NEUTRON AND GAMMA RADIATION EFFECTS ON THE VISCOELASTIC BEHAVIOUR OF POLY (ARYL ETHER ETHER KETONE)

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ABSTRACT

The effects of combined neutron and gamma radiation on the viscoelastic behaviour of two industrial semi-crystalline PEEK grades (VICTREX 150P and 450P) were investigated. Tensile test samples were processed on an ENGEL55 injection moulder, then irradiated in a reactor pool environment, against the reactor vessel wall of the SLOWPOKE-2 facility at the Royal Military College of Canada (RMC), for exposures resulting in dosages ranging from 10 kGy to 320 kGy. First, the morphology of the irradiated resins was characterized by differential scanning calorimetry (DSC), X-ray diffraction and density measurements. Secondly, the viscoelastic behaviour of the material was studied at three thermodynamic states, in order to define the nature of the structural damage suffered by PEEK, by comparing its degree of molecular motion with the dose received. Therefore, standard mechanical testing was performed at room temperature, stress relaxation near the glass transition temperature(T_g), at 140°C, and melt viscosity above the melting point (T_m), at 350 °C.

Results confirmed that PEEK is highly resistant to radiation, but also suggested that PEEK degrades faster under a combined neutron and gamma flux, in a reactor pool environment, than observed in previous work under electron beam or gamma alone. The density increased slightly over the range of irradiation (150P: 1300 to 1303 kg/m^3 ; 450P: 1296 to 1299 kg/m^3), while the crystallinity (150P: 27 %, 450P: 24 %), and the thermal properties, like T_g and T_m , remained unaffected. Therefore, the increases in density were attributed to transformations occurring mostly in the amorphous phase, which is also consistent with previous work. The viscoelastic behaviour analysis provided the following damage assessment for PEEK: the amorphous phase is subject to both crosslinking and chain scission; the effects of chain scission, on the viscoelastic behaviour of PEEK, are predominant for doses higher than 100 kGy; tie-molecules, at the crystalline and amorphous phase interface, are more sensitive and are prone to chain scission under radiation; and, crosslinking occurs predominantly near chain-ends. Overall, this research confirmed PEEK as a good candidate material for applications in nuclear reactor pool environments and for the disposal of radioactive waste.

INTRODUCTION

The aerospace, communications and nuclear industries rely increasingly on new polymeric materials for advanced engineering applications demanding high resistance to radiation. Among the most promising polymeric materials is poly (aryl ether ether ketone) (PEEK), a semi-crystalline thermoplastic which is resistant to high temperatures in addition to displaying superior mechanical properties and good stability in both chemically active and radiation environments. These characteristics make PEEK an excellent candidate material for nuclear applications.

PEEK was designed in 1978 by Imperial Chemical Industries (ICI) as a tough high temperature-resistant cable insulating material [1]. Since its commercialization in 1981, PEEK's excellent mechanical stability at high temperatures coupled with its ease of processing has made it a material of choice in a number of high technology applications including employment in radiation environments. PEEK is generally a tough, semi-crystalline thermoplastic with the following chemical structure (Figure 1)[2]:

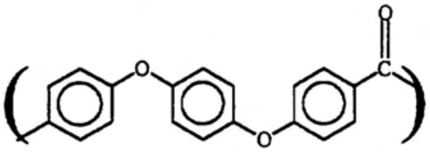


Figure 1: Chemical structure of poly (aryl ether ether ketone) (PEEK)

The special properties of this polymer can be attributed to its chemical structure. The *aromatic ring* is the dominant component in PEEK's composition, as shown above, and is mostly responsible for the strength, the high temperature and radiation resistance of the material [3]. The *ether* bond provided by oxygen in the backbone contributes toughness and flexibility. The last feature, is the *ketone* group which provides a side group resulting in greater intermolecular spacing, reducing the density and increasing both free volume and molecular movement. The repetitive sequence in PEEK's molecular structure, allows crystallization to occur, enhancing strength and chemical resistance.

