



Post-irradiation thermal degradation of PA6 and PA6,6

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ABSTRACT

PA 6 and PA6,6 sheets irradiated with electron beam were investigated in relation to their thermal stability in various environments (air, distilled water and NaCl 5% solution) at 70 °C. The preexposure doses were 100, 200, 400 and 600 kGy at a dose rate of 22.4 kGy/s. The FTIR spectra allowed the evaluation of the progress of sample oxidation by elucidating the contributions of each environment to the ageing of polyamides. The increases in the absorbance at 1652 cm⁻¹ placed the surrounding aggressive attack in the following sequence: air < water < NaCl solution. A scheme of degradation mechanism is proposed for the explanation on the involvement of amidic units.

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1. Introduction

The polymer processing by radiation has been established in large areas for different applications in biomedical items, electrical cables and wires, coatings, tires, footwear, commodities (Bhattacharya, 2000; Chmielewski et al., 2005). The durability of these products has to be controlled because their proper functionality determines the long-term operation and the maintenance of equipment in which they are component units.

The effects of high energy radiation on polyamides have been reported in several papers (Ueno, 1990; Li et al., 1996; Mizusawa and Baba, 2003; Ferro and Silva, 2004; Sengupta et al., 2006a, b; Rosales et al., 2007; Mészáros and Czvikovszky, 2007; Peres Araújo et al., 2008). The resistance of polymer to the action of various energetic stimuli depends on many factors, such as the nature of functional units that exist in the molecular backbone or branching on it, the ageing environment, the material formulation, the duration and the intensity of stressors. Nevertheless, the most important aspect that has to be considered is the competition between crosslinking and degradation, whose rate ratio determines the material stability when exposed to high energy radiation. The accomplishment of a certain material structure is assured by the level of dose rate and the total dose received by polymer. The radiation processing applied on polymers changes the physical and mechanical properties, and the resulting strength reflects the chemical modifications involved in the reactions of intermediates.

Polyamides which belong to the class of engineering plastics present excellent physico-mechanical properties, especially heat

resistance. They can be crosslinked (Lyons and Glover-jr, 1991; Feng et al., 2002; Dadbin et al., 2005) or they may be degraded (Buchalla et al., 2002; Sengupta et al., 2006a, b; Chytiri et al., 2008) as the consequence of their exposure to ionizing radiation. The easier decay of amide segments with increasing dose represents one manner of degradation that was mentioned earlier by Chapiro (1962).

The post-irradiation behavior of polyamides in connection with their chemical strength was not studied earlier. The characterization of degradation rate in correlation with the service environment would direct the applications towards certain areas, where the aggressive conditions are not applied. This paper presents the behavior of EB irradiated polyamide 6 (PA 6—caprolactam) and polyamide 6,6 (PA6,6—polyimidohexa-methyleneiminoadipoyl) to the heat treatment in various environments.

2. Experimental

2.1. Materials

Polyamide 6 (PA 6) and polyamide 6,6 (PA 6,6) samples were supplied by Radici Plastics Ltd. The injection equipment was Battenfeld TM 1000. The main properties of tested polyamides are listed in Table 1.

2.2. Sample preparation

The samples of PA 6 were injected in Battenfeld TM 1000 injector at 250 °C. The samples of PA 6,6 were injected in the same injector but at 275 °C.

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Table 1
The main characteristics of studied polyamides.

Sample	Density (g/cm ³)	Melting point (°C)
Polyamide 6	1.12–1.15	215–220
Polyamide 6,6	1.13–1.15	250–255

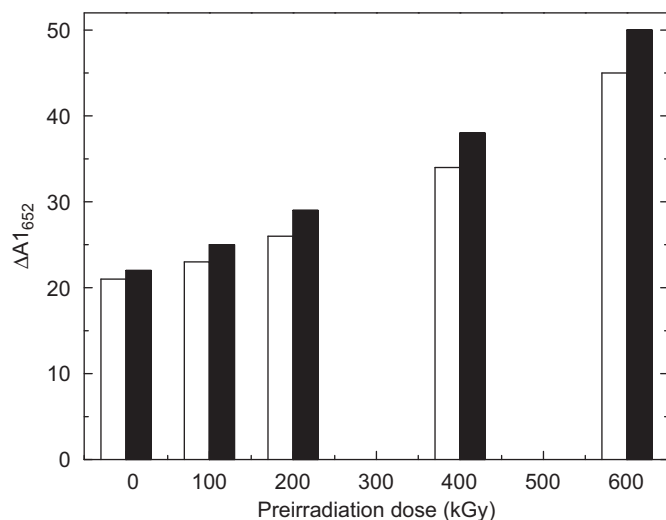


Fig. 1. The relative absorbance values of polyamide samples on preirradiation stage. (White) PA 6; (black) PA 6,6.

Table 2
The values of constants for the proposed degradation equation.

