HIGH POLYMER-BASED COMPOSITE CONTAINERS FOR THE DISPOSAL/STORAGE OF HIGH RADIOACTIVE WASTE

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ABSTRACT

Spent fuel disposal is one of the hottest topics in nuclear news, getting considerable amount of media coverage around the world. Canada as well as many other countries with nuclear electric generation plants has therefore been pushed to develop policy on this issue. One of the proposed and most widely supported strategies is to dispose of this so-called waste permanently in deep underground vaults. Through the use of engineered barriers including vault seals, vault composition, backfill and sophisticated containers this radioactive matter is isolated from the natural environment. According to a design developed by Atomic Energy of Canada[1], the seclusion must be maintained for approximately 500 years, which is a representative length of time it takes for the radioactive elements to decay to natural background levels. The purpose of the current study is to determine the feasibility of using poly(ether ether ketone), an advanced polymer, and continuous carbon fibre in a consolidated composite as a principal container component. Feasibility was determined by simulating the ultimate radioactive environment that the containers will be exposed to by exposing test specimens to neutron and gamma radiation fields at various temperatures (20°C - 75°C) for a variety of time intervals.

INTRODUCTION

The excellent mechanical and chemical stability of poly(aryl ether ether ketone) (PEEK) has made it a material of choice for many technologically advanced applications. Because of its desirable properties, the potential applications in the space and nuclear field were identified early, and has been investigated and examined since the early 1980's. Yoda[2,3] employed high-energy electron beams and both gamma and electrons were employed in a study by Hegazy et al[4,5]. In both of these investigations similar results were found in that amorphous PEEK tends to be more susceptible to radiation than crystalline PEEK and the cross-linking due to the radiation field occurs in the amorphous regions. This cross-linking has more recently been shown by Sasuga and Hagiwara[6,7,8] to cause changes in the molecular structure to the extent that changes in physical and thermal properties are seen. Also seen in this study was that ion radiation causes more variations than electron or gamma radiation. In a recent investigation by Pagé[9] using a mixed field radiation source produced by a SLOWPOKE-2 research reactor, the morphology and viscoelasticity effects were studied. Chain scission was determined to be a dominant factor in the polymer degradation, with the crystalline-amorphous

interface being a more susceptible region. It was also shown that this type of radiation produced a more rapid degradation when compared with electron radiation.

THEORY

When polymers are exposed to a radioactive environment, the high energy waves and particles produce a molecular rearrangement, which can ultimate lead to observable physical changes on a macroscopic scale. Not all polymers react to radiation equally, with some being much more resistant to this reorganization. PEEK polymer has a chemical structure of that in figure 1. This semi-crystalline polymer is tough, strong, and radiation and chemically resistant. The aromatic ring, which dominates the structure, contributes much of the resistance, strength and high temperature stability. The benzene-like structure is unusually stable, due to the multiple resonance structures and delocalized pi electrons[10].

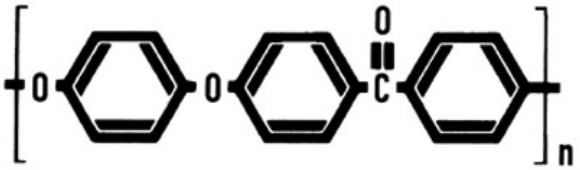

FIGURE 1: Chemical structure of poly(aryl ether ether ketone).

When irradiated, there are two main reactions that occur: chain scission and cross-linking. Scission is the splitting of the polymer chain or backbone. Scission occurs when the high energy particles interact with the bonds of the polymer, splitting the bond and producing two new molecules. Cross-linking is the recombination of adjacent polymer chains, resulting in a higher molecular weight. In PEEK, the weakest bonds (i.e. C-C or C-O) are generally targeted, while the aromatic rings and the ketone side group remains intact. Another area within PEEK that has been said to be more susceptible is the tie molecules at the amorphous and crystalline interface.

Radiolysis, or radiation-induced chemical reactions, is dependent on several interrelated factors: the molecular structure, crystallography, the reactive species created upon radiation treatment, and the freedom of movement of these species. Molecular movement tends to directly increase with temperature, and therefore it can be postulated that the reactive species have the ability to travel further and/or faster.

