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Procedia Materials Science 00 (2014) 000–000

Procedia Materials Science

www.elsevier.com/locate/procedia

20th European Conference on Fracture (ECF20)

Microstructure and Mechanical Properties Evolution in Electron Beam Irradiated isotactic Polypropylene

Eduardo A. Maeda[a], Alessandra F. Santos[b], Leonardo G. de Andrade e Silva[c], Cláudio G. Schön[d,*]

[a]*Centro Universitário Nove de Julho, Av. Dr. Adolpho Pinto, 109, CEP 01156 – 050, São Paulo, Brazil*

[b]*Faculdade de Tecnologia de Mauá, Centro Estadual de Educação Tecnológica "Paula Souza", Av. Antônia Rosa Fioravante, 804, CEP 09390-120 Mauá, Brazil*

[c]*Instituto de Pesquisas Enenrgéticas e Nucleares, Comissão Nacional de Energia Nuclear, Av. Prof. Lineu Prestes, 2242, CEP 05422-970, São Paulo, Brazil*

[d]*Escola Politécnica da Universidade de São Paulo, Av. Prof. Mello Moraes, 2463, CEP 05508-030 São Paulo, Brazil*

Abstract

Isotactic Polypropylene 3mm 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 and Raman FTIR), X-ray diffraction and by mechanical tests (tensile tests and instrumented indentation), with the aim to investigate the ability of the instrumented indentation test to identify the changes in the macroscopic properties which arise from the changes in the chain structure. The use of larger irradiation doses (industrial usage usually is limited to maximum 100kGy) showed an unexpected behavior. At the smaller doses (up to 60kGy) as expected, sample crystallinity decreases, characterizing irradiation induced amorphisation. For the 100kGy dose, however, the sample recrystallizes, returning to crystal/amorphous phase rations similar to the ones observed for the pristine material. These changes correlated with the progressive production of -C=O chromophores in the chain and with a loss in yield strength and Young modulus up to 200kGy (the sample subjected to 300kGy is brittle). In spite of this, the indentation test showed limited sensitivity to the changes in the macroscopic properties.

Selection and peer-review under responsibility of the Norwegian University of Science and Technology (NTNU), Department of Structural Engineering.

Keywords: Polypropylene, Degradation, Electron Beam, Crystallography, Instrumented indentation

1. Introduction

Instrumented indentation has been in use already for several decades, as a tecnique to probe mechanical properties of smell volumes of materialsDoerner and Nix (1986); Oliver and Pharr (1992). In metals, where the technique

* Corresponding author. Tel.: +55-11-3091-5726 ; fax: +55-11-3091-5243.
E-mail address: schoenr@usp.br

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was first applied, the technique allows to probe several macroscopic properties, like hardness, Young modulus, yield strength, strain hardening exponent, among others Giannakopoulos and Suresh (1999); Pintaúde et al. (2005).

There are, of course several works which deals with the extraction of macroscopic mechanical properties from instrumented indentation data in polymers (e.g. refs. VanLandingham et al. (2001); VanLandingham (2003); Cross et al. (2005); Santos et al. (2008); Menčik et al. (2011); Peng et al. (2012, 2013); Oliveira et al. (2014), just to quote a few), 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, where large variations should be expectedCross et al. (2005); Santos et al. (2008).

The primary aim of the present 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. Since the electron beam irradiation alters the molecular structure of the polymer, these changes have been monitored by chemical, spectroscopic and crystallographic methods, resulting in a rich picture of the structure evolution by influence of electron beam irradiation.

2. Materials and Methods

2.1. Material and samples

The resin employed in the present work was 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^{-2}, 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.

Since the primary objective of this work was to investigate the variation of mechanical properties, the material was processed to obtain 3 mm thick compression molded specimens, according to ASTM Standard D4703 (2010), using the flash mold configuration. Details of processing and additional specifications for the employed resin can be found in ref. Santos (2011). 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 (2010). 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 . Samples were placed in trays which were submitted to the electron beam at the prescribed speed. Total dose was obtained by multiple passings under the beam. Samples were submitted to doses of 20, 40, 60, 100, 200 and 300 kGy[1]. These electron beam settings were designed to warrant full penetration in the 3 mm, so that no gradient is expected to exist along the sample's thickness.

