CASTOR OIL POLYURETHANE AS A COATING OPTION FOR SPENT NUCLEAR FUEL DISPOSAL CONTAINMENT

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Abstract

Castor oil polyurethane (COPU) coatings are being proposed as an additional barrier in the design of the copper containers to store spent nuclear fuel in Canada. The present work investigates the variation in the physico-mechanical properties of two COPUs, based on an aliphatic and aromatic diisocyanate, as a function of ionizing radiation dose and dose rate. The changes in physico-mechanical properties have shown that radiation, regardless of dose rate and isocyanate structure, increases the values of the modulus and the ultimate tensile strength when compared with those of the unirradiated samples, with aromatic based polyurethanes being more susceptible to variation than aliphatic based ones.

Keywords: castor oil, polyurethanes, radiation, dose rate.

1. Introduction

In Canada, the proposed method for the ultimate disposal of spent nuclear reactor fuel and high-level radioactive waste consists of burying the radioactive waste underground in a deep geological repository (DGR) [1, 2]. The Canadian concept for the disposal of its waste consists of a multi-barrier system contained within a geological repository. The multi-barrier system is composed of the used nuclear fuel bundles themselves (i.e. fuel pellets and cladding), the filler material, the container, the buffer, sealing systems and the geosphere [1]. The multi-barrier system recognizes that, regardless of design, at some point all manufactured materials will fail. However, engineered barriers can be constructed so as to increase the time to failure. A multi-barrier system ensures that, although individual components of the system may succumb, the whole unit will act to delay the migration of radionuclides and diminish with time the hazards of the spent nuclear fuel.

The material presently proposed for the fabrication of the container is copper, more specifically, oxygen-free phosphorous doped copper. The used fuel container (UFC) design initially proposed by the AECL is a cylindrical container with dimensions 2250 mm high, and 620 mm inner diameter, containing 72 standard CANDU 37-element fuel bundles [1]. In the AECL report it was stated that on pessimistic assumptions, the estimates for the time failure by corrosion range from 30,000 to one million years for a 25 mm thick copper container; with a more realistic estimate of more than a million years [1]. The main cause of failure of copper is corrosion, which in the context of the DGR is at its most aggressive state during the warm oxidizing period during the early stages of emplacement (<100 years) [3]. The maximum predicted dose rate at the surface of the used fuel container within the DGR environment is 0.908 Gyh^{-1} at the beginning of the dwelling time of the container within the DGR [4]. The dose rate gradually decreases with time such that the total expected dose on the metal wall of the container over its lifetime of 500 years is 6.262 MGy [4].

The simultaneous exposure of the container's walls to the ionizing radiation field emitted by the spent nuclear bundles, the relatively high temperatures caused by the residual heat produced by the spent nuclear fuel, and the chemical aggression from the groundwater that would be in contact with the copper would all challenge the container's integrity. To that end, this work investigates the merit of introducing a polymer coating as an additional barrier to reduce the contact of the surrounding groundwater with the copper container. Through the addition of another physical barrier the intention is to significantly slow the rate of approach of the surrounding groundwater to the container. Thus, the end result will ensure the longevity of the copper container as the physical polymer barrier would have protected it in the most critical early periods (<100 years) when the copper container would have otherwise been at its most susceptible to corrosion. Therefore, the intent of the present work is to assure the reliability of the copper container through the insertion of the additional physical polyurethane coating.

The field of natural based polymers is a very active one, as industry strives to replace conventionally produced petroleum based polymers with biopolymers (natural polymers). The complex structure of the castor oil based polyurethanes, referred to in the document as COPU, provides an interesting backdrop for a variety of applications. The uniqueness of the castor oil component is that it imparts chain flexibility due to its long aliphatic chain component and, more importantly, it assumes several roles that promote crosslinking, which results from its tri-functional nature and proton donor ability. Castor oil based polyurethanes are chosen for this application because of their flexibility and mechanical resistance, important factors in the handling and transportation of the used nuclear fuel container.

