MIXED FIELD RADIATION MODIFICATION OF POLYURETHANES BASED ON CASTOR OIL

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Abstract

Polyurethane is among the polymers and polymer-based composite materials being investigated at the Royal Military College of Canada for the fabrication of leak-tight containers for the long-term disposal of radioactive waste. Due to the long aliphatic chain of the castor oil component of polyurethane, thermal curing of castor oil based polyurethane (COPU) is limited by increasing polymer viscosity. To enhance further crosslinking, COPUs were subjected to a range of doses (0.0 – 3.0 MGy) produced by the mixed ionizing radiation field of a SLOWPOKE-2 research nuclear reactor. The tensile mechanical properties of castor oil based polyurethanes (COPU), unirradiated and irradiated, were characterized by mechanical tensile tests. Increases in mechanical strength due to radiation-induced crosslinking and limitations of thermal curing were confirmed by tensile tests and changing ^{13}C-NMR and FTIR spectra.

Keywords: Radiation, Radioactive Waste Management, Castor Oil, Polyurethane, Mechanical Testing, ATR-FTIR, Solid State ^{13}C-NMR

Introduction

In looking towards the future, industry is always striving to manufacture more performant materials. Elastomeric polyurethanes are high performing materials that have found applications in inflatable structures, conveyor belts, protective coatings, biomaterials, among many others, where flexibility, high tensile strength, tear strength and abrasion resistance are of paramount importance [1].

Another application to which polymers are being used in radiation environments is with the nuclear industry. The present work is an extension of work done since 1997, at the Royal Military College of Canada (RMC) to investigate the use of polymer and polymer composites for the fabrication of containers to store low-, intermediate, and high-level nuclear waste [2,3]. Several of the polymer composite materials, such as polyurethane, epoxy, poly (etheretherkertone), researched at RMC were found to be quite resistant to radiation, exhibiting overall increases in density, Young's modulus, a decrease in the strain at break, and only minor changes in the strength [2,3].

Radiation crosslinking is one method by which the mechanical performance of some polymers may be improved. The world market for radiation curable raw materials in 2002 amounted to 195,300 tonnes, with radiation curable urethanes acrylates responsible for eighteen percent (18%) of the acrylated oligomers market [4].

Castor oil is chosen in the fabrication of elastomeric polyurethane because of its varied and favourable structural features. These features include three secondary hydroxyl groups amongst a long aliphatic chain that allows it to act as a proton donor, crosslinking agent, providing flexibility to the resulting polymer.

The use of natural oils, particularly castor oil, in the production of elastomeric polyurethanes is not a novel idea. Castor oil has been used to make fast-cured polyurethane ureas [5] and polyurethanes by several investigators [6-9]. Liu and Bui investigated the impact properties of castor oil based polyurethanes crosslinked with an aliphatic polyisocyanate resin based on Desmodur N-100 and hexamethylene diisocyanate, HMDI [7].

In this paper tensile strength values are reported in terms of MPa. This is because the tensile strength is the force (in Newtons) per unit area of the sample (m^2), resulting in a strength unit in Nm^{-2} or Pa. The tensile strength and modulus reported for the HDI-castor oil polyurethane samples in Liu and Bui's work were 0.987 MPa and 1.627 MPa respectively [7]. Kendaganna *et al* investigated the structure-property relationship of castor oil based diol extended polyurethanes. The work of Kendaganna *et al* reported tensile strengths of 0.99-1.18 MPa +/- 2% and modulus values of 2.8-3.8 +/- 2%[9].

The polymer in the present work was synthesized by the thermal curing reaction between castor oil and hexamethylene diisocyanate (HMDI) (Figure 1). As the polymerization progresses, the cured COPU develops in a star structure, with branches emanating outwards. During the thermal curing, the growing branched structure of the COPU increases the overall viscosity of the polymer. The increase in viscosity has a two-fold effect: reduced reaction rates and decreased diffusivity of unreacted monomers. As a result of these effects, the thermal curing of castor oil based polyurethanes is slow and results in some unreacted sites.

