INVESTIGATION INTO THE APPLICATION OF POLYETHERIMIDE TO NUCLEAR WASTE STORAGE CONTAINERS

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Abstract

The procedure of the analysis of the effects of irradiation on the mechanical and chemical properties of the polyetherimide (PEI) is outlined. Previous research in this field at the Royal Military College of Canada is presented. Samples of PEI will be exposed to a mixed radiation field, in the pool of a SLOWPOKE-2 nuclear reactor, then changes in mechanical properties, degradation product formation, and physical property changes will be assessed. Additionally, the heat transfer in the sample will be calculated in order to model the heat transfer rate and heat diffusion profile of PEI. The purpose of the proposed research is to determine the feasibility of using PEI for spent CANDU nuclear fuel and nuclear waste storage containers.

1. Introduction

In Ontario, over 52 % of the electrical energy used by the province is derived from nuclear energy, nationwide this percentage is 14.6 % **[1].** Since the first nuclear power reactor (the Nuclear Power Demonstration reactor (NPD)) began supplying electricity to the Ontario grid in 1962 [2], the percentage of energy derived from nuclear energy has increased from 20 MW in 1962, to 12,612 MW as of August 14 2007 [3]. This increase is a result of the limited petroleum resources, as well as the need for a sustainable energy source.

Nuclear fission is an efficient low CO_2 (22 g $(kW\ h)^{-1}$) [1] production pathway for electricity generation. In Canada, there are a total of 22 nuclear power reactors (18 of these 22 being operational at the present time), and 8 research reactors, all of which generate waste. Canada's unique reactor is the CANDU reactor (CANadian Deuterium natural Uranium reactor).

Nuclear waste, in Canada has been classified into three categories: low level radioactive waste (LLW), intermediate level radioactive waste (ILW) and high-level radioactive waste (HLW). It is common to forgo the classification of intermediate, and classify waste as either HLW or LLW. Spent nuclear fuel is considered as part of HLW. In Canada, there is presently an estimated 2 million used fuel bundles. Furthermore, if one assumes that a power plant has a service life of 40 years, then the expected production of used fuel bundles in Canada's existing power facilities will likely increase this number to 3.7 million [4]. Since there is no reprocessing of the used fuel in Canada, the spent fuel and other waste is being stored in temporary storage sites, in wet storage (pools), in dry storage (in concrete canisters). It is accepted that these methods are only temporary and a permanent solution is becoming imperative.

In this context, there is a need for a solution to the problem of nuclear waste. The Nuclear Waste Management Organization (NWMO) has considered several solutions to this problem. Namely: deep geological repository, which involves waste storage in the deep underground stable rock formations of the Canadian Shield. The Department of Energy Mines and Resources first proposed the concept of nuclear waste storage in the Canadian Shield in 1977. Moreover, it has also been investigated by AECL from 1978 to 2007 when it was officially adopted by the NWMO as the solution to nuclear waste disposal. AECL's solution involves the use of natural and engineered barriers for the storage of waste in vaults 500 to 1000 meters deep in the intrusive igneous rock (termed plutons) of the Canadian Shield. The fuel waste, sintered uranium dioxide pellets in zirconium alloy cladding, is to be stored in a container filled with glass beads or, as suggested by Miedema et al [11], thorium dioxide beads, and the container is to be placed in a vault which will be buffered with clay, sealed and back-filled. This idea represents a permanent solution to the problem of nuclear waste management. Canada has invested over 800 million dollars [4] in used fuel technology since 1978, and it is not the only country studying deep geological repository as a technique for waste storage, as Table 1 below shows.

Table 1. Deep Underground Repository Worldwide [6]

Country	Storage Media
Sweden	Bedrock
Switzerland	Bedrock/ Opalinus Clay
Argentina	Granite
Germany	Salt Dome
Japan	Sedimentary Rock
Finland	Bedrock
Czech Republic	Granite
France	Mudstone
United Kingdom	Igneous/metamorphic rocks/strong sedimentary rocks
United States	Ignimbrite and salt dome

The Ontario Power Generation is presently researching the feasibility of a deep geologic repository, for LLW and ILW, at 680 meters in the limestone/shale rock near the western waste management facility in Kincardine, Ontario. AECL has published research that was undertaken at the AECL's underground research laboratory in Lac-du-Bonnet, Manitoba. The research has touched upon many topics such as, stress, seismology and other issues related to deep geological storing [21]. The safety of geological barriers in underground storage in the biosphere can be illustrated by the example of the 16 natural reactors sites found in Oklo, Gabon. These reactors achieved criticality approximately 1.5 billion years ago and ran for thousands of years, and most of the fission products remained contained underground with no contamination to the biosphere until they were found in 1972 by French physicist Francis Perrin [7]. Nevertheless, containment is still a primary issue in safe waste storage. At the Nuclear Fuel Waste Disposal Concept and Environmental Assessment Panel (Seaborn Panel) in 1998, one of the issues that arose was the need for a robust long-lived container for the storage of the nuclear waste [4].