2.3. Tensile tests

Mechanical tests were conducted in an electromechanical universal testing machine, using a calibrated 1 kN load cell. In the total, ten specimens were tested for each condition. In some cases fracture occurred visibly at loads which are incompatible with the remaining results, these results were discarded, but at least seven valid results were obtained 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.

[1] The Gray (Gy) is the SI derived unit for irradiation absorbed dose and is defined as the absorption of one Joule of energy by one kilogram of matter.

Table 1. Settings for the electron accelerator

Parameter	Value
Beam Energy	1.103 MeV
Beam width	100 cm
Scan	71.5%
Beam current	4.74 mA
Tray speed	6.72 m min^{-1}
Estimated dose	23.39 kGy s^{-1}

2.4. Instrumented indentation

Instrumented indentation tests were performed in a Fischerscope H100V microindenter, available at the Laboratrio de Fenômenos Superficiais (LFS) of the Escola Politeécnica 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 $A(h)$ is the contact area. In the present area the following expression of $A(h)$ was used:

$$A(h) = 24.5h^2 + 4.7372h - 2.34786\sqrt{h} \tag{2}$$

which is calibrated for the Vickers indenter used in the LFS.

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

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A(h_c)}} \tag{3}$$

where $\beta = 1.034$ is a form factor for the Vickers indenter, S, is the contact stiffness, defined as:

$$S = \left.\frac{\mathrm{d}P}{\mathrm{d}h}\right|_{h_{max}} \tag{4}$$

and, E_r is the reduced Young modulus of the system indenter + sample, which is postulated to be definedDoerner and Nix (1986); Oliver and Pharr (1992) as:

$$\frac{1}{E_r} = \frac{\left(1-\nu^2\right)}{E} + \frac{\left(1-\nu_i^2\right)}{E_i} \tag{5}$$

with $E_i = 1029$ MPa and $\nu_i = 0.07$ being respectively the Young modulus and Poisson coefficient of the indenter material (diamond)Pulecio (2010) and $\nu = 0.38$ being the Poisson coefficient of the resin (estimated).

2.5. Structure characterization

2.5.1. Chain structure

The changes in the chain structure, caused by irradiation, were characterized by ultraviolet-visible spectroscopy (UV-VIS) and by Fourier Transform Infrared spectroscopy (FTIR) and by chemical methods.

The UV-VIS spectra were acquired in absorption mode using a Cary 50 Conc UV-Visible spectrophotometer. The samples were analyzed through the original thickness (3 mm), so that no special preparation was needed.

The FTIR spectra were acquired in a Thermo Scientific Nicolet 6700 FTIR spectrometer. The spectra were measured in transmission mode and corresponds to 128 scans at a resolution of 4 cm^{-1}. Due to limitations of the equipment the samples needed to be thinned by hot pressing. The final thicknesses of the measured films is given in table 2.

Table 2. Thicknesses of the films used for the FTIR experiments, as obtained after hot pressing

Dose (kGy)	thickness (mm)	std. dev. (mm)
Pristine (0)	0.09	0.004
20	0.09	0.010
40	0.07	0.005
60	0.06	0.001
100	0.10	0.001
200	0.12	0.006
300	0.20	0.006

Additionally, the samples were dissolved in boiling xylene to investigate the possibility of irradiation induced reticulation.

2.5.2. X-ray diffraction

X-ray diffraction experiments were made in 25 × 25 mm samples cut out of the heads of the tensile specimens, using a Rigaku Multiflex diffractometer, operating with a copper tube (CuKα radiation, $\lambda = 0.154184$, opperating at 40 kV and 20 mA). Patterns were acquired in the $\theta - 2\theta$ geometry, with parallel beams in the $3° \leq 2\theta \leq 90°$rante, with 0.2°step.

3. Results and Discussion

3.1. Mechanical behavior

Figure 1 summarizes the results of the tensile tests in the pristine and irradiated samples. The values for the 300 kGy irradiated sample are not included, because this material, consistently , fractured in a brittle mode.

The results shows a picture consistent with a continuous irradiation-induced degradation, which is more evident in the elongation results, but is also observed in the yield strength data for samples irradiated beyond 60 kGy. The brittle behavior of the 300kGy samples can be justified by the results of the boiling xylene dissolution, since this is the only case in which an appreciable degree of reticulation (4.32%) is observed.

