# Surface reactions of poly(ether ether ketone) with $He^{2+}$ ions

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Room temperature irradiation of poly(ether ether ketone) (PEEK) films with $He^{2+}$ ions in the range of $0.78 \times 10^{15}$–$12.5 \times 10^{15}$ ions $cm^{-2}$ produces surface changes detectable by X-ray photoelectron spectroscopy and Fourier transform infra-red spectroscopy. Rutherford backscattering spectroscopy, with a sampling depth of several micrometres, reveals no compositional changes during irradiation. Surface reactions that proceed during irradiation yield highly oxidized species, hydroxylated moieties and carbonized regions with loss of the aromatic character within the upper 5 nm of the surface. The surface compositions after various irradiation times are constant indicating that no loss of material takes place. This behaviour is compared to the surface evolution of PEEK following other types of surface modification methods.

**(Keywords: PEEK; surface reaction; irradiation)**

## INTRODUCTION

The development of thermoplastic matrices for composite applications has increased tremendously in recent years since new polymers with desirable properties have become commercially available[1,2]. Among these, poly(ether ether ketone) (PEEK) has shown exceptional mechanical properties and is described as being chemically inert to most solvents and radiation resistant[3,4]. PEEK has been also considered to be an alternative substitute of conventional thermoset resins since it may impart higher thermal stability to reinforced composites[5]. In addition, PEEK has also been reported as an excellent adhesive for various applications[6,7]. PEEK has a dielectric constant[8] of 3.3, which is lower than the values of conventional polymers used in microelectronic packaging[9]. Consequently, increased use of PEEK in this industry is expected[8].

Although the chemical and physical characterization of PEEK by a variety of techniques such as thermal analysis[1,10,11], X-ray scattering[12], infra-red (i.r.) spectroscopy[13] and nuclear magnetic resonance (n.m.r.) spectroscopy[14,15] has been reported, there is inconclusive information on the interaction of different types of radiation with PEEK. A literature survey indicates that a very limited number of reports on this subject have been published. For example, Sasuga *et al.* have described the effects of electron beam irradiation on the tensile properties of several aromatic polymers[16]. They reported that polyimides, namely Kapton-H and Upilex-S, had greater resistance than PEEK. Polysulphone and poly(phenylene oxide) had inferior resistance to radiation effects than PEEK. Yoda observed different mechanical behaviour in electron-irradiated crystalline and amorphous PEEK[17]. Beam exposure decreased the degree of crystallinity and the melting point of crystalline PEEK. Exposure of PEEK to a dose of 100–120 Gy of $\gamma$ radiation yields embrittled surfaces[8]. In a more recent study, electron beam damage occurring during the microscopic examination of polymers was reported for poly(*p*-phenylenebenzobisthiazole), poly(*p*-phenylenebenzobisoxazole), poly(benzoxazole), PEEK and poly(benzimidazole)[18]. Polymer damage was correlated to thermal stability and melt temperature of the material. In the studies described above, no chemical changes due to irradiation have been reported.

In general, polymers subjected to irradiation by ions, neutrals or metastables may undergo crosslinking or degradation reactions[19]. Rutherford backscattering spectroscopy (RBS) is a powerful technique for thickness measurements and compositional analysis of inorganic films. In recent work, this technique has been used in diffusion studies of organic films[20,21]. Because in conventional RBS analysis the specimens are irradiated with energies in the mega electronvolt range, irradiation effects must be minimized. This is especially critical for organic films. In addition, surface interactions between the ion beam and the organic film may occur even at low temperatures or short exposure times resulting in different compositions at the surface and in the bulk of the film. For example, polyimide films (pyromelliticdianhydride oxydianiline (PMDA-ODA)) undergo imide ring cleavage reactions and carbonization at low (−130°C) and room temperatures[22]. After irradiation, the polyimide surface contains a reduced level of imide carbonyls, carboxylate groups and carbonized domains as detected by i.r. and X-ray photoelectron spectroscopy (X.p.s.). These surface changes may be expected to induce different electrical, optical and chemical properties in the material[23–25].

In this study, the interaction of a partially crystalline commercial PEEK film with 2.1 MeV $He^{2+}$ ions with fluences in the range of $0.78 \times 10^{15}$ $12.5 \times 10^{15}$ ions $cm^{-2}$ is reported. The overall composition of the bulk within the penetration depth of the ions is followed during these experiments by conventional RBS and the surface changes are detected by X.p.s. and Fourier

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transform infra-red (*FT*i.r.) as a function of fluence. Chemical changes introduced by irradiation are described and compared to the results obtained by other surface modification methods.