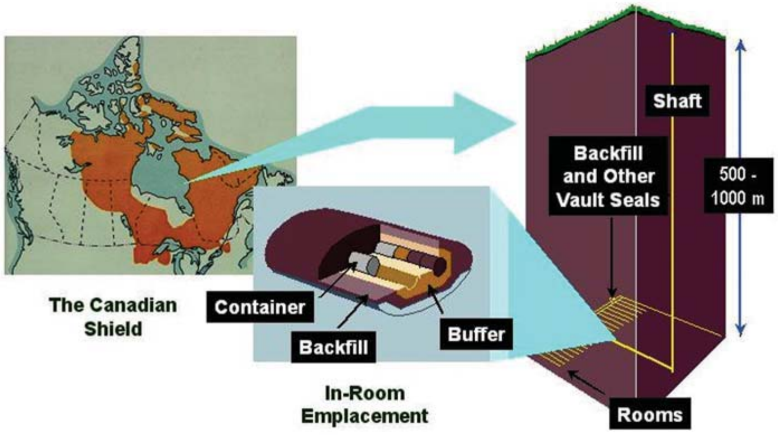

Figure 1. Proposed Deep Geological Disposal [8]

2. State of the art

2.1 Proposed AECL Storage Container

Several engineered barriers will be used to separate the waste from the biosphere; one of these barriers is the storage container. These containers must be corrosion resistant, mechanically strong (resist loads of up to 10 MPa) and radioactively stable, as well as be able to resist alkaline water and salinity, fluctuations in temperature, and be cost efficient. While no final design has been chosen, a few models have been proposed, one of these is a titanium shell packed particulate container (Figure 2) having the capacity of holding 72 fuel bundles. This allows for a total of 10 million used fuel bundles in storage within the vault. Another such design is a copper shell packed particulate container.

Figure 2. Proposed AECL Storage Container [9]

Some arguments for the use of copper are based on the availability of copper artefacts that can be used to approximate the container lifetime, and as for titanium and its alloys; they have excellent mechanical properties. The proposed titanium shell container has a projected safe lifetime of over 500 years which is the time necessary for the activity of the waste to decay by a factor of over 200 000 [10]. Radiation emitted by used fuel is 1.150 mSv/h (at 1.3 m) for a 50 year old bundle and subsequently drops to 0.82 mSv/h after 500 years of decay, and finally to 0.09 mSv/h after 1000 000 years [4]. Therefore one of the main motivations for investigating alternative construction materials is to increase the fail-safe container life and permit the storage of radioactive waste until the activity has decreased to a safe level.

The main problem with the use of a metal container in the presence of ground water (saline and alkaline) is corrosion. It is hard to predict the actual corrosion of the container in the storage conditions, and it is hard to accurately predict factors such as chlorine in groundwater, microbial effects, and oxidizing conditions, which can also accelerate corrosion.

2.2 The Problematic in Using a Metal Container

The AECL proposed storage container contains, as aforementioned, a copper or titanium shell. After burial of the container, the conditions in the storage vault are predicted to be warm and corrosive [26]. This environment is a result of the trapped O_2 in the vault, decay heat and the presence of oxidants created by the radiolysis of H_2O. Additionally, the ground waters of the deep Canadian Shield are slightly saline thus providing chloride ions to for the corrosion process. The concentration of chloride ions at the storage location is anticipated to range from 0.1 to 1 mol/dm^3 [25]. In such conditions, crevice corrosion of titanium is possible [26] as well as hydrogen induced cracking; resulting from the H_2 absorbed during the crevice corrosion process. In metals and alloys, exposure to radiation increases the rate of corrosion [27] as well as the rate of hydrogen embrittlement. Corrosion of the storage cylinder in the vault will be a function of the temperature, availability of oxidants and chloride concentration.

After 500 to 1000 years conditions in the vault are predicted to become cool and anoxic due to the decrease in decay heat and depletion of oxygen utilized in reactions.

2.3 Previous Research

Poly ether ether ketone (PEEK), a thermopolymer, was studied by Miedema et al. [11] at the Royal Military College in Kingston; the material was exposed to temperatures ranging from 20 to 75°C, and radiation doses up to 1MGy, with very little effect on the mechanical and material properties. Changes to the polymer did not exceed one standard deviation of the values of un-irradiated sample properties. PEEK displayed high radiation resistance and it was found to be resistant to mixed fields of radiation of up to ~10^{6} Gy. From this research it was found that, at low radiation doses, cross-linking of the polymer occurred, resulting in a reinforcement of the structure, whereas high doses lead to chain scission and a decrease in mechanical properties. Although PEEK displays excellent material and mechanical properties, it is not an ideal candidate for an application in the AECL project due to its high manufacturing cost.

Irradiation and mechanical testing of several polymeric samples was done recently by J.R Van Tine et al. [12] at the Royal Military College, where it was found that PEEK and PEI offered the best combination of radiation resistance, desirable mechanical properties, and cost efficiency. PEI was retained as the selected candidate for the design of the storage container due to its economic advantage over PEEK. Preliminary radiation testing was done on PEI by J.R Van Tine et al. [12], with exposure of 30% GF (Glass Fibre) PEI samples to a mixed field of radiation in the SLOWPOKE-2 reactor at the Royal Military College of Canada. The total dose received by the PEI container was 2.89 x 10^4 Gy, mechanical properties of the PEI were then investigated. It was found that under the given irradiation conditions, the modulus of elasticity increased of 5.63 % ± 0.23%.

3. Polymer Composites

Failure of metal containers results from containment breach caused by electrochemical corrosion. Polymer composites have comparable and even superior mechanical properties to metals and their oxides In addition, they do not corrode. Containment breach in polymers occurs from diffusion resulting from physiochemical degradation. The aim of this study is to investigate the feasibility of using polyetherimide (PEI) as a construction material for the storage container. The design of the container must be specified in a way to resist to pressures exceeding 12.5 MPa, mixed radiation fields, and temperatures up to 100°C without alteration of the mechanical and chemical properties in a way that would lead to failure.

3.1 Polyetherimide

Polyetherimide is an amorphous thermoplastic polymer with high thermostability, resistance to biological degradation, and resistance to long-term effects of chemicals. The polymer consists of a backbone of aromatic imides, propylidene and ether groups, it can have two structures: linear (L-PEI) or branched (B-PEI), the linear form is known as crystalline PEI [22].

