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# Effect of dose and temperature on the physical properties of an aliphatic thermoplastic polyurethane irradiated with an electron beam



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## HIGHLIGHTS

- Cross-linking predominated over scission for the e-beam irradiated aliphatic TPU.
- Both BD/EG-MDI hard segments and PTMG soft segments were affected by irradiation.
- Mechanical properties were reduced by cross-linking at amorphous phase.
- Irradiation temperature had not any significant effect.

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## ABSTRACT

The electron beam irradiation of a fully aliphatic thermoplastic polyetherurethane was carried out in air at doses ranging from 50 to 4000 kGy at room temperature and 100 °C and a dose rate of 5.1 kGy min<sup>-1</sup>. The effects of the irradiation on the chemical structure and the physical properties were studied. Gel was obtained already at the lower dose, increasing to almost 100% gel at the higher dose, with cross-linking predominating over chain scission. FTIR and DSC measurements proved that both, soft segment and hard segment, were affected by irradiation. Mechanical properties were adversely affected by irradiation mainly due to the cross-linking produced in the amorphous part of the material. Irradiation temperature did not have any significant effect except at the highest dose of 4000 kGy.

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## 1. Introduction

Electron beam irradiation has been used for practical applications since the 1950s, and has been expanding since that time. Currently, the most prevalent applications are the modification of many different plastic and rubber products, mainly cross-linking of cable jackets, heat-shrinkable plastic tubing and film, plastic pipe, foam and pellets, and partial curing of rubber sheet for automobile tire components (Cleland, 2006). In the case of rubber cross-linking, it has been reported that, in 2009, more than 90% of the tires were produced with a partial curing by electron beam irradiation (Machi, 2009). Cross-linking with electron beam irradiation, and in general with radiation, has the advantage over chemical cross-linking that no chemicals are added, and therefore, no by-products

are generated (Chmielewski et al., 2005). These by-products can be detrimental for biomedical and food-packaging applications. In addition, radiation cross-linking can be performed at ambient temperature whereas chemical systems need heating (Lyll and Becker, 1984). Besides cross-linking, electron beam irradiation is used for the sterilization of medical devices, although the radiation needed for this purpose is of the order of 25 kGy, lower than that needed for polymer cross-linking (Benson, 2002). The electron beam excites and ionizes atoms and polymer molecules on the targeted substrate, and the produced radicals promote the decomposition and/or cross-linking of the polymer, as well as the formation of new functional groups, which depends on the surrounding media during the treatment.

Polyurethanes (PUs) are one of the most useful commercial classes of polymers that are widely used in both industry and everyday life. Polyurethanes exhibit a broad range of physico-chemical and mechanical properties, due to their structural diversity. In the case of linear thermoplastic PUs (TPUs), they consist

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of a hard and soft segments connected by means of urethane linkages, which either mix or segregate depending on chemical composition and produce phase mixed or phase separated morphologies due to their immiscibility. In phase separated TPUs, hard segments provide physical cross-links within the soft segment matrix (Oertel, 1994; Randall and Lee, 2003; Szycher, 2012).

Due to their outstanding blood-contacting performance, coupled with excellent oxidative bio-stability, biocompatibility, processability and desirable mechanical properties such as abrasion resistance, toughness, flexibility, durability and tensile strength, these materials became the choice for a wide variety of biomedical devices (Harsici, 1991; Lamba et al., 1998).

When PUs are employed in the manufacture of medical devices that are implanted it is critical that the final product is sterilized before use. Sterilization processes like dry steam, ethylene oxide, heat and high energy irradiation can have unfavorable effects on medical grade polymers such as extensive material degradation and plastic deformation. Sterilizing techniques can either act physically or chemically leading to alterations of the structure or function of macromolecules which can result in chain scission, oxidation, cross-linking, melting and hydrolysis (Matthews et al., 1994; Skiens and Williams, 1983).

Polyurethanes are qualified as materials possessing excellent radiation stability. However, depending on the molecular architecture and composition, radiation resistance of polyurethanes differs significantly (Walo et al., 2014). Irradiation is known to produce changes in the bulk of polymers such as scission, cross-linking and oxidation of polymer chains (Chapiro, 1995), including PUs. Few papers have been published concerning the effects of ionizing radiation on TPUs, either with gamma irradiation (Shintani et al., 1990, 1991; Abraham et al., 1997; Maxwell et al., 2003; Nouh and Abutalib, 2011) or electron beam irradiation (Pierpoint et al., 2001; Guignot et al., 2001; Janik, 2004; Dannoux et al., 2005; Abd El Ail, 2007; Mrad et al., 2009, 2010; Wetzel et al., 2010; Nouh and Abutalib, 2011; Kim et al., 2013; Murray et al., 2013; Walo et al., 2014), mainly in the last decade for the later. Most of the studied TPUs, were aromatic, and only a scarce number were fully aliphatic (Abraham et al., 1997; Guignot et al., 2001). These aliphatic TPUs are used in biomedical applications, and because electron beam irradiation could be used for sterilization, it is of interest to study with as much detail as possible the effect of electron beam irradiation on the structure and properties of fully aliphatic TPUs.