The SLOWPOKE-2 reactor produces a large variety of different radiation. At half power, the normal operating mode, the reactor produces a total dose rate of 3.7×10^4 Gy/h. The ionizing particles produced are as follows: 3.2×10^4 Gy/h (86%) for the electrons, 2.6×10^3 Gy/h (7%) for the gamma photons, 1.0×10^3 Gy/h (2.7%) for the recoil protons, and 0.5×10^3 Gy/h (1.4%) for the fast and thermal neutrons. As each of the particles have different penetration power and energy, each have differing interactions with the polymer. This is quantitatively described as the Linear Energy Transfer (LET), which is the amount of energy transferred to the matter per unit length. It has been estimated that the LET of recoil protons and neutrons is 10 and 2.5 times, respectively, greater than that of electrons or gamma rays. Penetration power is important because such radiation as electron beams and alpha radiation are strongly attenuated and only result in surface effects. However, fast neutrons can travel much greater distances, and travel

throughout the irradiated sample, causing damage uniformly through the sample.

MATERIALS

The PEEK/graphite composites used in the current study was obtained from Applied Fiber Systems, Clearwater, FA, USA. This material consists of woven continuous graphite fibre in a 2×2 twill in a matrix of Victrex Grade 150 PEEK. This polymer has a reported M_W and M_{WD} of 14 000 g/mol and 2.5, respectively[11]. The graphite, grade HTA G30-500, was obtained in strand form from Toho Besfight Carbon Fibres. The specimens were obtained from the manufacturer in nominal 1" × 3" × 0.125" coupons. These samples were cut from a 17" × 17" panel produced by stacking plies of woven fabric pre-impregnated with PEEK resin powder and compression molded into a consolidated sheet. These coupons would become the samples to be irradiated. Virgin PEEK 150 will also be studied for comparison to the composite. These samples will be in ASTM standard dog-bone shape, produced by injection moulding. This polymer has the same specifications as the composite matrix, and also is irradiated in the same manner.

EXPERIMENTAL

During the irradiation sequences, the samples were placed beside the SLOWPOKE-2 reactor core in the reactor pool in a specially designed support, as in figure 2. The total dose for the samples ranged from 0 to 10^6 Gy. To determine mechanical and chemical changes within the material, several different analysis procedures were employed. Overall mechanical properties were determined using flexural testing. This was conducted on an Instron Model 4206 in accordance with ASTM D 790, using a 16 to 1 span-to-depth ratio. To determine changes in the polymer matrix differential scanning calorimetry and wide angle X-ray scattering was used. Attempts were also made to determine density changes using the water displacement method described in ASTM D792-A, however the experimental error was too great and any changes detected were deemed not significant. A DSC 2010 was used with a TA Instruments 9900 thermal analyzer and Data Analysis 6.1 to analyze endothermic and exothermic transitions. During the scans, a heating rate of 10°C/min to 400°C was used and then cooled at a rate of 10°C/min. WAXS results were obtained using a Scintag Diffractometer with a θ-θ geometry goniometer coupled with DMS2000 Diffraction Management System software. From the WAXS, crystallite sizes and overall crystallinity of the polymer could be determined.

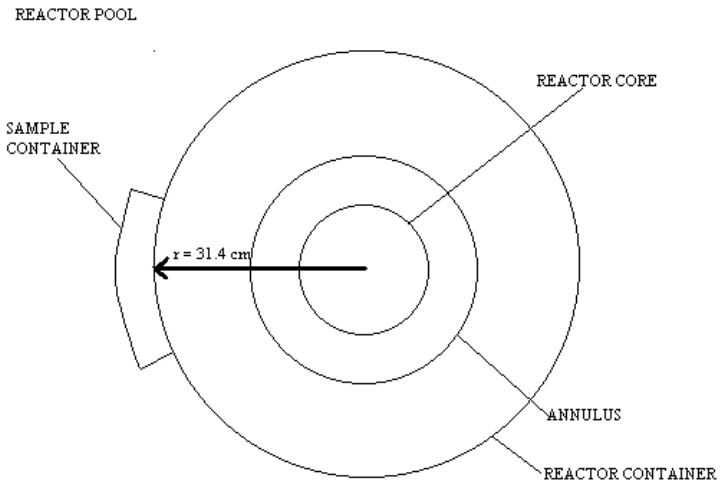

FIGURE 2: Irradiation Set-up

RESULTS AND DISCUSSION

It is expected that the carbon fibre is unaffected by the radiation because of the relatively small neutron cross-section and especially strong bonding. The main effects to be observed would be in the matrix material, the PEEK resin. Table 1 shows the changes the results obtained from the various tests. Only the results from the 20°C irradiations are shown, as the other simulations have not been analyzed as yet.