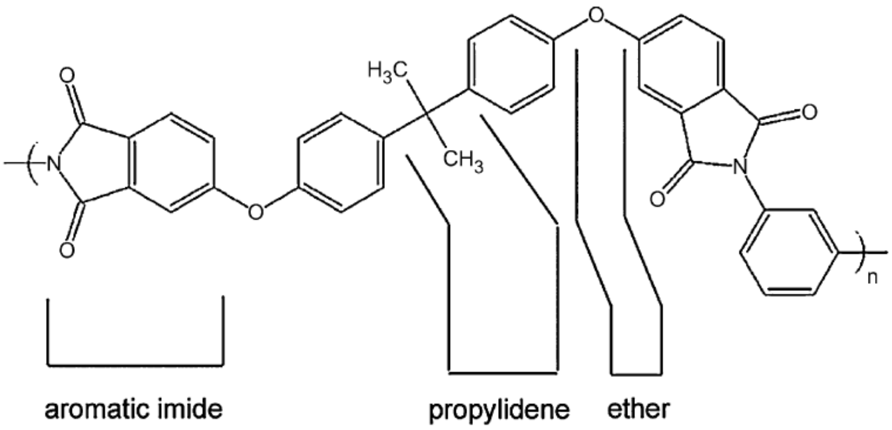

Figure 3. Structure of PEI [13]

Aromatic structures in polymers result in high radiation resistance because the imparted energy is retained in a way that does not modify the structure of the compound; aromatic groups absorb excitation energy and decay to ground state with very little bond breaking. Benzene rings have resonant energy dissipation as a result of the resonant structure, which prevents bond breaking. [14] It can therefore be assumed that, due to its high aromatic ring content, PEI will display excellent radiation resistance, as it will be capable of dissipating the absorbed energy into heat.

PEI is manufactured under the name Ultem. From the material data sheet of Curbell plastics PEI and 30% GF (Glass-Fibre), PEI is listed to have the following physical and mechanical properties:

Table 2 Properties of PEI and 30 % Glass-Fibre PEI [15]

Property	Ultem (Unfilled)	Ultem (30 % GF)
Specific gravity	1.27	1.51
Water absorption (24hr. 23°C)	0.25%	0.16%
Tensile strength at break (PSI)	15,200	24,500
Tensile elongation at break (%)	7	3
Flexural Strength (PSI)	22,000	33,000
Flexural Modulus (PSI)	480,000	1,300,000
Compressive strength (PSI)	21,900	30,700
Compressive modulus (PSI)	480,000	938,000

4. Diffusion Testing

4.1 Theory

The process of diffusion is the movement of atoms from one site to a vacancy driven by a concentration gradient of the diffusing species. The mechanism of diffusion is a random process which occurs until a state of equilibrium is attained in the system. At temperatures other than ambient the driving force becomes a contribution of a temperature and concentration gradient. Thermal diffusion is not a random process; the flow of solute follows a temperature gradient.

For diffusion to occur, the diffusing species must be able to move into a vacancy site, the energy needed to achieve this is termed activation energy. Activation energy is thermal energy and is analogous to the energy needed to break the bonds holding the atom in the lattice and to move this atom to another vacancy site.

In order to evaluate the applicability of PEI to nuclear waste storage containers the water sorption and diffusion characteristics of the material must be examined.

Several characteristics of polymers influence their resistance to diffusion. The degree of crystallinity of a polymer is a measure of the order of the matrix; crystalline regions of a polymer create higher resistance to diffusion than the less ordered amorphous regions. [28] The crystalline regions are more permeable to diffusion and create regions where diffusion occurs much less than in the amorphous regions. Since diffusion requires the movement of molecules from vacancy to vacancy, higher ordered, impurity free and defect free polymers permit less diffusion. As radiation damages polymer, vacancies and defects can be created resulting in higher diffusion in the matrix. Alternatively if cross-linking occurs from exposure to radiation, the ability of the polymer to promote mass transfer is reduced. In composite polymers diffusion can be increased or decreased depending on the chemistry of the reinforcement.

At temperatures above ambient, absorption of water molecules causes a softening on the polymer structure [29] change to the polymer properties occurs from the water molecules connected by hydrogen bonds to the polymer chains. The imide group in PEI is a polar group and therefore, a possible hydrogen bonding site.

Previous research on water absorption in polymers has shown that absorption of water leads to a reduction in modulus, Tg and enlarges fracture strain as well as impact strength [33].

Van der Waals interactions other intermolecular bonds are a factor in the magnitude of the modulus of polymers; higher intermolecular interactions result in higher modulus. Providing sufficient thermal energy causes intermolecular bonds break causing the material to become glassy with an insignificant modulus. [30]

Assuming that the time to attain uniform temperature in the material by heat transfer is much less than the time required to achieve saturation of the material; our system can be modeled as Fickian diffusion. To gauge the effects hydrothermal and acidic aging on PEI, the saturation water content was measured. The saturation water content indicates changes in the structure of the polymer (increase in amorphous regions, chain scission and the presence of hydrolytic reactions). From these values the diffusion coefficient is calculated. The diffusion coefficient is a measure of the ability of the material to promote mass transfer; it represents the amount of solvent diffusing through a given volume per unit time.

Research has shown the hydrolytic stability of PEI at high temperatures (up to 180ºC) and in acidic conditions (pH of 2) [31]. The presence of imide groups, the site of the hydrolysis reaction, did not render the material hydrolytically unstable.

