

Coloring of Radiation Damages in Ion-Implanted Poly(aryl ether ether ketone): LiCl Uptake and Thermal Desorption

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ABSTRACT: Poly(aryl ether ether ketone) (PEEK) films irradiated with 2 MeV O⁺ and Ar⁺ ions to fluences in the range 10¹¹–10¹³ cm⁻² were treated with 5 mol/L LiCl aqueous solution at 100°C for 1 h. After removal of excessive, weakly bound LiCl the samples were annealed at temperatures from 50 to 250°C for 1 h to check the mobility of the incorporated LiCl. The amount of incorporated LiCl and its depth profile were determined using the neutron depth-profiling (NDP) technique, which makes use of the ⁶Li(*n*_{th}, ⁴He) ³H nuclear reaction. Up to the maximum annealing temperature no significant escape of the LiCl was observed. With increasing annealing temperature, a gradual migration of LiCl dopant toward the sample surface was observed on the irradiated PEEK samples. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2780–2784, 2002; DOI 10.1002/app.10253

Key words: ion beam; poly(aryl ether ether ketone); LiCl doping; neutron depth profiling

INTRODUCTION

Poly(aryl ether ether ketone) (PEEK) is a high-temperature and radiation-resistant thermoplastic material that is used in an increasing number of technical applications.¹ For various applications the PEEK surface properties can be modified, for example, by laser light¹ or by ion irradiation.^{2,3} Ion irradiation leads to rather pronounced changes in polymer surface composition

and structure and, in turn, to changes in surface polarity, wettability, electrical conductivity, mechanical strength, and biocompatibility. The effects of ion irradiation in PEEK were extensively studied by positron annihilation,^{2,4} IR, UV–Vis spectroscopies, X-ray diffraction (XRD) technique³ and the neutron depth-profiling (NDP) method.^{5,6} In the latter study the PEEK samples irradiated with 1–2 MeV O⁺ were doped at room temperature from an aqueous solution of LiCl. Then the depth profile of the incorporated Li was measured by the NDP method. It was found that the LiCl solution easily penetrates the radiation-damaged PEEK surface layer and is captured preferentially in the radiation-damaged material. The amount of incorporated LiCl is an increasing function of the ion fluence applied. The subsequent leaching in distilled water showed that a significant part of LiCl was rather strongly bound

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in the polymer matrix.⁶ The measured Li depth profiles in pristine and irradiated PEEK were described by Case II diffusion with a depth-dependent diffusion coefficient.⁵

This study is a continuation of previous investigations mentioned above. The PEEK foils irradiated with 2 MeV O⁺ and Ar⁺ ions to fluences in the range 10¹¹–10¹³ cm⁻² were doped with LiCl and the stability of doped polymer was examined by thermal desorption technique.

EXPERIMENTAL

Semicrystalline PEEK foils (thickness, 200 μm; density, 1.286 g/cm³; Sumimoto Chemical Co., Tokyo, Japan) were used in the present experiment. The foils were irradiated with 2 MeV O⁺ and Ar⁺ ions to fluences in the range 10¹¹–10¹³ cm⁻². The irradiation was accomplished at an electrostatic accelerator (2 MeV model; High Voltage Engineering), with the ion current density being kept between 3 and 8 nA/cm² to avoid polymer thermal degradation. The irradiated samples were doped with 5 mol/L aqueous solution of LiCl at 100°C for 5 h and an excessive, weakly bound LiCl was removed by rinsing in deionized water at room temperature for 0.5 h. This procedure was previously proved to be sufficient for removal of all excessive, weakly bound LiCl.⁶ The samples were then annealed at temperatures from 50 to 250°C for 1 h, performed in darkness and in air. The total amount of the incorporated LiCl dopant and its depth profile in the as-doped and annealed PEEK samples were measured by the NDP technique, which makes use of the ⁶Li(*n*_{th}, ⁴He) ³H nuclear reaction.⁸ The nondestructive NDP technique allows one to determine Li depth profiles up to the depths of about 5 μm, with a depth resolution of about 20 nm at the sample surface. The conversion of the NDP energy spectra into Li depth profiles was accomplished using stopping powers calculated with the RSTOP procedure of TRIM (91 version) code.⁷ Doping and annealing experiments described below were performed 5 years after the ion irradiation. Meanwhile, the PEEK samples were stored at room temperature, in darkness and in air.