A literature research has revealed many valuable works performed on the physico-mechanical properties of castor oil based polyurethanes; and the effects of chain extenders, isocyanate structure, and hard-to-soft ratio [5, 6, 7]. The studies of radiation effects on polyurethanes have for the most part excluded polyurethanes based on castor oil and have focused on single sources of radiation versus a mixed field. The results of some of the works done on radiation and polyurethane polymers by researchers such as Ravat *et al.*[8] and Cao *et al.*[9], have shown that the resulting effects of the radiation strongly depend on the composition of the polyurethane as well as the type of radiation. A positive increase in the physico-mechanical properties of mixed field ionizing radiation on aliphatic castor oil based polyurethane has been reported in previous works[10, 11].

The goal undertaken in the present work was to build on previous works through further investigation of the effects of higher accumulated doses and varying dose rates, as well as isocyanate structure on COPUs. The properties and effects imparted by different isocyanate structure and dose rate on the physico-mechanical performance of the COPU as a function of accumulated dose were analyzed. In this work, the physico-mechanical behaviour of the COPUs was monitored by means of tensile testing. In addition, the thermal properties were investigated using two techniques, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Moreover, these two techniques can relate the thermal properties to the COPUs structure and assess the suitability as a coating material.

2. Materials

Castor oil, hexamethylene diisocyanate (HMDI), and 2,4-toluene diisocyanate (TDI) were obtained from Sigma-Aldrich Company, Inc, and were used as received (Figure 1). The equivalent weight per hydroxyl group for castor oil was 345g and per NCO group were 84g and 87g for hexamethylene diisocyanate and 2,4-toluene diisocyanate respectively. In this report, the castor oil based polyurethanes based on HMDI and TDI are referenced as COPUH and COPUT respectively. The castor oil polyurethanes samples were prepared by the simple addition reaction of the castor oil and the respective isocyanate at a NCO/OH ratio of 1.5.

The samples were irradiated in the mixed radiation field provided by a SLOWPOKE-2 nuclear reactor. At the irradiation site, the mixed field is comprised of 87% electrons, 9% gamma photons, 3% recoil protons and 1% fast and thermal neutrons. The samples were positioned at 32cm in the radial direction from the reactor centre at mid-core height. At the aforementioned position, to achieve the desired dose rates, the reactor was operated at either half or three quarter power, corresponding to dose rates of 37 $kGyh^{-1}$ and 55.5 $kGyh^{-1}$ ± 28% [12].

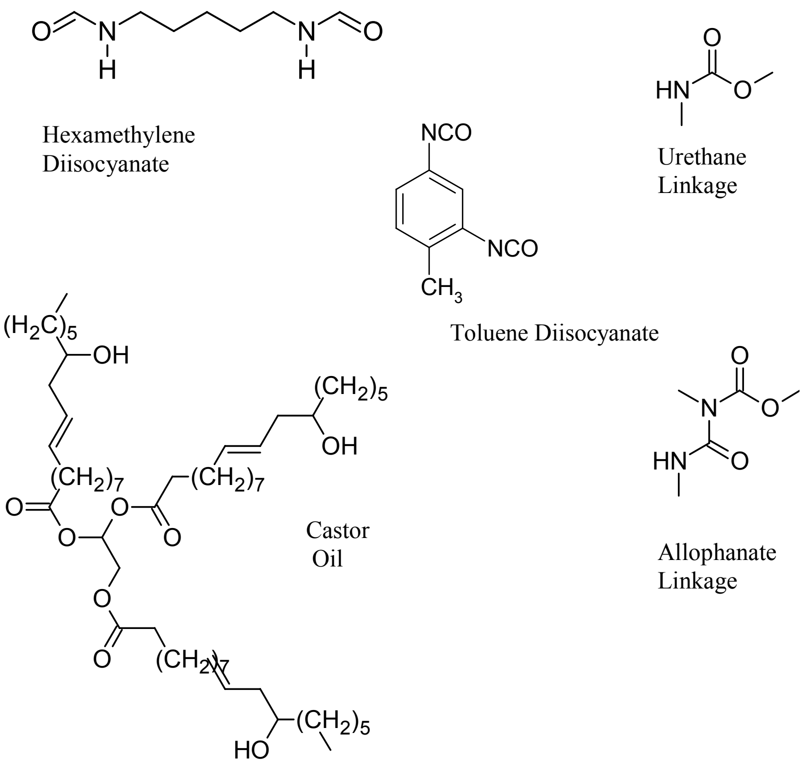

Figure 1: Components of Castor Oil Based Polyurethanes

2.1 *Characterization.*

In the present work, five samples were tested at each trial to ensure the reproducibility and reliability of the test samples and the results.

