

# Mixed Radiation Field Effects from a Nuclear Reactor on Poly(Aryl Ether Ether Ketone): A Melt Viscosity Study

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**ABSTRACT:** Poly(aryl ether ether ketone) (PEEK) is a high-temperature engineering thermoplastic used in the aerospace industry. To assess its suitability for nuclear industry applications, the effects of mixed field radiation from a nuclear reactor were investigated on two industrial semicrystalline PEEK grades (VICTREX 150P and 450P). Specimens were first processed on an ENGEL55 injection molder and then irradiated in the pool of a SLOWPOKE-2 nuclear research reactor. Specimens were thus exposed to a mixed field of radiation including gamma, electrons, protons, and neutrons, for exposures resulting in doses ranging from 0.15 to 15 MGy. Irradiated samples were characterized by viscosity measurements in the melt, differential scanning calorimetry (DSC), and density measurements. Melt viscosity of irradiated samples proved to be significant in detecting early molecular weight changes in PEEK and helped explain the interaction of competing chain scission and crosslinking reactions at various stages of the radiolysis. All results pointed toward the following transformation of the resin with increased dosage: chain scission of the tie-molecules between the amorphous and crystalline phases, crosslinking in the amorphous phase, followed by a general degradation of the molecular weight dominated by chain-scission. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2713–2719, 2002

**Key words:** radiation; morphology; viscosity

## INTRODUCTION

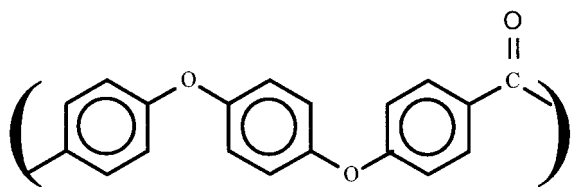
The excellent mechanical stability of poly(aryl ether ether ketone) (PEEK) at high temperature has made it a material of choice in a number of high-technology applications in the space, automotive, electrical, and chemical industries, among others. PEEK is an engineering semicrystalline thermoplastic that can be processed on conventional industrial equipment. Its melting point, crystallization temperature, and glass transition temperature are 334, 220, and 143°C, respectively. Key features in the structure of PEEK, shown in Figure 1, contribute to the superior performance of the polymer. The aromatic ring in the backbone is mostly responsible for the strength, heat, and radiation resistance of the material.<sup>1,2</sup> The ketone side group increases intermolecular spacing, whereas the ether linkage allows flexibility of the main chain, both contributing to the toughness of PEEK.<sup>1,3</sup>

The potential of PEEK for use in the nuclear and space industries was identified early. Yoda, in 1984, studied the effect of high-energy electron beams on the structure and properties of PEEK.<sup>4</sup> Other research followed,<sup>5–10</sup> using also gamma<sup>9</sup> and ion radiation.<sup>10</sup>

Although no significant differences in radiation damage were observed between high-energy electron beam and gamma radiation,<sup>9</sup> ion radiation yielded more damage, especially in the amorphous phase.<sup>10</sup> Ions similar to protons and neutrons possess a higher linear energy transfer (LET),<sup>11</sup> allowing them to better concentrate their energy deposition, causing more damage in the irradiated material. The energy deposition of gamma rays and electron energy in the irradiated material is more diffuse. Radiation damage was assessed with various means including differential scanning calorimetry (DSC),<sup>4,10</sup> X-ray diffraction (XRD),<sup>7</sup> gas evolution,<sup>9</sup> dynamic mechanical relaxation,<sup>8</sup> and tensile testing.<sup>5,6,10</sup> In all cases, the damage was related to components of the morphology of PEEK consisting of crystals, the amorphous phase, and the tie-molecules linking both phases. The crystallinity and melting temperature of PEEK were reported to start decreasing at doses of 10 MGy,<sup>4</sup> whereas at 260 MGy only a small fraction of the crystals remained.<sup>7</sup> The amorphous phase was found to be more sensitive to radiation than the crystals.<sup>9</sup> Tensile testing showed a decrease in elongation at break and the tensile strength of both amorphous and semicrystalline PEEK, whereas the tensile modulus increased for doses up to 50 MGy.<sup>5,6</sup> This effect was attributed to the crosslinking of molecules in the amorphous phase. Finally, comparison between dynamic relaxation results for irradiated semicrystalline and amorphous PEEK revealed that tie-molecules between the crystal-

