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Ionizing radiation effect studies on polyamide 6.6 properties

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Abstract

The automotive, electric and electronic component industries, employ more and more the engineering plastics as a viable alternative for cost reduction and increase of productivity without quality loss. Polyamide 6.6 is an engineering plastic with distinguished role on this category of polymers due to its high thermal and chemical resistance, and strength. The aim of this work is to present the results of crosslink density determination, calculated through the equilibrium swelling experiments of polyamide 6.6 with and without fiber glass reinforcement, irradiated by electron beam at different doses.

Keywords: Polyamide 6.6; Ionizing radiation; Electron beam

1. Introduction

It is a fact that the consumers are more and more demanding more elaborated patterns, increased quality and security of the products that are offered; this being the case, new materials are developed to meet that demand, like the engineering plastics (Saechtling, 1996).

Amongst those plastic materials, the polyamide 6.6 has a distinguished role in this context, because its mechanical characters, thermal and chemical resistances allows it to play an important role during the development of new applications.

Aliphatic polyamides have a greater distinction due to their low attrition coefficient, high fusion temperature, good impact resistance, high resistance to the fatigue and low specific mass when compared with metal (Kohan, 1973). The interaction of the ionizing radiation with polymers results in the transfer of energy to them, provoking mainly the molecular excitation and ionization, generating chemical reactions that can effect permanent modifications in the polymer's physicochemical structure (Bolt and Carrol, 1963).

The induced modifications may result in the degradation of the polymer or in improvement of its properties. In this case the process inserts crosslinking, improving their thermal, electrical and mechanical properties. One of the basic properties of that crosslinked molecular structure is the decrease of solubility (Clegg and Collyer, 1991).

The aim of this work is to study the effect of ionizing radiation on polyamide (PA), researching mainly the possibility of crosslink increase among polyamide 6.6 molecules with and without glass fiber reinforcement, submitted at different radiation doses. Determination of crosslink density (v_e) and swelling percentage in the equilibrium ($\%S$) were also researched.

These methods allow for the verification of the changes that happen in the structure of the polymeric molecules when submitted at radiation dose.

2. Experimental

Samples of polyamide 6.6 with and without 30% of glass fiber reinforcement were injected and the swelling assays were realized according ASTM D 3616-88 standard.

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The average molecular weight among crosslinks ($\bar{M}_c$) was obtained by

$$\bar{M}_c = \frac{M_n}{(v_e M_n + 2)}, \quad (1)$$

where $\bar{M}_c$ is the average molecular weight among crosslinks; M_n is the average molecular weight; and v_e is the crosslink density.

The crosslink density was calculated by the equation based on the theory of Flory–Rehner and may be estimated using Eq. (2) (Flory and Rehner, 1943):

$$v_e = -\left[\frac{\ln 1 - W_2 + W_2 + \chi W_2^2}{\bar{V}_1 \rho \left(W_2^{1/3} - (W_2/2)\right)}\right], \quad (2)$$

where v_e is the crosslink density; ρ is the polymer density; W_2 is the reduced volume (dry volume/swelled volume); $\bar{V}_1$ is the molar volume of pure solvent; and χ is the parameter for polymeric–solvent interaction.

The samples of polyamide 6.6 with and without glass fiber reinforcement, irradiated and non-irradiated, were heated at 80°C for 72 h in order to eliminate the humidity of the samples measuring their weights, and afterwards immersed in formic acid for 72 h. After that, the solvent was removed and the swollen samples were weighted. The assay was performed at room temperature and in the dark.

The swelling percentage (%S) was calculated using

$$\%S = \left(\frac{W - W_0}{W_0}\right), \quad (3)$$

where W is the final weight of the sample; and W_0 is the initial weight of the sample.

The samples of both types of polyamide 6.6 were irradiated on JOB 188 accelerator with an electron beam energy of 1.5 MeV in air with doses of 200, 300, 400, 500 and 600 kGy and a dose rate of 22.61 kGy/s.

3. Results and discussion

The results of the average molecular weight among crosslinks ($\bar{M}_c$) are summarized in Table 1. The results of the crosslink density (v_e) and the swelling percentage in the equilibrium (%S) are summarized in Tables 2 and 3. These results were obtained from the experimental immersion in the formic acid that was performed with samples of PA 6.6 and PA 6.6, reinforced with 30% of glass fiber, irradiated and non-irradiated.

