reversal of the surface oxidation, due to etching under energetic ions bombardment.

4. Conclusion

This study aimed to investigate on the efficiency of plasma treatment using the rf discharge, in order to improve the adhesion properties of polymer surfaces. In this respect, the chemical composition, hydrophilicity and roughness modification, induced under different plasma treatment conditions, were explored. Results obtained by various analysis techniques correlate well, showing that the surface oxidation is favoured for mild treatment conditions, in terms of rf power, gas pressure and treatment duration, whereas extended treatment is eventually leading to reversal of the surface oxidation, due to etching under energetic ions bombardment.

References

[1] W. Shen, Y. Filonanko, Y, Truong, I.H. Parker, N. Brack, P. Pigram, J. Liesegang, Coll. Surf. A **173** (2000) 117.
[2] R. Smith, R. Pitrola, Polymer **41** (2000) 9111.
[3] S. Vasquez-Borucki, C.A. Achete, W. Jacob, Surf. Coat. Technol. **138** (2001) 256.
[4] I.A.Rusu, G. Popa, J.L.Sullivan, J. Phys. D: Appl. Phys. **35** (2002) 2808.
[5] G. Beamson, D. Briggs, High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database, Wiley, Chichester, 1992.
[6] D.T. Clark, H.R. Thomas, J. Polym. Sci., Polym. Chem. Ed. **15** (1977) 2843.
[7] G. Marletta, S. Pignataro, A. Toth, I. Bertoti, T. Szekely, B. Keszler, Macromolecules **24** (1991) 99.

_____
*Corresponding author: g.borcia@uaic.ro