

Mixed field radiation effects on dry and acidic solution saturated polyamide 6,6

L. Brown, H.W. Bonin *, V.T. Bui

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ont., Canada K7K 7B4

Received 16 August 2004; accepted 11 January 2005

Abstract

The disposal of Canada's radioactive waste materials has been the focus of ongoing research at the Royal Military College of Canada, in the use of polymer-based composite materials for the fabrication of disposal containers. An evaluation of the performance of polyamide 6,6 after exposure to radiation and acidic aqueous solutions provides the basis for the assessment of the lifetime performance of a polymeric-based storage container. This work demonstrates the importance of the combined effects of aqueous solution diffusion and radiation exposure on the mechanical performance and molecular structure of polyamide 6,6. Irradiation of dry samples initially results in a marked reduction of mechanical performance, however, post-irradiation aging allows for the return to pre-irradiation mechanical strength. Samples irradiated after exposure to either distilled water or 0.1 M sulfuric acid solutions exhibited increases in mechanical performance upon exposure to a mixed field radioactive environment.

© 2005 Published by Elsevier B.V.

PACS: 61.82.P; 66.30; 28.41.K

1. Introduction

1.1. Research goals

As part of the quest to find a solution for the disposal of Canada's radioactive waste, the Royal Military College of Canada has been conducting research on the use of polymeric materials for the design of radioactive waste storage containers. Previous work has determined that several of these materials exhibit the required mechanical strength and resistance to radiation to make them viable alternatives to the titanium alloys currently

proposed by Atomic Energy Canada Ltd. (AECL) for the fabrication of the storage containers in the Environmental Impact Statement on the Concept of Disposal of Canada's Nuclear Fuel Waste [1].

Bonin et al. demonstrated that composite materials such as those based on polyamide 6,6, polycarbonate, and polyurethane would perform well in the radioactive environment produced by low and intermediate level wastes [2,3]. Miedema investigated the use of polymer composites such as polyetheretherketone (PEEK)/graphite in the radioactive environment that is expected in the storage and disposal of spent nuclear fuel and high level radioactive waste [4]. Both research works determined that these types of materials, in combination with a packing material such as ThO₂ (which acts as a radioactive shield and heat conducting material),

* Corresponding author.

E-mail address: bonin-h@rmc.ca (H.W. Bonin).

would have the required mechanical strength to be viable alternatives to the titanium containers currently proposed.

As the titanium containers' mode of failure is electrochemical corrosion, it is important to evaluate the corresponding barrier properties of the polymeric materials. This will allow for an assessment of the lifetime of a polymer container based on its ability to restrict the flow of groundwater in and subsequently the leaching of radionuclides out of the container, as well as maintain mechanical performance integrity when exposed to a radioactive environment.

Polyamide 6,6 has been utilized as the initial test material due to its hydrophilic nature and ability to absorb relatively high amounts (>9%) of aqueous solution over a time period that was acceptable for the experimental timescale. It is also susceptible to radiation damage, due to the aliphatic nature of the molecular structure, and can provide a means of understanding the mechanisms governing the molecular response to radiation exposure.

Previous work has shown that polyamide 6,6 would be an acceptable material for the storage of low level radioactive waste. As such, it has been determined to be the best material for the initial development of testing procedures and techniques, and to provide detailed experimental results in order to form the basis of the lifetime evaluation of a polymeric container.

1.2. Radiation effects on polyamide 6,6

'Polymeric materials exhibit a wide range of radiation stabilities. Radiation resistance is strongly influenced by the basic macromolecular structure, the presence of certain types of additives, and the particular environmental exposure conditions' [5]. The environment surrounding the sample, specifically, the presence or absence of oxygen, greatly alters the extent of crosslinking or chain scission. Typically, a polymer undergoes both crosslinking and chain scission; however, one does dominate.

1.2.1. Hydrolysis

Due to the basic macromolecular structure and hydrophilicity of polyamide 6,6, the response to radiation is highly dependant on the environment surrounding the sample before, during, and after irradiation. Polyamide 6,6 is extremely susceptible to molecular scission arising from the association of water molecules with the amide groups, resulting in cleavage of the molecule at the amide linkage (hydrolysis).

Ishak and Berry studied the hygrothermal aging of polyamide 6,6 (short carbon fiber reinforced). 'Hygrothermal aging refers to the process in which the deterioration of the mechanical performance and integrity of

composite materials results from the combined action of moisture and temperature' [6].