Tensile Testing

Tensile testing was performed on an INSTRON Universal Testing Instrument, Model 4206. Tensile testing was based on a procedure according to ASTM D 638-96. The polymer test specimens were made in the form of standard dumbbell-shaped type IV bars. Measurements were taken with 50N and 5kN load cells at crosshead speeds of 10.0 and 20.0 mmmin^{-1} for the COPUH and COPUT correspondingly. Tests were run until break occurred or until the maximum displacement was reached. The parameters of interest included the modulus and the ultimate tensile strength (UTS).

Differential Scanning Calorimetry (DSC)

Differential scanning calorimeter data were obtained on a TA instruments Q100 series equipped with a liquid nitrogen cooling accessory. All DSC measurements were performed following the ASTM E1356-03 standard. Runs were performed on polymer samples of about 10mg at a heating rate of $20^{\circ}\text{Cmin}^{-1}$. The gas-cooling accessory was used to provide an experimental range that began at –100ºC and spanned to 100ºC. Two consecutive cycles were run on each sample. The midpoint of the slope change of the heat capacity plot of the second scan was taken as the glass transition temperature.

Dynamic Mechanical Analysis (DMA)

DMA data were collected on the TA instruments Q800 DMA series equipped with a liquid nitrogen cooling apparatus, using a single cantilever clamp setting. The DMA measurements were carried out using the ASTM E1640-99 standard. The multifrequency mode at a temperature ramp of 10ºCmin^{-1}, over a temperature range of –100ºC to 150ºC was used. To protect the thermocouples from damage a thermal shield was used over the sample during testing

3. Results and Discussion

The general trend exhibited by the reported data in Figures 2 and 3 from the tensile tests showed an overall increase in physico-mechanical properties of the COPUs. The unirradiated samples are presented as the straight lines, y = <number>, where the number is the value of the modulus or ultimate tensile strength at an accumulated dose of zero Gy.