## EXPERIMENTAL

Commercial PEEK film (Stabar SK-300) from ICI Americas was used. The film (75 $\mu$m thick) was cleaned in methanol and acetone and dried in vacuum at $1.3 \times 10^{-5}$ Pa before use. The degree of crystallinity of this film was estimated to be 15% by differential scanning calorimetry.

Irradiation with $He^{2+}$ ions was performed with a 1.7 MeV Tandetron accelerator (Department of Materials Science and Engineering, Cornell University) as previously described[26]. The samples were irradiated with an ion beam normal to the surface of the sample. The total current was kept at 20 nA while the total collected charge was varied between 2.5 $\mu$C and 40 $\mu$C. The irradiated spots had areas of 2 $mm^2$. The estimated ion fluences for these charges were in the range of $0.78–12.5 \times 10^{15}$ ions $cm^{-2}$. Spectral simulations were performed using the RUMP program[27].

The irradiated spots were analysed using a Surface Science SSX-100 small spot X.p.s. spectrometer. The analysed area was confined to the irradiated spot by using an aperture of 600 $\mu$m and a resolution of 25 eV. Survey and high-resolution spectra were collected. The resulting envelopes for the C 1s and O 1s spectral regions were curve-fitted using a standard program to derive the individual contributions under each envelope. Binding energies were referenced to the C–C groups in the original material assigned to have a binding energy of 284.6 eV. Atomic compositions were estimated by standard programs provided with the instrument.

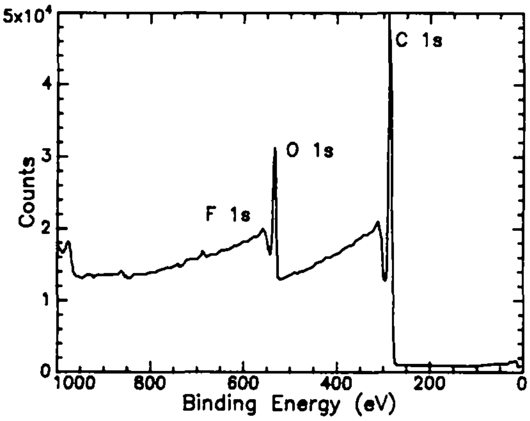

**Figure 1** X.p.s. survey spectrum of untreated PEEK film. The small signal at ~700 eV arises from residual fluorine from a reactant used in the polymer synthesis

*FT*i.r. analyses were performed on the same spots, using an IBM-44 *FT*i.r. spectrometer equipped with a Bruker i.r. microscope. The area of analysis was restricted to ~200 $\mu m^2$ within the irradiated spot. Transmission spectra with a resolution of 4 $cm^{-1}$ and 100 scans were collected for each sample.

## RESULTS AND DISCUSSION

X.p.s. analyses were performed on the commercial PEEK film to determine the contributions from the expected chemical environments and their binding energies. *Figure 1* shows a survey spectrum for a film after cleaning with methanol and acetone. The spectrum consists of two major signals assigned to oxygen (O 1s orbital) and carbon (C 1s orbital). In addition, a small signal assigned to F 1s at ~700 eV is clearly visible. Since the polymer is synthesized by the reaction of bis-4-fluorophenylketone with the potassium salt of bis-4-hydroxyphenylketone[28], the detection of low levels of fluorine in the final product is not unexpected. The atomic concentrations measured at the surface of the film yield: 83% C, 16% O and 1% F. The calculated concentrations of carbon and oxygen for the repeating unit of the polymer are 86.4 and 13.6%, respectively.

The high resolution X.p.s. spectra for the C 1s and O 1s regions detected for PEEK are shown in *Figure 2*. Based on the repeating unit, three different carbon environments are expected but because it has already been shown that the commercial films contain low levels of fluorine, a small contribution from carbon atoms attached to fluorine must be included. Finally, since the polymer is basically aromatic, a shake-up satellite arising from $\pi$–$\pi^*$ transitions is also detectable. Curve resolution of the C 1s envelope yields the three environments for the repeating unit of the polymer. The strongest signal at 284.6 eV is assigned to the C–C bonds in the aromatic rings, the ether groups in the repeating unit appear at 286.2 eV and the carbonyl group has a binding energy of 287.0 eV. A small and weak signal at 288.9 eV corresponds to residual C–F groups. The expected $\pi$–$\pi^*$ shake-up satellite is a broad signal centred at 291.3 eV. The calculated intensities for the three environments in the repeating unit that assumes two ether linkages and