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**Figure 1** Molecular structure for the repeating unit of Poly(aryl ether ether ketone).

line and amorphous phases were particularly vulnerable to radiation and prone to chain scission.<sup>8</sup>

The present study focuses on the effects of a mixed radiation field (gamma, electrons, protons, and neutrons), within a nuclear reactor facility, on two commercial PEEK grades. The degradation of a material due to the combined effects of a mixed radiation field is especially important to the nuclear industry. Also, the variation data of the molecular weight with increased dosage can be used in radiation processing to graft functional groups onto PEEK to enhance the chemical properties of the polymer. Melt viscosities were measured to assess the effects of the radiation damage on the overall molecular weight of the polymer. Other techniques such as density measurements and DSC were used to assess the irradiation damage on the polymer's morphology at the time of irradiation.

## EXPERIMENTAL

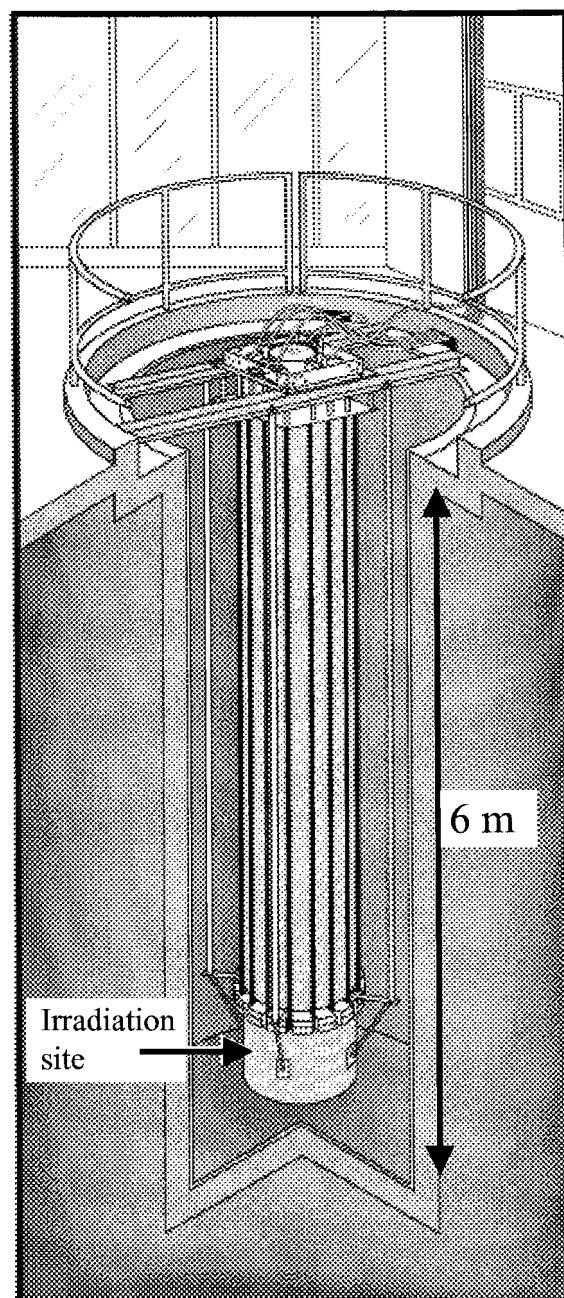
### Materials

Two industrial PEEK resins were purchased from VICTREX USA Inc. (West Chester, PA)<sup>12</sup>: 450P, with an average molecular weight of 43,000 g/mol, and, 150P, with an average molecular weight of 14,000 g/mol. Both grades had molecular weight distributions of 2.5. The resins were dried at 180°C for 4 h and then processed on an ENGEL55 injection molder to produce ASTM type IV tensile test specimens. The melt processing temperature was fixed at 370°C, and the molder was previously purged by using polysulfone at 350°C. The molded samples were annealed at 200°C, for 7 h, to maximize crystallinity and to relieve internal stress.