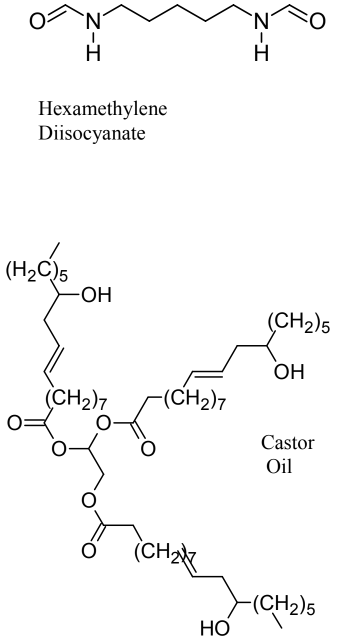


Figure 1: HMDI and Castor Oil Structure

In order to develop better quality and more performing polymeric materials, the goal of this research aims at using ionizing radiation as part of the curing process to improve the structure and properties of the castor oil based polyurethane. The formation of radicals, initiated by radiation, allows unreacted hydroxyl and diisocyanate groups present in the COPU polymer to react. The structure-property behaviour of the unirradiated and irradiated samples was investigated using mechanical testing and the determination of changes in the chemical transformations of the polymer monitored using FTIR and ^{13}C-NMR spectra.

Experimental

Materials

Castor oil and Hexamethylene diisocyanate were obtained from Sigma-Aldrich Company, Inc, and were used as received. The equivalent weight per hydroxyl group for castor oil was 345g and that of HMDI per NCO group was 84g.

Sample Preparation

The samples were prepared by simultaneously introducing a predetermined amount of castor oil and HMDI corresponding to a fixed NCO/OH ratio of 1.5 into a round bottom flask. The round-bottom flask was then placed in an oil bath for even heat distribution. The mixture was stirred vigorously under reflux, with a Teflon-coated magnetic stir bar, and heated to approximately 65°C for at least one hour to form the urethane prepolymer. After mixing, the blend was poured into moulds designed according to the tensile dumbbell shape prescribed by ASTM D638-96 [10]. To produce bubble-free samples, the moulds were degassed under reduced pressure, 76mmHg (10.13 kPa), and heated to 65°C for thirty minutes. Then the blends were cured in the moulds at 100°C for 9.5 h.

Irradiation Conditions

The samples were irradiated in the mixed radiation field from a SLOWPOKE-2 nuclear reactor. The mixed field comprised of 87% electrons, 9% gamma photons, 3% recoil protons and 1% fast and thermal neutrons [11]. The samples were positioned at 32 cm in the radial direction from the core at mid-core height.

At this position, the dose rate was determined to be 37 kGyhr^{-1} +/-28% [11].

Characterization

Tensile tests were performed using an INSTRON Universal Testing Instrument, Model 4206, at room temperature. Tests were performed according to the procedure set by the ASTM D 638-96, at a crosshead speed of 5 mm min^{-1}. The Young's modulus, the ultimate tensile strength and maximum strain were determined from the stress-strain curves. FTIR analysis was performed on a Nicolet Impact 410 instrument, which generated infrared spectra with a spectral range between 4000-350 cm^{-1}. The Solid State ^{13}C-NMR spectra were obtained using a VARIAN Mercury plus-300 MHz spectrometer, equipped with a double resonance solid-state probe, with variable temperature. The ^{13}C-NMR spectra were recorded at room temperature. Magnetic angle spinning (MAS) and high power proton decoupling, with zirconia rotor spinning speeds of the order of 3500Hz were used for the ^{13}C-NMR characterization tests.

Results and Discussion

The tensile mechanical properties of castor oil based polyurethanes (COPU) exhibit a steady increase below a cummulative dose of 1.0 MGy (Figure 2). As mentioned previously, the long aliphatic chain of castor oil acts as a steric hindrance during the thermal curing process, slowing down the reaction rate and resulting in an end product that contains unreacted castor oil and HMDI. Some remaining unreacted hydroxyl and isocyanate end groups, further react upon exposure to radiation. Above 1.0 MGy, the response of the COPU to higher radiation doses reaches a plateau. For a given stoichiometric combination of reactants, there are a limited number of reaction sites. As their irradiation increases, the number of available reactive sites decrease to the point that additional irradiation does not produce further bond formation. This is because all possible reaction sites are then exhausted; as is revealed by the plateau trend exhibited in the tensile graphs of Figure 2.