The authors cite two distinct sources that result in deterioration of the mechanical performance of a polymer. First, chemical interactions within the polymer on a molecular level, such as hydrolysis of bonds and subsequent dissolution or leaching out of water-soluble species from within the polymer matrix [7]. Secondly, physical interactions would include plasticization of the polymer matrix where the matrix would then become much more mobile.

1.2.2. Oxygen effects on the response to radiation of polyamide 6,6

In the absence of oxygen, mechanical and chemical effects are a function of overall dose and independent of dose rate. Therefore, it is acceptable that testing be done at high doses over short times and extrapolated to long times at a low dose. It is important to remember that this is only the case if it does not result in high temperature changes such as those exceeding the heat removal capacity of the system.

The radiation of polymeric materials in the presence of oxygen, particularly when both oxygen and radiation penetrate the material, results in much more degradation to the polymer. If the permeation of the oxygen into the sample is limited to the surface, as is the case for thick samples, oxidation takes place at the surface resulting in enhanced degradation of the surface layer. However, the interior behaves as though radiation was in an oxygen-free environment. Exposure to oxygen after irradiation also increases the degree of degradation. '...The influence of time and sample geometry can become of paramount importance, resulting in large dose-rate effects, post-irradiation effects, and environmental synergisms of radiation and temperature. These effects greatly increase the difficulty of predicting long-term radiation-degradation behavior under a particular set of environmental conditions...attempts to draw inferences on radiation-oxidative degradation, based on data for radiation effects under non-oxidizing or surface-oxidizing conditions can lead to serious underestimates of the damage' [5].

Other factors that affect the extent of oxidation include:

1. *Dose rate.* Lower dose rates increase oxidation and scission yields. Dose rate effects are observed when one of the chemical processes such as oxygen diffusion, or radical migration becomes the rate-limiting step.
2. *Temperature.* As with dose-rate, temperature can affect the rate at which the various processes occur, with the mobility of the radicals enhanced with higher temperatures.

3. *Post-irradiation.* Due to the oxidation process and subsequent formation of reactive radicals, as these molecules migrate over time, oxidation reactions may continue resulting in the continued formation of radicals even after radiation exposure has ended.

2. Experimental

2.1. Materials

Two different polyamide 6,6 materials were utilized for the present work: Dupont Zytel 101L[®] Nylon 6,6, ($T_m = 263\text{ }^\circ\text{C}$, $\rho = 1.18\text{ g cm}^{-3}$) and Sigma Aldrich Polyamide 6,6 (CAS 32131-17-2, $T_m = 250\text{--}260\text{ }^\circ\text{C}$, $\rho = 1.09\text{ g cm}^{-3}$). Both were studied as it was thought that the additives present in Dupont Zytel may alter the polymer response to radiation, therefore, Sigma Aldrich samples were also tested as they contained no such additives. Differences were indeed observed, but most of the time, they were not significant. In this particular work, the lack of significant differences in the results may be explained in that, due to the high radiation doses that the samples were receiving (500–2000 kGy), stabilizers could not provide much protection at such high doses. Unless otherwise stated, Nylon 6,6 results presented are for Dupont Zytel.

2.2. Irradiation experimental set-up

Sample irradiation was completed in the mixed radiation field of the pool-type SLOWPOKE-2 research nuclear reactor. Samples were placed in the reactor pool at a distance of $32 \pm 1\text{ cm}$ from the center of the reactor core, i.e. against the reactor vessel wall. The radiation at this position in the pool is a mixed field consisting of 1% neutrons, 3% protons, 87% electrons, and 9% gamma with a flux variation of <1% and a dose rate of $37\text{ kGy/h} \pm 28\%$ [8]. Fig. 1 is a representation of the sample placement within the SLOWPOKE-2 Research Reactor [9].

Doses are cumulative in that samples receive doses intermittently over many days. Thermocouples embedded in the samples allowed for a measure of the temperature during irradiation. It was demonstrated that no significant increase in temperature was noted for doses and dose rates used in this work. Therefore, it has been concluded that differences in molecular response arising from temperature effects from doses delivered intermittently or continuously could be considered as negligible.