Past research work has concentrated mostly on the study of the effects of electron beam [4-12] and gamma radiation [13] on PEEK among other thermoplastics. No research has been carried out on the effects of fast and thermal neutrons on this material, especially on its viscoelastic behaviour in the temperature region close to the glass transition temperature. In order to assess molecular damage and to better analyze the specific role played by the amorphous phase, the crystalline phase and their interface during radiolysis, the morphology of the PEEK resins were characterized using density measurements, differential scanning calorimetry (DSC) and X-ray diffraction. Then, the viscoelastic behaviour of the polymer was studied at three different thermodynamic states. The methodology used for this part of the research consisted first in performing stress relaxation testing just below T_g(140°C) to study the viscoelastic behaviour of the irradiated PEEK, then, these tests were complemented with tensile testing at room temperature to assess the elastic behaviour of the material, finally rheology tests were performed above T_m(350°C) to assess changes in the viscous behaviour of PEEK.

THEORY

Nuclear reactors produce a large variety of radiation. The nuclear reaction is initiated in the core by the spontaneous and neutron-induced fission of Uranium-235, and leads to a series of interactions producing radiation in the fuel rods, surrounding water and reactor vessel materials. While electron, beta, alpha particles and heavy ions are attenuated rapidly, neutron and gamma radiation can interact with materials far from the reactor core. This radiant behaviour is the result of different interaction mechanisms between radiation and matter[14].

Gamma-rays are photons which can ionize atoms through three important energy transfer processes[15]. First, the *photoelectric process*, [16-19] where low energy photons (< 0.05 MeV) interact with a tightly bound electron from an inner shell of the atom and causes one electron to be ejected out. Second, the *Compton scattering*, in which a low-to-high energy photon (0.1-10 MeV) interacts with several atoms, each time scattering off an orbital electron, which goes on to ionize more atoms. Compton scattering ends when the photon has decreased its energy low enough so that the photoelectric process may occur. The third process is the *pair-production*, where a photon of energy 1.02-20 MeV, converts its energy in the presence of an atomic nucleus to a positron-electron pair, which proceeds to interact with more atoms and molecules [20]. In most cases, Compton scattering is the principal radiation interaction mechanism for organic polymers. Overall, photon energy deposition tends to be fairly uniform within the irradiated material.

Neutrons ionize atoms along their paths by ejecting electrons, but also collide with and produce energetic recoil nucleus by *knock-on process*. In a polymer, fast neutrons (1-2 MeV), mostly produce energetic protons from the collisions with hydrogen atoms which, in turn, interact and cause far more damage than the incident neutron [20]. Neutrons of thermal energy (0.00253 eV) can also be absorbed by other nucleus which then become unstable radionuclides and undergo nuclear reaction or further radiation decay [14]. This type of reaction can induce radiation that can remain active a long time after the irradiation exposure is completed, especially in metals. Again, in most pure polymers, induced radiation is short-lived, because the radionuclides generated by C,O and H possess short half-lives, and decay mostly with the emission of beta and gamma-rays. The end result of neutron radiation is the generation of recoil protons and heavier ions, producing a different geometrical distribution of the energy deposition which tends to concentrate damages along specific tracks and in more localized sites [20].

Therefore, the level of damage caused by radiation depends not only on the quantity of the energy deposited in the material but also on how concentrated the energy deposition is, resulting in free-radical pairs along the path taken by the energized particle or photon[23]. The destructive potential of radiation is assessed in terms of linear energy transfer (LET) which is the amount of energy deposited per unit length of the ionization track [20,21], expressed as dE/dx. For example, gamma-radiation has a low LET of 3.5 keV/μm in water, whereas energetic protons and alpha-radiation have a high LET of 53 keV/μm in water. Since fast neutrons can generate several recoil protons along their paths, they are also attributed with a LET of 53 keV/μm in water. If the incident neutrons have energies lower than 10 keV, they are attributed with a lower LET of 7-10 keV/μm in water [14].

Radiation-induced chemically active species can react in different ways resulting in structural and molecular weight changes. Those chemical reactions occurring in the polymer as a result of irradiation are described as *radiolysis* [22-24]. Among those chemical transformations, crosslinking increases the molecular weight by the creation of new intermolecular bonds. Crosslinking can eventually result in the formation of an important network which radically alters transition temperatures, chemical and mechanical properties of the material [23]. Secondly, chain scission consists in the fractionation of macromolecules followed by the recombination of the newly formed free radicals with low molecular weight molecules, which causes a decrease in the overall molecular weight of the material. As a result of chain scission the general properties of the material are altered but in a more gradual way than crosslinking. Thirdly, the creation of low molecular weight products occurs resulting from chain scission and followed by abstraction and recombination reactions. These products are usually gases such as H_2, CO_2, CO and CH_4, but some polymers with particular structural groups may release other gases like SO_2, in the case of polysulfones, or HCl for polyvinylchloride [22]. Such small products impact on the overall molecular weight and create small gas pockets in the polymer which reduce mechanical properties. The last induced chemical change is the actual structural modifications by the appearance of new bonds creating new chemical groups or the elimination of existing ones. Such changes can alter both chemical and physical properties of the polymer.