### Radiation processing

The mixed field radiation produced by the SLOWPOKE-2 nuclear research reactor<sup>13</sup> was used for this research. PEEK tensile test specimens were inserted in doubled low-density polyethylene bags and installed on a rack made of poly(methyl methacrylate) and lowered at a rigorously repeatable irradiation site in the reactor pool against the reactor vessel wall shown in Figure 2 at 31.4 cm from the reactor center core. The

dose rate at the irradiation site, at reactor half-power, was characterized in separate investigations and is reported in Table I.<sup>14–16</sup> The sample irradiation profile consisted of several exposures between 4 and 16 h, at 20°C, until the targeted cumulated doses were achieved: 0.15, 0.47, 1.5, 4.8, and 15 MGy. Prior to any testing of irradiated specimens, a standard radioactive cooling-down period of 3 weeks was allowed for the decay of radicals. Cooling of irradiated samples was also necessary to bring the dose rate from radioisotopes produced through neutron activation processes



**Figure 2** Irradiation site in the SLOWPOKE-2 nuclear reactor facility at the Royal Military College of Canada, at the reactor core mid height, 31.4 cm from center core.

**TABLE I**  
**Experimental and Computational Radiation Dose Rates**  
**in the SLOWPOKE-2 Research Reactor at the Royal**  
**Military College of Canada**

Type of radiation	Dose rate (kGy/h)
Electron	32 ± 9
Proton	1.0 ± 0.1
Gamma	2.6 ± 1.4
Neutron	0.50 ± 0.05
Total	36 ± 11

Note: Half power (10 kW) at the reactor mid-height, 31.4 cm from center core.<sup>14-16</sup>

to a safe level of 24  $\mu\text{Sv h}^{-1}$  (2.4 mrem  $\text{h}^{-1}$ ) or less at the samples' surface. It is important to mention that although the error on the absolute dose rate reported in Table I is 28%, the SLOWPOKE-2 reactor produces a highly reliable, repetitive, and stable power with fluctuations of <0.5%. Consequently, the uncertainty on the comparative dose received by the samples is <1%.

### Measurement

The density of non-irradiated and irradiated samples was measured by following the ASTM D792-A procedure and by using a Mettler H35AR balance.<sup>13</sup> The sample was first weighed in air giving  $W_0$  and then thoroughly immersed and weighed in water giving  $W_1$ . The sample's density was calculated by using the density of water at 23°C with the following equation:

$$\text{Density} = 0.9976 [W_0 / (W_0 - W_1)] \quad (\text{g mL}^{-1}) \quad (1)$$

The crystallinity of the samples was determined by using a differential scanning calorimeter, DSC 2010, from TA Instruments. The heat of fusion of the polymer was measured at heating rates of 20°C  $\text{min}^{-1}$  and divided by the heat of fusion of PEEK crystals,<sup>17</sup> 130 J  $\text{g}^{-1}$ , to obtain the crystallinity.

The melt viscosities of both PEEK grades were measured by using a Capillary Rheometer Instron Model 3210 with rheology test (REO) software. The rheometer was mounted on an Instron Model 4206 universal testing machine. The temperature of the rheometer was then set to 350°C. The rheometer was equipped with a proportional integral derivative (PID) controller that kept the temperature in the barrel within one degree of the set point. Irradiated tensile test specimens were cut into small pieces and fed into the barrel of the rheometer. A standard preheat period was allowed for the melt to reach the set temperature of 350°C. The molten resin was then forced down by a plunger with a diameter of  $d_p = 0.9525 \pm 0.0005$  cm, from the barrel through a tungsten carbide capillary of dimensions,  $d_c = 0.1527 \pm 0.0005$  cm and  $L_c = 5.0940$

$\pm 0.0003$  cm. The crosshead speeds of the plunger were  $v_p = 1, 2, 4, 8, 16,$  and  $32$  mm  $\text{min}^{-1}$ . Because of the non-Newtonian behavior of most polymer melts, shear rates measured with a capillary rheometer must be corrected by using the power law defined in eq. (2), where  $\tau$  is the shear stress,  $\dot{\gamma}$  is the shear rate,  $k$  is the fluid consistency, and the  $n$  is the power law exponent<sup>18,19</sup>:

$$\tau = k\dot{\gamma}^n \quad (2)$$

The shear stress was calculated from eq. (3),<sup>20</sup> where  $F$  is the force applied on the plunger,  $A_p$  is the area of the plunger,  $d_c$  is the diameter, and  $L_c$  is the length of the tungsten carbide capillary, and

$$\tau = \frac{F}{4A_p(L_c/d_c)} \quad (3)$$

The apparent shear stress  $\dot{\gamma}_a$  was calculated from eq. (4),<sup>20</sup> where  $d_p$  is the diameter of the plunger and  $v_p$  is the crosshead speed of the plunger;