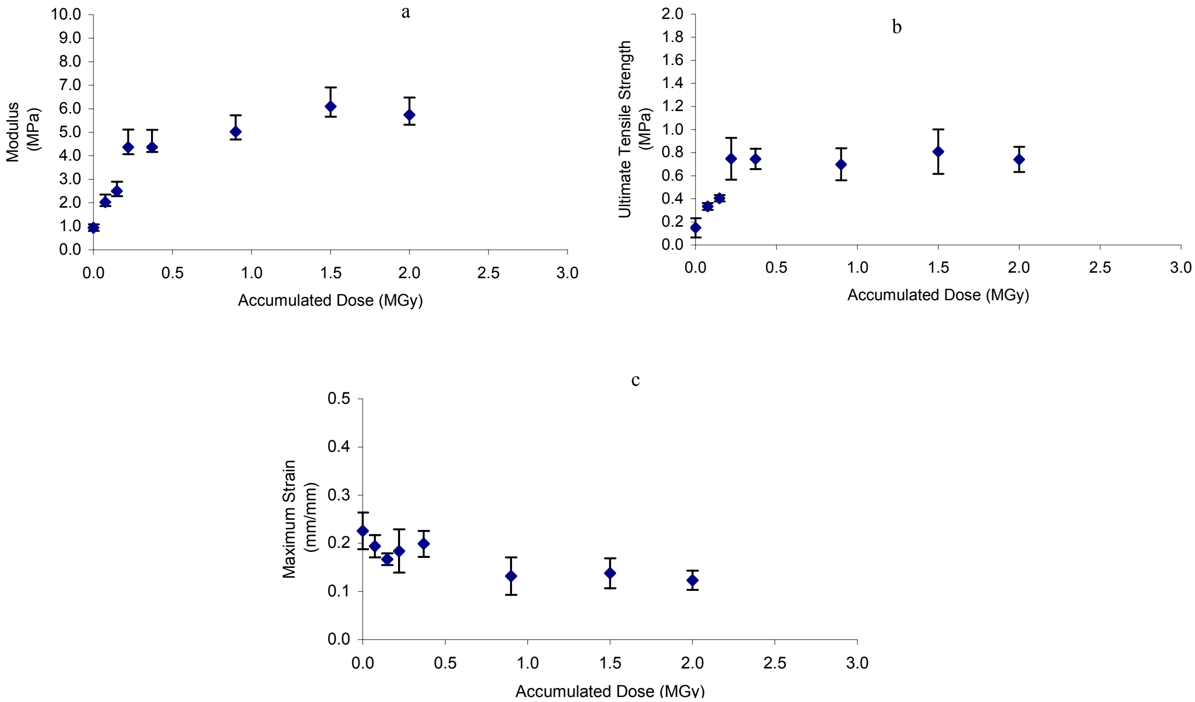


Figure 2: Mechanical Properties as a Function of Accumulated Dose. (a) Modulus; (b) Ultimate Tensile Strength; (c) Maximum Strain. The error on the accumulated dose is +/- 28%

Confirmation of the urethane structure and the presence of unreacted isocyanate groups in the unirradiated COPU sample are illustrated by FTIR spectra (Table 1, Figure 3). Of particular interest to this paper is the appearance of the isocyanate peak, O=C=N (2276-2240cm^{-1}) in the unirradiated sample which confirms earlier remarks that suggest the presence of unreacted isocyanate groups in the COPU.

The experimental results for tensile strength and modulus of the unirradiated COPU in this work are 0.149 +/- 0.083MPa and 0.930+/-0.130 MPa. As expected, the tensile and modulus values of the COPU reported in this work are less than those values reported in the work of Liu and Bui and Kendaganna *et al*. This is because Liu and Bui used a trifunctional isocyanate and Kendaganna *et al* used diol chain extenders to produce more branched PU structures than the COPU samples in this work.