The role played by the morphology in semi-crystalline PEEK, during radiation-induced molecular transformations, is not well understood. The kinetics of radiolysis is dependent on the reactive species created by radiation and also by the freedom of movement of those reactants. Since molecular movement increases with temperature as the polymer goes through various thermodynamic transition states[3] it can therefore be used to study the role played by the morphology during radiolysis, and also to assess the damage caused by radiation on the structure of the polymer.

The special mechanical properties of polymers are driven by their viscoelastic attributes. The *viscoelasticity* of a material is characterized by the Young's modulus which is the ratio of the applied stress to the material's strain response. The changes in the viscoelastic properties of polymers, exposed to aggressive environments such as radiation, are often an excellent indicator on the ability of polymeric materials to maintain the mechanical resistance required from them throughout the lifetime of their application. The viscoelasticity of a polymer is dependent on its molecular structure, defined by chemical bonds and chain length, but also by its *morphology* which is determined by the crystalline and amorphous phase composition and interface characteristics.

METHODOLOGY

The mechanical properties of polymers are dependent on their viscoelastic nature. The viscoelastic behaviour of polymers is best observed starting from their glass transition region up to their melting point, where both the effects of the elasticity provided by molecular conformation changes and the viscous flow created by chain segment movements, takes place on the same time scale. In order to verify if viscoelastic changes could be observed following irradiation, a series of stress relaxation tests were performed on irradiated polycarbonate and polystyrene for doses between 10 kGy and 100 kGy at temperatures going from (T_g-20°C) to (T_g +20°C). The best temperature region, providing for the optimal observation of stress relaxation and the repeatability of the results with a minimum standard deviation, was (T_g-10°C) to (T_g-3°C).

Two industrial PEEK grades were purchased from VICTREX USA, the 450P(MW 43k, MWD 2.5) and 150P(MW 14k, MWD 2.5). The resins were processed on an ENGEL55 injection moulder to produce tensile test samples and then annealed up to 200°C, for seven hours, to relieve internal stress. The tensile test samples were then irradiated with a combined gamma and neutron flux, against the reactor vessel wall of the SLOWPOKE-2 facility, for exposures ranging from 10^4 Gy to $10^{5.5}$ Gy. The total dose rate at the irradiation site in the SLOWPOKE-2 reactor pool was determined at 2400± 960 Gy/h [25,26], and consisting of a 75% gamma radiation contribution and 25% fast and thermal neutrons contribution. Following a cooling period of three weeks, morphological and thermal properties were determined by differential scanning calorimetry, X-ray diffraction and density measurements [27]. The studied dose range was set between 10 kGy and 320 kGy in order to identify early degradation in semi-crystalline PEEK, and also to assess molecular damage before the occurrence of significant morphological changes. The morphology was characterized with density measurements, differential scanning calorimetry (DSC) and X-ray diffraction. Then, the viscoelastic behaviour of the irradiated resins was investigated at three thermodynamic states as demonstrated in Figure 2, with stress relaxation tests conducted at 140°C, standard tensile tests at 24°C, and melt viscosity measurements at 350°C.

