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Chemical, physical, and mechanical properties evolution in electron beam irradiated isotactic polypropylene

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HIGHLIGHTS

- Instrumented indentation results do not correlate with the tensile results.
- Young modulus shows a large decrease for irradiation above 100 kGy.
- UV–VIS shows that degradation is continuous, by production of chromophores.
- XRD shows initially amorphization, but crystallinity is recovered above 100 kGy.

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ABSTRACT

Isotactic Polypropylene 3 mm thick tensile samples, prepared by compression molding, were subject to electron beam irradiation with doses 0, 20, 40, 60, 100, 200 and 300 kGy. These samples were characterized by spectroscopic methods (UV spectroscopy), X-ray diffraction and mechanical tests (tensile tests and instrumented indentation), with the aim to investigate the ability of the instrumented indentation test to detect the changes in the macroscopic properties which arise from the changes in the chain structure. The use of larger irradiation doses compared with the commercial levels led to an unexpected behavior. At the smaller doses (up to 60 kGy), as expected, sample crystallinity decreases, characterizing irradiation induced amorphization. For the 100 kGy dose, however, the sample recrystallizes, returning to crystal/amorphous phase ratios similar to the ones observed for the pristine material. These changes correlated with the progressive production of –C═O and –C═C– chromophores in the chain and with a loss in yield strength and Young modulus up to 200 kGy (the sample subjected to 300 kGy is brittle). In spite of this, the indentation test showed limited sensitivity to the changes in the macroscopic tensile properties.

1. Introduction

Instrumented indentation has been in use already for several decades, as a technique to probe mechanical properties of small volumes of materials [1,2]. In metals, in which the technique was first applied, the technique allows to probe several macroscopic properties, like hardness, Young modulus, yield strength, strain hardening exponent, among others [3,4].

There are, of course several works which deal with the extraction of macroscopic mechanical properties from instrumented indentation data in polymers [5–12], the algorithms, however, are more complex than those used for metals and alloys and sometimes the results are disappointing, showing no variation of the predicted mechanical properties, when large variations should be expected [7,8].

The primary aim of the present work is to report instrumented indentation data on an isotactic Polypropylene resin, as received and after electron beam irradiation. Since the main purpose was to test the mechanical properties, samples were extracted from compression molded plates and the samples themselves were subject to irradiation prior to testing. Electron beam irradiation alters the molecular structure of the polymer, hence these changes

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have been monitored by chemical, spectroscopic and crystallographic methods.

2. Materials and methods

2.1. Material and samples

The resin employed in the present work is an isotactic Polypropylene (iPP) compounds, designated as HA722J, furnished by Nova Petroquímica (at the time, a division of Suzano Petroquímica SA, Mauá, Brazil). It is described as an iPP homopolymer with density between 0.89 and 0.91 g cm^{-3}, with high crystallinity, low fluidity and high stiffness, designed primarily for plastic parts injection molding. The material was furnished in granules of approximately 3 mm diameter. Melt flow index was measured, resulting in 0.35 ± 0.01 g $(10\ min)^{-1}$ [13].

The material was processed to obtain 3 mm thick compression molded specimens, according to ASTM Standard D4703 [14], using the flash mold configuration. Details of processing and additional specifications for the employed resin can be found in ref. [13]. The produced specimens were visually inspected, and found to be free of defects. The specimen geometry corresponded to dumbbell tensile specimens with dimensions according to class IV of ASTM standard D638 [15]. One set of samples was reserved for the investigation of the unirradiated material (pristine) and the remaining were subject to electron beam irradiation.

2.2. Electron beam irradiation

Sample irradiation was performed in Dynamitron Job 188 electron accelerator available at the Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN-SP, Brazil). The irradiation settings are given in Table 1. Samples were placed in trays which were submitted to the electron beam at the prescribed speed. Total dose was obtained by multiple passes under the beam (5 kGy per pass). Samples were submitted to doses of 20, 40, 60, 100, 200 and 300 kGy. These electron beam settings were designed to warrant full penetration in the 3 mm, so that a gradient is expected to exist along the sample's thickness, but the applied dose is the same on both sides and constant through the whole section [16].