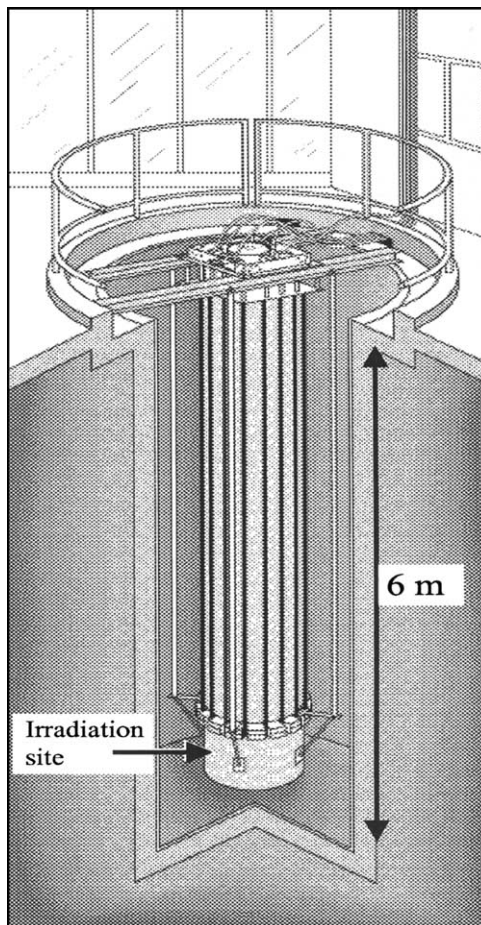


Fig. 1. Irradiation site of the SLOWPOKE-2 research reactor.

At the outset of irradiation, the set of samples is positioned far from the reactor core, at half-depth in the pool, i.e. at a position in the pool that is shielded from the radiation produced by the SLOWPOKE-2 nuclear reactor. The samples were then allowed to decay at half pool depth for a period of approximately seven days, before being removed from the reactor pool and subsequently tested. This time is referred to as the ‘cooling down’ period (in a radioactive sense). The purpose of this cooling down period is to let the radioactivity induced within the samples decay to levels ensuring safe exposure rates to the personnel and equipment during removal from the reactor pool and subsequent handling.

2.3. Experimental techniques

Experimental techniques for diffusion, mechanical testing, and dilution viscometry have been described in detail by Brown et al. [10]. A brief summary is provided below.

2.3.1. Diffusion

The weight gain method of determining moisture uptake in polymeric materials, ASTM D570-95 [11], was utilized. Flexural bars were placed in 100 mL test tubes, which were then filled with the diffusing solution and lowered into a water bath. The water bath was entirely insulated with flexible foam sheets to minimize heat loss and to maintain the system at the experimental temperature (± 1 °C). Periodically throughout the experiment, samples were removed from the test tube, dried well with absorbent paper to remove the surface moisture, and allowed to air dry for 5 min at room temperature. These samples were then weighed to the nearest 0.0005 g on an analytical balance, and finally, returned to the test tube.

2.3.2. Mechanical testing

Flexural testing was carried out on an Instron Universal Testing Instrument, Model 4206, according to ASTM D790-02, three point bending test [12]. The crosshead speed was maintained at 13.65 mm/min for all experiments. Measurements were taken with a 5 kN tension/compression load cell. Tests were run until break occurred or until the maximum displacement was reached. The use of a load cell, which is sensitive to very small forces, produces results that exhibit less than 5% error.

2.3.3. Dilution viscometry

Dilution viscometry was completed on a Lauda Intrinsic Viscosity Measurement System (Model D15 KP) with Ubbelohde viscometers. Initial sample concentrations were approximately 0.005 g cm^{-3} . A series of dilutions were carried out for each sample at intervals of 0.0005 g cm^{-3} beginning at 0.0045 g cm^{-3} and finishing at 0.0015 g cm^{-3} . The temperature was maintained at 25 °C, with an initial stirring period of five minutes to ensure constant temperature. Nylon 6,6 samples were dissolved in m-cresol at room temperature prior to testing with a Type II viscometer.

A comparison of the pure solvent flow time to the flow times of the solutions through the viscometer capillary for each of the serial dilutions was used to calculate the relative viscosity of the solution at each concentration. These relative viscosities were then used to calculate the inherent viscosity and reduced viscosity based on the following relationships:

$$\eta_{\text{inh}} = \ln(\eta_{\text{rel}})/C, \quad (1)$$

$$\eta_{\text{red}} = (\eta_{\text{rel}} - 1)/C. \quad (2)$$

The inherent and reduced viscosities were then plotted for each concentration, which resulted in two linear plots that intersected at zero concentration. This point of intersection represented the intrinsic viscosity of the solution. The intrinsic viscosity could then be related

to the molecular weight of the polymer via the Mark-Houwink coefficients (K and a) according to the following equation:

$$\text{MW} = ((1/K) * (\eta_{\text{int}}))^{1/a}. \quad (3)$$

However, due to these coefficients dependence on the structure of the polymer molecule, it was determined that available data would not provide accurate correlations for all samples due to degradation resulting from acid or radiation exposure. It was therefore determined that comparisons would be made between intrinsic viscosity results and chain length inferences made based on these values.

