



ELSEVIER

Contents lists available at ScienceDirect

## Radiation Physics and Chemistry

journal homepage: [www.elsevier.com/locate/radphyschem](http://www.elsevier.com/locate/radphyschem)

# Polyamide-6: The effects on mechanical and physicochemical properties by electron beam irradiation at different temperatures

E. Adem<sup>a,\*</sup>, G. Burillo<sup>b</sup>, L.F. del Castillo<sup>c</sup>, M. Vásquez<sup>a</sup>, M. Avalos-Borja<sup>d</sup>,  
A. Marcos-Fernández<sup>e</sup>

<sup>a</sup> Instituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico

<sup>b</sup> Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico

<sup>c</sup> Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico

<sup>d</sup> Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, A. Postal 2681, Ensenada, B.C., Mexico. On leave at IPICYT,

División de Materiales Avanzados, San Luis Potosí, S.L.P., Mexico

<sup>e</sup> Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain

## HIGHLIGHTS

- Electron beam irradiation in polyamide-6 produced higher crosslinking than in polyamide-6,6.
- Crosslinking took place mainly in the amorphous phase of the polymer.
- Polyamide-6 melting point slightly decreased with the increase in irradiation dose and crystallinity remained practically unchanged.
- Mechanical properties were strongly affected by irradiation dose.
- Irradiation above  $T_g$  significantly increased the changes in thermal and mechanical properties respect to irradiation at ambient temperature.

## ARTICLE INFO

### Article history:

Received 15 October 2012

Accepted 6 November 2013

Available online 22 November 2013

### Keywords:

Polyamide-6

Electron beam irradiation

Thermal properties

Tensile properties

## ABSTRACT

The electron beam irradiation of polyamide-6 (PA-6) films was carried out in air over a range of 50–1000 kGy at varying temperatures and a dose rate of  $5.1 \text{ kGy min}^{-1}$ . The effects of the irradiation at temperatures above and below the glass transition temperature ( $T_g$ ) on the thermal and mechanical properties were studied. Melting and crystallization temperatures decreased significantly with the increase in irradiation dose, whereas percent of crystallinity varied only slightly and  $T_g$  slightly increased for irradiated samples respect to non irradiated one with no significant effect of the dose. Mechanical properties were affected by irradiation. The material became more rigid with a direct relationship between the mechanical properties and the irradiation dose. The irradiation above  $T_g$  led to a larger variation in the thermal and mechanical properties respect to the irradiation below  $T_g$ . The changes in properties were related to the crosslinking produced in the amorphous part of the polymer by the electron beam irradiation.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Radiation modifications of polymers have been widely studied and used to produce heat-resistant wire cable, polyethylene foam, shrinkable tubes, gaskets, etc. Normally, polymeric materials are exposed to radiation in an air atmosphere at ambient temperatures. The chemical reactions are known to depend on the irradiation temperature. Polytetrafluoroethylene (PTFE), which degrades via chain scission by ionizing radiation, crosslinks at temperatures above its melting temperature (Oshima et al., 1995);

polystyrene (PS) crosslinks at ambient temperature, but above its glass transition temperature ( $T_g$ ), it largely undergoes chain scission (Takashika et al., 1999); the Rockwell hardness and resistance to wear of polycarbonate and polysulfone can be improved through irradiation at their glass transition temperature (Seguchi et al., 2002). The radiation crosslinking of polyamide-6,6 (PA-6,6) has been reported by several researchers (Ueno, 1990; Lyons and Glover, 1990; Sengupta et al., 2003, 2005), but only one published work has dealt with the irradiation of PA-6,6 at high temperature (Sengupta et al., 2006). Moreover, although polyamides have high heat stability, the absorption of thermal, light or mechanical energy by the polymer, can lead to deterioration of its physical and mechanical properties (Gonçalves et al., 2007). The thermal oxidation of polyamides occurs predominately through the

\* Corresponding author. Tel.: +52 55 56 22 50 49.

E-mail address: [esbaide@fisica.unam.mx](mailto:esbaide@fisica.unam.mx) (E. Adem).

abstraction of a hydrogen atom from the methylene group close to the amide group  $-\text{CONH}-\text{CH}_2-$ . The resulting radical can produce crosslinks or chain scission, with the final properties depending on the preferential route.

For polyamide-6 (PA-6), the published reports on the effect of electron beam irradiation (Zohdy et al., 2004; Pramanik et al., 2009; Aytac et al., 2010), is even more scarce than for PA-6,6. In two of these works, the effect on mechanical properties was studied, but at low irradiation doses, lower than 75 kGy, that is the range required for the surface treatment of textiles (Zohdy et al., 2004) and for the prevulcanization of tyres (Pramanik et al., 2009). Only in one work the range for the irradiation dose is wide, from 100 to 600 kGy (Aytac et al., 2010), and none of these works studied the effect of the irradiation temperature and all irradiations were carried out at ambient temperature. The effect of irradiation on the mechanical properties in these works gave contradictory results, with an increase in the tensile strength with the dose in the work performed in a wide range of irradiation dose (Pramanik et al., 2009) and a decrease (Aytac et al., 2010) or a constant value (Zohdy et al., 2004) in the works performed in a narrower range of irradiation dose. In addition, the effect of irradiation on thermal properties was not followed in these works.

In a previous work, we studied the influence of the irradiation of PA-6 at different temperatures on the radiation chemical yield of scission and crosslinking (Burillo et al., 2013). Now, we present a detailed effect of the irradiation on the thermal and mechanical properties of PA-6 at different temperatures within a wide range of irradiated doses, up to 1000 kGy, in order to establish clear relationships and clarify the contradictory results found for the mechanical properties in the literature.

## 2. Materials and methods

### 2.1. Irradiation of the films

PA-6 of molecular weight ( $M_n$ ) 35,600  $\text{g mol}^{-1}$  was received from Goodfellow (Coraopolis, PA, USA) as a 0.6-mm-thick film. Type 3 dumbbell test pieces (according to ISO 37) and squares of 1 cm  $\times$  4 cm were cut from the films for mechanical testing and for the rest of the tests, respectively. The samples were introduced into 9 cm  $\times$  6 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  $\mu\text{A}$  at a dose rate of 5.1 kGy  $\text{min}^{-1}$  and doses from 50 to 1000 kGy in air at temperatures ranging from room temperature to 70  $^\circ\text{C}$ .

### 2.2. Crosslinking and viscosity measurements

The crosslinking was determined following the method described by Burillo et al. (2013). To evaluate the gel content, the 1 cm  $\times$  4 cm irradiated samples were weighed, immersed in 15 mL formic acid for 72 h at room temperature, filtered through a fritted glass crucible, and the remaining solid weighed. The crosslinked PA-6 (gel%) was calculated from the weight ratio of the insoluble fraction after irradiation ( $W_f$ ) and prior to irradiation ( $W_i$ ). The viscosity of the PA-6 solutions (1%) diluted with formic acid was measured using an Ubbelohde viscometer.

### 2.3. Thermal Properties

Thermogravimetric analysis (TGA) was used to measure the thermal stability and the water content of the samples. Experiments

were carried out by triplicate in a Thermal Analysis Q500 instrument. Disc samples cut from films with weights between 27 and 33 mg were tested. Water content was determined as the weight loss in an isothermal experiment under nitrogen at 190  $^\circ\text{C}$  for 1 h. In this experiment, sample weight reached a plateau. Immediately after, thermal stability was determined in a dynamic scan in Hi-Resolution mode from 190 to 800  $^\circ\text{C}$ . In this mode, 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  $^\circ\text{C min}^{-1}$  under a flux of nitrogen.

Thermal properties were measured in a Mettler Toledo DSC822e instrument. Discs weighting 18–20 mg were sealed in aluminium pans with perforated cover. Samples were heated at 10  $^\circ\text{C min}^{-1}$  from 25 to 250  $^\circ\text{C}$  followed by cooling at a rate of  $-10$   $^\circ\text{C min}^{-1}$  from 250 to 25  $^\circ\text{C}$ . After 5 min at 25  $^\circ\text{C}$ , samples were reheated from 25 to 250  $^\circ\text{C}$  at 10  $^\circ\text{C min}^{-1}$ . All scan were carried out under a constant nitrogen purge. The melting point ( $T_m$ ) and crystallization temperatures ( $T_c$ ) are given as the maximum of the endothermic transition and the minimum of the exothermic transition, respectively. Glass transition temperature ( $T_g$ ) is given as the midpoint of the change in heat capacity. The percent of crystallinity ( $X_c$ ) was calculated from the endothermic peak area  $\Delta H_c$  by  $X_c = (\Delta H_c / \Delta H_0) 100$ , where  $\Delta H_0$  is the heat of fusion for perfect PA-6 crystals (188  $\text{J g}^{-1}$ ) (Dadbin et al., 2005).

### 2.4. Mechanical properties

Tensile properties were measured in a MTS Synergie 200 testing machine equipped with a 1000 N load cell. Type 3 dumbbell test pieces were tested. A crosshead speed of 5  $\text{mm min}^{-1}$  was used with an initial gauge length of 20 mm. Strain was measured from crosshead separation and referred to 10 mm initial length. The reported values are the average of at least 6 specimens.

## 3. Results and discussion

### 3.1. Gel content

Burillo et al. (2013) demonstrated the acceleration in both the crosslinking and chain-scission reactions for irradiated PA-6 when the temperature was increased from room temperature to above glass transition temperature ( $T_g$ ). A value of 1.3 for the ratio of the radiation chemical yield of scission ( $G_s$ ) to the radiation chemical yield of crosslinking ( $G_c$ ) ( $G_s/G_c$  in which the radiation chemical yield indicates the number of scission or crosslinked chains produced by 100 eV of received energy) was calculated for irradiation at room temperature, similar to the value of 1.5 found in literature (Pramanik et al., 2009), proving that scission was predominant at room temperature, below  $T_g$ . However, the ratio decreased when temperature was raised above  $T_g$  reaching a value of 0.91 at 70  $^\circ\text{C}$ , thus, at this temperature, crosslinking was the predominant effect. The increased tendency toward crosslinking with temperatures of irradiation above the  $T_g$  of the polymer may derive from the improved mobility of the PA-6 molecules. Compared with the  $G_s/G_c$  values reported for PA-6,6 (Sengupta et al., 2005, 2006), scission dominates in PA-6,6, whereas crosslinking dominates in PA-6.

The radiation dose for incipient gel formation at different temperatures was approximately 200 kGy, in agreement with the value found by other authors for PA-6 irradiated at room temperature (Pramanik et al., 2009). The same dose was required for gel formation in PA-6,6 irradiated at ambient temperature (Sengupta et al., 2005), although the gel content value was much lower (3.5% weight) respect to PA-6, in agreement with the results for the ratio  $G_s/G_c$ . The dose needed to crosslink PA-6 by electron

beam irradiation is lower than the dose needed when irradiated by gamma radiation (350 kGy) (Dadbin et al., 2005), showing that electron beam irradiation is more efficient in crosslinking.

Before gel is formed at 200 kGy, inherent viscosity increased as a consequence of chain branching. This result is in agreement with the results found by Dadbin et al. (2005) for PA-6 and contrary to the decrease in viscosity reported for irradiated PA-6 from a tyre cord (Aytaç et al., 2010). The increase in the inherent viscosity prior to gel formation for those samples irradiated at room temperature (below the  $T_g$ ) was lower than that for samples irradiated above the  $T_g$ , because the mobility of the amorphous polymeric chains increased above the  $T_g$ , and therefore the probability of radical recombination increased at higher temperature.

### 3.2. Thermal properties

It is known that PA-6 and PA-6,6 absorb water, and this absorbed water, mostly diffused in the amorphous regions, can produce a plasticizing effect that can affect the thermal and the mechanical properties of the material (Pai et al., 1989). It is therefore very important to determine the amount of water absorbed in PA samples. TGA analysis showed that the amount of absorbed water, 2.2 to 2.4% weight, was practically the same for all the samples, irrespective of the irradiation dose and of the irradiation temperature. Thus, the effect of absorbed water will be the same for all the samples. Temperature of maximum rate of weight loss was in between 422 and 426 °C for all the samples, with no trend with the irradiation dose and of the irradiation temperature. Residual carbon at 800 °C was very small, as expected, from 0.7 to 1% weight. In this case, residual carbon increased linearly with the increase in the irradiation dose, although this change is small.

Changes in thermal properties with irradiation dose were measured by DSC. Samples were measured by triplicate to estimate the dispersion of the results. The general shape of the DSC trace was the same for all the samples. In the first heating, a broad endotherm span from ambient temperature to approximately 170 °C, attributed to the release of the water in the material, followed by a sharper endotherm due to the melting of the PA-6 crystals. The shape of the curve is similar to the heating curves presented in Fig. 3 of Sengupta et al. (2006). Because of the merging of both endotherms, the percentage of PA-6 crystallinity could not be calculated. In the cooling step, a single crystallization exotherm appeared. In the second heating, a  $T_g$  was observed at low temperatures due to the amorphous regions of PA-6, and an endotherm at high temperature due to the melting of the PA-6 crystals. The melting endotherm of the second heating presented a bimodal distribution with two maxima for the non irradiated sample, that has been related to the presence of two crystal forms,  $\alpha$  and  $\gamma$ , for the maxima at higher (main peak from which  $T_m$  was measured) and lower temperature, respectively (Friedrich et al., 2007; Yu et al., 2010). The maximum for the less stable form diminished with the increase in dose becoming a shoulder.

In Figs. 1–3 the changes in melting point and crystallization temperature can be seen. For the melting point, in the first run (Fig. 1), the initial melting temperature at approximately 220 °C decreased to approximately 212 °C after 1000 kGy irradiation dose at room temperature. The decrease was larger when irradiated at 70 °C, above  $T_g$ , with a final value of approximately 208 °C. The data fitted a quadratic curve when irradiated at room temperature and a line when irradiated at 70 °C. In general, the dispersion of the data increased with the increase in dose. The same trend was found for the three set of data, with a decrease with the increase in the dose, larger at higher irradiation dose. The decrease in  $T_m$  with the increase in irradiation dose has also been found for PA-6,6 (Sengupta et al., 2006) and other semicrystalline polymers such as

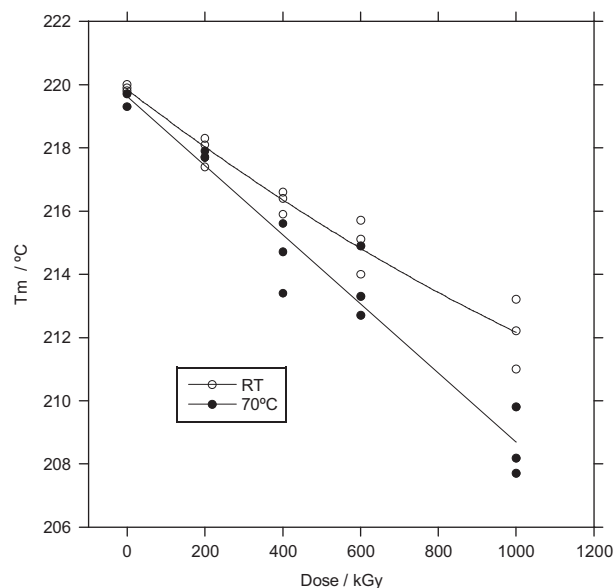


Fig. 1. Melting point of PA-6 in the first DSC scan irradiated at different doses at room temperature (empty symbols) and at 70 °C (filled symbols).

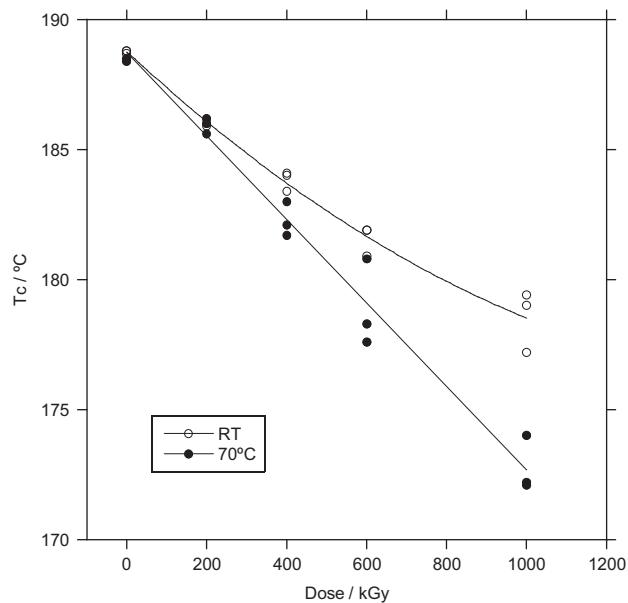


Fig. 2. Crystallization temperature of PA-6 irradiated at different doses at room temperature (empty symbols) and at 70 °C (filled symbols).

polyethylene (PE) (Cerrada et al., 2009). In both cases, the change in  $T_m$  was stated to be consistent with crosslinking and branching taking place mainly on the amorphous regions and on the boundaries of crystallites. For PA-6 irradiated up to 150 kGy, below the critical dose for gel formation, no significant changes were found for  $T_m$ , but when a crosslinker was added to PA-6, a decrease was found, again related to branching and crosslinking in the amorphous polymer and at the crystallites interface (Dadbin et al., 2005). The same argument is valid to our results on PA-6 irradiated at higher dose, and the effect of temperature, leading to a larger decrease in  $T_m$ , also found for PA-6,6 (Sengupta et al., 2006), is consistent with the increase in crosslinking found by gel content measurements. This crosslinking also disturbs the formation of crystals on cooling, producing a delay on the crystallization, as already found for PE (Cerrada et al., 2011).

The changes in the  $T_g$  measured in the second heating run were rather small. From the initial value of 54.5 to 55 °C,  $T_g$  increased

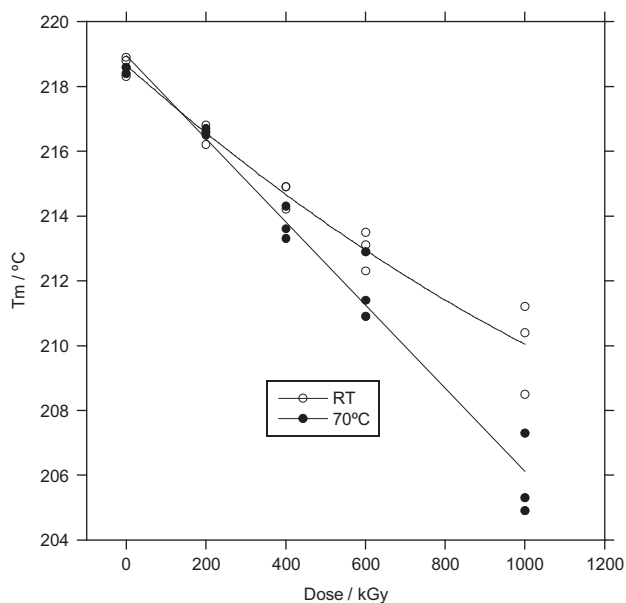


Fig. 3. Melting point of PA-6 in the second DSC scan irradiated at different doses at room temperature (empty symbols) and at 70 °C (filled symbols).

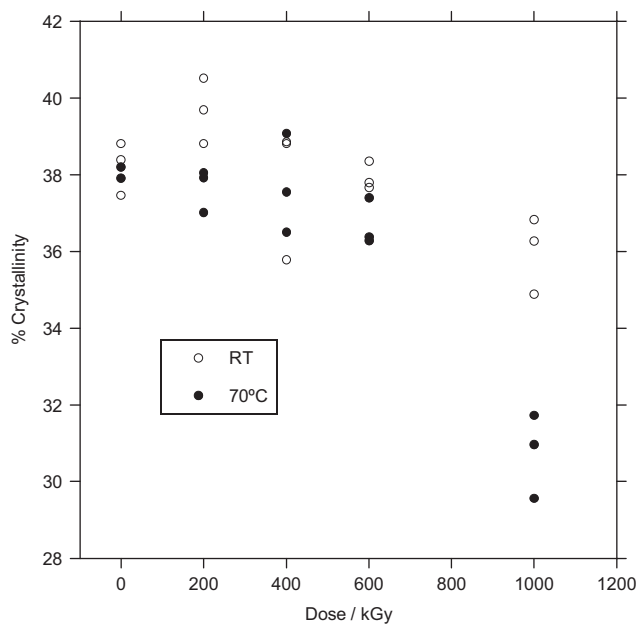


Fig. 4. % Crystallinity of PA-6 in the second DSC scan irradiated at different doses at room temperature (empty symbols) and at 70 °C (filled symbols).

when irradiated, reaching a value of 56 to 57 °C. At different irradiation doses, the values were scattered around 56–57 °C irrespective of the dose and irradiation temperature. The initial increase in  $T_g$  value from non-irradiated samples to irradiated samples is consistent with the crosslinking in the amorphous regions of the polymer, although a certain increase with the increase in dose was expected. Chain scission, that produces shorter chains and decreases  $T_g$ , takes place simultaneously to crosslinking and could account for the relatively invariance of  $T_g$  with dose.

From the second scan, the percentage of crystallinity was calculated and it is represented in Fig. 4. Similar results are found for the exotherm value during crystallization (not shown). From the initial crystallinity of around 38%, the value seems to slightly decrease without any noticeable effect of the irradiation temperature up to

600 kGy irradiation dose (less than 3% decrease in crystallinity respect to the non irradiated sample). A decrease in crystallinity with the increase in dose has been described for PA-6,6 (Sengupta et al., 2006), noticeably larger (13% decrease in crystallinity for the sample irradiated for 500 kGy at room temperature respect to the non irradiated sample) than for our PA-6 samples, that was only slightly affected by the irradiation temperature (lower crystallinity at higher temperature). Taking into account that chain scission is more predominant in PA-6,6 than in PA-6 and crosslinking is lower, it is deduced that chain scission leads to a higher loss in crystallinity than crosslinking.

At 1000 kGy irradiation dose, the decrease is again very small when irradiation is carried out at room temperature, but is very significant when irradiation is carried out at 70 °C, with a drop of 18% respect to the initial value. This result cannot be easily explained because gel contents (Burillo et al., 2013) and  $T_g$  values were similar at both temperatures.

From the shape of the endotherms, initially with two maxima, it seems that chain scission and crosslinking affected more to the less stable  $\gamma$  crystalline form, leading to the almost complete disappearance of the maxima at lower temperature related to it.

### 3.3. Mechanical properties

Fig. 5 shows the stress–strain curves for several irradiation doses, and Figs. 6–9 the values for the mechanical properties.

PA-6 behaved as a tough plastic. After a very stepped stress growth at low strain, it went through a yielding point. At this point, it could visually be observed the formation of a neck on the narrow part of the test specimen. Once yielding was passed, stress dropped to a lower value and remained almost unchanged until a certain strain was reached. At this point (approximately at 200% strain), necking had advanced through all the narrow part of the test specimen and reached the part of the specimen where it widens. As a consequence, the curve changed the slope and the stress increased almost linearly with the strain.

From Fig. 5 it is evident that the shape of the curve remained the same irrespective of the irradiation dose. The effect of increasing the dose was the decrease of the strain that led to a decrease in the tensile strength, and the increase in the value of the stress at yield. The plot of the properties confirmed the trends.

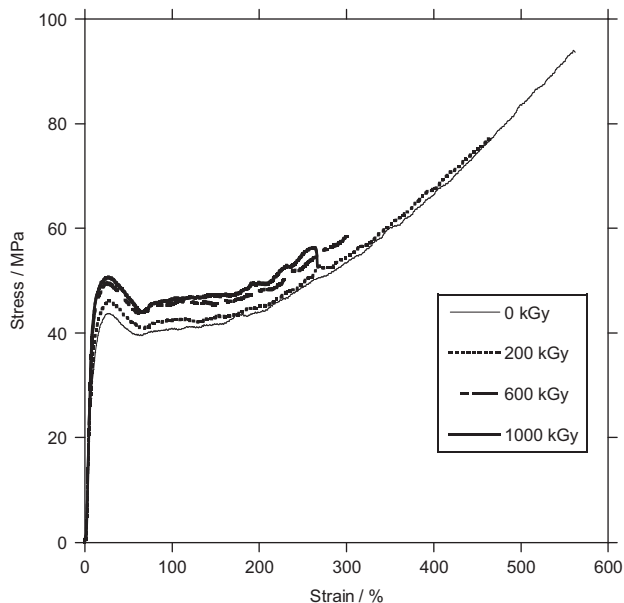


Fig. 5. Representative stress–strain curves for PA-6 irradiated at different doses.

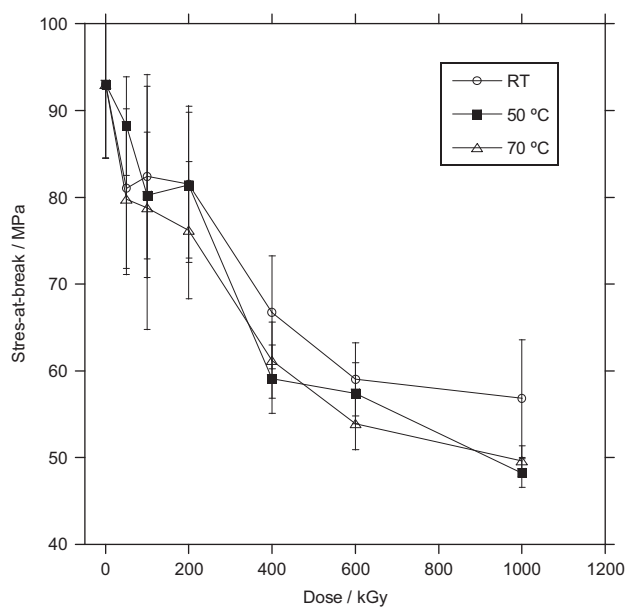


Fig. 6. Stress-at-break values for PA-6 irradiated at different doses.

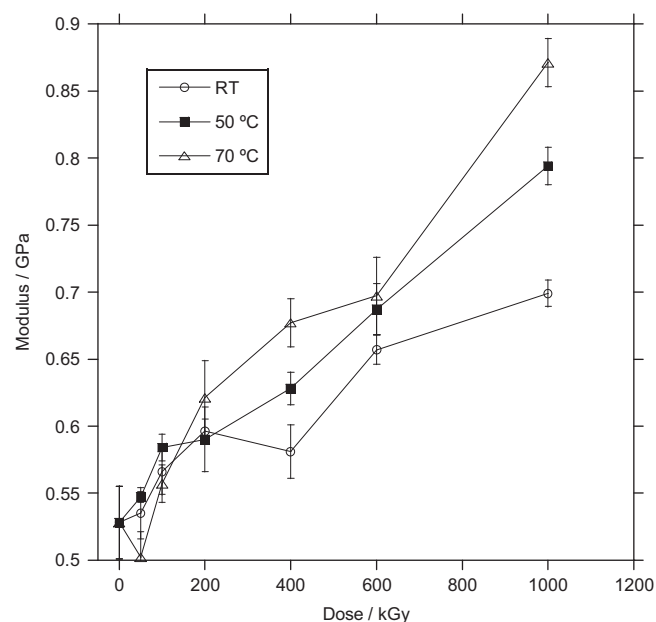


Fig. 8. Modulus values for PA-6 irradiated at different doses.

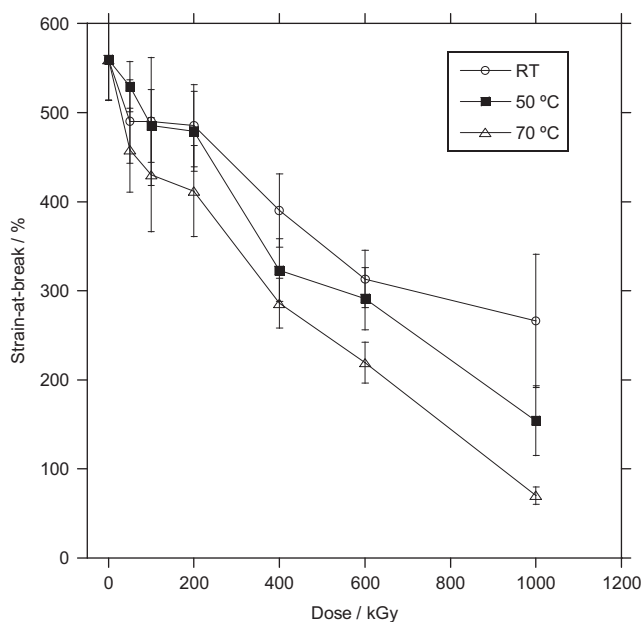


Fig. 7. Strain-at-break values for PA-6 irradiated at different doses.

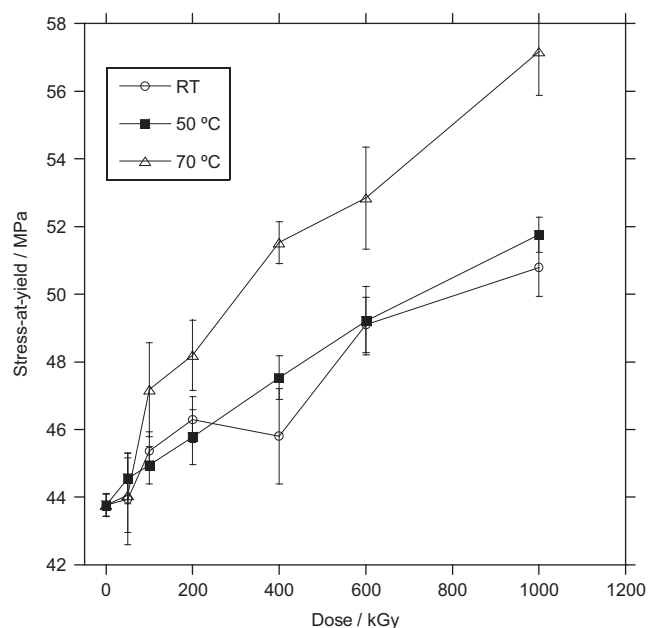


Fig. 9. Stress-at-yield values for PA-6 irradiated at different doses.

A continuous decrease in the stress-at-break (Fig. 6) and in the strain-at-break (Fig. 7) was observed with the increase in dose, whereas Young's Modulus (Fig. 8) and stress-at-yield (Fig. 9) increased with the increase in dose. The value of strain-at-yield varied in between 26 and 31% and tended to slightly decrease with the increase in dose. Irradiation temperature did not have a significant effect on stress-at-break and strain-at-yield, but strain-at-break decreased and Modulus and stress-at-yield increased with the increase in temperature. Crystallinity is one of the primary factors that influence the mechanical properties of polymers (Nielsen, 1974), but for these samples, crystallinity (see Fig. 4) slightly decreased with the increase in irradiation dose, and therefore, a decrease in Modulus and in stress-at-yield and an increase in strain-at-break should be expected. The crosslinking of the material in the amorphous phase accounts for the results. When irradiation dose increased, crosslinking

increased, and the ability of the chains in the amorphous state to slip was increasingly restricted, decreasing the strain-at-break of the material. At the same time, the amorphous material became more rigid and Modulus and stress-at-yield increased. This increase in rigidity produced by the crosslinking of the amorphous phase has also been described by electron beam irradiated PE (Cerrada et al., 2009). The increase in temperature increased the predominance of crosslinking over scission, bringing about an increase in Modulus and in stress-at-yield and a decrease in strain-at-break respect to the values for samples irradiated at lower temperatures.

The comparison with the data reported in literature for PA-6 is difficult due to the differences in the experimental test conditions. For PA-6 tyre cord irradiated up to 75 kGy, a slight decrease in

stress-at-break and strain-at-break was reported (Aytaç et al., 2010), in agreement with our results, but for PA-6 of non specified thickness irradiated up to 150 kGy and tested at 50 mm min<sup>-1</sup> of crosshead speed, mechanical properties remained constant at a value of approximately 44 MPa for stress-at-break and 260% for strain-at-break (Dadbin et al., 2005), well below the value obtained for our non irradiated sample. And for very thick PA-6 (3 mm) irradiated up to 600 kGy (Pramanik et al., 2009), strain-at-break strongly decreased from a very low initial value of approximately 38%, Modulus increased moderately and stress-at-break slightly increased with the increase in irradiation dose. The last result is in complete disagreement with our results and can be explained by the low strain-at-break of these samples, that hardly reached the yield point according to the results for our PA-6, and therefore the stress-at-break data given by Pramanik et al. (2009) must be more properly compared with our stress-at-yield data, that do slightly increase in samples irradiated at room temperature.

The slow crosshead speed used for our samples gives the material more time for rearrangement during stretching and as a consequence the values reached for the mechanical properties are higher, which allows in our case for a better appreciation of the variations in properties due to irradiation. The measured errors were fairly good, less than ±12% for stress-at-break (except one sample), less than ±15% for strain-at-break (except two samples), less than ±5% for Modulus, less than ±3% for stress-at-yield and less than ±8% for strain-at-yield.

It was also difficult to compare the data in this study with the data reported for PA-6,6 (Sengupta et al., 2006). The PA-6,6 used was tested at 50 mm min<sup>-1</sup> and the values for the non irradiated samples showed that the material just reached an extension above the yield point with 63% strain-at-break and the value for the Modulus (2.45 GPA) demonstrated that this material was more rigid than the PA-6 used in the present study (crystallinity was also higher for non irradiated PA6,6, 44%). An optimum irradiation dose of 200 kGy was found for the mechanical properties, coincident with the critical dose for gel formation, the same critical dose for gel found for the PA-6 in this work, although no optimum dose for mechanical properties was observed for our PA-6. The properties for PA-6,6 were explained by the relative weight of four factors with respect to the absorbed dose and temperature: the crystallinity (that decreased continuously with dose), crosslinking, chain scission and the loss of molecular hydrogen. By contrast, crosslinking of the material in the amorphous phase can explain the changes in mechanical properties for the PA-6 in this study, that is higher than in the case of PA-6,6 (> 40% for PA-6 vs. < 25% for PA-6,6 at a dose of up to 500 kGy). The effect of increasing temperature in PA-6,6 showed the same trend than the results presented here for stress-at-break, that very slightly decreased, and for strain-at-break, that strongly decreased, but not for the Modulus, that very slightly decreased whereas for PA-6 in this study Modulus increased significantly.

#### 4. Conclusions

The effects of electron beam irradiation at temperatures above and below the glass transition temperature on the thermal and mechanical properties were studied for polyamide-6 (PA-6).

Chain scission and crosslinking took place simultaneously during irradiation, with chain scission being predominant below  $T_g$  and chain crosslinking above  $T_g$ . The radiation dose for incipient gel formation at different temperatures was approximately 200 kGy, as for PA-6,6. Gel content demonstrated that crosslinking was much higher for PA-6 than for PA-6,6.

Melting and crystallization temperatures decreased with the increase in irradiation dose due to branching and crosslinking in

the amorphous part of polymer and at the crystallites interface. Percent of crystallinity did not vary significantly except for the sample irradiated for 1000 kGy above  $T_g$ , that showed a small decrease, in contrast to the behavior reported for PA-6,6 that reduced its crystallinity significantly.  $T_g$  value increased slightly for the irradiated samples respect to the non irradiated sample due to the crosslinking of the amorphous phase, without any significant effect of dose or irradiation temperature. Irradiation above  $T_g$  significantly decreased the melting point respect to irradiation at ambient temperature.

Mechanical properties were strongly affected by irradiation. Stress-at-break and strain-at-break were strongly reduced and Young's Modulus and stress-at-yield were significantly increased by the increase in dose. These changes were consistent with an increase in the crosslinking within the amorphous phase. These trends were in agreement with the results reported in literature for PA-6. Irradiation at higher temperature significantly increased the changes in mechanical properties respect to irradiation at ambient temperature.

#### Acknowledgements

We acknowledge the financial support of DGAPA grants IN-112509 and IN-111112 in México and Ministry of Science and Innovation grant MAT2011-25513/MAT in Spain. We acknowledge the technical support provided by E. Palacios and M. Cruz from ICN, Gladys Labrada from IPICYT, E. Sánchez from IIM-UNAM and C. Magaña from IFUNAM.

#### References

- Aytaç, A., Deniz, V., Şen, M., Hegazy, E.-S., Güven, O., 2010. Effects of gamma and electron beam irradiation on the properties of calendered cord fabrics. *Radiat. Phys. Chem.* 79, 297–300.
- Burillo, G., Adem, E., Muñoz, E., Vázquez, M., 2013. Electron beam irradiated polyamide-6 at different temperatures. *Radiat. Phys. Chem.* 84, 140–144.
- Cerrada, M.L., Benavente, R., Fernández-García, M., Pérez, E., Campos, J.M., Ribeiro, M.R., 2009. Crosslinking in metallocene ethylene-co-5,7-dimethylocta-1,6-diene copolymers initiated by electron-beam irradiation. *Polymer* 50, 1095–1102.
- Cerrada, M.L., Benavente, R., Fernández-García, M., Pérez, E., Campos, J.M., Ribeiro, M.R., 2011. Metallocene ethylene-co-(5,7-dimethylocta-1,6-diene) copolymers crosslinked using electron beam irradiation: a tunable alternative. *Polym. Int.* 60, 1309–1317.
- Dadbin, S., Frounchi, M., Goudarzi, D., 2005. Electron beam induced crosslinking of nylon 6 with and without the presence of TAC. *Polym. Degrad. Stab.* 89, 436–441.
- Friedrich, J., Zalar, P., Mohorčić, M., Klun, U., Kržan, A., 2007. Ability of fungi to degrade synthetic polymer nylon-6. *Chemosphere* 67, 2089–2095.
- Gonçalves, E.S., Poulsen, L., Ogilby, P.R., 2007. Mechanism of the temperature dependent degradation of PA6,6 films exposed to water. *Polym. Degrad. Stab.* 92, 1977–1985.
- Lyons, B.J., Glover Jr., L.C., 1990. Radiolytic crosslinking and chain scission in aliphatic and alkyl-aromatic polyamides. Part 1. *Radiat. Phys. Chem.* 35, 139–147.
- Nielsen, L.E., 1974. *Mechanical Properties of Polymers and Composites*. Dekker, New York.
- Oshima, A., Tabata, Y., Kudoh, H., Seguchi, T., 1995. Radiation induced crosslinking of polytetrafluoroethylene. *Radiat. Phys. Chem.* 45, 269–273.
- Pai, Ch.-Ch., Jeng, R.J., Grossman, S.J., Huang, J.-Ch., 1989. Effects of moisture on thermal and mechanical properties of nylon 6,6. *Adv. Polym. Technol.* 9, 157–163.
- Pramanik, N.K., Haldar, R.S., Bhardwaj, Y.K., Sabharwal, S., Niyogi, U.K., Khandal, R. K., 2009. Radiation processing of nylon 6 by e-beam for improved properties and performance. *Radiat. Phys. Chem.* 78, 199–205.
- Seguchi, T., Yagi, T., Ishikawa, S., Sano, Y., 2002. New material synthesis by radiation processing at high temperature—polymer modification with improved irradiation technology. *Radiat. Phys. Chem.* 63, 35–40.
- Sengupta, R., Tikku, V.K., Somani, A.K., Chaki, T.K., Bhowmick, A.K., 2003. Electron beam irradiated polyamide-6,6 films-I: Characterization by wide angle X-ray scattering and infrared spectroscopy. *Radiat. Phys. Chem.* 72, 625–633.
- Sengupta, R., Tikku, V.K., Somani, A.K., Chaki, T.K., Bhowmick, A.K., 2005. Electron beam irradiated polyamide-6,6 films-II: Mechanical and dynamic mechanical properties and water absorption behavior. *Radiat. Phys. Chem.* 72, 751–757.

- Sengupta, R., Tikku, V.K., Somani, A.K., Chaki, T.K., Bhowmick, A.K., 2006. Effect of ambient-temperature and high-temperature electron-beam radiation on the structural, thermal, mechanical, and dynamic mechanical properties of injection molded polyamide-6,6. *J. Appl. Polym. Sci.* 99, 1633–1644.
- Takashika, K., Oshima, A., Kuramoto, M., Seguchi, T., Tabata, Y., 1999. Temperature effects on radiation induced phenomena in polystyrene having atactic and syndiotactic structures. *Radiat. Phys. Chem.* 55, 399–408.
- Ueno, K., 1990. The radiation crosslinked process and new products. *Radiat. Phys. Chem.* 35, 126–131.
- Yu, J., Tonpheng, B., Andersson, O., 2010. High-pressure-induced microstructural evolution and enhancement of thermal properties of nylon-6. *Macromolecules* 43, 10512–10520.
- Zohdy, M.H., Mohamed, S.S., El-Naggar, A.W.M., 2004. Crease recovery, mechanical and thermal properties of synthetic fabrics treated with electron beam irradiation. *Nucl. Instrum. Methods Phys. Res., Sect. B* 222, 105–113.