Increased branching results in increased strength and modulus values. At the point where the mechanical property plateaus, the tensile strength and modulus values of the irradiated COPU are 0.747 +/_ 0.088 MPa and 4.365 +/_0.299 MPa respectively.

Table 1: Typical Infrared Spectra of Polyurethane [12]

Wavenumber (cm^{-1})	**Functional Group Assignment**
3360-3310	N-H Stretching
1760-1700	Urethane Carbonyl Absorption
1730	Free C=O Stretching
1605	Bonded C=O Stretching
1550	N-H Bending
1525	Allophanate LInkage
1250	C-O Stretching

Therefore from the results of this work, it can be shown that including ionizing radiation as part of the curing process does indeed improve the structure and properties of COPU.

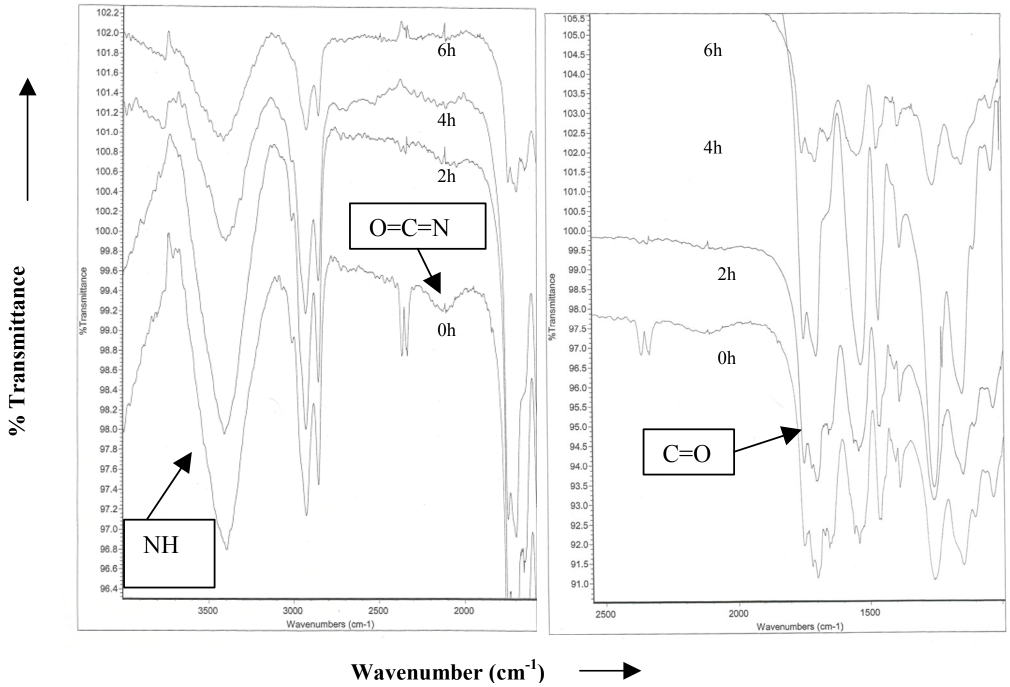
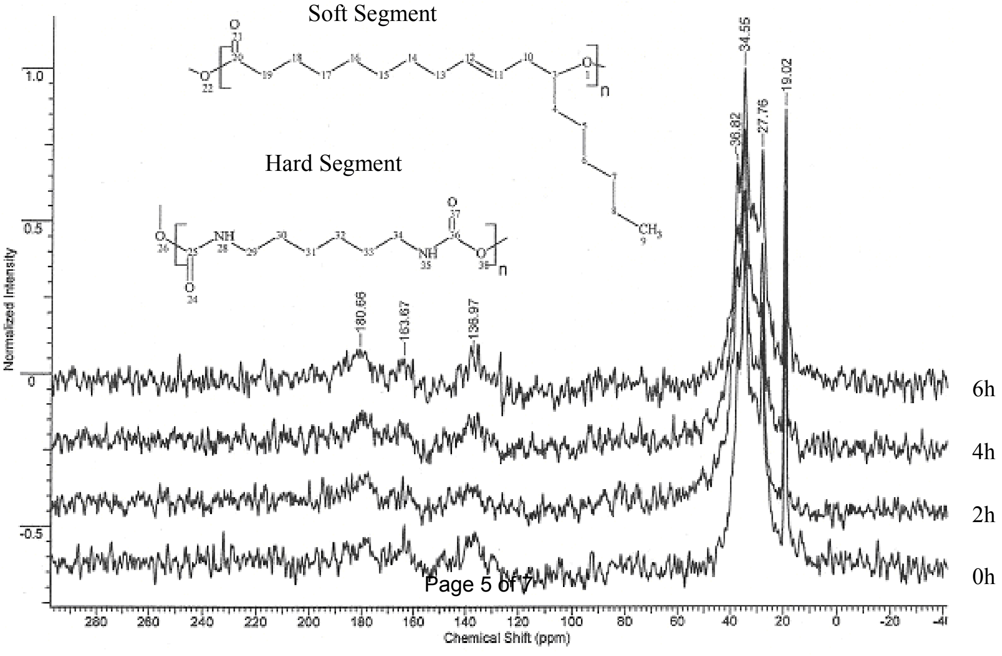