3. Results and discussion

3.1. Apparent diffusion coefficients

Diffusion studies via weight gain were carried out for materials that had been exposed to radiation. After radiation exposure, the samples were placed into test tubes containing water or 0.1 M sulfuric acid and maintained at 40 °C until saturation was achieved.

Apparent diffusion coefficients were obtained prior to radiation exposure, as well as for samples that were irradiated either dry or which absorbed the pool water during the irradiation and ‘cooling down’ periods and then placed in the diffusing solution. The diffusion rate is dependant not only on the temperature, but also on the chemical environment (pH) and on the exposure to radiation. Fig. 2 shows the difference in apparent diffusion coefficients before and after irradiation for the case where the samples are kept dry during irradiation and that in which the samples are exposed to the pool water and thus allowed to begin the diffusion process during irradiation.

The samples were placed into the reactor pool at the beginning of the irradiation sequence and remained in the pool until after the cooling down period. This resulted in the samples being in the reactor pool for many

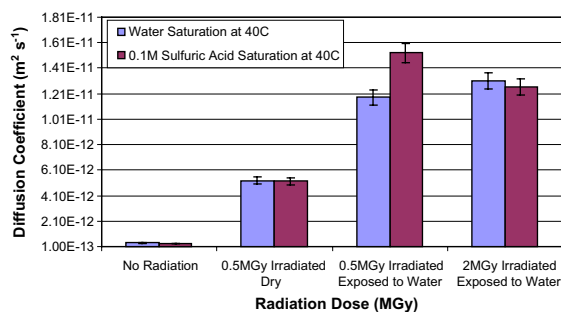


Fig. 2. Apparent diffusion coefficients.

weeks even if the total time required to receive the required dose was only 54 h. Due to temperature and operational restrictions placed on the SLOWPOKE-2 Research Reactor, radiation exposure was possible only during regular reactor operations. This resulted in samples being left in the reactor pool for many hours when radiation levels were negligible. Temperatures ranged from 15 to 30 °C depending on the state of operation of the reactor. The extent of diffusion was dependant on the time required to complete the radiation process. Fig. 3 is an example of the diffusion profile for these samples.

Time $t = 0$ corresponds to the moment when the samples were first placed into the reactor pool. It is expected that the diffusion curves for samples exposed to water during irradiation would exhibit a lower slope initially as diffusion would be occurring at lower temperatures. As it is not possible to measure weight gain when samples are being exposed to radiation, it is also not possible to acquire data to produce a complete graph. However, since the diffusion process is still in the linear portion of the curve, as evidenced by the data collected for diffusion after removal from the reactor pool, it is possible to extrapolate back to time zero and observe that both materials exposed to water during the irradiation process would fall on the same diffusion curve, resulting in an apparent diffusion coefficient of $7.6\text{E}-14\text{ m}^2\text{ s}^{-1}$. The average reactor pool temperature calculated during these experiments was 14 °C. This apparent diffusion coefficient is lower than that found for water at 20 °C ($1.4\text{E}-13\text{ m}^2\text{ s}^{-1}$), and would therefore correspond seemingly to the temperature of 14 °C based on the data following an Arrhenius relationship with the data points at the lower temperatures (14 and 20 °C) showing the apparent diffusion coefficient approaching zero as temperature continues to decrease [10].

During the irradiation process, scission of the polymer molecules may result in low molecular weight fragments being produced. These fragments are often times volatile and if produced near enough to the surface of

the sample, may migrate out of the sample, resulting in a weight loss being observed. This loss in weight due to volatile fragments, in combination with an increase in weight due to diffusion of the water molecules into the sample, will result in an overall lower observed weight gain, which will result in a lower apparent diffusion coefficient. Careful observation of Fig. 3 demonstrates that the loss of volatiles during irradiation may indeed be occurring as the maximum weight gain noted for samples that were irradiated dry and then saturated, is lower than that observed for samples saturated without prior radiation exposure.

This demonstrates the importance of not only considering the environment into which the radioactive waste containers will be placed, but also realizing that, as the groundwater diffuses through the container, diffusion rates will be changing as the radiation dose imparted to the container wall increases. The radioisotopes present within the spent nuclear fuel and/or the radioactive waste materials stored in the container create a radioactive environment affecting the container wall material. This results in changes to the diffusion profiles of the groundwater. As can be seen from Fig. 2, when this material is exposed to radiation, the diffusion coefficient is increased. The groundwater can then migrate at a faster rate into the container.

