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Material Properties

Mechanical behavior and microstructural changes in polyurethane exposed to high doses of X rays, gamma rays or neutron irradiation

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ABSTRACT

Polymeric materials are widely used in applications where the environmental conditions entail their exposure to different sources of irradiation (in most cases ultraviolet or low dose of electromagnetic irradiation for sterilization). In contrast, in this study we have assessed the modifications undergone by a series of polyurethane joints exposed to high radioactive doses of either X-rays or gamma rays (with doses of 20.5, 100, 300 and 900 kGy) or neutron irradiation (with a fluence of $7.23 \cdot 10^{10}$ n/cm^2) which are typical of the environment of nuclear reactors. Tensile tests were carried out to assess the change in mechanical properties derived from the radioactive exposure. Three mechanical parameters were used to monitor the evolution of strength, ductility and toughness: the tensile strength (σ_{max}), the strain corresponding to σ_{max} ($\varepsilon_{\sigma max}$) and the density of energy absorbed prior to maximum load ($U_{\sigma max}$). With regards to X and gamma rays, a negative impact of radiation on strength, ductility and toughness was observed. The detailed statistical analysis of the results has shown that a threshold dose of 300 kGy must be overcome to trigger the damage process. For the fluence employed in this study, neutron irradiation produced very little change in the mechanical properties. The SEM fractographic study has allowed the influence of irradiation on the material failure mechanisms to be identified. Thus, the fracture surface of unirradiated samples shows evidence of plastic deformation and ductile tearing. In contrast, the fracture surface of those samples exposed to a dose of 900 kGy corresponds to brittle fracture. In a consistent way, samples exposed to neutron irradiation have a fracture surface similar to that of the non-irradiated material. In summary, electromagnetic radiation for doses above the threshold leads to the embrittlement of polyurethane.

Raman spectroscopy was employed to identify the microstructural changes induced by the different sources of radiation at the molecular level. The band corresponding to the vibration of the C-H bending bonds present in the polyurethane was measured as a function of the dose, finding a strong correlation between its vibration frequency and the dose of exposure to electromagnetic radiation. This shift is more sensitive than the mechanical material response since the frequency is affected at doses of 100 kGy, below the threshold previously identified for any of the mechanical properties. This correlation opens the door for the use of Raman spectroscopy as a novel non-destructive tool to characterize the microstructural effect of irradiation on polyurethane.

1. Introduction and aim

Radiation may degrade the mechanical properties of materials so that they are no longer mechanically suitable. This is of particular concern in the environment of nuclear reactors where the materials are usually exposed to a variety of sources of radiation including X rays, gamma rays and neutrons. The effects of radiation on concrete and metals have been extensively studied, due to their relevance for the structural integrity of components in nuclear facilities [1]. Polymeric materials are increasingly used for technological applications under irradiation environmental conditions. In addition, radiation-processing has the potential to play an expanding role in polymer manufacturing

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since ionizing radiation is a powerful means of modifying polymers. For these reasons, describing, quantifying and understanding the effects derived from exposing polymers to ionizing radiations is becoming increasingly important. For instance, polymers are used as insulators, cable systems or packing materials in nuclear plants and high intensity proton accelerators [2]. In addition, polymer-based medical devices are commonly sterilized by means of gamma rays and electron-beam irradiation.

The ability to predict lifetimes when materials are irradiated is still a limiting factor in a number of existing radiation technologies [3]. Even although polymeric materials generally possess a lower structural responsibility in nuclear facilities, there is no doubt that their possible deterioration by radiation can lead to undesirable situations from the logistic and economic viewpoints. Thus, as stressed by Cassidy et al. [4], "Degradation mechanisms in polymers due to gamma irradiation also impact the reliability of instrumentation and power cable systems necessary to maintain safe operation and extend the lifetimes of Light Water Reactors (LWRs) for nuclear power".

Polymers may exhibit a wide range of radiation effects; the formation or rupture of chemical bonds usually results in irreversible effects changing the chemical, thermal or mechanical properties of the material. The reactions undergone by irradiated polymers can be broadly grouped in two types, namely, cross-linking and chain scission. The cross-linking results in the formation of new chemical bonds between polymer molecules while chain scission implies the fracture of polymer molecules. In general, cross-linking improves the strength of the polymer materials whereas the opposite occurs under chain scission. However, the degree and direction of the change is extremely material-sensitive.