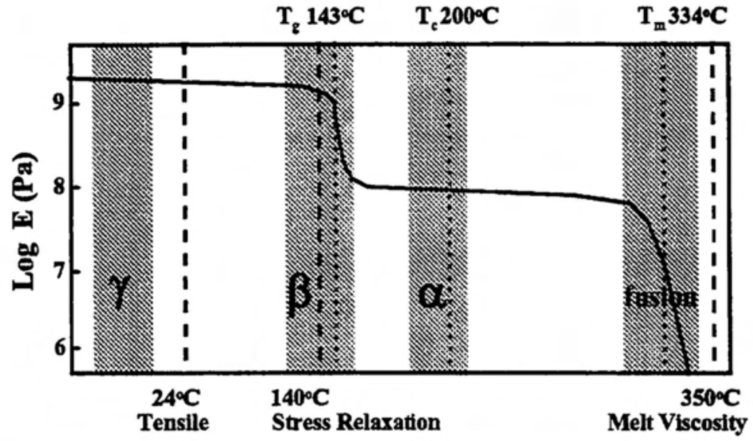
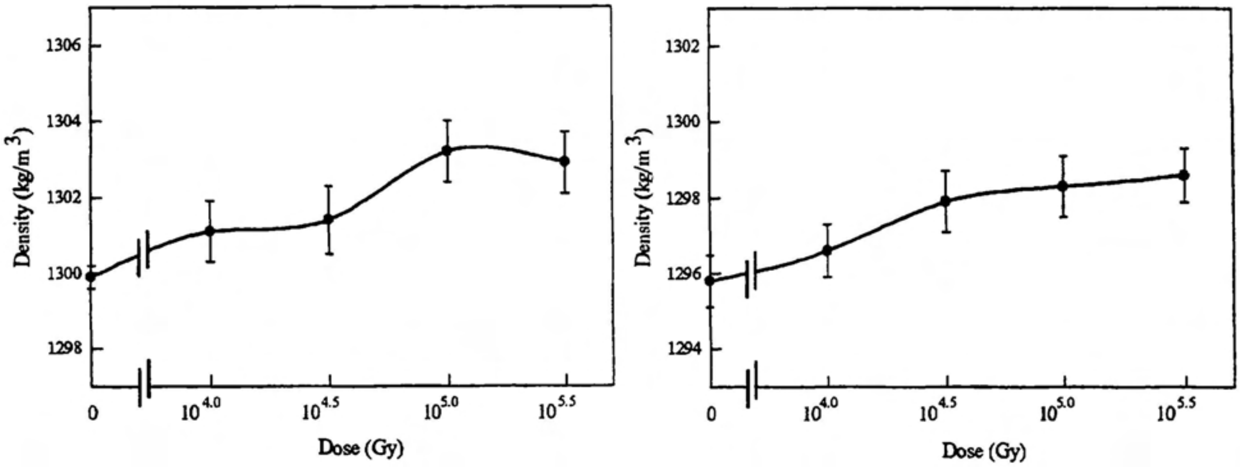


Figure 2: The Young's modulus of PEEK in relation with its γ,β and α phase transitions and thermal properties, and the selected temperatures for the three viscoelastic tests.

RESULTS AND DISCUSSION

The density increased slightly over the range of irradiation (150P: 1300 to 1303 kg/m^3, 450P: 1296 to 1299 kg/m^3) as demonstrated in Figures 3 and 4, which can be attributed to crosslinking. Changes in thermal properties like the glass transition and melting temperatures were not detected, as well as no changes were detected in the crystallinity (450P: 24 %, 150P: 27 %) within the precision of the equipment. This leads to the belief that most of the changes occurred within the amorphous phase, identified in Figure 5, which is consistent with previous work [4,5,28].

The results of the three viscoelastic tests tend to demonstrate polymer degradation dominated by chain scission, in both resins, after receiving a combined neutron and gamma dose of $10^{5.5}$ Gy. Although the performance of PEEK is still outstanding in such irradiation conditions in a reactor pool environment, the results in comparison with previous work, suggest a more significant degradation mechanism than for electron beam [10] or gamma radiation alone [4].



Figures 3 & 4: Density as a function of the dose received for the PEEK resins 150P and 450P respectively.