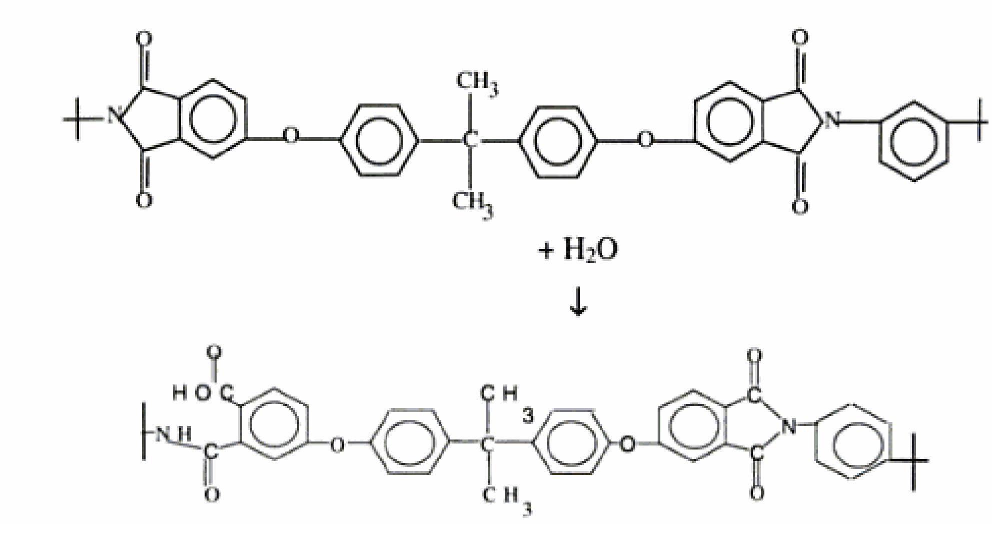

Figure 4. Hydrolytic Degradation of PEI [31]

Furthermore it was shown that a rise in temperature results in a rise in equilibrium water content of the material and a rise in value of the diffusion coefficient. It was shown that immersion in water for 21 days at 180ºC did not result in any noticeable chemical structure changes and that 6-8 days immersion at 170ºC and 180ºC lead to a mass reduction of about 1%. The hydrolysis process can be monitored in the material by the rate of degradation product formation (acid and amides) and an increase in molecular weight.

It was observed that at a temperature of 100ºC and a pH of 2 the hydrolysis reaction was very low, Merdas et al. explained this by the possibility that at this temperature the reserve reaction occurs and the hydrolysis reaction becomes a loop between the hydrolysis and the condensation reaction.

Further research has shown the hydrolytic stability of PEI. It was shown that after 10 000 hours of immersion in water at 100°C, the tensile strength decreased by less than 10% [17] and by less than 5% at 23°C [18].

The diffusion process of water into PEI, as modeled by Merdas et al, follows three steps:

(1) Disassociation of the polymer water complex
(2) Migration
(3) Formation of the polymer water complex

Since the disassociation requires more energy for high polarity compounds and from comparisons of the rate constants of the water-polymer complex formation and the disassociation, the limiting step was concluded to be the disassociation of water-polymer complexes. [31]

The reactions sites for the degradation of PEI are the ether, isopropylidene and phenyl-phtalimide groups. The mechanism of thermal degradation of this polymer has been studied by Kuroda et al. [34], it was found that four possible reactions exist during exposure to high temperatures.

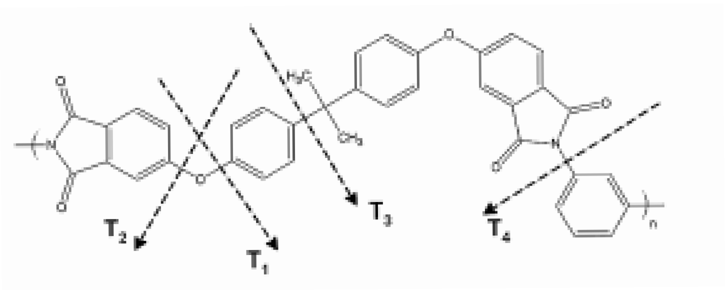

Figure 5. Thermal Degradation Reactions in PEI [13]

The first two reactions consist in the scission of ether bonds followed by a C-H hydrogen transfer reaction. The third degradation reaction is the disproportion of the isopropylidene group in the bisphenol-A group again followed by hydrogen transfer reactions. Finally, the last reaction to occur is the scission of the phenyl-phtalimide bond followed by hydrogen transfer reactions.

These reactions all occur above 400°C. The degradation process results in the formation of free radicals which will further react with PEI to degrade the material or alternatively, form cross-linking .

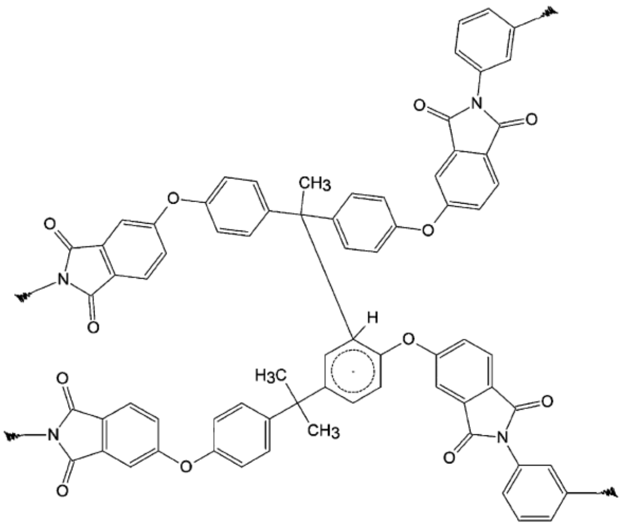

Figure 6. Thermal Cross-linking of PEI Caused by Free-Radicals [13]

Cross-linking of the polymer is believed to occur from the linking of two radicals produced in the chain-scission of isopropylidene and substitution of a phenyl radical into the benzene ring [13]. During thermal degradation of PEI, cross-linking dominates over chain scission, due to the presence of ester and imide bonds, resulting in an overall increase in molecular weight [16].