$$\dot{\gamma}_a = (2/15)v_p \frac{d_p^2}{d_c^3} \quad (4)$$

$k$  and  $n$  in eq. (2) were determined by plotting the log of shear stress against the log of the apparent shear rate. To find the true viscosity of a polymer melt, the corrected shear rate  $\dot{\gamma}_c$  must be calculated by using the Rabinowitsch correction factor  $(3n + 1)/4n$  through eq. (5)<sup>18,19</sup>;

$$\dot{\gamma}_c = \dot{\gamma}_a (1 + 3n)/4n \quad (5)$$

Corrected viscosities for shear rates between 2 and 200  $\text{s}^{-1}$  were calculated by using the Rabinowitsch correction<sup>18,19</sup>:

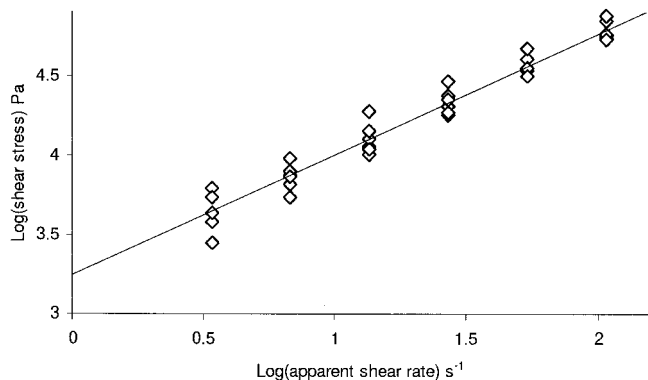
$$\eta = \tau / \dot{\gamma}_c \quad (6)$$

Bagley's correction for end effects was not applied in this work because of the high  $L/R$  ratio of the capillary. The error due to end effects is estimated to be small and to be the same for all measurements.

## RESULTS AND DISCUSSION

### Melt viscosity

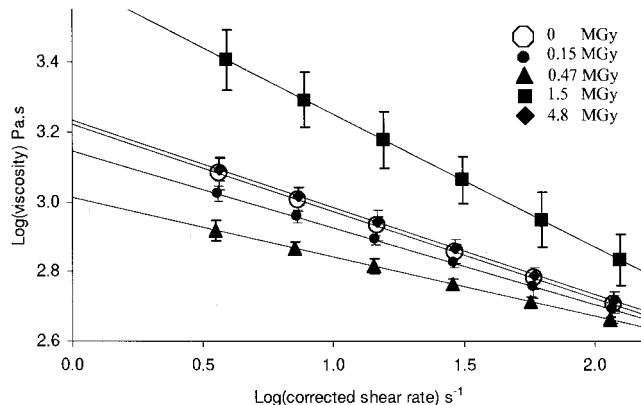
The melt viscosity was measured at 350°C for both irradiated and non-irradiated grades of PEEK. At 350°C, the morphology of the polymer was completely erased; only the net effect of melted polymer chains on viscosity remained. Figure 3 shows a log/log plot of the shear stress in Pascals against the apparent shear rate in  $\text{s}^{-1}$  for non-irradiated 150P PEEK grade at



**Figure 3** Shear stress as a function of shear rate from a capillary rheometer at 350°C for PEEK 150P grade in the melt. Fitted with  $k = 1780$  and  $n = 0.75$ .  $R^2 = 0.96$ .

350°C over five runs. The results were fitted with the power law with  $k = 1780 \text{ Pa s}^{-n}$  and  $n = 0.75$ . Power-law parameters for the non-irradiated 450P and all resins after irradiation are reported in Table II.

A log/log plot of viscosity against the corrected shear rate is shown in Figure 4 for the irradiated and non-irradiated 150P PEEK grade. The resin melt viscosity was clearly affected by the radiation. Higher melt viscosities attest to evidence of crosslinking, while lower viscosities show evidence of chain scission. All samples displayed a shear thinning behavior of the viscosity, typical of molten polymer. In Figure 5, the melt viscosity is reported against dose received by the 150P PEEK grade for four corrected shear rates, 3, 10, 30, and  $100 \text{ s}^{-1}$ . The general shape of the curve clearly indicates a complex radiolysis mechanism with competing crosslinking and chain-scission reactions during the irradiation period. The trend supports earlier findings<sup>4–10</sup> explaining the polymer degradation and changes in polymer morphology due to irradiation. The decrease in melt viscosity, after doses between 0.15 and 0.47 MGy, indicated a reduction of the molecular weight, which was attributed to the degradation of the tie-molecules between the amorphous and crystalline phase.<sup>8</sup> A potential explanation for the vulnerability of the tie-molecules could be that they are under tension,<sup>21</sup> being partly folded in crystals and entangled in the amorphous phase. Once broken, the



