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THERMAL ANALYSIS OF IONIZING RADIATION EFFECTS ON RECYCLED POLYAMIDE-6

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Abstract

The aim of this work is to study the ionizing radiation effects on thermal properties of the recycled polyamide-6. This polymer was irradiated with an electron beam of 1.5 MeV with different doses. The thermal properties of the samples were determined by TG, DSC and DMA measurements. It was observed that the irradiated samples of recycled polyamide-6 undergo a crosslinking process.

Keywords: crosslinking, DMA, DSC, polyamide-6, recycled polyamide-6, TG

Introduction

Successive recycling promotes changes in several material properties, such as breaks of structures, increase of melt index, decrease of molecular mass and of mechanical resistance. These changes depend on the kind of recycled plastic resin, how and how long the recycle process takes place and the temperature and shearing strain applied [1, 2].

The interaction of the ionizing radiation with polymers results in energy transfer to them. This phenomenon may cause permanent modifications in the structure of the molecules. The induced modifications may bring degradation of the polymer or improvement of its properties by crosslinking, which are simultaneous and competing processes, depending on the radiation dose applied. The ionizing radiation has sufficient energy to convert at least one electronically neutral atom or molecule in an ion pair. The energy released by this kind of radiation is so intense that the molecular species can be broken and, possibly, rearranged after a short period. This is the base for polymer research using ionizing radiation [3].

Studies of structural and many physical effects of gamma and electron beam irradiation on virgin poliamide-6 have been made previously, but controversies exist [4–8]. There is no investigation on the ionizing radiation effect on recycled polyamide-6.

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In this work, electron beams were the only radiation to be concerned with. When the radiation interacts with the material, the primary electrons from the accelerator transfer part of their energy to the orbital electrons from the material, allowing them to move to higher energy orbits (excitation), or to become free (ionization) [9].

Polyamide-6 is a semicrystalline polymer with a high crystallinity degree, and is among the top of three engineering plastics due to its use in high performance machine parts [10]. The main characteristics of polyamide-6 are the resistance to oils, grease, solvents, fatigue and repeated impact. Other important features include a low friction coefficient, high tensile strength and toughness, besides moderate temperature resistance. Its limitations are the high moisture absorption resulting in dimensional and mechanical property changes, high mold shrinkage and notch sensitivity, unless suitably blended for toughness [6]. Typical applications of some polyamide-6 are manufacturing of wind-shield wiper gears, speedometers, engine fans, break fluid tanks, car mirror frames, mechanical components of house appliances, hammer handles, machine mobile parts, electric plugs, food packaging, threads for cloths, food and cloth processing equipment, brushes, fishing threads, sports goods, etc [11, 12].

Among the thermal analysis techniques utilized to study polymer property changes are thermogravimetry (TG), differential scanning calorimetry (DSC), dynamic thermomechanometry (DMA). A polymer with a high degree of crystallinity has a reduced amorphous phase and, therefore, a weak physical transition. DMA is more sensitive than DSC to chemical and physical material structure changes and yields more information than other mechanical and thermal techniques [13].

This work presents ionizing radiation effects on the virgin and recycled polyamide-6 thermal properties.

Table 1 Experiment results with different doses

Sample polyamide-6	Dose/ kGy	V_e crosslinking density/mol g^{-1}	M_c number average molecular mass/g mol^{-1}	Swelling/%
Virgin	0	–	–	dissolved
	200	5.49E–6±5.19E–7	47.765±1.287	2.525±97
	300	5.04E–6±8.77E–7	44.005±1.697	1.992±162
	500	6.20E–6±8.44E–7	41.863±1.477	1.806±113
	600	4.96E–6±2.18E–7	44.127±423	1.996±41
Recycled	0	–	–	dissolved
	200	2.83E–6±9.82E–8	48.709±233	2.600±43
	300	5.52E–6±1.25E–6	43.140±2.319	1.918±202
	500	7.90E–6±7.93E–7	39.088±1.211	1.614±74
	600	3.93E–6±1.82E–7	46.246±390	2.228±48

Table 1 presents the results of crosslinking density (V_e), number-average molecular mass between crosslinks (M_c) and swelling percentage (swelling agent-formic

acid) of virgin and recycled irradiated polyamide-6 [14]. These results were calculated through the equilibrium swelling experiments, using the Flory–Rehner theory [15]. The crosslink density in a polymer network is inversely proportional to the number-average molecular mass between crosslinks (M_c) and swelling percentage.