Most thermal damage to the polymer occurs at the site of the weakest bond; the isoproylidene group.

4.2 Materials

The PEI used in this research was obtained from SABIC Polymershapes, under the trade name ULTEM, in the form of sheets. Sheets of ULTEM 1000 (pure PEI) and ULTEM 2300 (30% Glass Fibre PEI) were obtained and cut into sample bars 76.2 mm long, 24.5 mm wide and 3.2 mm thick. These dimensions comply with the ASTM for flexural testing and water sorption of plastics and simplify the modelling of the diffusion process.

4.3 Methodology

To study the water absorbency capacity of PEI, diffusion testing was undertaken. Samples were placed in sulfuric acid solutions in water baths at different temperatures; this was done to evaluate the combined effect of acidity and temperature on diffusion in the polymer. The selected temperatures were 60°C, 40°C and 20°C and the selected acid concentrations were: 1M, 0.5M and 0.1 M. The ASTM D570-98 for water sorption of plastics was followed for long term immersion. The water content in the sample was measured every 24 hours until the water content in the material had reached equilibrium.

The apparatus used in the water sorption testing of the material consisted of a water bath containing 16 samples in test tubes filled with sulphuric acid. The temperature of the bath was maintained at the set point using a Haakee temperature controller.

Following the ANSTM D570-98, weight gain was plotted versus diffusion time. The weight gain of each sample was calculated from the following relation:

$$Weight\ Gain\ (\%) = \frac{wet\ weight - dry\ weight}{dry\ weight} \qquad [1]$$

A plot of the weight gain versus the square root of the immersion time provides the diffusion profile in the sample. As a result of the dimension of the samples, diffusion in the material must be modeled in two dimensions, for the same reason, edge effects can be neglected.

Following immersion the mechanical properties of the material were measured via flexural testing, the property used to gauge mechanical strength was the modulus. The modulus is a measure of the stiffness of the material; if any significant hydrolytic reactions had occurred, a decrease in modulus would be observed.

5. Effects of irradiation and temperature on polymers

5.1 Theory

Free radicals created from irradiation by ionizing radiation lead to chain-scission and cross-linking; the number of cross-links is proportional to the dose. At very high doses, when the cross-linking density exceeds the critical value [14], the gel point is reached, and a three dimensional network is formed between molecules. When cross-linking occurs, the elongation of the polymer is decreased, but its tensile strength and modulus are increased. Chain-scission leads to increased brittleness and fracturing [19]. Irradiation causes ionization and excitation, as energetic particles interact with the molecules of the polymer: gamma and electron particles form anions, cations, excited states, and radicals. In PEI, the radicals undergo further reaction in the polymer para-substituted dipheneylether as principal radiation damage sites, and damage to the imide groups [20].

High temperatures lead to the oxidation of polymers. Temperature resistant groups are similar to radiation resistant groups in the manner that they are able to absorb energy with limited bond breaking; aromatic groups are very stable at high temperatures.

The process of degradation of PEI following exposure to ionizing radiation is by chain-scission. Previous research on the behavior of PEI during irradiation has shown dual processes occurs during irradiation; chain scission and cross-linking [32]. As well as cross-linking in the polymer (on the imide ring) which only occurs at doses exceeding 16 MGy [32]. Furthermore, it has been shown that irradiation by Co60 for 1000 hours, for a total dose of 500 Mrad, resulted in negligible changes in tensile strength (less than 5 %) [18].

5.2 Methodology

To determine the feasibility of using PEI as a material of construction for the HLW storage container, it’s resistance to radiation and temperature, must be assessed. To do so, the polymer will be exposed to doses of radiation comparable to the lifetime dose exposure of the storage container calculated by Miedema et al [11], to be 12 MGy for glass bead filling and 56 kGy for thorium dioxide filling. The method followed by Miedema et al. [11] with PEEK will be used with PEI.

The irradiation of the samples will be done in the SLOWPOKE-2 reactor at the Royal Military College of Canada. This reactor is a 20 kWth reactor which is usually operated at half power, at steady state. The samples will be placed in the reactor pool against the reactor vessel, 31.4 cm from the centre of the core and in line with the reactor core at mid-plane. At the chosen irradiation site the flux has been calculated to be 37 kGy h^{-1} ± 28 % [23]. The irradiation field is a mixed field consisting of 1% neutron, 3 % proton, 9% gamma and 87 % electrons. [23].

In addition to the exposure to radiation, the samples will be placed in a heated chamber during irradiation to achieve simultaneous irradiation at high temperatures. The range of temperatures will range from the reactor pool temperature (about 20°C) to 80°C. It will be attempted to reach an irradiation temperature of 100°C, since this is the temperature listed by AECL as the possible temperature from the decay of waste. A system will have to be designed to achieve stable temperature in the irradiation chamber.

Irradiation will be done for varied periods of time dependent on the desired dose. Following exposure, samples will be left to safely decay below a dose rate of 2.5 μSv h^{-1}, in a lead container, prior to analysis. The mechanical and material properties of the samples will be measured and compared to the un-irradiated samples to determine the damage incurred.

5.2.1 Experimental Setup

Samples are to be placed in a polyethylene box; temperature in the box will be maintained by flow of heated water. The selected temperatures for the irradiation process are of; ambient, 40°C, 60°C and 80°C.

