Investigation of the ageing of plasma oxidized PEEK

W. J. Brennan
Wilton Materials Research Centre, ICI plc, Wilton, Middlesbrough, UK

and W. J. Feast*, H. S. Munro and S. A. Walker
Department of Chemistry, University of Durham, South Road, Durham, UK
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Oxygen plasma treatment can be used for increasing the hydrophilicity of polymer surfaces, however, it is widely known that this effect decays significantly with time. This ageing phenomenon is thought to be caused by both migration of low molecular weight fragments and reorientation of modified polymer chains. It has recently been shown that the aged surface becomes transiently hydrophilic before attaining a final surface energy significantly lower than the initially treated surface. X-ray photoelectron spectroscopy (XPS) and contact angle measurements were used to monitor the changes in surface chemistry of plasma oxidized poly(ether ether ketone) (PEEK) during post treatment storage. The decay and transient increase in hydrophilicity were found to be dependent upon crystallinity and storage temperature.

(Keywords: PEEK; ageing; X-ray photoelectron spectroscopy)

INTRODUCTION

The oxygen discharge treatment of polymers has been extensively reported, particularly in studies on improving wettability and adhesive properties. Much is known about the immediate changes produced in a variety of substrates, such as polyethylene[1], polydimethylsiloxane[2] and poly(ethylene terephthalate)[3], and by a number of techniques, including corona discharge[4] and both radio frequency[5] and microwave[6] plasmas. It has been shown that after the initial treatment there is an increase in the contact angle with water which levels off to a plateau value after a few days[7]. It has been suggested that this decrease in hydrophilicity is due to a combination of two processes. One involves rotation of surface polar groups into the bulk of the material to reduce the surface energy[8]. The other is due to migration of low molecular weight, polar fragments into the polymer matrix[9]. It has been shown recently[10] that the aged surface becomes transiently hydrophilic before attaining the final plateau value of contact angle. This latter observation suggests that the dynamics of plasma treated surfaces are more complex than originally envisaged.

In this work we have used contact angle measurements and X-ray photoelectron spectroscopy (XPS) to follow changes in surface chemistry of four oxygen plasma modified samples of poly(ether ether ketone) (PEEK) (see *Figure 1*) of different crystallinities and degrees of orientation.

EXPERIMENTAL

Materials

Samples of PEEK were provided by ICI plc. Four different types of film were investigated: amorphous, A; 10% crystalline and uniaxially oriented, B; 20–23% crystalline and unoriented, C; 35% crystalline and biaxially oriented, D. Samples were washed in Micro detergent as supplied by the International Products Corporation. They were thoroughly rinsed in water followed by hot methanol, until XPS showed them to be clean. All samples had an initial contact angle of 87 ± 2° with water.

Plasma treatment

Samples were treated in a Polaron E2000 Plasma Asher/Etcher, using a 30 W oxygen plasma for 30 s at a pressure of 0.2 mbar. The samples were then stored in air at either −18°C, 2°C, 21°C, or 45°C. All were stored at ambient humidity (r.h. 40–60%) except those at −18°C which were stored in a desiccator to prevent formation of ice on the surface.

Contact angle measurements

Contact angle measurements were performed using the sessile drop technique[11] using a 1 μl drop of distilled water. Averages of at least three measurements were taken, these averages were found to be consistent within ±2° for contact angles greater than 20° and ±3° for contact angles of less than 20°.

XPS measurements

Core level spectra for C_{1s} and O_{1s} regions were recorded on a Kratos ES200 electron spectrometer using $Mg_{K\alpha}1,2$ X-rays and an operating pressure of 10^{-7} Torr.

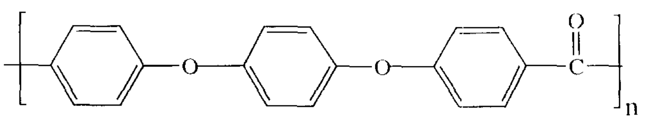

Figure 1 Structure of poly(ether ether ketone)

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* To whom correspondence should be addressed

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Electron take-off angles of 70° and 35° were used to investigate the vertical homogeneity of the sample. A take-off angle of 70° samples a depth of *c*. 15 Å for carbon and *c*. 10 Å for oxygen. At 35° the sampling depth is *c*. 35 Å for carbon and *c*. 25 Å for oxygen[12]. Atomic ratios were measured to ±1 oxygen per 100 carbon atoms. Peak fitting was performed according to the method of Clark *et al.*[13]. Because of limited spectrometer time XPS spectra were only obtained for amorphous PEEK (sample A) stored at 45°C.