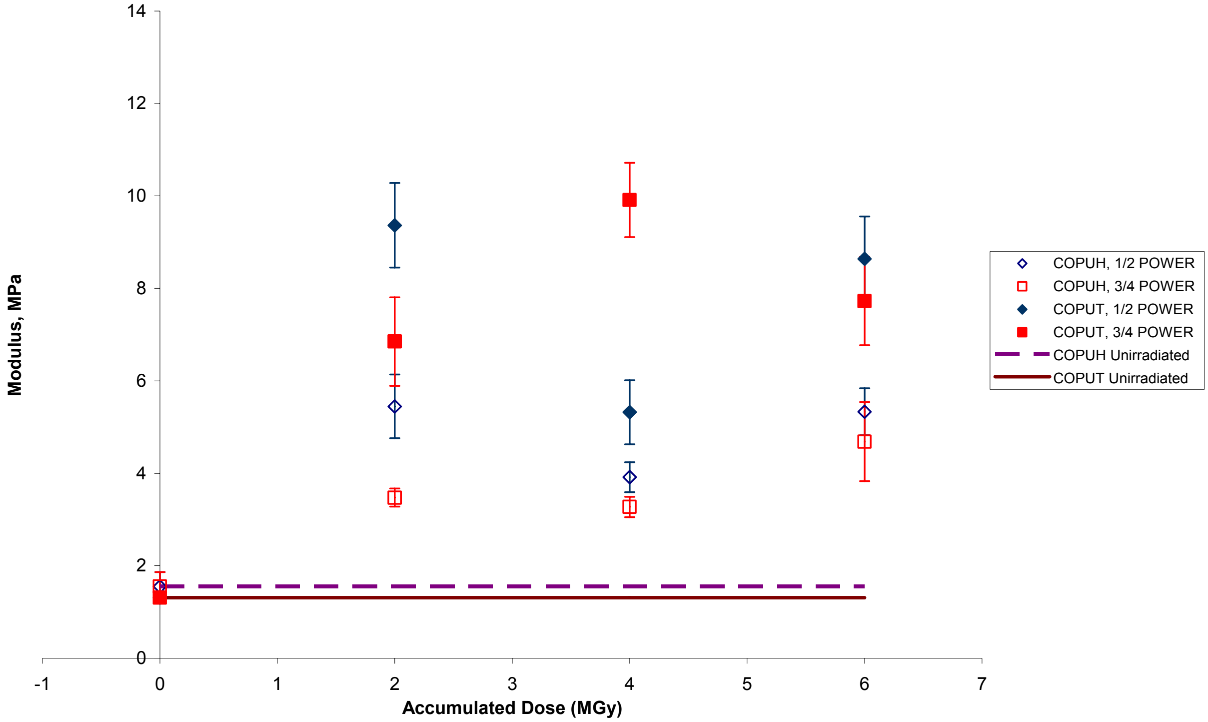

Figure 2: Modulus as a Function of Accumulated Dose.