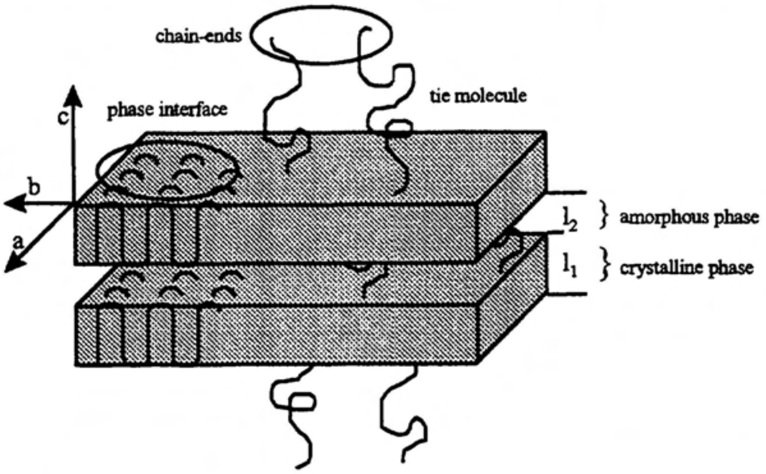
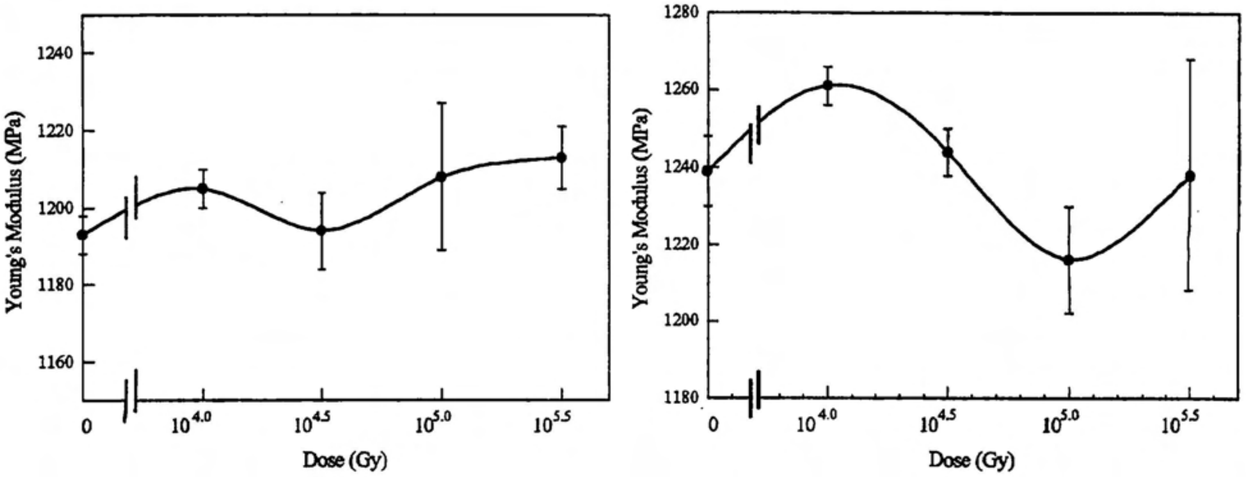


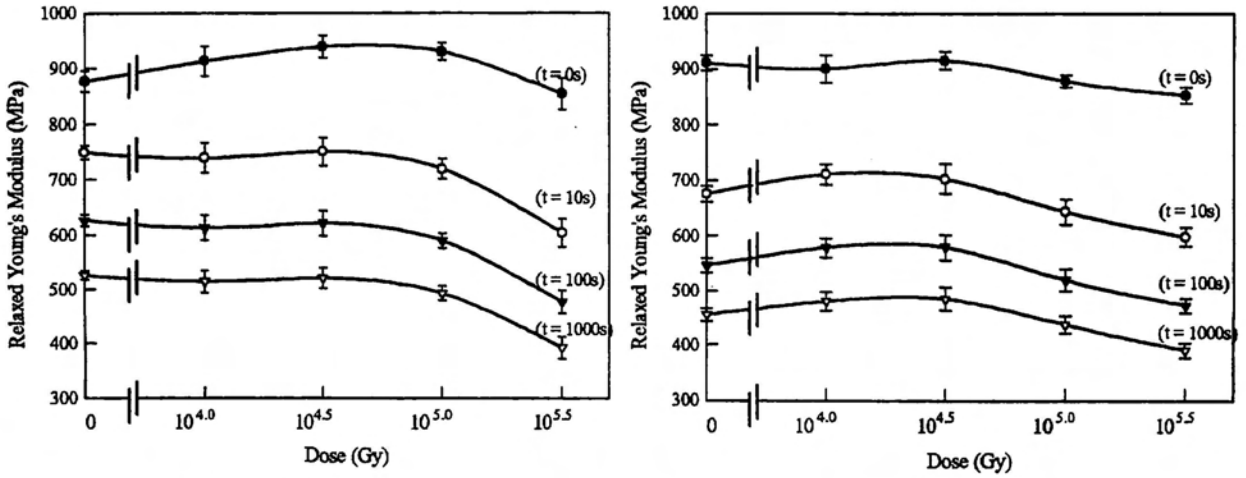
Figure 5: Molecular arrangement of PEEK in its semi-crystalline state.