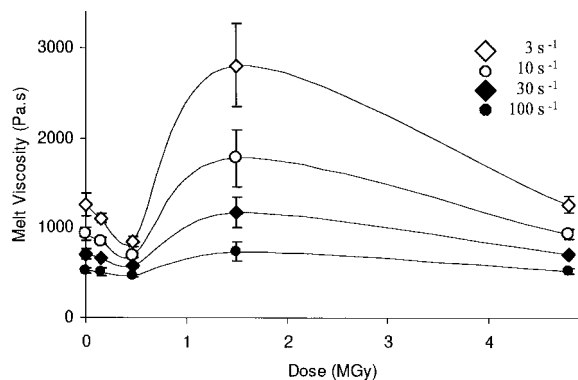
**Figure 4** Melt viscosity at 350°C for irradiated PEEK 150P grade as a function of the power law corrected shear rate.

loose ends of those molecules are pulled apart by tension, which makes the possibility of both ends crosslinking at the phase interface difficult, therefore resulting in an overall molecular weight reduction. The increase in melt viscosity between 0.47 and 1.5 MGy for both resins supports the crosslinking occurring in the amorphous phase,<sup>5,6,9</sup> which is equivalent to an increase in molecular weight. Crosslinking is diffusion dependent, with free radicals being able to move more freely in the amorphous phase to achieve crosslinking with a neighboring chain. However, the crosslinking occurring in PEEK due to irradiation at room temperature is limited because of the high  $T_g$  of the resin, and the degree of crosslinking is not high enough, once the polymer has melted, to create a microphase inside the melt. Finally, the decrease of the melt viscosity for samples irradiated at doses higher than 1.5 MGy supports the beginning of a more extended degradation of the molecular weight of the polymer<sup>4,7</sup> that can be explained by a predominance of chain-scission reactions over those involving crosslinking.

A log/log plot of viscosity against the corrected shear rate is shown in Figure 6 for the irradiated and non-irradiated 450P PEEK grade. The resin melt viscosity again appears to be affected by the radiation. Higher melt viscosities are evidence of crosslinking, whereas lower viscosities show evidence of chain scission. All samples displayed a shear thinning viscosity

**TABLE II**  
Power Law Fluid Consistency ( $k$ ) and Power Law Exponent ( $n$ ) for the Melt Viscosity at 350°C for the Two PEEK Irradiated Grades

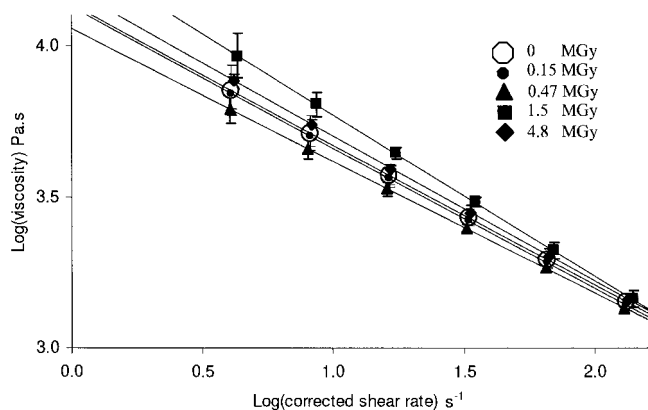
Dose (MGy)	PEEK 150P		PEEK 450P	
	$k$ ( $\text{Pa s}^{-n}$ )	$n$	$k$ ( $\text{Pa s}^{-n}$ )	$n$
0	$1780 \pm 150$	$0.75 \pm 0.02$	$15100 \pm 1000$	$0.53 \pm 0.02$
0.15	$1480 \pm 100$	$0.78 \pm 0.02$	$14800 \pm 700$	$0.54 \pm 0.02$
0.47	$1070 \pm 50$	$0.83 \pm 0.02$	$12600 \pm 600$	$0.56 \pm 0.02$
1.5	$4400 \pm 1000$	$0.63 \pm 0.04$	$22900 \pm 900$	$0.47 \pm 0.02$
4.8	$1820 \pm 100$	$0.76 \pm 0.02$	$17000 \pm 500$	$0.52 \pm 0.01$