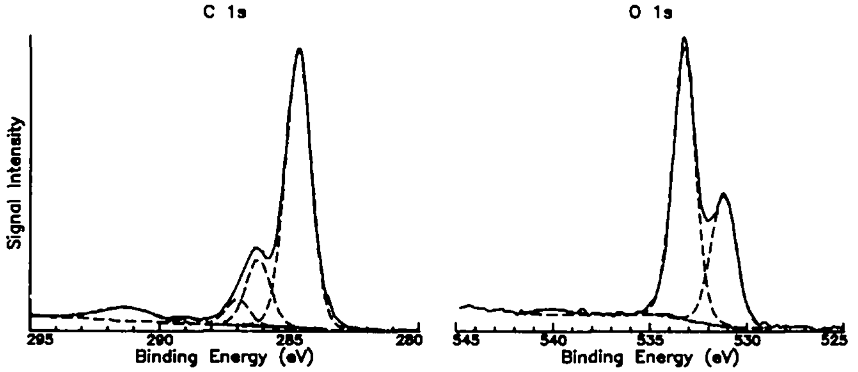

**Figure 2** High resolution X.p.s. spectra for the C 1s and O 1s regions of PEEK. The broken lines correspond to the calculated contributions for the assignments described in the text

one carbonyl group are 74% (C–C bonds), 21% (C–O–C bonds) and 5.3% (C=O bonds). The relative contributions obtained by curve resolution were 76, 18 and 6%.

The O 1s region of the X.p.s. spectrum contains two environments identified as carbonyl (531.2 eV) and ether groups (533.3 eV). A small and broad signal at 540.1 eV is a $\pi$–$\pi^*$ shake-up satellite. After curve resolution, the resulting areas have a ratio of 1.9 to 1.0. These results confirm the assumed repeating unit.

During the irradiation studies, a sample of the film was mounted on the sample block of the instrument and exposed to a flux of 2.1 MeV $He^{2+}$ ions for a specified time to yield a variable amount of collected charge while other instrumental conditions were kept constant. In this manner, exposures in the range of $0.78 \times 10^{15}$ $12.5 \times 10^{15}$ ions $cm^{-2}$ were obtained. In order to maximize the penetration of the impinging ions into the film, the samples were placed perpendicular to the direction of the beam. The estimated penetration depth of 2.1 MeV $He^{2+}$ ions into PEEK is ~10 μm. *Figure 3* presents the RBS spectra for three of these experiments performed after the collected charges were 10, 20 and 40 μC. For a spot size of 2 $mm^2$, these experiments correspond to fluences in the range of $3.1 \times 10^{15}$–$12.5 \times 10^{15}$ ions $cm^{-2}$. The spectra are displayed as a function of channel number or increasing energy *versus* the normalized yield per atomic type. In RBS, the heavier atomic number elements appear at higher energies. Thus, in the spectra, the oxygen signal is located approximately at channel 160 while the carbon signal begins at channel 120. The plateau between these two numbers corresponds to the distribution of oxygen within the sampling depth of the film and it indicates the compositional uniformity of the film. Since the spectra shown are essentially identical, the RBS experiment does not detect specific changes occurring near the surface. In addition, the ratios of carbon and oxygen do not change with exposure time indicating that the irradiation does not produce preferential loss of carbon or oxygen from the sample as previously detected for the irradiation of poly(ethylene terephthalate)[29].

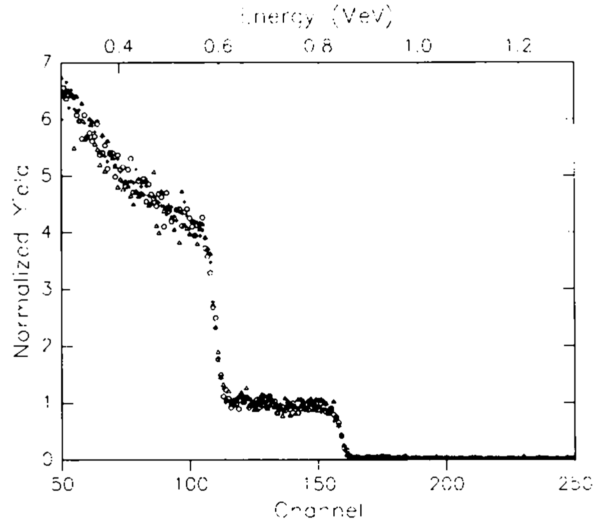

**Figure 3** RBS spectra for PEEK film exposed to $3.1 \times 10^{15}$, $6.2 \times 10^{15}$ and $12.5 \times 10^{15}$ $He^{2+}$ ions $cm^{-2}$ (collected charge of △, 10, ○, 20 and +, 40 μC in an area of 2 $mm^2$)