As a result of the irradiation process, the recycled polyamide-6 samples undergo a high crosslinking density as the virgin ones. The values of V_e increase while the radiation doses increase up to 500 kGy, for virgin and recycled samples. At doses as high as 600 kGy, it was observed that V_e decreases. It may be related to the degradation of the samples promoted by the high radiation dose.

Experimental

Radici Plastics Ltda. supplied the virgin and recycled polyamide-6 test specimens (1.13 g cm^{-3}, T_m=220°C, T_g=50°C). These samples were irradiated at the Nuclear and Energetic Research Institute (IPEN) irradiation facility, in a JOB 188 model accelerator, with a 1.5 MeV electron beam, with doses of 50, 100, 200, 300 and 500 kGy, and dose rate of 22.61 kGy s^{-1}.

Thermal analyses were carried out using a Shimadzu TGA-50 and DSC-50, under a flow rate of 50 mL min^{-1} of synthetic air and pure nitrogen, respectively, and heating rate of 10°C min^{-1}. The sample mass was around 4 mg.

Also, DMA-983 from TA Instruments was applied for testing the samples. They were held in the equipment by vertical clamps under a $70 \cdot 10^{-2}$ Nm torque separated 15 mm from each other. Then, they were cooled until –70°C using liquid nitrogen (LNCA), kept under isothermal conditions for 3 min and heated up to 200°C at 3°C min^{-1}. A 1 Hz frequency was utilized along with 0.2 mm oscillation amplitude, length correction of 0.5 and Poisson's constant of 0.5. Another sample of virgin polyamide-6 was pre-heated up to 100°C in the DMA equipment, kept under isothermal conditions for 5 min, cooled and analyzed as the previous samples. This procedure was adopted in order to eliminate the moisture absorption effect on DMA data.

The calibration of the thermal analysis equipment was done as suggested by the manufacturer. All tests were performed in triplicate.

Results and discussion

TG curves shown in Fig. 1 indicate that virgin polyamide-6 samples, irradiated or not, undergo thermal decomposition in a two stage process. The first one presents final temperature at 480°C, and corresponds to a mass loss of about 70%; in the second stage, the final temperature is about 620°C. The recycled polyamide-6 samples show little difference in the mass-change behavior when compared to the virgin ones.

DSC curves in Figs 2 and 3 allow to follow the crosslinking process of the virgin and recycled samples as a function of the radiation dose. The pre-melt crystallization exothermic peak, characteristic of the first heating of these samples and associated with the amorphous fraction, gradually disappears with the increasing doses of radiation. For the recycled samples, a second endothermic peak is observed at 245°C in the

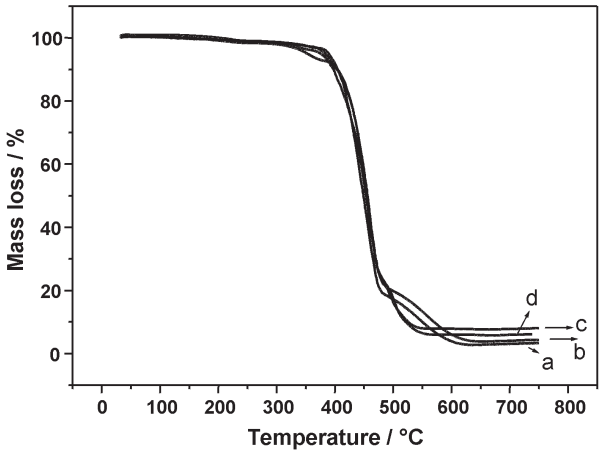

Fig. 1 TG curves of polyamide-6: a – virgin, not irradiated, b – virgin, irradiated with 200 kGy, c – recycled, not irradiated and d – recycled, irradiated with 300 kGy

DSC curve, also disappearing with the increase of the radiation dose. The degree of crystallinity was calculated based on the heat of melting for 100% crystalline polyamide-6 (ΔH_m=190 J g^{-1}) [16]. DSC data of the virgin samples make it possible to observe a significant change in the heat of melting, corresponding to an increase in the crystallinity of the irradiated material. This effect was not observed in the recycled samples. The virgin irradiated samples present very close melting temperature while the recycled samples show a more pronounced reduction in the melting temperature with the increase in the radiation dose, about 10°C for the highest dose. These values are shown in Table 2.