The role of the morphology on the radiolysis of the polymer was also considered. Standard tensile tests were performed at 24°C. At that temperature, PEEK is above its γ–transition temperature where molecular movement is limited mostly to chain-ends in the amorphous phase and repeat units at the phase interface [9]. Stress-strain diagrams revealed that the higher molecular weight PEEK (450P) possessed a second yield point which could be associated with the presence of a crystalline network where molecular chains are long enough to be part of several crystalline layers. The lower molecular weight (150P) did not display that kind of behaviour which would indicate that its strain is limited by the effect of chain entanglement in the amorphous phase. For that reason, the Young's modulus of the two PEEK grades, reacted differently to radiation as demonstrated in Figures 6 and 7. The 450P displayed a clear reduction in its Young's modulus after receiving $10^{4.5}$ Gy while the 150P showed a slight increase with dosage. The reduction in modulus, was explained by the higher radiation vulnerability [9] of the tie molecules at the phase interface due to the presence of some tension between two phases of different densities. The behaviour of the 150P was attributed to the higher concentration of chain-ends, about three times that of 450P, which, by their mobility potentially favoured crosslinking.



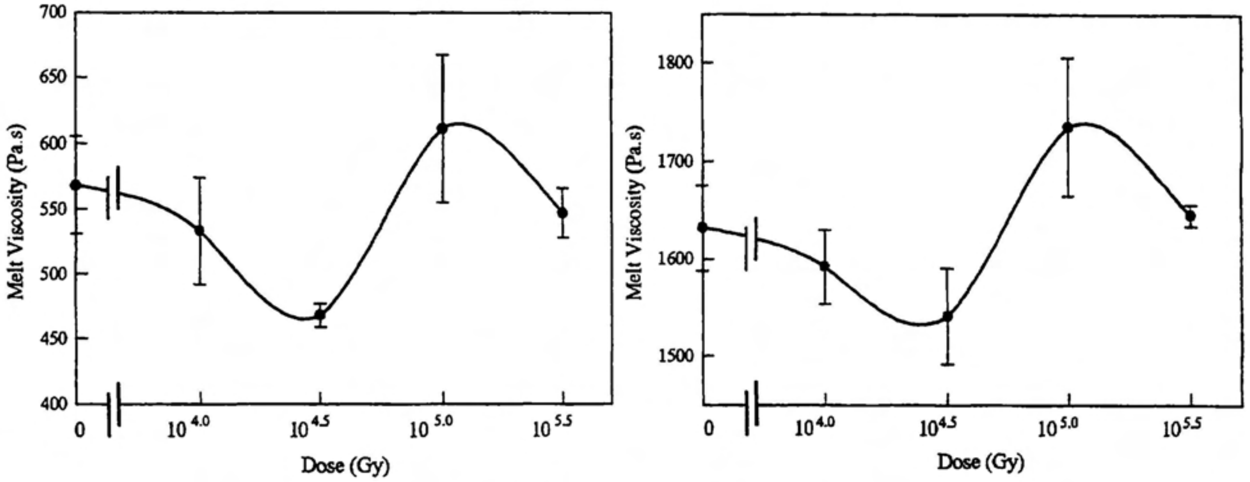
Figures 6 & 7: Young's modulus as a function of the dose received for the PEEK resins 150P and 450P respectively.

The stress relaxation test was performed at 140 °C on tensile test bars after rapidly applying a 4.8% strain. At that temperature, PEEK is in its β–transition where movement is dominated by molecular backbone movement in the amorphous phase. The relaxed Young's modulus $E_r(t)$ was measured against time with a statistical deviation error of 10 to 30 MPa based on five samples for each point. The results in Figures 8 and 9, representing the measured relaxed Young's modulus, displayed a marked decrease for samples that received doses of 10^5 Gy or more. The higher molecular weight grade (450P) displayed a slight maximum in $E_r(t)$ after receiving a dose between 10^4 Gy to $10^{4.5}$ Gy. The small variations in $E_r(t)$, even at a temperature of 140 °C, confirmed the very high stability of the neutron irradiated semi-crystalline PEEK and are indicative of the competition occurring within the amorphous phase between the crosslinking and chain scission processes. Although $E_r(t)$ seemed at first only slightly affected by radiation, a marked decreasing trend appeared for doses between $10^{4.5}$ Gy and 10^5 Gy. Therefore, at this dose range, molecular backbone movement in the amorphous phase seems to become more important, probably caused by an increase in lower molecular weight products resulting from chain scission. On a segmental scale of several repeat units, the effect of chain scission in the amorphous phase becomes predominant over crosslinking after a dose of $10^{4.5}$ Gy and contributes more effectively to the reduction in the mechanical properties of irradiated PEEK.



Figures 8 & 9: Relaxed Young's modulus at 140°C as a function of the dose received for the PEEK resins 150P and 450P respectively.

Lastly the rheology test was performed at 350 °C to measure the melt viscosity as demonstrated in Figures 10 and 11. At that temperature, PEEK is above the melting temperature in one homogeneous phase and its viscosity is determined by full molecular motion. For this test, both resins yielded similar results. A maximum viscosity was reached for a dose of 10^5 Gy followed by a decrease at higher dose. This maximum, can be attributed to the presence of larger molecules resulting from crosslinking. However, from those results, it is not clear whether crosslinking occurred only in the amorphous phase or also in the crystalline phase.



Figures 10 & 11: Melt viscosity at 350°C and 100 s^{-1} as a function of the dose received for the PEEK resins 150P and 450P respectively.

This research work showed that the degradation under a combined flux of neutron and gamma in the SLOWPOKE-2 is more significant than evidenced in previous work for PEEK irradiation under electron beam or gamma. Also, the parallel work of mechanical testing at room temperature, relaxation near T_g and melt flow above T_m provided an effective method to better understand the role of the morphology during the radiolysis of the semi-crystalline PEEK. Mechanical testing confirmed the sensitivity of tie molecules between the two phases to chain scission, and the contribution of chain-ends to crosslinking. Stress relaxation near T_g, demonstrated both the occurrence of crosslinking and chain scission in the amorphous phase and greater relaxation with radiation, especially for doses of 10^5 Gy and up. Chain scission appeared to induce more movement on a molecular segment scale caused by the possible increase in the number of small radiolysis products. Melt viscosity revealed the viscous behaviour of PEEK on a full molecular scale including molecules from the crystalline phase. Both resins displayed the same behaviour, with a maximum viscosity at 10^5 Gy followed by a decrease at higher dose. This trend supports the occurrence of crosslinking producing larger molecules up to 10^5 Gy. The subsequent reduction in viscosity at higher dose can be attributed to the predominance effect caused by chain scission over the crosslinking of only a few larger molecules.

CONCLUSION

This study has confirmed PEEK as a resistant material to radiation and provided a better understanding of the mechanical performance of semi-crystalline PEEK under the effects of neutron and gamma radiation in a reactor pool environment. Three types of viscoelastic tests were carried out on non-irradiated and irradiated PEEK as follows: standard tensile tests at 24°C, stress relaxation tests at 140°C and melt-viscosity measurements at 350°C. The results of those three tests tend to demonstrate polymer degradation dominated by chain scission, in both resins, after receiving a combined neutron and gamma dose of $10^{5.5}$ Gy. Results also pointed toward the crystalline/amorphous phase interface as a weak point in the morphology of semi-crystalline PEEK. Although the performance of PEEK is still outstanding in such irradiation conditions in a reactor pool environment, the results in comparison with previous work, suggest a more significant degradation of the mechanical properties of PEEK than for electron beam radiation [10].

Tools made of PEEK could be used in nuclear reactors for long periods of time without significant lost in mechanical properties. Owing to its high mechanical strength and chemical resistance, PEEK could also be used in the construction of containers for the transport of nuclear fuel waste without risking hazardous container deterioration. PEEK could be used as a coating on metal (copper) container to prevent corrosion or as the resin with carbon or boron fiber to produce all made composite containers. In this research, semi-crystalline PEEK resins were studied up to a maximum dose of 320 kGy in the SLOWPOKE-2. This dose corresponds to an equivalent exposure of 3.23 years for a PEEK composite nuclear waste container [29] holding fuel bundles with glass as a filler and 700 years using Thorium dioxide as a filler. Composite containers would definitely provide a handling advantage over the currently used heavy titanium alloy containers.

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