Sample	C (%)	k (kGy ⁻¹)
Polyamide 6	21	0.001266
Polyamide 6,6	22	0.001372

2.3. Irradiation and thermal conditioning

Irradiation of the PA 6 and PA 6,6 samples was carried out in air at room temperature using 1.5 MeV electron beam of Dynamitron linear accelerator dc 1500/25-JOB 188 model at different irradiation doses 100, 200, 400 and 600 kGy at a dose rate of 22.4 kGy/s.

The heat treatment was performed at 70 °C in an air-circulation oven at various times. To the samples repeated cycles heating/spectral measurement were applied for the characterization of oxidative product accumulation.

2.4. Spectral evaluation

FTIR spectra were recorded with ATR JASCO 4200 provided with ZnSe crystal detector. 60 scans were selected for good imaging spectra. The band at 1652 cm⁻¹ was selected, because the most significant variations could be noticed.

3. Results and discussion

The first irradiation stage on the history of polyamide samples induced certain level of degradation as it may be noticed from Fig. 1. There is a slight difference between the augmentations in the absorbance at 1652 cm⁻¹ for both the types of polyamides.

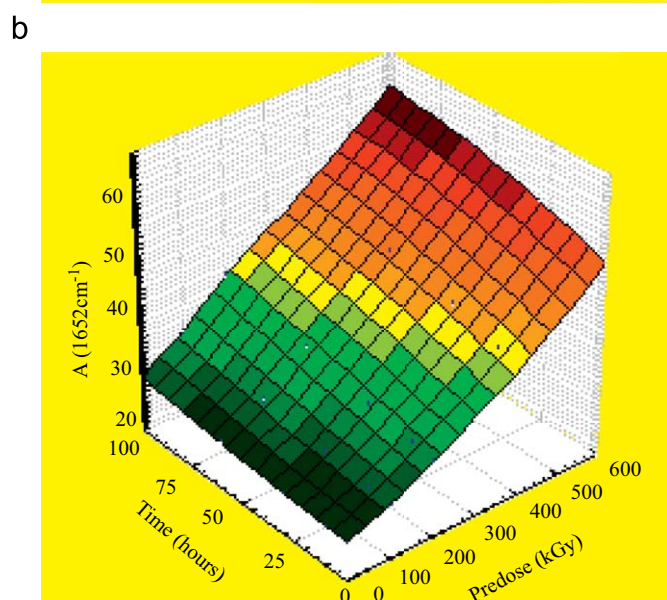
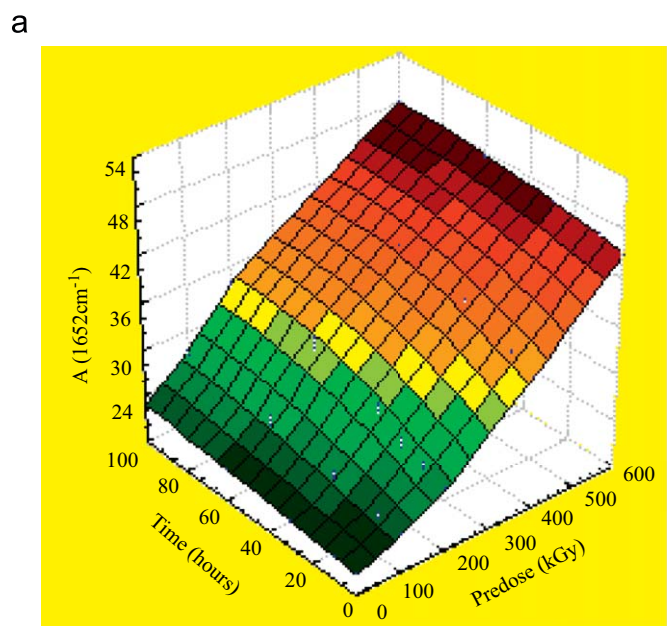


Fig. 2. Evolution of absorbance at 1652 cm⁻¹ recorded for PA 6 (a) and PA6,6 (b) samples heated in distilled water.

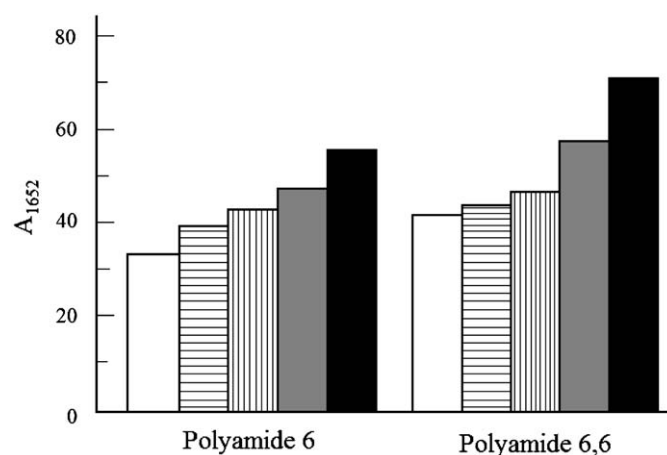


Fig. 3. The absorbances at 1652 cm⁻¹ for all preirradiated samples heated for 100 h at 70 °C in NaCl solution. (White) control; (horizontal lines) 100 kGy; (vertical lines) 200 kGy; (grey) 400 kGy; (black) 600 kGy.