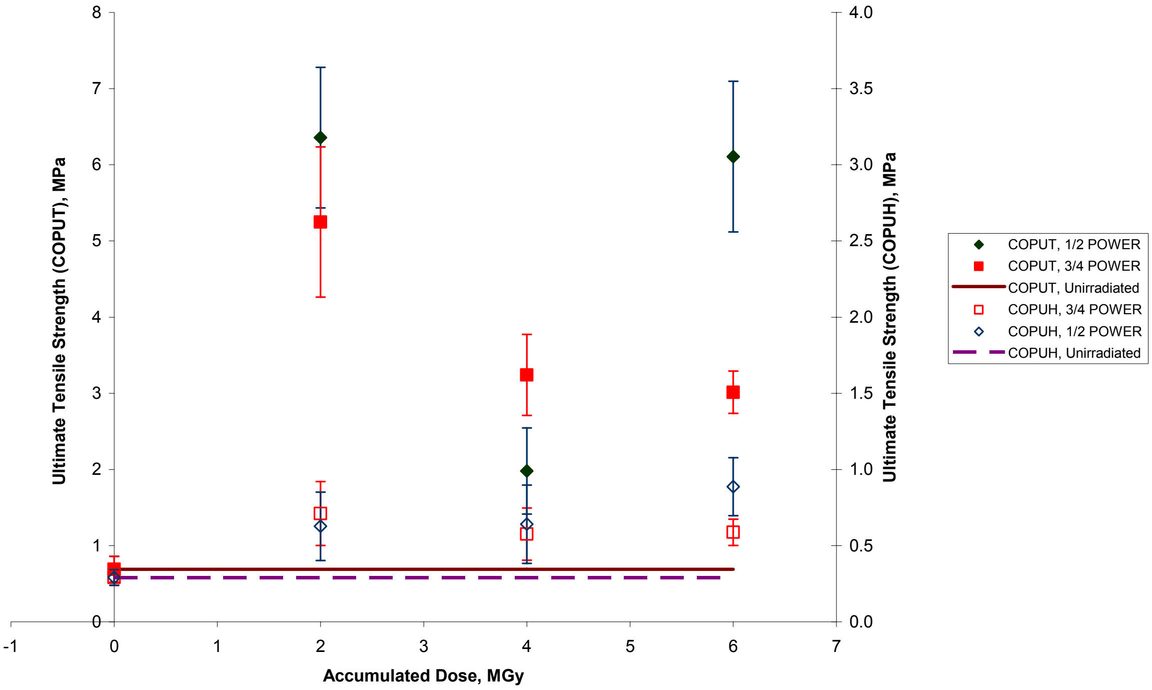

Figure 3: Ultimate Tensile Test as a Function of Accumulated Dose

The unirradiated values of modulus and ultimate tensile strength for the COPUH and COPUT polymers are relatively close and are: 1.55 ± 0.30MPa , 0.29 ± 0.051 MPa; and 1.31 ± 0.12 MPa, 0.69 ± 0.167 MPa; respectively. Some references concerning the tensile and the modulus value of castor oil based polyurethanes have been reported and range from 0.987 MPa to 9.27 MPa, and 1.62 MPa to 6.70 MPa respectively [5, 6]. The differences in these reported values are attributed to differences in the isocyanate structure. The values in this work are within the range of those found by other investigators. In the present work, the values for modulus demonstrate little favourability to whether the COPU is based on the aromatic or aliphatic isocyanate. This implies that the materials stiffness and hence its modulus is more a function of the large castor oil component, while the materials strength is dependant on the isocyanate structure. There is a noticeable difference between the UTS values of the COPUT and COPUH values, with the former value almost doubled that of the latter one. Therefore the stiffness imparted by the aromatic ring increases the strength of the resulting polymer.

It is evident from Figures 2 and 3 that the COPUT values for the modulus and the ultimate tensile strength (the solid points) are markedly more affected by the increasing accumulated dose than those of the COPUH values (the unfilled points). The long chain component of the castor oil polyol that is so appealing for the flexibility it imparts to the COPUs also hinders the reaction rate of the growing polymer chain. As evident from this work and past works, the initial effect of ionizing radiation is one which may cause an increase in the reaction rate. The increase in reaction rate may be attributed to unreacted polyol and diisocyanate sites left dormant during the thermal curing process, which may further react upon exposure to radiation. The combination of the long castor oil chain and the rigid aromatic structure may yield more unreacted hydroxyl and isocyanate end groups during thermal cure. Therefore, upon irradiation the aromatic based polyurethanes show an increased response to accumulated dose when compared with the corresponding aliphatic based polyurethanes. In addition to the increased polyurethane reaction, based on data presented elsewhere, it has been shown that allophanate bonds (Figure 1) as well as increased hydrogen bonding contribute to the initial increase in physico-mechanical properties upon exposure to the mixed ionizing radiation [10].

Under ionizing radiation conditions, polymers are known to undergo competing chain scission and crosslinking reactions. These competing reactions result in a weaker or degraded polymer with lower molecular weight when chain scission is predominant. Conversely, predominant crosslinking results in a stronger polymer developed from the formation of an insoluble gel which in turn increased the molecular weight. The weakness or strength of a polymer can also be related to its modulus and UTS. Hence an increase or decrease in modulus and UTS can be correlated to increased chain scission or crosslinking, respectively. From Figures 2 and 3, it is clear these competing reactions are more strongly felt in the COPUTs than the COPUHs. The value of the modulus and UTS for the COPUHs remains relatively constant as the accumulated dose is increased, implying that neither chain scission nor crosslinking is the dominant reaction. On the other hand, the COPUTs exhibit noticeable changes depending on the accumulated dose, implying that the isocyanate structure does indeed affect the outcome of the physico-mechanical properties of the polymer.

The effect of dose rate, which is controlled by whether the reactor is operated at half or three-quarter power (37 $kGyh^{-1}$ and 55.5 $kGyh^{-1}$ ± 28%), on the COPUs based on Figures 2 and 3 is highly dependant on the isocyanate structure. The aromatic based COPUTs are influenced by dose rate, while the COPUH polymers seem indifferent to dose rate. The rigid aromatic structure of the COPUTs, unlike the flexible aliphatic structure of the COPUHs, does not facilitate easy movement within the chains and hence the COPUTs produce more distinct results at different dose rates and doses.

Changes in the polymers physico-mechanical properties are clearly dependant on the isocyanate structure and can be related to their glass transition temperatures, T_gs. The glass transition temperature is a secondary transition which can be related to conformational changes within a polymer and can therefore be connected to the polymers' flexibility, strength, and modulus. Table 1 reports the glass transition temperatures of both the aliphatic and aromatic polymers at half and three quarter power. The glass transition temperatures were analyzed using two methods: dynamic mechanical analysis and differential scanning calorimetry. Table 1 shows that, at the least, there is a thirty degree difference between the two methods. The differences between the two methods arise because the DMA method relies on the changes in the relaxation times and conformational movements within the polymer, i.e. second order transitions, while DSC responds to changes in first order transitions. Therefore DSC measurements of T_g give an approximate value which is acquired over a long time frame and large temperature ranges, while the DMA records a more accurate representation of T_g. The glass transition temperatures generated by DSC for COPU have been shown by several investigators to vary between -35ºC to 52ºC [6,13]. As such the castor oil polyurethanes in this work are well within the range of those studies.