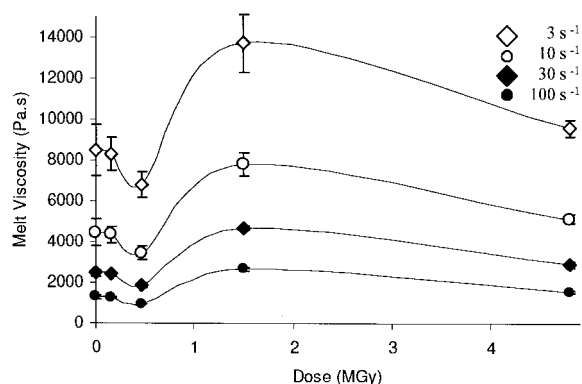
**Figure 5** Melt viscosity at 350°C for PEEK 150P grade as a function of the dose received. Melt viscosity is presented at four corrected shear rates, 3, 10, 30, and 100  $s^{-1}$ .

behavior. In Figure 7, the melt viscosity is reported against dose received by the 450P PEEK grade for four corrected shear rates, 3, 10, 30, and 100  $s^{-1}$ . The viscosities reported are three to four times larger than the ones reported in Figure 5 for the 150P grade. This is consistent with the higher molecular weight of the 450P grade. The general shape of the curve indicates the same trend as that reported in Figure 5 and supports the same degradation mechanism with competing crosslinking and chain-scission reactions at the time of irradiation.

Overall, the changes in melt viscosity were attributed to radiation damage to the solid polymer morphology at the time of irradiation and not to post-irradiation effects occurring in the melt state. Although post-irradiation reactions could have occurred in the melt, those reactions, if predominant, should have promoted either crosslinking or chain scission for all specimens regardless of the dose received. The resulting trends showed evidence of successive viscosity decrease followed by an increase and decrease again, and the trends were the same for both resins. Also, the concentration of free radicals should be very limited given the post-irradiation cooling period of 3



**Figure 6** Melt viscosity at 350°C for irradiated PEEK 450P grade as a function of the power law corrected shear rate.



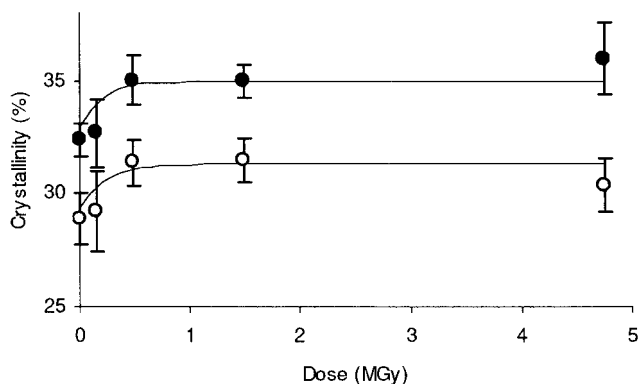
**Figure 7** Melt viscosity at 350°C for PEEK 450P grade as a function of the dose received. Melt viscosity is presented at four corrected shear rates, 3, 10, 30, and 100  $s^{-1}$ .

weeks. Therefore, post-irradiation reactions in the melt, if occurring at all, were considered negligible.