In the reported work we focused on the quantification of the effects of electron beam irradiation on the properties of a fully aliphatic TPU through a diverse array of characterization techniques. The material was irradiated at doses from 50 to 4000 kGy in an air atmosphere at two different temperatures, room temperature and 100 °C.

## 2. Materials and methods

Aliphatic polyurethane in the form of a translucent sheet with a thickness of approximately 650  $\mu\text{m}$  was received from Goodfellow (Coraopolis, PA). Samples for testing were cut directly from the sheet.

Nuclear magnetic resonance (NMR) spectra were obtained on Varian spectrometers (Inova 300 and Inova 400) using  $\text{CDCl}_3$  as solvent. The residual signal of the deuterated solvent was used as the internal reference (7.26 and 77.0 ppm for proton and carbon respectively).

Attenuated total internal reflectance-Fourier transform infrared analyses (ATR-FTIR) were performed at room temperature using a PerkinElmer Spectrum One infrared spectrometer equipped with an ATR accessory. 16 scans taken directly from the samples at a

resolution of  $4\text{ cm}^{-1}$  were averaged to get the FTIR spectra

A Thermal Analysis Q500 instrument was used for thermogravimetric study of the polyurethane (TGA). A disc sample cut from the sheet with a weight of approximately 20 mg was tested. The test was done in Hi-Resolution mode, where the heating rate is automatically adjusted in response to changes in the rate of weight loss, which results in improved resolution, with an initial heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under a flux of nitrogen.

Differential scanning calorimetry (DSC) analyses were carried out in a Mettler Toledo (DSC 822e) calorimeter equipped with a liquid nitrogen accessory. Discs cut from the samples weighing approximately 20 mg were sealed in aluminum pans with perforated cover. Samples were heated at  $10\text{ }^\circ\text{C min}^{-1}$  from 25 to  $200\text{ }^\circ\text{C}$  followed by cooling at the maximum cooling rate accessible for the instrument to  $-90\text{ }^\circ\text{C}$ , held at this temperature for 10 min and reheated at  $10\text{ }^\circ\text{C min}^{-1}$  from  $-90\text{ }^\circ\text{C}$  to  $200\text{ }^\circ\text{C}$ . All scan were carried out under a constant nitrogen purge. Melting points (Mp) were taken as the maximum of the endothermic transition, whereas glass transition temperatures ( $T_g$ ) were taken as the midpoint of the change in heat capacity.

SAXS measurements were performed at the beamline BL-11 NCD at ALBA Synchrotron Light Facility (Barcelona, Spain). Wavelength of the X-ray beam was 0.999 Å. Detector calibration was done with rat tail tendon, and the characteristic distance  $L$  was calculated from the scattering vector ( $q=4\pi(\sin\theta)/\lambda$ ,  $\lambda$ =wave length,  $2\theta$ =scattering angle). A disc cut from the polyurethane sheet was placed in a Linkam hot stage and heated at  $10\text{ }^\circ\text{C min}^{-1}$  while the SAXS spectra were recorded. Calibration of temperature gave a difference of approximately  $7\text{ }^\circ\text{C}$  between the temperature reading at the hot stage display and the real temperature at the sample.

Tensile properties were measured at ambient temperature in a MTS Synergie 200 testing machine equipped with a 100 N load cell. Type 3 dumbbell test pieces (according to ISO 37) were cut from the samples. A cross-head speed of  $200\text{ mm min}^{-1}$  was used. Strain was measured from cross-head separation and referred to 12 mm initial length. At least six samples were tested for each irradiation dose.

### 2.1. Irradiation of the samples

Square samples of dimensions approximately  $4.5\text{ cm} \times 4.5\text{ cm}$  were cut from the polyurethane sheet. The squares were introduced into  $9\text{ cm} \times 6\text{ cm}$  polyethylene bags and placed in a holder for heating to different temperatures. The device was specially designed and purpose built at the Institute of Physics, UNAM. The samples were irradiated with an electron-beam accelerator, using a Van de Graaff source, 1.3 MeV energy and a beam current of  $5\text{ }\mu\text{A}$  at a dose rate of  $5.1\text{ kGy min}^{-1}$ . Doses covered the range 50–4000 kGy in air at room temperature and the range 300–4000 kGy in air at  $100\text{ }^\circ\text{C}$ .

### 2.2. Gel content

To evaluate the gel content, 150–200 mg of irradiated samples were immersed in 10 mL chloroform for 2 h at room temperature. Chloroform was decanted and 10 mL of fresh chloroform were added. After 24 h at room temperature, chloroform was decanted, 10 mL of fresh chloroform was again added and left for further 24 h. Finally chloroform was decanted, and the resulting gel was dried in air for 2 h and in vacuum at room temperature overnight. The remaining dry solid was weighed. The gel content was calculated from the weight ratio of the insoluble fraction after irradiation and prior to irradiation.

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