Figure 3: FTIR Spectra for COPU irradiated for 0h, 2h, 4h, and 6h

Increased urethane linkages upon exposure to radiation are reflected by an increase in modulus and ultimate tensile strength (Figure 2a and 2b), and a reduction in maximum strain (Figure 2c). The aforementioned trends occur because the polyurethane becomes one larger molecule as crosslinking increases. In response to the additional bonds, the growing molecule becomes stronger, and harder to distort, and also requires greater applied forces to strain or pull apart. Upon irradiation, increases in mechanical strength may also be attributed to the formation of allophanate linkages between terminal isocyanate groups and active hydrogen present in the urethane groups of the COPU polymer. As a result of and in addition to the increased bond formation upon irradiation, there is also increased strength as a result of increased hydrogen bonding.

The progress of the increased crosslinking due to radiation-induced reactions is monitored by the disappearance of the N=C=O absorption peak and by the spreading and splitting of the N-H stretching and C=O absorption peaks of the FTIR spectra. The spreading and splitting of the absorption peaks of the previously mentioned functional groups



indicate a change in the surrounding environment caused by increased interactions due to hydrogen bonding and bond formation. An absorption peak around 1525 cm^{-1} confirms the presence of allophanate linkages. Allophanate formation is caused by the reaction of urethane groups with isocyanate groups

The ^{13}C-NMR spectra of the unirradiated and irradiated samples may be viewed in Figure 4. The most distinctive feature of the spectra in Figure 4 is that there are no observable differences in the ^{13}C–NMR spectra of the various irradiated COPU samples. In other words, the peaks are of similar areas and occur within the same chemical shift regions, thus implying that the overall integrity of the COPU is not degraded significantly by small doses of ionizing radiation.

Figure 4: ^{13}C-NMR Spectra for COPU irradiated for 0h, 2h, 4h, and 6h

Conclusions

Thermally cured castor oil based polyurethanes were modified using intermediate dose radiation from a mixed ionizing radiation field. This work shows that:

- Thermal curing of castor oil is indeed limited, as confirmed by the presence of unreacted isocyanate groups in the FTIR spectrum of the unirradiated/thermally cured COPU;
- Increased curing can be achieved by radiation induced curing of the thermally cured COPU;
- Increased bond formation was confirmed by favorable increases in mechanical properties and changes in the FTIR spectra upon exposure to intermediate accumulated radiation doses;
- Intermediate radiation doses, such as those used in the present study, do not jeopardize the integrity of the COPU by degradation.
- Since the integrity of the COPU is not degraded when exposed to intermediate levels of radiation dose, then it may be considered a suitable material for the fabrication of containers for radioactive waste disposal.

Acknowledgments

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