RESULTS

Directly after treatment most samples were completely wetted by water or had contact angles too small to be measured with any degree of accuracy. After approximately 5 min contact angles could be measured and were found to be in the region of 4° to 15°, tending to be lower for the less crystalline samples. However, the large relative errors in this region make meaningful comparison difficult if not impossible. Most samples show a decay curve as illustrated in *Figure 2*, with plateau and drop in contact angle occurring as outlined in *Table 1*. The semi-crystalline and drawn samples tend to show a slower rate of increase in contact angle and the onset of the sudden drop in contact angle is delayed compared to the amorphous polymer.

The effect of increasing the temperature is marked. The rate of relaxation of the surface is increased as manifest by the more rapid attainment of plateau contact angle, which is higher at higher temperature, and the earlier occurrence and the brevity of the transient increase in hydrophilicity. The semi-crystalline and biaxially drawn samples do not appear to undergo a transient increase in hydrophilicity (see *Figure 3*). It is possible that the phenomenon does not occur under these conditions or that it occurs between measurements. It is not practically possible to continuously monitor the contact angle.

The XPS spectrum of untreated PEEK (see *Figure 4*) shows within experimental error that there are the expected 16 oxygen atoms per 100 carbon atoms. The C_{1s} spectrum shows a shoulder to higher binding energy relative to the main photo-ionization peak at 285 eV indicating carbon singly and doubly bonded to oxygen and a shake-up satellite at a shift of 7 eV due to

Table 1 Effect of sample and storage conditions on contact angle decay

			TIH[a]	
Conditions	°C	Plateau value	Time	Duration (days)
Amorphous	−18	25[b]	21	3
	2	40	18	2
	21	43	15	2
	45	48	9	1
Uniaxially drawn	−18	31	24	3
	2	40	21	3
	21	45	17	2
	45	49	10	1
Biaxially drawn	−18	34	25	3
	2	38	22	3
	21	42	–[c]	–[c]
	45	47	–[c]	–[c]
Semicrystalline	−18	30	23	3
	2	40	20	2
	21	40	17	2
	45	49	–[c]	–[c]

[a] TIH = transient increase in hydrophilicity
[b] Samples kept at −18°C did not always reach a plateau value
[c] TIH not experimentally observed