The interaction of the $He^{2+}$ ions with the polymer surface can be detected by X.p.s. using a sampling area within the irradiated spot. *Figure 4* presents the high resolution spectra of the C 1s and O 1s regions after various irradiation conditions. The spectra for the non-irradiated film are shown for comparison. The C 1s region gradually evolves from a well defined envelope into a broader signal. The broadening detected increases at high and low binding energies. These changes can be interpreted as the creation of more oxidized carbon-containing species (higher binding energy signals) and carbonization (broadening developed below 284.6 eV). The O 1s region, with two well defined signals before irradiation, also broadens but the lower binding energy components increase with irradiation time. This change may also suggest that more oxidized groups, e.g. moieties containing C=O groups, are formed. Although it may be possible to fit the envelopes following irradiation to various components, more information from other techniques can provide a better understanding of surface modification.

The presence of the $\pi$–$\pi^*$ shake-up satellite in the C 1s spectrum of the unmodified film is an indication of the aromatic character of the surface. During irradiation, the change in intensity of this band can be used to assess the preservation of the aromatic character of the polymer. In *Figure 5*, the $\pi$–$\pi^*$ satellites for the surfaces following irradiation are shown. In this figure, the intensity of the C 1s envelope was normalized to a constant number of counts. As can be seen, the aromatic character within the sampling depth of X.p.s. (~5 nm) is lost after exposures of >20 μC ($6.2 \times 10^{15}$ ions $cm^{-2}$).

Additional information on surface modification is obtained by *FT*i.r. spectroscopy. *Figure 6* presents the *FT*i.r. spectra obtained for films of PEEK after 0, 10 and

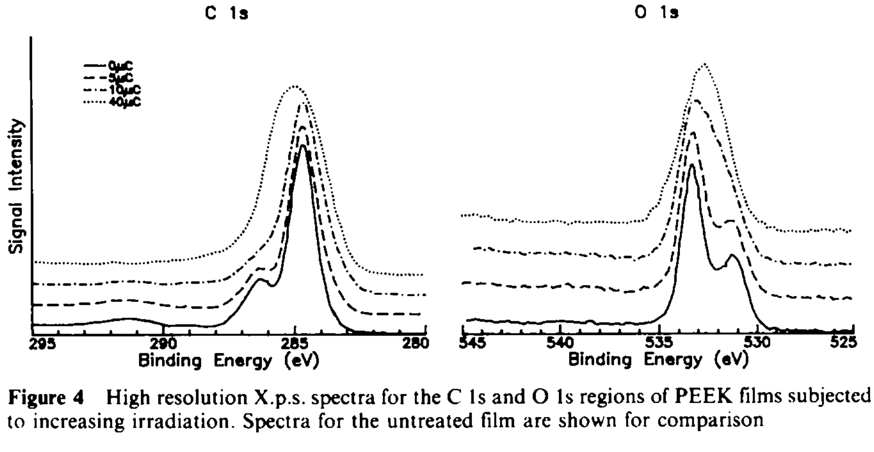

**Figure 4** High resolution X.p.s. spectra for the C 1s and O 1s regions of PEEK films subjected to increasing irradiation. Spectra for the untreated film are shown for comparison

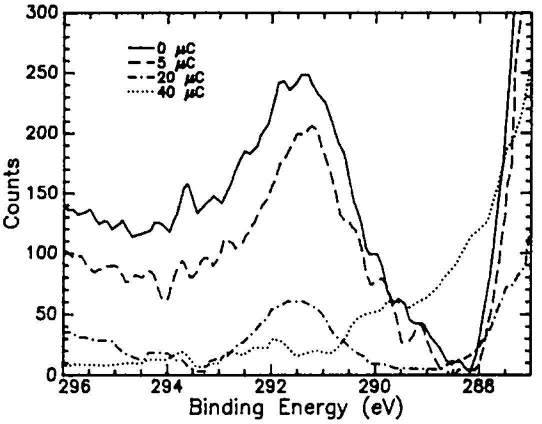

**Figure 5** High resolution X.p.s. spectra of the C 1s $\pi$–$\pi^*$ shake-up satellite region for PEEK showing the reduction in signal intensity with irradiation conditions