Table 2 Melting temperature (T_m), heat of melting (ΔH_m) and crystallinity degree obtained from the DSC curves for the virgin and recycled samples of polyamide-6 not irradiated and irradiated at different doses

Sample	Properties	Dose/kGy					
		Not irradiated	50	100	200	300	500
Virgin	T_m/°C	220.0	220.0	219.0	216.0	218.0	216.0
	ΔH_m/J g^{-1}	50.0	63.0	61.9	61.7	62.2	59.6
	Crystallinity/%	25.8	33.2	32.6	32.5	32.7	31.4
Recycled	T_m/°C	218.0	217.0	215.0	214.0	212.0	208.0
	ΔH_m/J g^{-1}	43.4	44.7	47.4	48.6	44.9	43.3
	Crystallinity/%	22.9	23.5	25.0	25.6	23.6	22.8

Figure 4 presents tanδ curves for the virgin and recycled polyamide-6 samples, obtained through DMA. Curves a and b represent the virgin samples submitted to different thermal pre-treatment as it was previously described. These samples presented relative

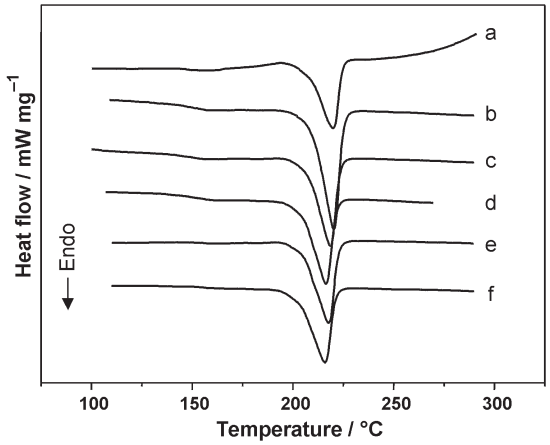

Fig. 2 DSC curves of virgin polyamide-6: a – not irradiated and irradiated with b – 50 kGy, c – 100 kGy, d – 200 kGy, e – 300 kGy, f – 500 kGy

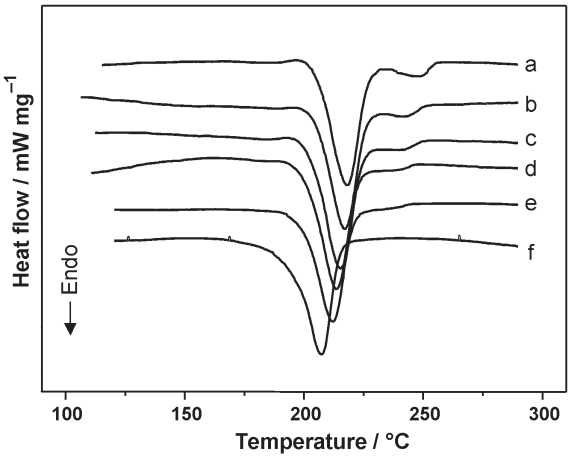

Fig. 3 DSC curves of recycled polyamide-6: a – not irradiated and irradiated with b – 50 kGy, c – 100 kGy, d – 200 kGy, e – 300 kGy, f – 500 kGy

changes in their glass transition temperatures. As observed in curve a, there is a second peak besides the main peak in tanδ curve. It is well-known from literature that moisture strongly affects polyamide-6 T_g. This increases the plasticity of polymer, allowing higher chain mobility and reducing T_g. Curve b corresponds to the virgin sample subjected to preheating in order to eliminate humidity. It presents a higher T_g and does not show a second peak as curve a. The recycled samples present an increase in T_g as a function of the radiation process until doses up to 300 kGy, as it can be seen in curves c and d in Fig. 4. The molecular mobility is hindered by crosslinking, shifting the glass transition tempera-