3.2. Assessment of the effects of radiation exposure on Nylon 6,6

3.2.1. Mechanical performance

The maximum stress at yield and flexural modulus for both the non-irradiated and irradiated (0.5, 1.0, and 2.0 MGy) samples, which have been irradiated in a dry environment, saturated with water or 0.1 M sulfuric acid prior to radiation exposure, or exposed to the water during irradiation were measured. Flexural testing was completed on the samples after approximately seven days cooling down at half pool depth. As

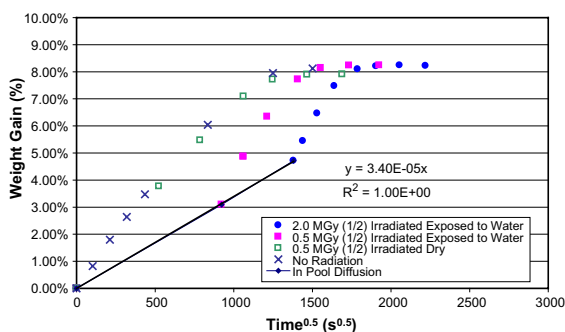


Fig. 3. Diffusion profile for water at 40 °C in Nylon 6,6 exposed to water during irradiation.

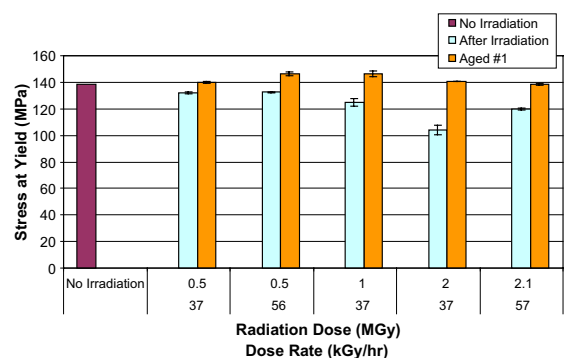


Fig. 4. Stress at yield for Nylon 6,6 irradiated dry and aged in a dry environment.

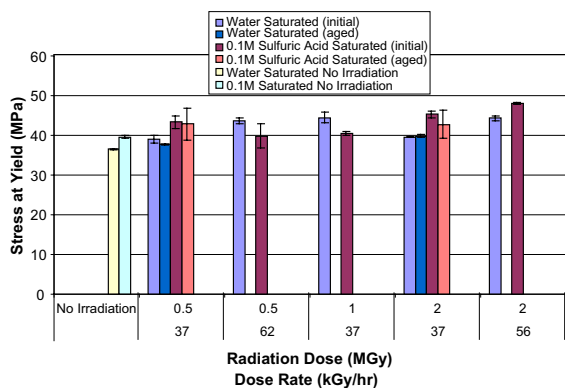


Fig. 5. Stress at yield for Nylon 6,6 saturated with water or 0.1 M sulfuric acid before irradiation exposed to the saturation solution.

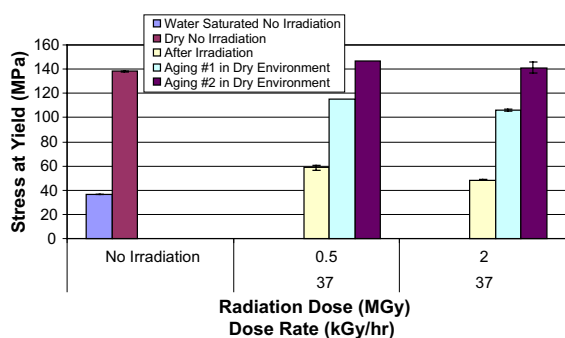


Fig. 6. Stress at yield for Nylon 6,6 irradiated exposed to water and aged in a dry environment.

post-irradiation curing is significant in Nylon 6,6 samples, indication of the aging times is also included in the presentation of the data.

Figs. 4–6 represent the effect of irradiation in a variety of environments on the flexural stress at yield, which is a measure of the mechanical performance of the material. There are a number of factors that affect the mechanical strength of these materials. In samples that were irradiated dry, there is a decrease in yield stress; however, this decrease is relatively small. Also interesting to note is the increase in yield stress after aging periods resulting in a return to the non-irradiated values, and in the longer term, even an improvement over the non-irradiated values.

The dose rate (Fig. 5) seems to have the opposite effect as one would expect, higher dose rates produce samples with higher yield stress than those which received the same dose but at a lower dose rate. This seems to be due to the higher dose rate imparting more energy into the samples, which allows for a higher degree of rearrangement of the molecules.