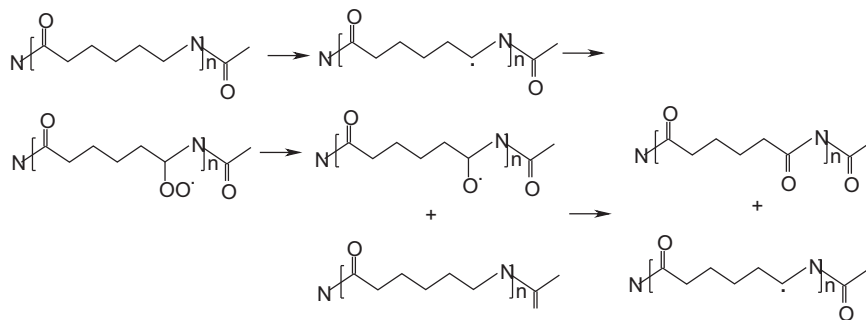


Fig. 4. Degradation mechanism proposed for studied polyamides.

The equation that depicts the changes in this spectral parameter I an exponential function:

$$A_{1652} = C \exp(kD)$$

where A is the measured absorbance at 1652 cm^{-1} , C a constant that is the initial absorbance, k an accumulation constant that denotes the sensitivity of irradiated material to the action of high energy radiation and D is the exposure dose. The calculated values for constants C and k are listed in Table 2. The lower values for both characteristics are explained by the higher radiation stability of polyamide 6 in comparison with polyamide 6,6. This behavior is in accordance with the earlier reported results (Cerrutti et al., 2003). The oxidative degradation of polymers in the radiation field may be evaluated by the triggering activity of peroxy radicals whose concentration is related to the total absorber dose. The increased irradiation dose causes the larger accumulation of reactive intermediates (peroxy radicals and hydroperoxides), which promote the chain process of degradation. These entities became the degradation promoter for further thermal treatment.

The degradation activity of salt solution was already demonstrated (Zaharescu and Mihalcea, 1997; Zaharescu and Podinã, 1998). The basic process of the accelerated degradation in salt solution is the charge transfer process occurred between chloride ions and hydroperoxides placed on the outer first molecular layers of polymer matrices (Zaharescu, 1994). The progress in the oxidation of polyamide can be explained by the attack of oxygen onto the methylene fragments that are placed in the vicinity of nitrogen atoms of amido groups (Cerrutti et al., 2003). The dependences of absorbance on preirradiation dose and time of heating for the 1652 cm^{-1} band recorded in the thermal degradation of polyamides 6 and 6,6 are presented in Fig. 2. The evolutions of the modifications in the oxidation state of PA6 and PA6,6 are similar for the other two ageing media (air and aqueous salt solution). However, the course of alteration processes got different amplitudes; in air, polyamides were lighter degraded, but in salt solution, the downgrading was more advanced for both types of materials. The enhance in the absorbance at 1652 cm^{-1} is due to the accumulation of the carbonyl units whose peak is overlapped on the band ascribed to primary and secondary amide structures. The increase in the intensity of this spectral region is more prominent for the samples aged in NaCl solution. The degradation rates are different for the three testing environments. The rates of oxidative attack sustained by applied environments place them on the following sequence based on the increase in their values:

air < distilled water < NaCl (5%) aqueous solution.

In Fig. 3 the comparison of thermal stability for polyamides 6 and 6,6 degraded in all three environments is presented. The higher absorbances for polyamide 6,6 display its availability to oxidation in comparison with polyamide 6.

Based on our results and on other similar investigation (Lánská et al., 2001; Feng et al., 2002; Cerrutti et al., 2003; Davis et al., 2003; Pramoda et al., 2003), a mechanism concerning the oxidation by thermal degradation of irradiated polyamides is presented in Fig. 4. It explains the accumulation of oxygenated entities via the formation of peroxy intermediates.

The density of reactive places that are formed during irradiation determines the propagation of oxidation, but the contribution of harmful factors of environment must not be disregarded, because their interference in the oxidation brings about major effects.

4. Conclusion

The thermal degradation of irradiated polyamides 6 and 6,6 occurs faster in the aggressive environment, for example aqueous salt solutions. The preexisting hydroperoxides interact with chloride ions and an additional ageing as solute accelerate the ageing of materials. The durability of irradiated polyamides in air is longer than in water and salt solutions. Nevertheless the improvement in the further stability of radioprocessed PA6 and PA6,6 would presume the presence of suitable antioxidants.

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