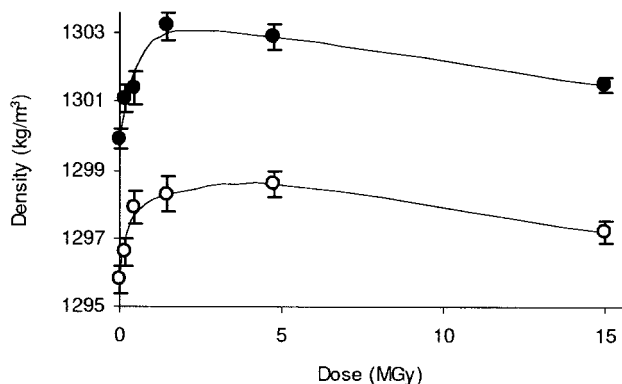
## Morphology

### Crystallinity

The crystallinity of all PEEK samples was evaluated by DSC. Figure 8 shows the crystallinity against the dose received by the resin. The values determined from DSC were based on the heat of fusion<sup>17</sup> of crystalline PEEK, 130  $J g^{-1}$ . Overall, DSC results for both grades indicated an increase in crystallinity of about 2% at a dose of 0.47 MGy. The slight increase in crystallinity supports the chain-scission effect of the tie-molecules at the lower dose, promoting further chain folding onto the crystalline phase.<sup>22,23</sup> The crystallinity remained constant at a higher dose.<sup>3,16</sup> The presence of high LET radiation, similar to protons and neutrons, did not seem to degrade the crystals because of their small 4% contribution to the overall dose composed mostly of electrons and gamma radiation.<sup>10,11</sup>



**Figure 8** Crystallinity determined by DSC for the irradiated PEEK 450P grade (○) and the PEEK 150P grade (●).



**Figure 9** Density as a function of dose for PEEK 450P (○) and PEEK 150P (●) grades.

### Density

The measured densities for all studied samples are presented in Figure 9 as a function of the irradiation dose for PEEK grades 150P and 450P. As expected, the densities of the two non-irradiated PEEK grades were different. The distinct density of each grade was attributed to the molecular weight because the processing conditions and the cooling rate were the same. Higher molecular weight chains take a longer time to crystallize because of their higher degree of chain entanglement.<sup>3</sup> Consequently, the shorter chains of the 150P grade achieved a slightly higher degree of crystallinity under the same cooling conditions and yielded a higher density for 150P samples. In Figure 9, both PEEK grades show an increase in density with accumulated dose up to 1.5 MGy, being indicative of morphological changes in the polymer resin. The increase in crystallinity shown in Figure 8 provides the reason for the increase in density. The decrease in melt viscosity in Figures 5 and 7 at the lower dose supports the scission of the tie-molecules at the crystalline and amorphous phase interface allowing molecules, liberated from tension due to entanglement in the amorphous phase, to achieve further chain folding on crystals,<sup>22,23</sup> thus increasing the density of the polymer. Crosslinking in the amorphous phase<sup>8,10</sup> would also contribute to the increase in density as would the increase in crystallinity. At higher doses, both resins showed a decrease in density explained by a more extended degradation of the polymer dominated by chain scission.

### Summary of results

The transformations observed in semicrystalline PEEK, under a mixed radiation field, were closely linked to the morphology of the polymer at the time of irradiation. At doses up to 0.47 MGy, changes in the polymer were dominated by the effect of chain scission of the tie-molecules at the phase interface. Con-

sequently, both studied grades showed decreases in melt viscosity, indicating a reduction of the overall molecular weight, while the density and the crystallinity of the irradiated samples increased. It is hypothesized that the chain scission of the tie-molecules at the phase interface promotes further chain folding onto crystals. The next dose range, between 0.47 and 1.5 MGy, was dominated by crosslinking in the amorphous phase. As a result, both grades showed increases in melt viscosity, indicating a higher overall molecular weight, while the crystallinity remained constant after the initial increase observed at lower dose. Finally, at doses above 1.5 MGy, chain scission started to predominate in the amorphous phase over crosslinking reactions. Both grades showed a decrease in melt viscosity and density, while the crystallinity appeared to suffer no significant reduction for this last dose range,<sup>6</sup> despite the presence of some high LET radiation.

### CONCLUSION

The results of this work detected significant changes in PEEK from doses as low as 0.5 MGy,<sup>6,10,11</sup> showing evidence of competition between crosslinking and chain-scission reactions during the irradiation of the polymer. Melt viscosity results proved to be an effective method in detecting the effects of those competing crosslinking and chain-scission reactions on the overall molecular weight. All results pointed to the following transformations of the polymer in its solid state, with increased dosage: chain-scission of the tie-molecules between the amorphous and crystalline phases, crosslinking in the amorphous phase, and a general degradation of the molecular weight of the polymer dominated by chain scission. The crystals proved to be resistant to radiation for the studied dose range despite the presence of some high LET radiation.

The data presented in this work could be used as an indication of the changes occurring in PEEK during radiation processing applications such as grafting. The performance of PEEK under a mixed radiation field of a nuclear reactor could lead it to potential nuclear industry applications such as the transport of spent fuel and the disposal of radioactive waste.

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