RESULTS AND DISCUSSION

The projected ranges of 2 MeV O⁺ and Ar⁺ ions in pristine PEEK calculated by TRIM code⁷ are 2.6

and 2.0 μm, respectively. For the initial ion energy the electronic energy loss is by about two orders of magnitude higher than the nuclear energy loss for both ion species, the total stopping power of which was about 10% higher for Ar⁺ ions. The ion irradiation results in rather deep changes in the PEEK elemental composition and chemical structure, especially in splitting of aromatic rings and production of excessive conjugated double bonds.³ Part of the volatile, low mass degradation products are supposed to escape the sample during the ion irradiation. In this way carbon-rich structures are formed and excessive free volume is produced in the irradiated material.² The excessive free volume may facilitate penetration and incorporation of LiCl dopant. The local density of the radiation defects is expected to be roughly proportional to the density of the energy deposited by an incoming ion at a particular depth, which in turn is proportional to the ion-stopping power. Because the stopping power depends on the ion immediate energy, the depth distribution of the radiation effects in the PEEK surface layer, affected by the irradiation, is highly inhomogeneous.

The dependency of the LiCl depth profile on the ion fluence for the PEEK irradiated with 2 MeV O⁺ ions is illustrated in Figure 1. The profile evolution indicates that with increasing ion fluence the PEEK permeability and ability to incorporate the dopant increase dramatically. The form of the depth profiles can also be affected by a limited doping time, during which a saturated state need not be achieved. For lower fluences intermediate profile forms are observed, corresponding to only partial dopant penetration and incorporation in the sample. For the highest ion fluence an anomalous profile is observed with a near-surface region of high Li concentration, extending to a depth of about 3 μm, which is obviously attributable to preferential dopant capture in the radiation-damaged surface layer and much weaker tail extending well beyond the 2 MeV O⁺ ion projected range of 2.6 μm. This finding is in accordance with previous observations^{5,6} on the PEEK samples LiCl doped at room temperature. The penetration of LiCl dopant beyond the radiation-damaged surface layer deserves attention. It cannot fully be explained by a regular LiCl diffusion into bulk, pristine PEEK, which is insignificant according to the present observation. The deep LiCl penetration/incorporation may be facilitated by the presence of microvoids produced by mechanical strain between radiation-damaged

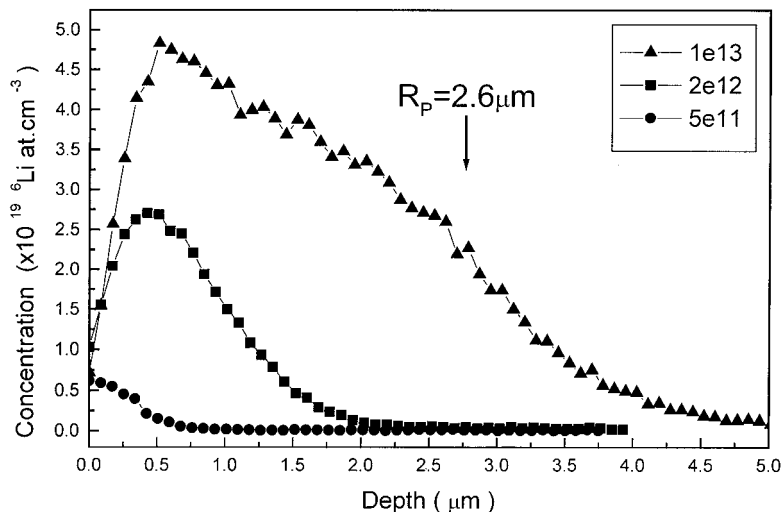


Figure 1 Depth profiles of ${}^6\text{Li}$ atoms measured using NDP technique on PEEK samples irradiated with 2 MeV O^+ ions to fluences indicated. The projected range of O^+ ions calculated by TRIM code⁷ for pristine PEEK is shown for illustration. The concentration decrease near the sample surface is an artifact attributed to limited depth resolution of the NDP technique.