Figures 2 presents the results derived from the indentation tests. The values for the Young modulus (Fig. 2(a)) shows a drastic difference of behavior for the resin when irradiated under and above 100 kGy. At lower doses, the modulus slightly increases with dose, but a sharp transition is observed at 100 kGy, and the modulus decreases to values about half the ones observed for the pristine resin. Values of universal hardness (HU, Fig. 2(b)), on the other hand, show almost no variation with irradiation dose. In both cases, the results obtained in the indentation tests and in the macroscopic tensile tests cannot be reconciled.

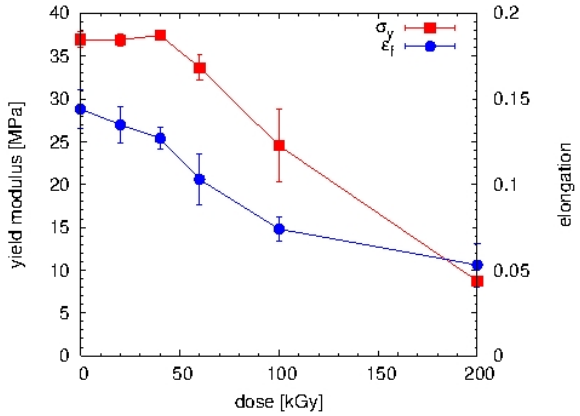

Fig. 1. Results of the tensile tests (reported values are averages of 10 specimens and bar height corresponds to the standard deviation). The point corresponding to null dose is the value for the pristine resin.

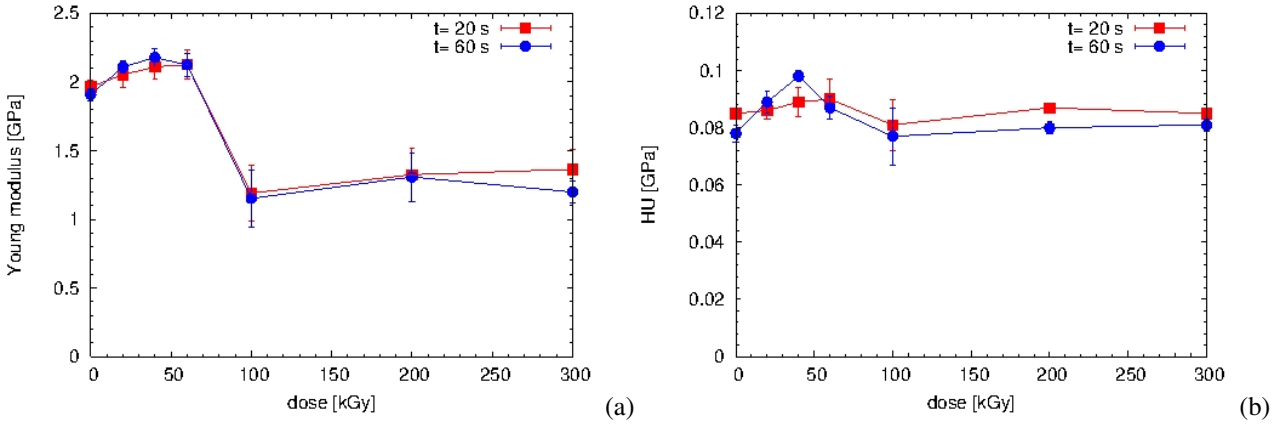

Fig. 2. Results of the indentation tests (reported values are averages of 10 specimens and bar height corresponds to the standard deviation). Young modulus (a) and Universal hardness as function of irradiation dose. The point corresponding to null dose is the value for the pristine resin.