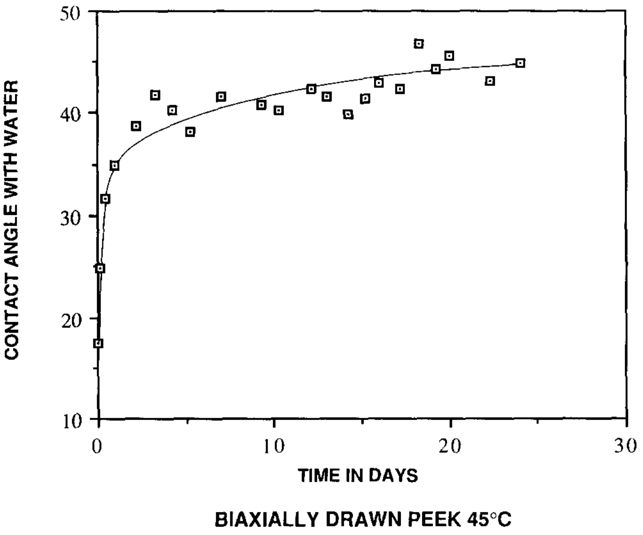

Figure 3 Contact angle without TIH

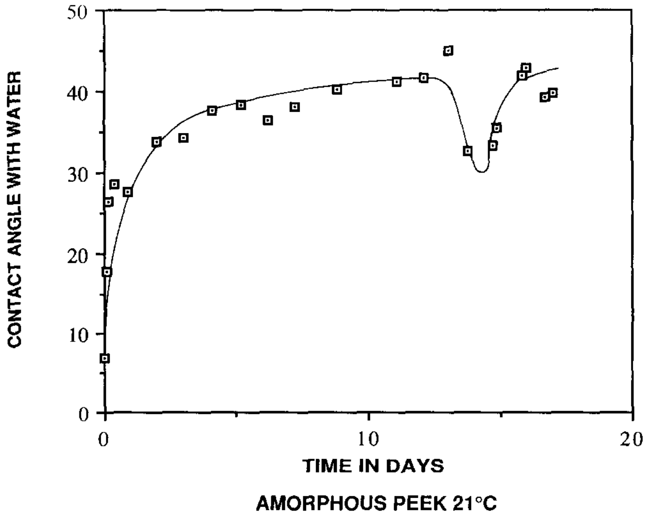

Figure 2 Typical contact angle decay curve

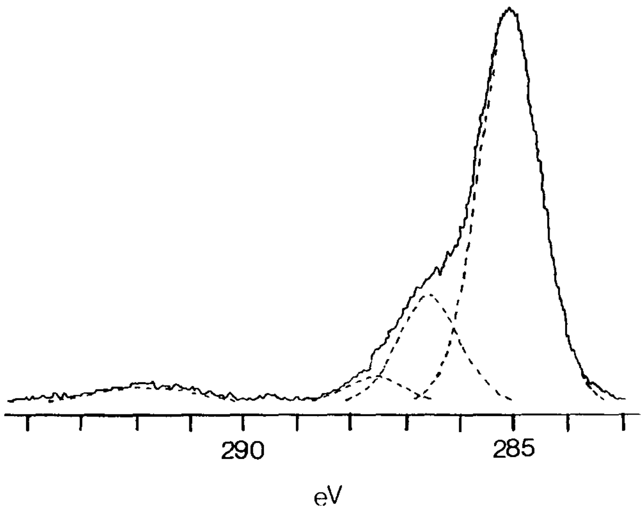

Figure 4 XPS spectrum of pristine PEEK

aromaticity[12]. The O_{1s} spectrum of pristine PEEK indicates the presence of two oxygen environments namely ether and carbonyl. After plasma treatment the increased complexity of spectra (see *Figure 5*) indicates that a variety of new functionalities have been formed. Peak fitting the C_{1s} envelope reveals the presence of C–O, C=O and O=C–O in relatively large quantities and a smaller amount of carbonate (see *Table 2*). XPS spectra directly after plasma treatment show an oxygen to carbon ratio of 35 to 100.

After about two days the oxygen content drops to a steady value of about 28 oxygens per 100 carbons, the shake-up satellite becomes more apparent and the general appearance of the O_{1s} envelope begins to resemble that of the starting material. Initially there were differences in the O_{1s}:C_{1s} ratio obtained from spectra recorded at take-off angles of 70° and 35° (see *Table 2*), after about two days both sets of spectra have identical O_{1s} to C_{1s} atomic ratios, although those with take-off angles of 70° show a relatively higher proportion of hydrocarbon carbon compared to oxygen functionalized carbon in the peak fitting of the C_{1s} envelope.

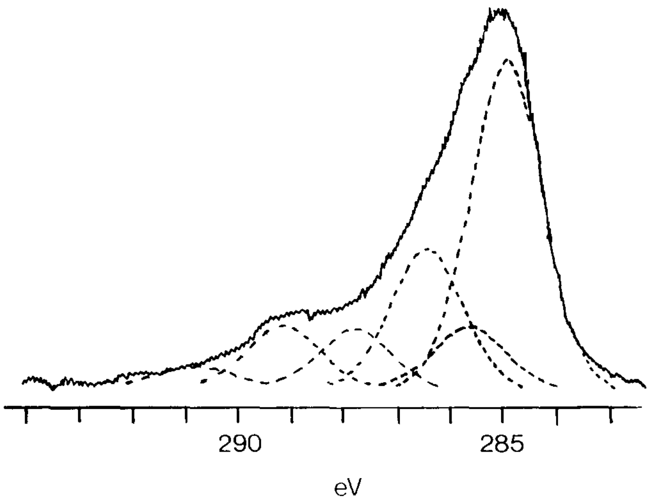

Figure 5 XPS spectrum of plasma oxidized PEEK

During the transient increase in hydrophilicity no increase in O_{1s}:C_{1s} atomic ratio is observed. However, a significant increase in the extent of oxidation is seen in the C_{1s} envelope.

DISCUSSION

From the contact angle data it is apparent that reorganization of the surface is taking place within the region sampled by the contact angle experiment, i.e. *c.* 5 Å (ref. 14), the initial very rapid change in contact angle observed in the first few minutes after plasma modification is probably due to the reorientation of highly mobile fragments created by the treatment. The changes in the surface over the next few days were observed with both XPS and contact angle measurements suggesting that these changes are due mainly to migration of fragments from the surface into the bulk. Subsequently, a further slight decrease in the amount of oxidation at the surface and a similar increase in the contact angle with water was observed. At the transient increase in hydrophilicity a discrepancy in the XPS and contact angle data was seen.