The flexural strength (see figure 3) and modulus both remain within experimental error of the non-radiated sample. Upon radiation exposure polymers tend to display a molecular reorganization, such as cross-linking and chain scission, which leads to changes in the mechanical properties. However because the matrix has such a small contribution to the expressed mechanical properties in a composite such as the one in this study, the changes are not seen. For comparison, the tensile strength of PEEK is just 4% of the fibres (~100 GPa versus ~4 GPa). However, this does show that even at a high dose of 10^6 Gy, the traditionally weak interfacial region between the fibres and matrix does not show significant change. If this region was affected the bonding would be altered, resulting in changes in the mechanical characteristics, which would be observed in these tests.

Dose		Simul'n Temp (C)	Flexural Strength (MPa)	SD*	Flexural Modulus (MPa)	SD*	Density (g/cm^3)	SD*	T_g (C)	T_m (C)	ΔH_f (J/g)	Crystallite Size (A)
0	0 Dose	20	851.944	44.431	49666.426	1191.1	1.5089	0.06403		338.20	14.81	175
1E+05	Low Dose	20	821.647	46.424	47560.035	1867.3	1.5222	0.06330	164.12	338.83	46.25	147
1E+06	Med. Dose	20	843.091	40.924	49321.40	1468.1	1.5098	0.06123	n/a	337.78	17.63	157
1E+07	High Dose	20	860.012	32.112	50385.281	745.13	1.5190	0.06404	164.77	338.96	41.46	75

TABLE 1: Test results for 20°C irradiated Carbon/PEEK composites (* SD = standard deviation).

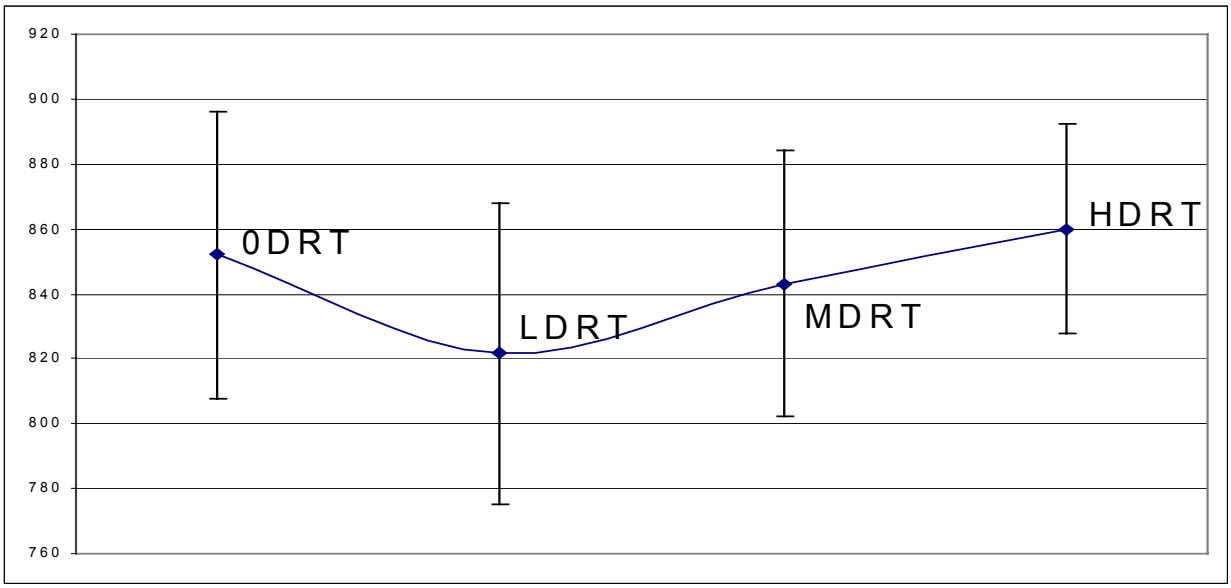

FIGURE 3: Flexural strength at various doses. (0D = zero dose, LD = low dose, MD = medium dose, HD = high dose. RT = room temperature)

The glass transition and melting temperatures were unaffected by the studied radiation doses, indicating that changes produced are so slight that these thermal properties were unaffected. Both cross-linking and an increase in crystallinity can lead to increases in temperature of the thermal transitions of the polymer, but in this study there was no indications of this phenomenon. This indicates that any changes that occur are most likely due to chain scission.