In Table 2, at 400 kGy we can observe an increase of the crosslink density of PA 6.6 and PA 6.6 reinforced with 30% of glass fiber, while in Table 1 we can observe a decrease in the average molecular weight among crosslinks at 400 kGy. These results indicate that the crosslinking increases after 400 kGy.

Table 1
Results of average molecular weight among crosslinks of Polyamide 6.6 and Polyamide 6.6 with 30% of glass fiber reinforcement at different radiation doses

Radiation dose (kGy)	Average molecular weight among crosslinks $\bar{M}_c$ (g/mol)	
	PA 6.6	PA 6.6 30% GF
0	69.54	38.76
200	92.76	4376.37
300	4901.96	11030.22
400	12359.90	7807.62
500	12350.25	6257.82
600	12217.17	5365.38

Table 2
Results of crosslink density of Polyamide 6.6 and Polyamide 6.6 with 30% of glass fiber reinforcement at different radiation doses

Radiation dose (kGy)	Crosslink density v_e (mol/g)	
	PA 6.6	PA 6.6 30% GF
0	0.014300000	0.02572000
200	0.010700000	0.00014850
300	0.000124000	0.00001066
400	0.000000907	0.00004808
500	0.000000970	0.00007980
600	0.000001853	0.00010638

Table 3
Results of swelling percentage of Polyamide 6.6 and Polyamide 6.6 with 30% of glass fiber reinforcement at different radiation doses

Radiation dose (kGy)	Swelling percentage (%S)	
	PA 6.6	PA 6.6 30% GF
0	−86.62	−62.15
200	−83.69	90.66
300	3220.22	878.53
400	2574.10	409.12
500	2464.24	350.10
600	1758.81	321.71

In Table 3 it is shown that when polymer crosslinking increases, its swelling percentage decreases because less acid is absorbed by the polymer.

In Fig. 1 we can see the samples of PA 6.6, without glass fiber reinforcement, non-irradiated and irradiated at 200 kGy, dissolved completely in formic acid. The sample irradiated at 300 kGy turned into a white gel meanwhile the ones irradiated with 400, 500 and 600 kGy turned into white frail solid. According to the experimental data, it is possible to conclude that there was crosslinking from 300 kGy.

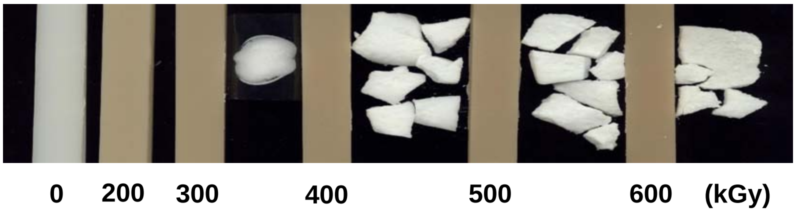

Fig. 1. Polyamide 6.6 samples non-irradiated and irradiated at different doses, after 72 h of immersion in formic acid.

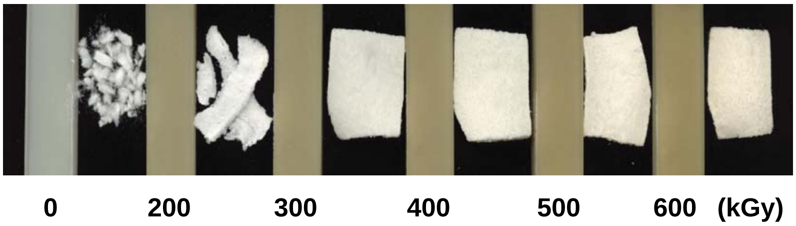

Fig. 2. Polyamide 6.6 samples with 30% of glass fiber reinforcement and non-irradiated and irradiated at different doses, after 72 h of immersion in formic acid.

Fig. 2 shows the samples of PA 6.6, with 30% of glass fiber reinforcement, non-irradiated dissolved completely, remaining only the glass fiber that did not dissolve in the formic acid. From 200 kGy is possible to verify some kind of resistance to the formic acid because the sample did not dissolve completely. From 300 kGy the resistance to the formic acid was greater. In this case, due to the glass fiber present in the polymer, it is noticeable that the radiation allowed a greater interaction between the fiber and the polymer.

Figs. 1 and 2 shows the Polyamide 6.6 without glass fiber reinforcement, when irradiated with doses starting from 300 kGy, decreases its solubility in formic acid after 72 h, and the Polyamide 6.6 with 30% of glass fiber reinforcement, irradiated with doses higher than 200 kGy, has its solubility decreased in formic acid after 72 h, increasing the crosslinking of the polymer.

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