and underlying pristine material. On the other hand, the subsequent LiCl leaching from deeper regions may be hindered by the necessity to overcome the near-surface, highly damaged, and doped layer. Similar profile evolution with increasing ion fluence is also observed for the PEEK samples irradiated with Ar^+ ions.

As a first attempt to explain the observed profile form we assume that the observed, anomalous depth profile simply reflects the depth distribution of the radiation defects on which the penetrating dopant is captured. Because the radiation defects are produced by ions by electronic (S_e) and/or nuclear (S_n) energy loss, the relative role of which is still unknown, the measured depth profile should be compared with depth profiles of electronic and nuclear energy loss or a combination of both. Several attempts have shown that the anomalous depth profile from the sample irradiated to a fluence of $1 \times 10^{13} \text{ cm}^{-2}$ cannot reasonably be approximated by any linear combination of S_e and S_n . This indicates that the whole process of dopant penetration and incorporation is much more complicated. In Fink et al.⁵ the penetration and incorporation of LiCl dopant in pristine and ion-irradiated PEEK was successfully described as Case II diffusion,⁹ with a depth-dependent diffusion coefficient. The role of excessive free volume, produced by the ion irradiation, polymer swelling, and transformation from glassy to rubbery state upon solvent uptake was also

considered. A certain deficiency of this approach is a large number of free parameters, the values of which cannot be unambiguously determined from the few experimental data available.

In Figure 2 the dependency of the number of ${}^6\text{Li}$ atoms incorporated in the 5- μm -thick PEEK surface layer on the ion fluence is shown for the samples irradiated with both ion species. For the low fluences the number of atoms remains practically unchanged and nearly the same as that for pristine PEEK, although above the fluence of $2 \times 10^{11} \text{ cm}^{-2}$ it increases rapidly with increasing ion fluence. The increase is roughly linear and about twofold faster for the samples irradiated with Ar^+ ions. The larger LiCl uptake for the samples irradiated to the same ion fluence with Ar^+ ions obviously cannot be explained by the almost 10% difference in the total stopping power of 2 MeV Ar^+ and O^+ ions. A tentative explanation can be found in the much larger role of nuclear stopping in the case of heavier Ar^+ ions. This supposition is in agreement with conclusions of Fink et al.,⁵ that is, that the diffusional mobility of LiCl dopant in radiation-damaged PEEK is governed by nuclear energy transfer.

The result of thermal annealing at temperatures of 50–250°C of the PEEK samples irradiated with O^+ ions to the ion fluence of $1 \times 10^{13} \text{ cm}^{-2}$ is shown in Figure 3. For the samples annealed to temperatures below the PEEK glass-transition temperature ($T_g = 148^\circ\text{C}$ as deter-