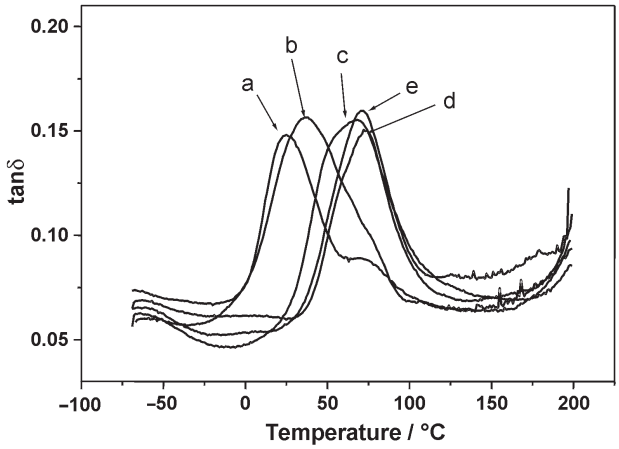

Fig. 4 Radiation effects on the tanδ of polyamide-6: a – (T_g=24.9°C), b – virgin, not irradiated, pre-heated up to 100°C (T_g=36.7°C), c – recycled, not irradiated (T_g=66.2°C), d – recycled, irradiated with 300 kGy (T_g=71.9°C), e – recycled, irradiated with 500 kGy (T_g=70.5°C)

ture to higher values. The recycled polyamide-6 irradiated with dose as high as 500 kGy shows lower glass transition temperature than the samples irradiated with lower doses. It may be related to some degradation of the sample.

Conclusions

- Thermogravimetry allowed to observe that the thermal stability of polyamide-6 is not affected by recycling or radiation process.
- The results from DSC showed that the recycling process did not affect the sample crystallinity. However, the virgin sample crystallinity is more affected by the radiation than the recycled one.
- The glass transition temperature of the studied samples cannot be observed in DSC curves. T_g values determined by DMA increased as the radiation dose increased. From DMA results obtained, it may be concluded that recycled samples became crosslinked after irradiation process. However, doses higher than 300 kGy may promote degradation of polyamide-6.

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References

1 H. Wiebeck, A. Bernardo, A. M. Martini, A. Asciuttis, M.G. Oliveira and C. H. Yai, In: VIth Latin American Symposium on Polymers, October 25–28, Chile 1998, p. 200.
2 L. D. B. Machado, L. G. A. Silva and H. Wiebeck, In: 5th Brazilian Congress on Polymers, Brazil, November 1999, CD-Rom, p.1550.

3 E. A. Abramyan, Industrial Electron Accelerators and Applications, Institute for High Temperatures, USSR Academy of Sciences, Hemisphere Publishing Corporation, London 1988.
4 E. J. Lawton and A. M. Bueche, Electron Irradiation of Preformed Polyamide Resin, United States Patent Office 2,858,259, New York 1958.
5 E. Lawton, Irradiation of Nylon, United States Patent Office 2,967,137 New York 1961.
6 N. Thorp, Cross-Linked Polyamides, The Patent Office 1,184,599, London 1970.
7 L. P. Singh and N. K. Chaudhuri, Proc. of Symp. on Industrial Polymers and Radiation, Sardar Patel University, Vallabh Vidyanagar, Gujarat, February 12–14, 1979.
8 M. C. Gupta and R. R. Pandey, γ-Irradiation of Nylon 6, J. Polymer Sci., 26 (1998) 491.
9 D. W. Clegg and A. A. Acollyer, Irradiation Effects on Polymers, Elsevier Applied Science, London 1991.
10 H. Wiebeck, In: 4th Brazilian Congress on Polymers, Brazil, September 28–October 2, 1997.
11 M. I. Kohan, Polyamides (PA), in Engineered Materials Handbook, Engineering Plastics, ASM International, 2 (1988) 124.
12 W. E. Nelson, Nylon Plastic Technology, The Plastic and Rubber Institute, London 1976.
13 S. V. Canevarolo, In: 1st Brazilian Congress on Polymers, Brazil, May 1991.
14 M. C. Evora, L. C. Lopérgolo, H. Wiebeck and L. G. Andrade e Silva, In: 12th International Meeting on Radiation Processing, Conference Programme and Abstracts (www.atriplei.com/imrp Abstacts, Session III, P08, IMRP 3-15), March 25–30, France 2001, p. 195.
15 P. J. Flory and J. Rehner Jr., J. Chem. Phys., 11 (1943) 512.
16 E. Kaisersberger, S. Knappe, H. Möhler and S. Rahner, TA for Polymer Engineering: DSC, TG, DMA, TMA. Netzsch Annual for Science and Industry, v. 3, Selb-Würzburg 1994.