3.2. Scructural changes

Figure [3(a) presents the UV-VIS spectra of the pristine and irradiated specimens. The pristine polymer presents a natural absorption peak around λ = 195 nm. With irradiation (up to 60 kGy) the continuous development of a band around 190 to 222 nm is observed. The formation of this band and its broadening with irradiation is usually attributed to de development of chromophore groups (dienes) in the chain. At higher doses (above 100 kGy) an additional contribution around 222 and 270 nm is observed, which is usually attributed to the formation of triene. The picture of irradiation damage is completed by the development of a sharp peak around 195 nm (superposed to the previously described diene contribution), which is attributed to the formation of carbonyl groups in the chainWorkman (2001). The development of these contributions in the UV-VIS spectra correlates with a visual alteration of color in the specimens (yellowing).Santos (2011)

These results are corroborated and complemented by the analysis of the FTIR spectra. The irradiated samples show the progressive increase of a band with wavenumber 1727 cm^{-1} which is attributed to the formation of carbonyl groups, up to 60 kGy dose. For larger doses, the carbonyl peak decreases in intensity and twp new peaks at wavenumbers 2150 and 1544 cm^{-1} develop. These are attributed, respectively to the diene and triene groups, detected in the UV-VIS spectra.Workman (2001)

Figure 3(b) shows the results of the X-ray diffraction in the pristine and irradiated samples. Table 3 presents the corresponding calculated crystallinities.As observed, the behavior is distinct below and above 100 kGy. At first,

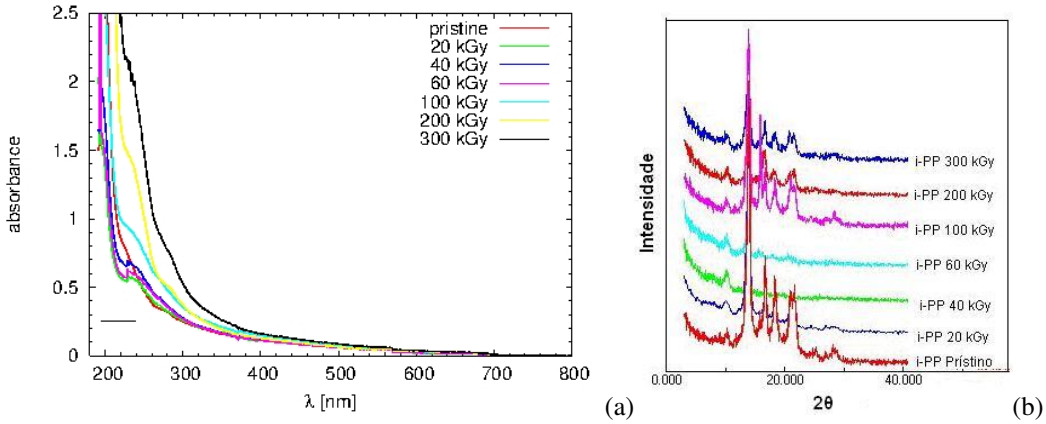

Fig. 3. UV-VIS spectra (a) and X-ray diffractograms (b) of the pristine and irradiated specimens

electron beam irradiation continously reduces crystallinity, characterizing radiation-induced amorphization. In the case of the 100 kGy sample, however, crystallinity reverts to values close to the ones observed in the pristine sample. Polyproplene is characterized by three polymorphs, one of which is known to be metastable. The possibility of radiation-induced phase transformation was investigated, but the reformed structure corresponds to the same existing in the pristine sample (the monoclinic α phase)Santos (2011). Above 100 kGy, the crystallinity decreases again, but the material seems to stabilize at a cruystallinity level slightly above 10%. This strange behavior is subject of an ongoing investigation, but it clearly correlates with the large drop in Young modulus (Fig. 2(a)).

Table 3. Calculated crystallinities of the pristine and irradiated samples.

Dose (kGy)	Crystallinity [%]
Pristine (0)	21
20	19
40	11
60	12
100	21
200	15
300	17

4. Conclusions

In the present work, samples of an isotactic Polypropylene resin were subject to electron beam irradiation, in order to obtain large variations in mechanical properties in chemically similar polymers. The obtained results showed that electron beam irradiation leads to degradation as evidenced by the tensile results: both strength and ductility decrease with increasing dose.

The materials were, then, investigated by instrumented indentation. It is unlikely that the results of Young modulus and Hardnerss could correlate with the macroscopic property changes. The technique is, however, sensitive enough to detect a large change in propeorties for the samples which were irradiated with doses above 100 kGy (in the Young modulus data).

Irradiation induces chages in the chemical structure of the polymer, producing chromophores (dienes, trienes and carbonyl groups). These changes are cummulative. These changes, however, are continuous and cannot justify the large change in Young modulus for samples irradiated with doses above 100 kGy.