As mentioned, T_g can be related to structure and flexibility of the polymer chain. The T_g is affected by free volume, chain flexibility and side group interactions such that the more ordered and flexible the chain the lower the T_g. This point is illustrated in Table 1 where the values of T_g for the more flexible aliphatic based polyurethane are much lower than those of the rigid aromatic based polyurethanes.

Table 1: Glass transition temperatures of the COPUs

Glass Transition Temperature, T_g, (ºC)								
Polymer	**COPUH**				**COPUT**			
Reactor Power	½	¾	½	¾	½	¾	½	¾
Accumulated Dose (MGy)	**DMA**	**DMA**	**DSC**	**DSC**	**DMA**	**DMA**	**DSC**	**DSC**
0	11.10	11.10	-21.27	-21.27	44.36	44.36	10.44	10.44
2	8.21	0.53	-21.25	-22.23	53.12	54.08	14.90	20.03
4	8.94	3.45	-16.19	-19.24	28.76	42.19	6.66	18.42
6	9.57	18.62	-10.99	-12.67	53.91	55.76	19.78	24.32

The glass transition temperature is a standard by which the practical application and utility of a polymer can be judged. In other words the T_g gives an idea of the polymers ability to be moulded, compounded, sprayed, etc., and is therefore of particular importance. In terms of processing this means that when heated to a temperature above room temperature, both the COPU polymers will be in their rubbery stage. The aliphatic polymer would require slightly higher temperatures to compensate for its lower T_g value. In the DGR temperatures are expected to fluctuate from its highest at 97ºC to 20-30ºC over 10^4-10^5 years [1]. Thus, the COPUs will be above their T_gs, which means the COPUs will maintain their rubbery integrity and will not become brittle and crack over its time in the DGR.

4. Conclusions

Ionizing radiation improves the physico-mechanical properties of the COPUs, as the physico-mechanical property values of both the COPUH and COPUT polymers are greater after being irradiated than those of the unirradiated values. The effects of radiation and dose rate on castor oil based polyurethanes are dependant on the structure of the polyurethanes, and more specifically the hard segment provided by the isocyanate component. The effect of isocyanate structure is further supported by the glass transition temperature measurements. The lower T_gs of the COPUHs over those of the COPUTs were attributed to the flexibility of the linear aliphatic HDI diisocyanate versus that of the more rigid aromatic TDI diisocyanate. Due to the inherent flexibility of the aliphatic polyurethanes, they are more readily able to recombine after radiative chain scission, than the more rigid aromatic polyurethanes. The result being that the aromatic COPUTs show definite changes depending on the dose and dose rate, while the aliphatic COPUHs show only slight variations.

The maximum predicted dose rate at the surface of the used fuel container within the DGR environment is 0.908 Gyh^{-1} and that the total expected dose on the metal wall of the container over its lifetime of 500 years is 6.262 MGy [4]. Also, the temperature within the deep geological repository is predicted to vary from its highest at 97ºC to 20-30ºC over 10^4-10^5 years [1]. Thus based on these experimental findings, the COPUs can be considered as suitable material in the application as a coating material for the used fuel copper container walls because the physico-mechanical properties were not compromised by radiation or temperature.

Future work geared towards the viability of using the polymer coatings as an additional barrier for the used fuel storage containers within the DGR conditions is ongoing. The conditions in the DGR are comprised of changing radiation, temperature, and pH. Thus, future developments include investigations into the sequential and simultaneous exposure of the castor oil based polyurethanes to temperature, radiation and solvents of varying pHs. The results of the sequential and simultaneous experiments will be analyzed through critical experiments on mechanical strength, glass transition temperature measurements, mass spectroscopy, and nuclear activation analysis.

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