Polymer irradiation under air, at room temperature, may result in trapped charges and radicals, which lead to post-treatment reactions, particularly due to the constant supply of oxygen. Mowery et al. [17], for example, investigated these reactions after γ irradiation of PP using ^{13}C Nuclear Magnetic Resonance (NMR). These authors reported linear or logarithmic kinetics for these reaction in a timespan of 700 days. On similar grounds, Fel et al. [18] recently investigated γ irradiation of PP and PE using Electron Paramagnetic Resonance (EPR). These authors focused on the signal arising from trapped radicals in the samples and report a time constant of ca. 73 h for decay of alkylperoxyl (O_2) radicals in PP as the most time resilient process. Neither the radical decay products, nor the time dependent reactions were characterized in the present work, but tests were performed as close as possible from irradiation, not superseding 40 h after the irradiation. This period, assuming Mowery et al. [17] results could be extrapolated to represent the present case, is insufficient for the occurrence of appreciable changes in the polymer matrix. The only exception to this rule was observed in the X-ray diffraction experiments, which, due to technical reason, could be performed only one month (30 days) after irradiation. Results of some preliminary tests performed just after irradiation, however, were indistinguishable from the ones presented here, therefore they are believed to be representative.

As stated before, the irradiation settings were chosen such that most electrons have enough energy to trespass the cross section of the sample, even after a few collision events. Some of these electrons, however, may perform multiple collision events in the matrix, loosing enough energy to become trapped as free charges. It is expected that the density of such trapped charges will be greater for the higher doses, but the present authors consider that this density is sufficiently low, not affecting the results.

Table 1
Settings for the electron accelerator.

Parameter	Value
Beam energy	1.103 MeV
Beam width/scan	100 cm
Beam current	4.74 mA
Tray speed	6.72 m min^{-1}
Dose rate	23.39 kGy s^{-1}

2.3. Tensile tests

Mechanical tests were conducted in an electromechanical universal testing machine, using a calibrated 1 kN load cell. Ten specimens were tested for each condition. Samples were tested under displacement control, with crossbar displacement set at 50 mm min^{-1}. No extensometer was used in the present tests. Ten specimens were tested for each condition.

Fracture surfaces in selected samples were observed using a XL30 Phillips electron microscope. Images were produced in the secondary electron mode, using 20 kV acceleration in gold sputtered surfaces.

2.4. Instrumented indentation

Instrumented indentation tests were performed in a Fischerscope H100V microindenter, available at the Laboratório de Fenômenos Superficiais (LFS) of the Escola Politécnica da USP, using a Vickers diamond pyramidal indenter. The maximum load (P_{max}) was set to 150 mN. Load, P was registered as a function of the instantaneous penetration depth, h, in a loading/holding/unloading cycle. The loading portion was set to 30 s, with acquisition time of 0.5 s (i.e. 60 points in the loading curve). The load was kept at its maximum value for 20 and 60 s (respectively 40 and 120 acquisition points) and the unloading portion took 50 s (100 acquisition points).

Samples were prepared for the indentation tests by grinding (using 220, 320, 400, 600, 1000 and 4000 mesh SiC paper) and polishing in metallographic cloth (without adding diamond paste) using detergent as lubricant. This procedure was found to produce acceptable surfaces for the indentation tests. Ten measurements were made in each sample.

Results are evaluated in terms of the universal hardness, HU, defined as:

$$HU = \frac{P_{max}}{A(h_{max})} \tag{1}$$

where h_{max} is the maximum penetration depth (the penetration depth at maximum load) and $A(h) = 24.5h^2 + 4.7372h - 2.34786\sqrt{h}$ is the contact area. This expression of $A(h)$ is calibrated for the Vickers indenter used in the LFS.

A second parameter is the Young modulus, E, estimated using the expression: