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THE EFFECT OF PEROXIDATION METHOD ON POLYPROPYLENE FILM USING GAMMA RADIATION

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ABSTRACT

In this work the ionizing irradiation on polypropylene (PP) films was carried out by peroxidation method under cobalt–60 gamma rays source, at room temperature. The material was submitted to 5, 10 and 15 kGy doses with a dose rate of 10.7 kGy h^{-1}. The objective of this study is evaluating the influence of oxygen atmosphere and irradiation dose on the mechanical and thermal properties. The thermal properties were evaluated by Differential Scanning Calorimeter and Thermogravimetric Measurement (TG). For the mechanical test, the samples were cut into pieces of 15 mm x 100 mm and the measurement was made at melting temperature (160 °C) to eliminate the crystallinity influence. In this test all samples (pure and irradiated) did not break and the extension was over 120mm, which is the equipment limitation, but the irradiated films had lower tension stress. In order to compare the mechanical resistance another test were made at room temperature. In this case the pure samples did not break (extension over 500%) and the irradiated break with around 50% elongation and reduce in the tensile stress. This decrease in the tensile stress in the mechanical tests can be attributed to the process of chain scission of the strained tie molecules after gamma- irradiation degradation. The present study shows that the PP irradiation at room temperature in air affects both molecular structure of the chains and the crystallinity of PP films.

1. INTRODUCTION

One of the major techniques to modified and/or improve properties in polymer is ionizing radiation. This process leads to degradation, crosslinking and grafting polymerization, depend on the require property.

Studies on the interaction of high-energy radiation with polymers have attracted the attention of many researchers. This is because high-energy radiation can induce both chain scission and/or crosslinking. During irradiation process polypropylene suffers crosslinking and chain scission (degradation) reactions at the same time and rate which leads to degradation of physical properties. Gamma irradiation in the presence of air strongly degraded the properties of PP materials and several studies about this conditions and consequences in PP have been reported [1, 2].

When polypropylene is exposed to gamma radiation under oxygen atmosphere, the radicals generated by chain scission can combine with oxygen and initiate chain reactions. After gamma radiation the oxidation process continues for a long period and one explanation is that the free-radicals persist after irradiation in the crystalline phase [3, 4] and is possible to

migrate to the crystalline/amorphous boundary and react with the oxygen. Another explanation for this degradation reaction after radiation process is a slow decomposition of hydroperoxides groups [5].

This work shows results of polypropylene films exposed to gamma irradiation process at 5, 10 and 15 kGy under oxygen temperature. The effects of peroxidation method in mechanical and thermal properties will be evaluated in this work.

2. EXPERIMENTAL

2.1. Materials

Polypropylene films with 100 μm thickness was submitted to gamma radiation at 5, 10 and 15 kGy at dose rate of 10.7 kGy h^{-1} under oxygen atmosphere in order to evaluate the changes in the mechanical and thermal properties.

2.2 Characterization

Thermogravimetric (TG) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in dynamic atmosphere from 25 to 700 °C at a heating rate of 10 °C min^{-1} under inert atmosphere.

Differential Scanning Calorimeter (DSC) measurement was carried out in a 822 Mettler-Toledo under nitrogen atmosphere at a heating rate of 10 °C min^{-1} and temperature range of -50 to 280 °C. The crystallinity degree for PP 100% crystalline is 209 J g^{-1} [6].

Mechanical properties were measurement at room temperature using a EMIC machine and at 160 °C using an Instron equipment. The tests were performed at a cross head speed of 50 mm min^{-1}.

The infrared spectroscopy by ATR-IR was carried out on FTIR of Thermo Nicolet spectrometer to record the spectra of pure and irradiated samples.

3. RESULTS AND DISCUSSION

The infrared spectra are shown in Fig. 1 and in spite of the irradiation process made under oxygen atmosphere the peaks refer to the carbonyl (1700 cm^{-1}) and hydroxyl (3500 cm^{-1}) groups do not appear, probably because the low dose used in this study didn't cause high degradation in the polymer chain.