The WAXS results show some significant changes in crystallography of <110> sample. Large changes in crystallite sizes can be seen, with a general reduction in size as the dose absorbed increases. At the highest dose, we have an almost 55% drop in crystallite size, leading to a speculation that the crystals are being split, leaving behind significantly smaller crystalline regions. It has been seen in other studies that the amorphous regions and areas surrounding crystallites are more susceptible. As there are differing crystal regions within the polymer, it can be assumed that it is the more susceptible regions being attacked first.

It can also been seen from the diffraction patterns that there are slight changes in overall crystallinity. Although we cannot deduce quantitative values from the patterns because of the presence of the carbon fibre halo, qualitatively we can see that the scattering intensities, specifically the <110> peak (see figure 4), are greatest after a medium dose. Scattering intensity is directly related to the crystallinity, therefore the medium dose is the most crystalline, with the least amount of crystallinity after the highest dose.

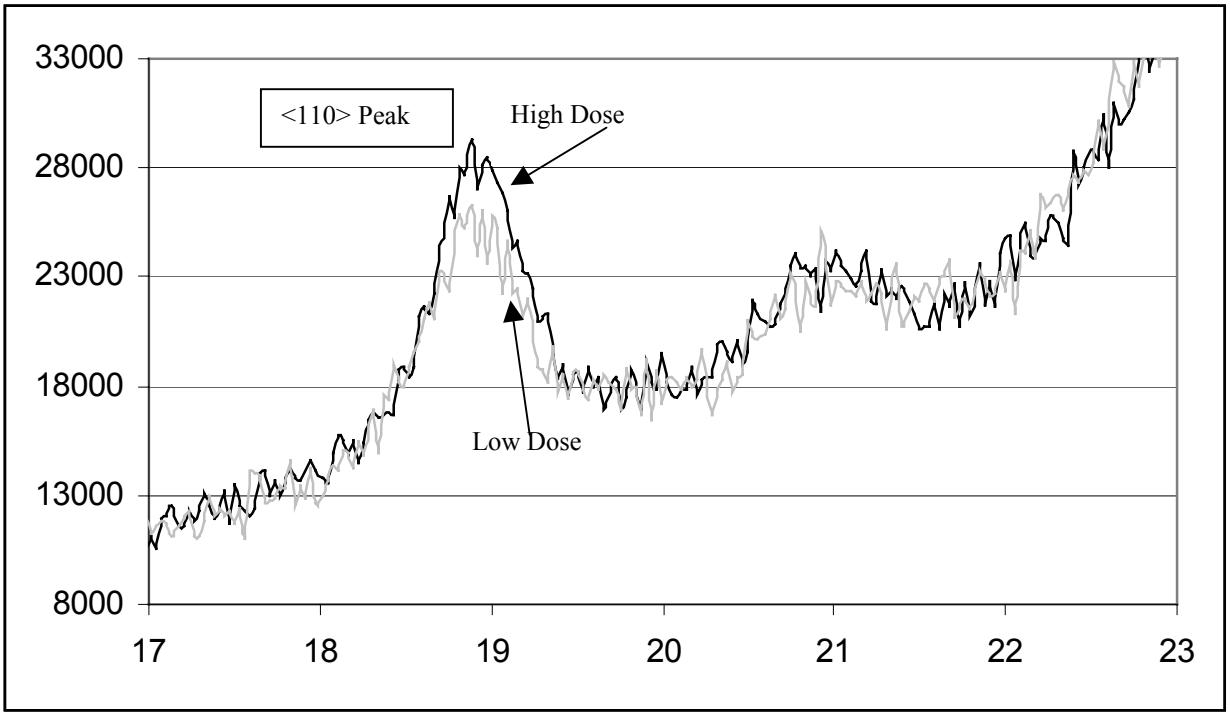

FIGURE 4: Comparison of high dose and zero dose X-ray diffraction patterns.

CONCLUSIONS

From the results obtained thus far in this study, it can be seen that the composite material is especially resistant to the neutron and gamma radiation produced by the SLOWPOKE-2 reactor. The mechanical tests preformed show that the samples degraded very slightly, and the changes that were seen are within experimental error. Crystallography studies show that the damage is incurred, with a crystallite sizes being reduced and crystallinity also being reduced. Chain scission appears to be the dominant destructive phenomenon, with little or no cross-linking being observed. In deducing the feasibility to apply this composite to the nuclear waste containers, from the results thus far we can conclude that it would be an excellent choice, as there has been no degradation in the physical characteristics. Further study with higher temperature irradiations will give a more accurate assessment on the use of PEEK/carbon composites for spent fuel containers.

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