5.2.2 Measuring material properties

Changes in material properties are an indirect way to measure changes occurring to the polymer structure from irradiation. It is also a way to determine whether the effects of irradiation will affect the material properties in a way that will render the material unsuitable to an application to waste storage containers. Differential scanning calorimetry is a thermoanalytical method that will be used to obtain:

- The glass transition temperature (T_g),
- The crystallisation temperature (T_c),
- The melting temperature (T_m),
- The re-crystallization temperature (T_{rc}).

Wide angle x-ray scattering is a material analysis method that will be used to determine the degree of crystallinity of the polymer. This will allow the measuring of the increase or decrease in the degree of crystallinity, and therefore the changes in the strength of the material.

5.2.3 Determining changes in chemical properties

In order to understand the combined effects of temperature and irradiation, the chemical changes to the polymer will be investigated using Fourier-Transform Infrared spectroscopy. This technique aims at obtaining information on the changes in chemical structure, the rate of appearance of degradation products, and the changes in degree of crystallinity.

5.2.4 Imaging the surface

Fibre damage from irradiation and break pattern following flexural testing will allow one to determine the method of failure and the damage imparted to the material. Scanning electron microscopy provides magnification of up to 250 000 times, and permits imaging of details from 1-5nm in size. Surface imaging will allow the observation of physical damage at the surface of the polymer.

5.2.5 Mechanical changes

Flexural testing will be done on the samples to obtain the flexural strength, flexural stress at different strain levels, and the flexural modulus. Flexural testing measures the strength needed to bend a sample using three contact points on the sample. These properties indicate the mechanical strength of the polymer. The strength of the polymer must remain at a level where safe containment can be ensured, and the overall material performance must be unaffected or negligibly affected by irradiation.

5.2.6 Modelling heat transfer

The heat transfer across the PEI sample will be measured using thermocouples and the temperature profile will be calculated from the heat transfer equations applied to the heat diffusion in the sample at the given conditions. It is planned to use the COMSOL™ [24] software to do the computer modelling of the heat transfer through the container. This will be done to model the heat transfer in the polymer and therefore determine the effect of the decay heat of the nuclear waste on the container.

6. Results and Discussion

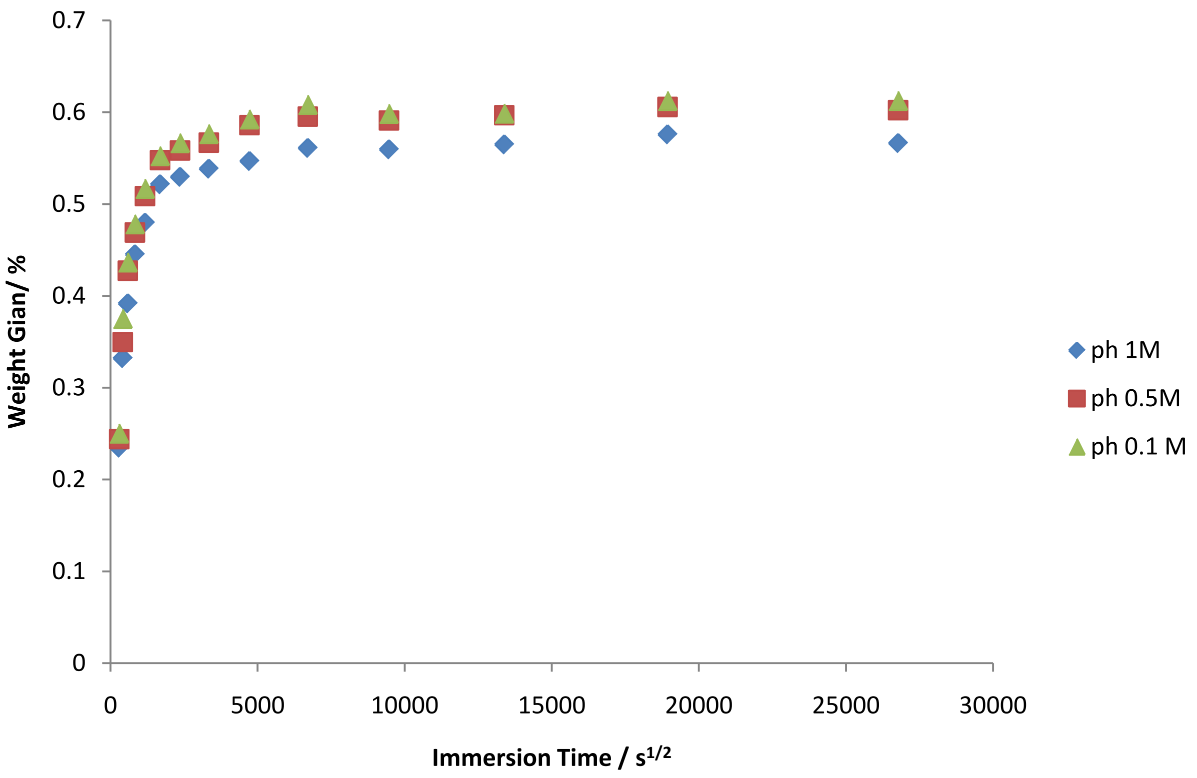

Figure 7. Weight Gain versus Immersion Time, 60°C

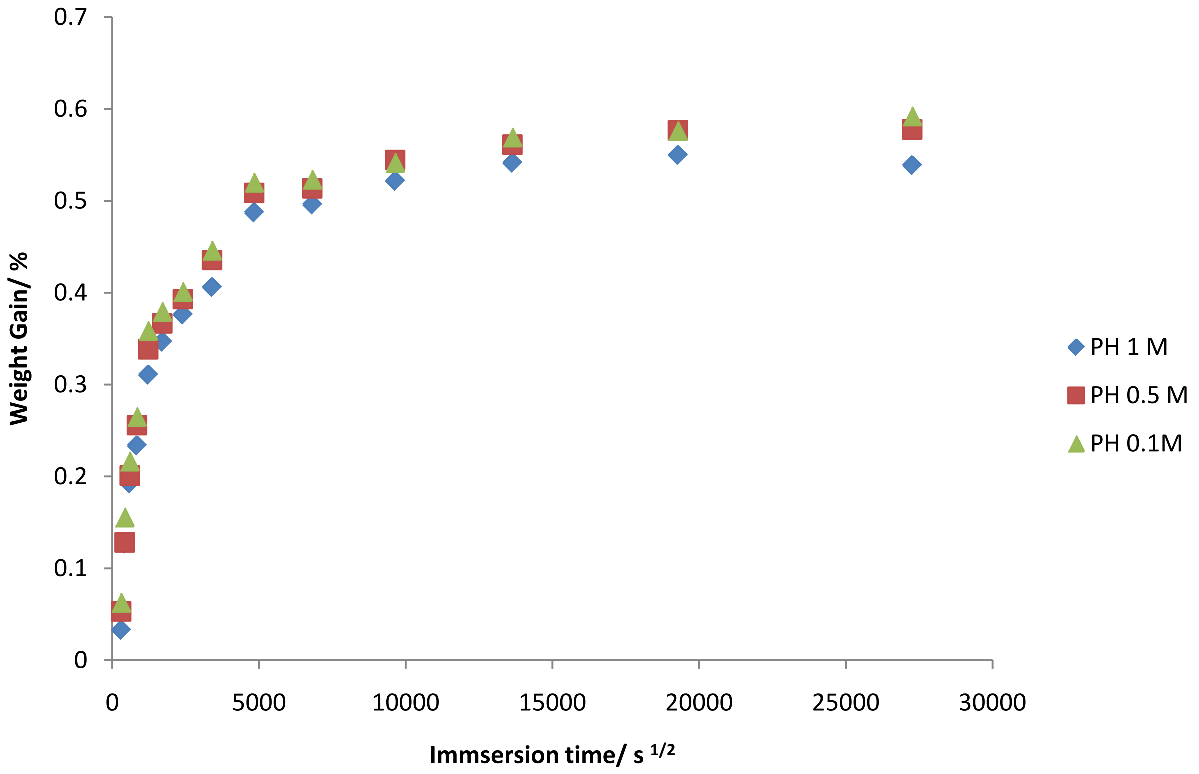

Figure 8. Weight Gain versus Immersion Time , 40°C

Calculation of the diffusion coefficiant was done preliminarly in one dimension using J. Cranks solution for diffusion with uniform intial conditions in symetrical samples [35]:

$$D = \frac{\pi}{16}\left[\left(\frac{M}{T^{1/2}}\right)\frac{h}{Mn}\right]^2 \qquad [2]$$

Where $\frac{M}{T^{1/2}}$ is the slope of the linear portion of the diffusion curves, h is the thickness of the samples and Mn is the saturation weight gain.

Table 2. Approximation of the Diffusion Coefficient

	PH 1 M	PH 0.5 M	PH 0.1 M
Temperature/ °C	D (m/s^2)		
60	2.09E-09 ± 6.48E-07	2.13E-09 ± 5.12E-07	2.27E-09 ± 6.74E-07
40	5.5982E-13 ± 2.98E-08	5.79198E-13±2.12E-08	6.93380E-13 ±2.07E-09

Overall, the diffusion testing shows that the material is rather hydrophylic, and the maximum water content does not exceed 0.6057 ± 0.003 . This is a desirable property for a storage container, since only limited amounts of groundwater will be absorbed into the polymer and hence degradation due to the distortion of the polymer structure by ingression of water molecules, which would lead to swelling and, ultimately, bond breaking, will be minimal.

An increase in temperature leads to an increase in weight gain; increasing the temperature increases the disassociation of water-polymer complexes which is the limiting step in the diffusion process and so the diffusion coefficient is increased. Additionally, the increase in temperature also increases the rate of the degradation reactions caused by sulfuric acid, therefore increasing the weakening of the polymer network. As a consequence of this, a higher amount of water molecules are able to penetrate the polymer resulting in an increase in maximal weight gain.

Increasing the concentration of acid leads to lower weight gain althought the decrease small it is not contained whitin the error. The higher the concentration of sulfuric acid, the lower the concentration of water, it is possible that the difussion process of water into PEI is selective to only water molecules and therefore the sulfuric acid molecules are not able to enter the material and diffuse into it. An increase in sulfuric acid concentration would lead to a decrease in weight gain since the concentration of water molecules is decreased. However, the diffusion constant is increased with acid concentration due to the damage caused by the sulfuric acid to the polymer which allows for quicker initial penetration of water molecules into the bulk to the sample.

Flexural testing of the samples showed that variations in the modulus of the material were inside the margins of error and therefore it can be concluded that exposure to heat and acidic conditions had to detrimental effects on the strength of the material.

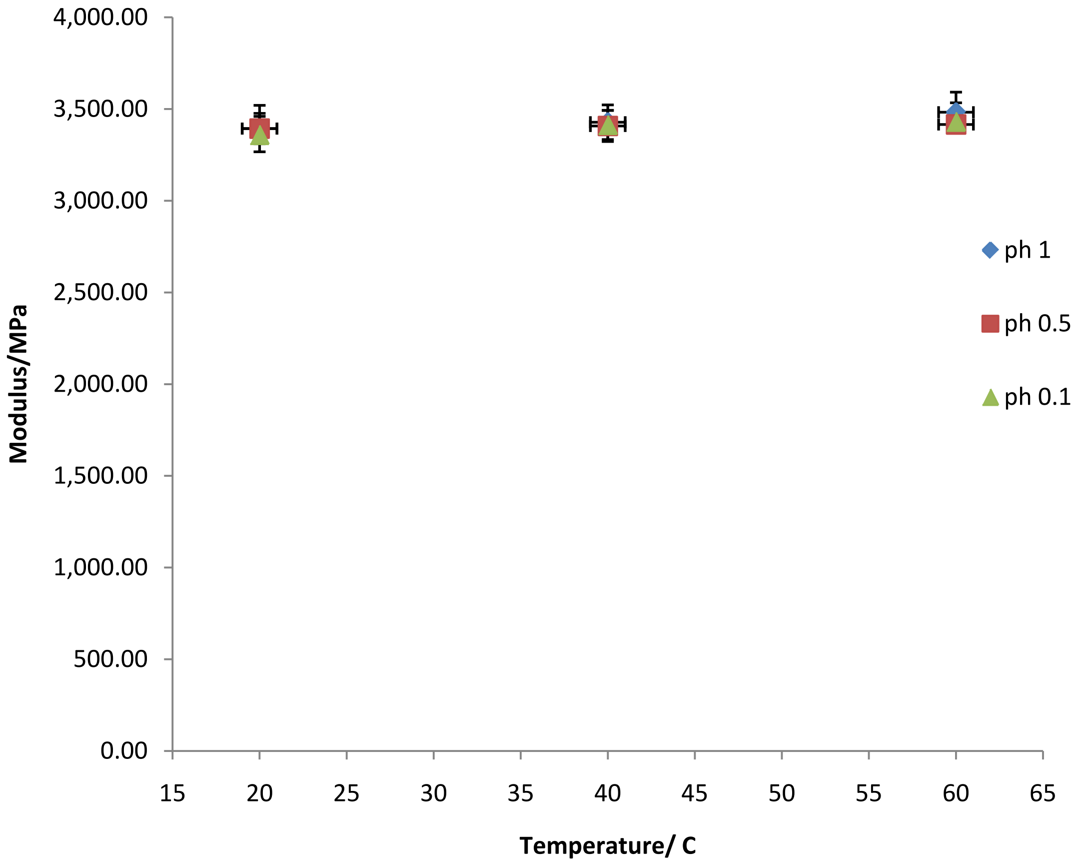

Figure 9. Modulus versus Temperature

Furthermore, it must be noted that under the condition of the flexural test, fracture of the samples did not occur. Elastic deformation occurred but the flexure extension versus load diagram, figure 10. ,shows the material had not yet entered the plastic region such that all deformations to the material were reversible.

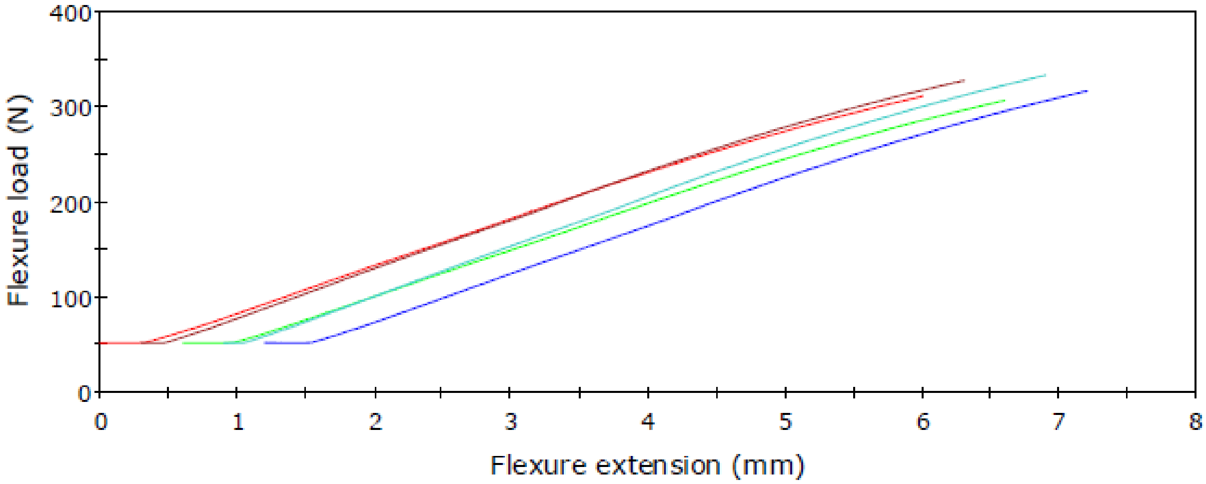

Figure 10. Flexure Extension versus Load, 60C and 1M

7. Conclusions

Flexural testing of samples of polyetherimide showed no changes in mechanical strength of the material following hydrogeothermal ageing in sulphuric acid solutions. Diffusion testing was undertaken at 40°C and 60°C as well as acid concentrations of 1 M, 0.5 M and 0.1 M to obtain the diffusion coefficient and diffusion profile. The experimental procedure that will be followed in the irradiation testing was been outlined as well as the direction of future work on this research project. Irradiation of samples of PEI to doses up to 1 MGy will be done in the SLOWPOKE-2 reactor, at the Royal Military College of Canada, in Kingston. Samples will be irradiated at set temperatures. Following irradiation, select properties of the polymer that translate to strength and enable the assurance of safe containment will be measured. Additionally, heat transfer through the samples will be investigated via experimental measurements and computer modelling.

8. References

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