The combined effects of irradiation and saturation are also a focus of the current work. It is observed that samples that are saturated either with water or a sulfuric acid solution and then exposed to radiation exhibit a higher yield stress than samples that are not irradiated. This is due to the plasticization effect, which provides the molecules with more freedom of movement. This, in combination with radiation energy, results in the molecules being able to recombine after scission in such a fashion as to produce a ‘stronger’ material.

Samples that were exposed to the environment of the pool water during irradiation exhibited a lower yield stress than the dry samples. This is an expected result when compared with the results of the saturated samples without radiation exposure. When a liquid is introduced into the polymer sample, it acts as a plasticizer and provides the molecules with more freedom of movement. This increase in freedom reduces the entanglement of the polymer molecules resulting in a decrease in the ability of the sample to withstand forces, ultimately reducing the stress at yield.

The higher stress at yield observed in the samples which received lower doses was simply due to the shorter time in which the samples were in the pool environment and thus did not absorb as much water as those receiving a higher dose, which were in the pool for a longer period of time.

For comparison, Tables 1–3 provide data collected for Sigma Aldrich Nylon 6,6 samples. The results obtained differ only slightly from the Dupont Zytel data. The additives present in the Dupont materials do not appear to alter the polymer response to the ionizing radiation energy at the doses studied.

3.2.2. Dilution viscometry

Dilution viscosity is a tool that may be used to determine the molecular configuration of a polymeric material. The intrinsic viscosity of Nylon 6,6 was found experimentally to be approximately 130 mL/g for samples saturated with water at 40 °C, and 100 mL/g for samples saturated with 0.1 M sulfuric acid at 40 °C. Figs. 7–9 summarize the inherent viscosity measurements for Nylon 6,6 samples exposed to a variety of conditions.

The data presented in Fig. 7 are unique in that dry samples were irradiated in a dry environment and stored to age in a dry environment. Previous work has focused on pre-saturation of samples as the method of irradiation.

Table 1
Stress at yield for Sigma Aldrich Nylon 6,6 samples prior to irradiation

Saturation	Yield stress (MPa)	Modulus (MPa)
Dry	136.9 ± 0.4	3110 ± 14
H ₂ O saturated at 40 °C	37.9 ± 0.2	670 ± 10

Table 2
Stress at yield for Sigma Aldrich Nylon 6,6 samples irradiated at 37 kGy/h

Dose (MGy) \pm 28%	Saturation	Aging time (days)	Yield stress (MPa)	Modulus (MPa)
1.0	Dry	13	125 \pm 3	3030 \pm 70
		39	146 \pm 2	3470 \pm 90
2.0	H ₂ O saturated before irradiation	14	42.9 \pm 0.1	718 \pm 8
	0.1 M H ₂ SO ₄ saturated before irradiation	14	48.1 \pm 0.4	798 \pm 5
0.5	Exposed to water during irradiation (\sim 20% saturated)	8	60.3 \pm 0.7	1100 \pm 3
		40	123 \pm 1 ^a	3370 \pm 17 ^a
		98	137 \pm 4 ^a	3400 \pm 135 ^a
2.0	Exposed to water during irradiation (\sim 50% saturated)	8	44.8 \pm 0.5	784 \pm 8
		42	101 \pm 2 ^a	2700 \pm 14 ^a
		100	130 \pm 2 ^a	3220 \pm 11 ^a

^a Placed in a dry environment at room temperature after radiation exposure.

Table 3
Stress at yield for Sigma Aldrich Nylon 6,6 samples irradiated dry at higher dose rates

Dose (MGy) \pm 28%	Average dose rate (kGy/h)	Aging time (days)	Yield stress (MPa)	Modulus (MPa)
0.5	56	8	127 \pm 1	2940 \pm 19
		44	140.0 \pm 0.3	3192 \pm 8
2.1	57	8	103 \pm 1	2300 \pm 54
		57	141 \pm 4	3200 \pm 110

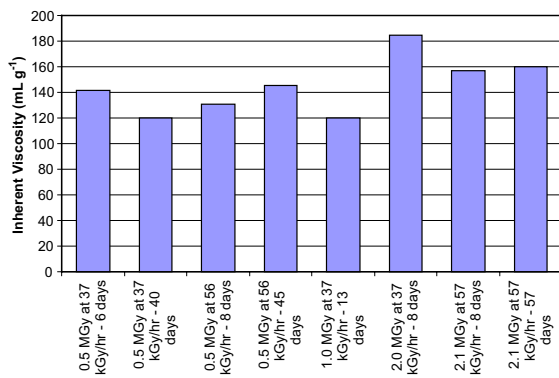


Fig. 7. Inherent viscosity of dry Nylon 6,6 after irradiation.

tion requires submersion in the reactor pool. Fig. 7, in conjunction with Figs. 8 and 9, demonstrates that the condition of the polymer sample prior to irradiation is an important criterion in the determination of its response to radiation exposure.