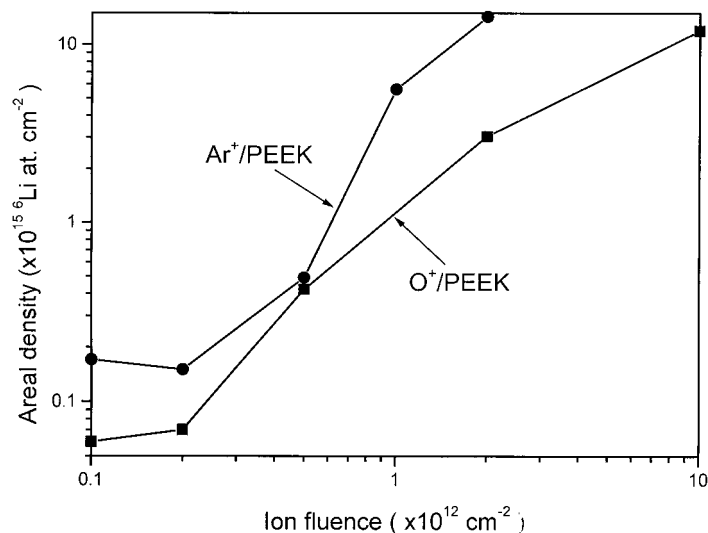


Figure 2 Dependency of number of ^6Li atoms incorporated in PEEK surface layer (5 μm thick) on fluence of O^+ and Ar^+ ions.

mined in Švorčík et al.³) the form of the ^6Li depth profile remains practically unchanged. Above this temperature, however, a significant dopant migration toward the sample surface is observed. The higher dopant mobility above T_g is obviously connected with enhanced mobility of segments of polymeric chains and with an increase of free volume fraction. No significant decline in the total amount of the LiCl dopant (in 5- μm -thick surface layer) and no dopant blooming were observed during the annealing procedure. The only change is

the above-mentioned dopant migration toward the PEEK surface, the rate of which is an increasing function of the annealing temperature. Similar but less-pronounced effects were observed on the PEEK samples irradiated with Ar^+ ions and the samples irradiated with both ion species to lower fluences. The preferential migration toward the sample surface could be explained, at least partially, by the depth-dependent diffusion coefficient introduced in Fink et al.⁵ and the presence of unsaturated capturing sites near the surface.

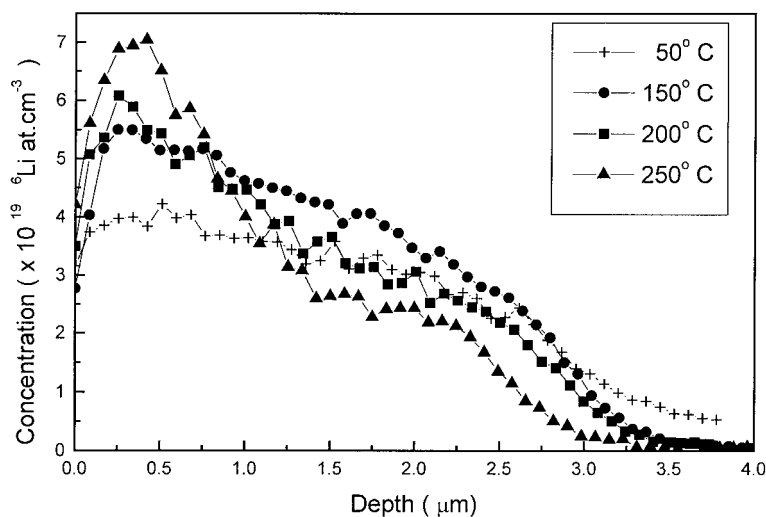


Figure 3 Evolution of ^6Li depth profile with annealing temperature for PEEK sample irradiated with O^+ ions to fluence of $1 \times 10^{13} \text{ cm}^{-2}$. Annealing time was 1 h.

CONCLUSIONS

The doping of PEEK irradiated with 2 MeV O⁺ and Ar⁺ ions to fluences in the range 10¹¹–10¹³ cm⁻² from an aqueous solution of LiCl was studied using the neutron depth-profiling technique. The LiCl uptake is an increasing function of the ion fluence and it is much faster for the samples irradiated with Ar⁺ ions. With increasing ion fluence the depth profiles of incorporated Li change dramatically and their form indicates an anomalous, non-Fickian mechanism of dopant penetration and incorporation in PEEK. The annealing of the PEEK samples to temperatures up to 250°C does not lead to a measurable escape of the LiCl dopant from the samples. Above 150°C a significant migration of Li atoms from the sample interior toward the sample surface is observed.

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