The X-ray diffraction data show that, initially, irradiation induces amorphization, but this amorphization is reverted for the 100 kGy dose, which correlates with the large reduction in the Young modulus data.

Acknowledgements

This work has been finantially supported by the Brazilian National Research, Development and Innovation council (CNPq, Brasília, Brazil).

References

ASTM Standard D4703, 2010. Standard practice for compression molding thermoplastic materials into test specimens, plaques or sheets, ASTM International, West Cornshohocken, PA. URL: http://www.astm.org, doi:10.1520/D4703-10A.

ASTM standard D638, 2010. Standard test method for tensile properties of plastics, ASTM International. URL: http://www.astm.org, doi:10.1520/D638-10.

Cross, G.L.W., O'Connel, B.S., Pethica, J.B., Schulz, H., Scheer, H.C., 2005. Instrumented indentation testing for local characterization of polymer properties after nanoprint. Microelectronic Engineering 78 – 79, 618 – 624.

Doerner, M.F., Nix, W.D., 1986. A method for interpreting depth-sensing indentation instrument. J. Mater. Res. 1, 601 – 609.

Giannakopoulos, A.E., Suresh, S., 1999. Determination of elastoplastic properties by instrumented sharp indentation. Scripta Mater. 40, 1191 – 1198.

Menčik, J., He, L.H., Němeček, J., 2011. Characterization of viscoelastic – plastic properties of solid polymers by instrumented indentation. Polymer Testing 30, 101 – 109.

Oliveira, G.L., Costa, C.A., Teixeira, S.C.S., Costa, M.F., 2014. The use of nano- and micro-instrumented indentation tests to evaluate viscoelastic behavior of poly(vinidilene fluoride) (PVDF). Polymer Testing 34, 10 – 16.

Oliver, W.C., Pharr, G.M., 1992. An improved technique for the determination of hardness and elastic modulus using load and displacement sensing indentation experiments. J. Mater. Res. 7, 1564 – 1583.

Peng, G., Feng, Y., Huan, Y., Zhang, T., 2013. Characterization of the viscoelastic – plastic properties of UPVC by instrumental sharp indentation. Polymer Testing 32, 1358 – 1367.

Peng, G., Zhang, T., Feng, Y., Huan, Y., 2012. Determination of shear creep compliance of linear viscoelastic – plastic solids by instrumented indentation. Polymer Testing 31, 1038 – 1044.

Pintaúde, G., Cuppari, M.G.V., Schön, C.G., Sinatora, A., Souza, R.M., 2005. A review on the reverse analysis for the extraction of mechanical properties using instrumented Vickers indentation. Z. Metallk. 96, 1252 – 1255.

Pulecio, S.A.R., 2010. Modelamento do ensaio de indentação instrumentada usando elementos finitos e análise dimensional – análise de unicidade, variações experimentais, atrito e geometria do indentador. Ph.D. thesis. Escola Politécnica da Universidade de São Paulo. São Paulo, Brazil. URL: http://www.teses.usp.br/teses/disponiveis/3/3151/tde-16082010-135510/en.php. (in Portuguese).

Santos, A.F., 2011. Efeito da irradiação por feixe de elétrons sobre as propriedades físicas e químicas de uma resina de polipropileno. Ph.D. thesis. Escola Politécnica da Universidade de São Paulo. São Paulo, Brazil. URL: http://www.teses.usp.br/teses/disponiveis/3/3133/tde-05082011-141252/en.php. (in Portuguese).

Santos, A.F., Wiebeck, H., Souza, R.M., Schön, C.G., 2008. Instrumented indentation testing of an epoxy adhesive used in automobile body assembly. Polymer Testing 27, 632 – 637.

VanLandingham, M.R., 2003. Review of instrumented indentation. J. Res. NIST 108, 249 –265.

VanLandingham, M.R., Villarubia, J.S., Guthrie, W.F., Meyers, G.F., 2001. Nanoindentation of polymers: an overview. Macromol. Symp. 167, 15 – 43.

Workman, J., 2001. Handbook of organic compounds: NIR, IR, Raman, and UV-VIS spectra featuring polymers and surfactants. Academic Press, San Diego.