The XPS data obtained during this work consistently showed no significant increase in the amount of oxygen at take off angle of either 70° or 35°. However previous work using more vigorous plasma oxidation and storage at 20°C[10] does show a significant increase in oxidation for a sampling depth of 25 Å during the transient increase in hydrophilicity. Although in this work no increase in the total amount of oxygen present was observed, the C_{1s} envelope does show an apparent increase in the proportion of oxygen functionalized carbon to hydrocarbon.

It is probable that plasma modification produces highly fragmented species at the surface, and further into the bulk fragmentation becomes progressively less. The mobility of the species created at the surface is high and the larger fragments in the subsurface have a correspondingly lower mobility. Directly after treatment the species

Table 2 Effect of storage on C_{1s} envelope

Day	Take-off angle	Relative area under C_{1s} envelope						
		C–C/H	C–O	C=O	O–C=O	CO_3	π–π*	O_{1s}/C_{1s}
0	70	58	21	9	9	3	0	0.33
1		59	19	9	7	3	2	0.29
8		77	15	3	3	1	2	0.29
8.5		74	15	6	3	2	3	0.28
9		72	16	4	4	2	2	0.29
9.5		66	20	5	4	3	3	0.29
11		74	15	4	3	1	3	0.28
0	35	64	20	5	5	3	3	0.35
1		64	22	5	4	2	3	0.32
8		64	20	5	3	4	3	0.29
8.5		63	21	5	3	4	4	0.28
9		63	21	5	4	3	3	0.29
9.5		65	22	5	3	3	2	0.28
11		63	21	5	4	3	4	0.28
Untreated		70	19	5	0	0	6	0.16

at the surface reorient very quickly and begin to migrate into the bulk. As smaller species migrate into the bulk, larger species will replace them at the surface, reorienting as they are exposed. The reasonable hypothesis that the larger fragments of polymer chain reorient at a slower rate than migration of the smaller species[9], provides a basis for a possible explanation for the transient increase in hydrophilicity. Thus, the low contact angle observed results from the presence of oxidized species in the surface. These species reorient or migrate into the bulk at different rates and also have different extents of oxidation.

Munro and McBriar[10] suggested that migration of small polar fragments could result in an incompatibility between these fragments and the less polar subsurface layers, thus providing a driving force for a reorganization via a transient higher surface energy intermediate.

An effect that has not been considered so far is that of atmospheric interactions. The newly modified material is likely to contain free radicals, radical ions and other reactive species at the surface, it is possible that these will undergo reaction with moisture and oxygen in the air which could lead to a classical auto-oxidative degradation process[15] which will compete with the reorientation and migration processes. It is possible that this could lead to the observed temporary increase in the polarity of the surface. It is also possible that during the ageing process free radicals initially within the subsurface are uncovered and then react with atmospheric components water and oxygen, further complicating the observed surface characteristics.

From the above discussion it is clear that the dynamics of the ageing of plasma modified polymer surfaces is very complex and governed by many parameters: the nature of the treatment, the polymer, and the storage conditions. The processes occurring at the transient increase in hydrophilicity are not fully understood. The hypotheses outlined above are all reasonable yet do not completely explain all the complexities seen in this or previous work. It is possible that the anomaly between the O_{1s}:C_{1s} atomic ratios and the changes in the C_{1s} envelope at the time of the transient increase in hydrophilicity (see *Table 2*) is due to the greater sensitivity of the O_{1s} peak to hydrocarbon contamination within the spectrometer, thus causing the measured O_{1s}:C_{1s} atomic ratios to be apparently less than the true value.

No explanation has been advanced for the apparent disappearance of the transient increase in hydrophilicity at higher temperatures for the more crystalline samples. The trends suggest that if the decrease in contact angle occurs at lower temperatures it should occur sooner at higher temperatures, and it may be of such short duration that it escapes observation.

Increasing the crystallinity and orientation of the samples increases the degree of order and reduces the free volume in a significant proportion of the polymer matrix. This hinders the movement of the polymer chains and therefore slows the ageing processes of migration and reorientation. This, in turn, causes the delaying of the conditions which lead to the onset of the increase in hydrophilicity. Conversely, raising the temperature of the PEEK increases the mobility of the polymer chains, thus causing the ageing processes to occur at a faster rate.

CONCLUSIONS

The data presented here show that the ageing and transient increase in hydrophilicity of plasma treated PEEK is dependent upon the mobility of the sample as characterized by its relation to crystallinity and temperature. The increase in hydrophilicity suggests that the observed decay in contact angle results from a complex set of interacting processes, which are not yet fully understood.

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