When irradiated samples were saturated with water prior to irradiation and compared to samples saturated with water, but not irradiated, very little decrease in viscosity was observed, indicating little change to the molecular structure for low dose at low dose rates. Higher doses resulted in increased viscosity, indicating some

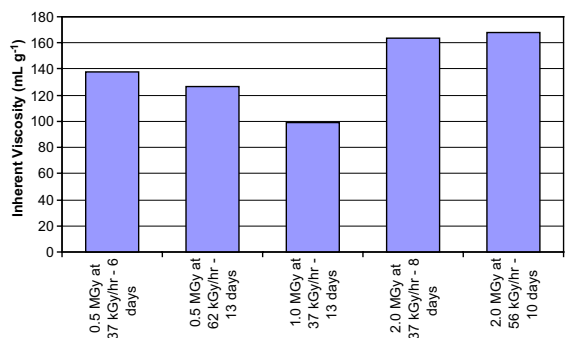


Fig. 8. Inherent viscosity of Nylon 6,6 saturated with distilled water prior to irradiation in distilled water.

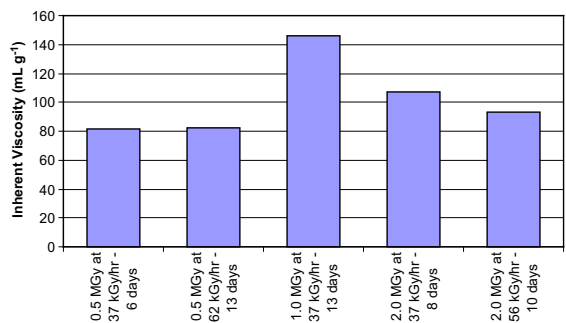


Fig. 9. Inherent viscosity of Nylon 6,6 saturated with 0.1 M sulfuric acid prior to irradiation in 0.1 M sulfuric acid.

degree of branching along the main chain. When samples are saturated prior to irradiation, the effect of dose rate becomes much less prominent. When samples were exposed to 1.0 MGy radiation doses, the damage to the polymer chains was observed to be quite severe. The lower viscosity values may be attributed to the higher dose, compared to 0.5 MGy, which results in a higher incidence of chain scission. Since chain scission and

recombination are competing processes, it appears that, at this dose, chain scission is the dominant process. As the dose is increased, the recombination of fractured chains to form branched molecules results in higher intrinsic viscosities.

When samples are pre-saturated with 0.1 M sulfuric acid solution, the results are quite different from the other results, and it becomes obvious that when these samples are exposed to radiation, the result is a decrease in intrinsic viscosity as compared to that obtained for the non-irradiated 0.1 M sulfuric acid saturated sample. The presence of sulfuric acid within the polymer matrix acts to enhance the chain scission effect and restrict the formation of branched molecules. As the decrease is slightly less in the samples exposed to higher doses than those exposed to lower doses, it may be concluded that the crosslinking and chain scission processes are still competing with the chain scission being dominant under these conditions. However, branching is still occurring, resulting in a slightly higher intrinsic viscosity for the higher doses. The dose rate is again important, as noted in the higher dose studies, in which the higher dose rate results in a lower intrinsic viscosity, and may be attributed to a higher incidence of chain scission.

The temperature of the samples was monitored during irradiation to ensure that significant increases in temperature were not occurring. It was determined that the rise in temperature as a result of irradiation at higher dose rates or longer irradiation times would not be significant to result in a difference between continuous and stepwise radiation exposure.

However, the results shown in the above tables and figures may provide some indication that in a material such as Nylon 6,6, which is not known to perform well in a strong radiation environment, may exhibit sensitivity to the continuity of radiation exposure due to factors other than temperature rise. The dose rates utilized in this work varied between 20 and 62 kGy/h. It is possible that a material such as Nylon 6,6 may show significantly different response when doses are received continuously as the polymer molecules are unable to offset the effects of the continuous influx of radiant energy resulting in a more enhanced change to the molecular structure.

If the dose were delivered intermittently, or continuously at low rates, the polymer molecules would have time to recover between or during exposure. However, this recovery period may result in a higher incidence of chain scission if there exists no other means of dissipation of the radiant energy. This would result in a greater reduction in chain length. If given sufficient time to recover, and if provided with other means of energy dissipation, such as in the case of molecules with aromatic rings in their structure, such materials would experience a lesser extent of reduction in chain length.