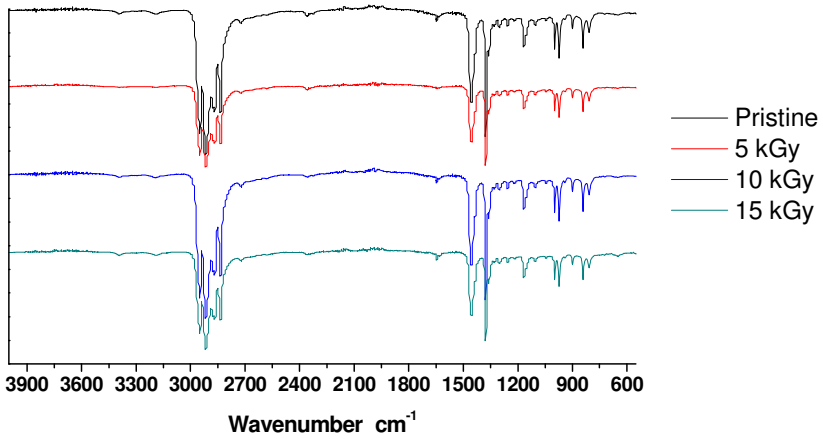

Figure 1. Infrared spectra (ATR-IR) for the samples.

The data for the mechanical tensile test at room temperature (25 °C) are demonstrated in Table 1. The results are in agreement with the literature which means that degradation is the effect caused by peroxidation method [4]. In this case the pristine samples did not break (extension over 500%) and the irradiated break with around 50% above of initial length and reduce in the tensile stress. This decrease in the tensile stress can be attributed to the process of chain scission of the strained tie molecules after gamma irradiation degradation.

The tensile tests at 160 °C were carried out for pristine and irradiated samples at 15 kGy. This temperature was used to eliminate the influence of crystalline phase (crystals) on the chain orientation. In this test these samples didn't break, the elongation was from 50 mm (initial length) until 120 mm which is the maximum of the Instron machine when the tests are done at high temperature. The irradiated samples suffer a decrease in the tensile at break value. This fact can be related to the reorganization of the crystalline phase during melting.

Table 1. Numerical results to the tensile test at room temperature

Sample	Initial length / mm	Elongation at break / mm	Tensile at break / MPa
Pristine	50	418.7*	21
5 kGy	50	112.5	5
10 kGy	50	78	4.5
15 kGy	50	78	3.5

* Sample didn't break

Thermogravimetric curves are in Fig. 2 and reveal the same profile for all samples. The initial degradation temperature wasn't affected with exception the irradiated polymer at 5 kGy which had a decrease in this temperature, from 440 °C for unirradiated to 424 °C for irradiated.

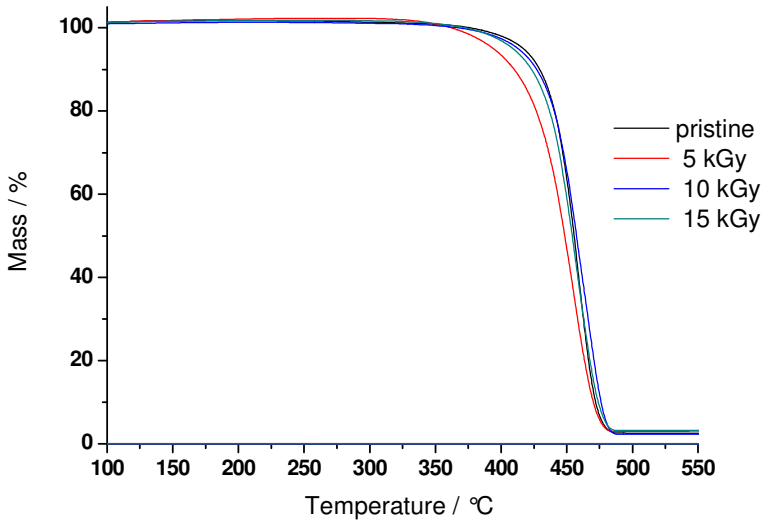

Figure 2. Thermogravimetric curves for all samples

The results obtained during first and second scanning of heating are demonstrated in Table 2 and the DSC curves for these values are showed in Fig. 3. The melting temperature is observed about 160 °C (Table 2) for all samples. The values of crystallinity degree (W_c) decrease as consequence of irradiation, that interacts with crystalline phase and produces more defective crystals.