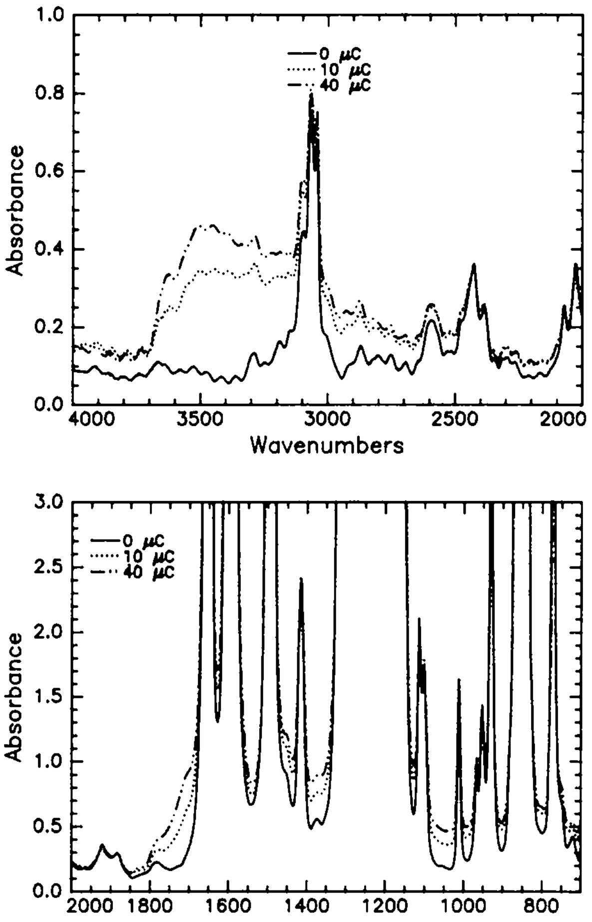

**Figure 6** *FT*i.r. spectra obtained for PEEK films before and after two different irradiation conditions (3.1 × $10^{15}$ and 12.5 × $10^{15}$ ions $cm^{-2}$). Spectra are shown in the region between 4000 and 750 $cm^{-1}$

40 μC exposures. Although the film used in this experiment is thick, the spectra contain information from the unmodified as well as the modified regions of the film. The i.r. spectrum of PEEK has been reported by Nguyen and Ishida[13]. The characteristic bands for the polymer appear at 1655 (carbonyl group), 1599 and 1492 (aromatic ring), 1277 and 1190 (diphenyl ether vibrations) and 1160 $cm^{-1}$ (in-plane vibrations of the aromatic hydrogens). It is also worth noting that PEEK does not show any characteristic bands between 1800 $cm^{-1}$ and 1660 $cm^{-1}$. Because of the aromatic rings, C–H vibrations are observed at 3080 $cm^{-1}$. With increasing exposure time, a new band at ~3500 $cm^{-1}$ gradually increases in intensity. This signal is assigned to newly formed hydroxyl groups. The slight broadening in the region between 1800 $cm^{-1}$ and 1660 $cm^{-1}$ is assigned to additional C=O groups formed by irradiation.

Recently, the surface modifications of PEEK films by means of oxygen plasma ashing[30], treatment downstream from an $O_2$ microwave plasma[31], and photo-oxidation[32] at wavelengths of >290 nm have been reported. These treatments enhance the hydrophilic character of the films. Plasma treatments as a function of microwave power and treatment time induce a thin oxidized layer (<5 nm) that contains carbonyls and other oxidized carbon species. In addition, loss of aromatic character also occurs but the surface layer does not contain carbonized networks[31]. Photo-oxidation of PEEK proceeds through oxygen uptake and the formation of carboxylate, carbonyl and carbonate groups with some aromatic ring-opening reactions[32]. Both of these surface modification processes show oxygen uptake while the irradiated film with $He^{2+}$ ions does not. This is evident by noticing that the carbon to oxygen ratio remains constant at ~5 for the irradiation range. The calculated carbon to oxygen ratio for the unirradiated film was 5.2.

## CONCLUSIONS

The interaction of 2.1 MeV $He^{2+}$ ions with fluences in the range of 0.78 × $10^{15}$–12.5 × $10^{15}$ ions $cm^{-2}$ proceeds by inducing compositional changes on the surface of the polymer and along the interaction track of the particles. Although RBS does not show any stoichiometric change within its sampling depth of ~10 μm, the surface changes are detectable by X.p.s. and *FT*i.r. Surface modification by $He^{2+}$ ions proceeds through aromatic ring opening reactions with the redistribution of carbon and oxygen atoms and the formation of oxidized species, some of them containing hydroxylated moieties. In addition, carbonization reactions similar to those detected during the irradiation of aromatic polyimides also occur. As opposed to other surface modification techniques, such as plasma or photo-oxidation reactions, external oxygen uptake is not required to break the aromatic rings. The resulting surfaces are expected to be hydrophilic and possess some conductivity.

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