When higher doses or lower doses at higher dose rates are received, the energy imparted into the system

can be large enough to allow the polymer chains to recombine with radicals to form branches on the main chain. This appears to result in an increase in the intrinsic viscosity, as was observed in the samples that received higher doses at lower dose rates or comparable doses, but at higher dose rates.

3.2.3. Long-term performance

As the container will be used in the long-term storage of radioactive materials, extrapolation of these short-term studies is required. This is the focus of ongoing research, which is aimed at determining if the short term results presented here are representative of long term performance expectations based on factors such as radiation exposure, dose rate, and the storage environment.

High doses and high dose rates have been the focus of experimental results presented here, however, these will not be representative of the dose or dose rate expected over the container lifetime. The polymeric materials are expected to show different responses when dose rates are reduced, such that extrapolation of the results obtained to date will require consideration of the specific radiation environment expected from the radioactive waste material within the container.

4. Conclusions

Dose and dose rate are important variables in determining the response of Nylon 6,6 to radiation exposure. Due to a lack of radiant energy absorbers in the molecular structure, the predominant response is chain scission, however, it has been demonstrated that the competitive mechanism of crosslinking or chain branching is dominant under certain conditions and exposure regimes.

Post-radiation diffusion and performance have been studied and have shown that radiation exposure affects the diffusion profile as well as increases the apparent diffusion coefficient. Mechanical performance is time dependant resulting in initial performance evaluations exhibiting poor results when compared to virgin materials. However, increased aging times often result in mechanical performance superior to the same material and exposure conditions prior to irradiation.

The results from this research work demonstrate that even materials such as Nylon 6,6, which are known to absorb high amounts water or other aqueous solutions (>9%) and which are susceptible to chain scission in a radioactive environment, would be an acceptable material for use in an environment such as that expected in the storage of radioactive materials.

A decrease in the materials hydrophilicity and an increase in its resistance to radiation damage, would result in a reduction to the damage induced when the material is exposed to a radioactive environment as well as de-

crease the loss of mechanical performance due to plasticization. Materials, such as polyamide 6,6 copolymer and polycarbonate, would be two such materials, and are the focus of current work. Both are expected to be viable polymer-based composite material candidates for the fabrication of radioactive material disposal containers.

Acknowledgments

This work is supported by the Natural Sciences and Engineering Research Council of Canada, the Academic Research Program at the Royal Military College of Canada, and Defence Research and Development Branch for the Royal Military College of Canada. The assistance of the technical personnel of the SLOWPOKE-2 Nuclear Reactor Facility and the Department of Chemistry and Chemical Engineering at the Royal Military College of Canada is gratefully acknowledged.

References

- [1] Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste, AECL-10711, COG-93-1, 1994.
- [2] H.W. Bonin, M.W.M. Walker, V.T. Bui, Nucl. Technol. 145 (1) (2004) 82.
- [3] M.W.M. Walker, Polymeric radioactive waste disposal containers, an investigation into the application of polymers vice metals to house low and intermediate level radioactive waste, MSc thesis, Royal Military College of Canada, April 2001.
- [4] I. Miedema, Application of advanced polymer composites to spent nuclear fuel disposal containers, MSC thesis, Royal Military College of Canada, 2002.
- [5] R.L. Clough, in: H.F. Mark, N.M. Bikaks, C.G. Overberger, G. Menges (Eds.), Radiation Resistant Polymers, Encyclopedia of Polymer Science and Engineering, vol. 13, 2nd Ed., John Wiley, New York, 1985.
- [6] Z.A.M. Ishak, A. Ariffin, R. Senawi, Eur. Polym. J. 37 (1635–1647) (2001) 1635.
- [7] Z.A.M. Ishak, J.P. Berry, J. Appl. Polym. Sci. 51 (2145–2155) (1994) 2145.
- [8] G.B. Lamarre, Experimental and computational determination of radiation dose rates in the Slowpoke-2 Research Reactor at the Royal Military College of Canada/College militaire royal du Canada, Royal Military College of Canada, 1999.
- [9] D.J.Y.S. Pagé, H.W. Bonin, V.T. Bui, P.J. Bates, J. Appl. Polym. Sci. 86 (2002) 2713.
- [10] L. Brown, V.T. Bui, H.W. Bonin, J. Appl. Polym. Sci. in press (2005).
- [11] ASTM D570-95, Standard Practice for Water Absorption of Plastics.
- [12] ASTM D790-02, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.