There are currently few publications on the changes in properties of polymers exposed to high radioactive doses. As noted above, this is because this type of material is not commonly used in environments as hostile as nuclear reactors. In contrast, numerous studies have been carried out in which the influence of ultraviolet radiation on various properties of different polymers is analyzed, such as [5–8]. The present study assesses the influence of high doses of X rays, gamma rays and neutron irradiation on the mechanical properties of the polyurethane constitutive material of a series of junctions that are part of pneumatic clamping modules. These modules are employed under very adverse conditions, in contact with metallic materials previously exposed to high doses of radiation (spent fuel rods, for instance). In this study, the strength, ductility and toughness of polyurethane were determined by means of quasi-static tensile tests on unirradiated samples and on specimens exposed to electromagnetic radiation with doses of 20.5, 100, 300 and 900 kGy or to neutron irradiation with a fluence of $7.23 \cdot 10^{10}$ n/cm^2. These doses are typical of the environment of nuclear reactors. To the best of these authors' knowledge, there are no previous works in the scientific literature in which the consequences of exposure to high radioactive doses on the mechanical properties of polyurethane are addressed.

A review of the specialized literature allows two main groups of studies related to the exposure of polyurethane to radioactive sources to be distinguished. On the one hand, works in which the polyurethane was exposed to ultraviolet radiation to assess the changes undergone by different properties (microstructural, thermal, mechanical, etc.). Within this first group, there is a small number of studies focused on the mechanical properties. For instance, Boubakri et al. [9] studied the changes in appearance and morphology, thermal properties and mechanical properties of thermoplastic polyurethane exposed to ultraviolet rays (through accelerated aging). According to their results, there was competition between chain scission and crosslinking mechanisms. Thus, the Young's modulus and the stress at a strain of 200% initially decreased and then increased progressively, revealing an increase in crosslink density.

There are also a number of contributions in which the polyurethane is sterilized by exposure to electromagnetic radiation. For instance, Gorna and Gogolewski [10] exposed different biodegradable medical polyurethanes (with varying hydrophilic-to-hydrophobic segment ratios) to gamma radiation at a dose of 25 kGy (which is the standard dose for sterilization). They found that the mechanical degradation is strongly material-sensitive. Thus, the decrease of tensile strength was 12% for the more hydrophobic polyurethanes and 50% for the more hydrophilic polyurethanes. Abraham et al. [11] studied the changes in mechanical behavior induced by sterilization through gamma irradiation on two commercial medical-grade segmented polyurethanes (Biospan™ and Chronoflex™). They obtained the stress–strain curves of these materials before irradiation and after being exposed to doses of 37.6 and 61.6 kGy, respectively. None of these materials showed significant changes in the secant moduli at 50% elongation or in the elongation at failure.

Within this context, one of the main novelties of our work lies in the doses to which the polyurethane has been exposed (reaching 900 kGy for gamma rays and a fluence of $7.23 \cdot 10^{10}$ n/cm^2 for neutron irradiation). The thorough statistical study carried out has allowed the influence of radioactive exposure and mechanical properties to be properly addressed, identifying the threshold that must be overcome to trigger the mechanical damage in this material. The relation between failure micromechanisms and the type and amount of radiation was elucidated through a fractographic study. Finally, Raman spectroscopy was employed to determine the microscopic changes in the material after being exposed to irradiation. As a result of the present work, we have identified the modifications of the mechanical behavior of the material derived from the exposure to the radioactive environment and these changes have been correlated with the micromechanisms developed in the polyurethane. The findings derived from the study by Raman spectroscopy have made it possible to develop a novel non-destructive method to monitor the damage undergone by the material which could prove extremely valuable in carrying out on-site inspections regarding the level of accumulated damage in polyurethane from exposure to radioactive sources.

2. Material

The pneumatic clamping modules consist of a fixed metal part that carries the pneumatic drive input coupled to a polyurethane joint, which is actioned by pressurized air (6–7 bar) making the joint press on the part to be held or lifted. Specifically, this type of clamping module is employed to hold metallic rings in nuclear facilities (nuclear fuel rods, for instance). The typical irradiation conditions are a dose of 100–200 Gy/h and a flux of 10^4-10^5 n/cm^2/s. Fig. 1 (a) shows a diagram of a tube-holding element consisting of three clamping modules while Fig. 1 (b) presents a photograph of one of the modules. The lower part (grey) corresponds to the metal casing and the upper part (black) to the polymeric joint.

A total of 60 polyurethane joints were available for this study. They were subjected to either X and gamma rays at different doses or neutron irradiation. Fig. 2 shows a picture with several samples while Table 1 summarizes the experimental groups involved in the research. It is worth noting that the experimental part was conducted under single blind conditions, that is to say, the designer of the research was in full possession of the information but the experimenter (in charge of carrying out the tensile tests, the fractographic or Raman studies) did not know the origin of the samples or the group they belonged to. This measure was applied to avoid skewing the results (which is of particular relevance for the fractographic study, based on visual inspection of the samples).

The density (ρ) and hardness shore D (H_{SD}) [12] of the samples were measured in the as-received condition obtaining the following results: $\rho = 1.22 \pm 0.03$ g/cm^3, $H_{SD} = 29.6 \pm 0.6$.