Table 2. DSC values

Sample	T_{m1} / °C	T_{m2} / °C	W_c / %
Pristine	160	---	47.5
5 kGy	159	162	45.7
10 kGy	158	164	48.7
15 kGy	157	164	47.2

T_{m1}: melting temperature; W_c: crystallinity degree

The DSC curves show two different melting temperature (one likes a shoulder in the endotherms) of the irradiated polymer, which means that crystals with different size are melting in different temperature. This fact can be attributed to structural instability after recrystallization step as consequence directly of the irradiation process [7, 8]. These imperfect crystals were created due to oxygen present in the atmosphere that introduces irregularities in crystalline phase.

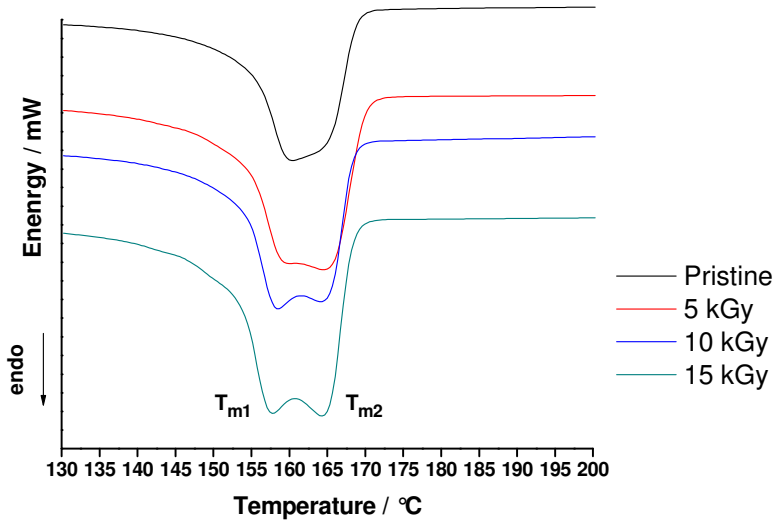

Figure 3. DSC curves for all samples

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4. CONCLUSIONS

By ATR-IR was not possible to verify the presence of carbonyl and hydroxyperoxide groups. But with the mechanical test and thermal analysis is possible to confirm the degradation process due to a decrease in these properties. By DSC is observed that there are different sizes of crystals in crystalline phase and appearance of double endotherms, both as a result of irradiation process in the presence of oxygen that interacts and cause irregularities in this phase.

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REFERENCES

1. U. A. Sevil, O. Guven "Spectroscopy, viscosimetric and mechanical characterization of γ- irradiated isotactic polypropylene syringes", *Rad. Phys. Chem.*, **46,** pp. 875-878 (1995).
2. N. Touati, M. Kaci, H. Ahouari, S. Bruzaud, Y. Grohens "The Effect of g-Irradiation on the Structure and Properties of Poly(propylene)/Clay Nanocomposites", *Macromol. Mater. Eng.*, **292**, p. 1271–1279 (2007).
3. D. J. Carlsson, C. J. B. Dobbin, D. M. Wiles "Direct observations of macroperoxyl radical propagation and termination by electron spin resonance and infrared spectroscopies", *Macromolecules*, **18** (10), p. 2092–2094 (1985)
4. F. Khoyluu and A A. Katbab "Radiation degradation of polypropylene", *Radiation Physics and.Chemistry,* **42**,(1-3), p. 219-222 (1993).
5. D. J. Carlsson, C. J. B. Dobbin, D. M. Wiles, "Reactivity of Polypropylene Peroxyl Radicals in the Solid State", *Macromolecules*, **18**, pp. 1791-1793 (1985).
6. J. Brandrup, E. H. Immergut *Polymer Handbook*, Ed. Wiley – Interscience, New York, **V – 27 a V – 33** (1989).
7. C. Y. Huang, C. L. Chen "The effect of plasma surface modification from a rotary plasma reactor on the styrene grafting onto a polypropylene surface", *Surface and Coatings Technology*, **153**, p. 194-202 (2002).
8. J. Karger-Kocsis *Polypropylene: Structure, Blends and composites*. Londres: Chapman & Hal, **1**, p. 56 (1995).