

Radiation stability of polyamide composites containing rice husk ash

T. ZAHARESCU^{*}, L. G. ANDRADE E SILVA^a, S. JIPA^b

INCDIE ICPE-CA, 313 Splaiul Unirii, P. O. Box 149, Bucharest, Romania

^aRadiation Technology Center, Institute for Nuclear Energy Research, Av. Prof. Lineu Prestes, 2242, São Paulo, Brazil

^b“Valachia” University of Targoviste, 18-22 Unirii Av., Targoviste 130082, Romania

This paper presents the radiation stability behavior of polyamide composites containing rice husk ash as filler. Samples consisting of polyamide 6 and 0, 10, 20 and 30 % (w/w) filler were EB irradiated at following doses: 0, 100, 200, 600 and 1000 kGy. The evaluation of radiation stability was accomplished by FT-IR spectroscopy and chemiluminescence. The assessment on characteristic bands of amide group was studied during the thermal degradation. The spectral and chemiluminescence investigations allowed the evaluation of propitious contribution promoted by rice husk ash in polyamide 6 composites in relation with radiation stability of studied substrates.

(Received March 3, 2011; accepted March 16, 2011)

Keywords: Polyamide 6 compound, Stability, Chemiluminescence, FTIR

The degradation of polymeric materials often limits their service life. To improve their durability the mechanisms responsible for their degradation must be correctly understood in correlation with the ageing action of stressors. Degradation occurs as the result of an environment-dependent chemical or physical attack. The degradation process can be very complex since it may involve several chemical and physical reactions. For example, in outdoor or special applications polymers can be exposed to UV light, elevated temperatures, chemical and radiation attacks. The understanding of the degradation mechanisms is further complicated by factors such as formulation, diffusion processes and interactions of polymer with filler.

The thermal oxidation perishing of polyamides is accomplished by the reaction of aldehyde and ketocarbonyl groups with amino end groups [1]. However, the depreciation in material characteristics following accelerated action of high energy radiation takes place in different manner, which emphasizes the contribution of filler to the depletion of free radicals [2-7].

The degradation of ammonium end-group during thermal treatment at about 200 °C was reported, when the virgin PA 6 chain modification was pointed out by NMR analysis [8].

The irradiation with accelerated electrons has revealed the crosslinking effects on polyamide-6 blends [9], which implies the availability of radicals generated by PA 6 further involved in reactions of material conducting to the improvement in thermal and radiation resistances.

The modification practice applied on polyamides has been extended onto various formulations, which may clarify the contributions of fillers to the behavior of base polymer matrix [10-15].

Chemiluminescence investigations on the thermal stability of polyamides were scarcely reported [16, 17]. They emphasize the generation of oxidation products from polyamide degradation causing the loss functional properties like mechanical strength accompanied by yellowish to brownish coloring and the appearance of brittleness.

The radiation effects on polyamides were previously studied [8-22], but the contribution of each structural unit to oxidative degradation was not detailed.

The present paper presents the radiochemical behavior of modified polyamide 6, which was modified with rice husk ash for the improvement in fire retardancy.

2. Experimental

2.1. Materials

PA 6 is an injection molding product manufactured by Radici Plastic Ltda (Brazil) delivered as Radilon[®]. Some main properties are listed below:

- density: 1.13 g/cm³
- ensile modulus: 2900 MPa (1 mm/min)
- stress at break: 70 MPa (5 mm/min)
- stretch at break: 5% (5 mm/min)
- flexural modulus: 2800 MPa (2 mm/min)
- flexural strength: 90 MPa (2 mm/min)

The technological parameters applied during sample preparation are mentioned for the characterization of manufacturing process of samples:

- processing temperature: 230 – 275 °C
- mold temperature: 30 – 60 °C
- injection speed: medium/high
- pressure: medium

2.2. Sample preparation

The combustion of rice husk generates ashes with structural variable states (amorphous and/or crystalline), which are defined on both type equipment used for the burning, time and cooking temperature. The rice husk burnt in controlled conditions (500 °C) was heated for three hours in a microwave oven generating residual ash where the major product was silicon dioxide in crystalline form of quartz. Further heat treatment lead to silica in amorphous state, which does not present any risks to human health [23, 24]. The rice husk ash used in this work was obtained from the burning of the rice husk under controlled temperature of 500 °C for three hours being afterwards ground and sifted in grills of 325 mesh. The residue has black coloration due to its incomplete combustion. As the main part with PA 6 is elaborated in black color, the contamination with carbon in the rice husk ash displayed for the injected plastic part.

The polyamide 6 composites containing rise husk ash were prepared by extruding at maximum working temperature of 300 °C.

The composites were injected in an injection molding machine Batenfeld, model TM 1000/25, command Unilog B2 of 100 t closing.

2.3. Irradiation

For irradiation a Electron Beam Accelerator JOB 188 (Dynamitron®, energy 0.86 MeV, beam current 5.05 mA, scan 100 cm and dose rate 28 kGy/s) was used. The obtained samples consisting of polyamide 6 and 0, 10, 20 and 30 % (w/w) filler were irradiated with electron beam in air, at room temperature at following doses: 0, 100, 200, 600 and 1000 kGy. Dosimetry was accomplished according with the procedure previously reported [25].

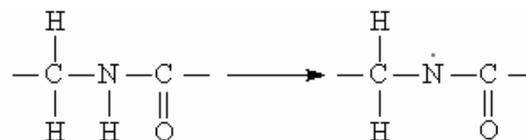
2.4. Measurements

Chemiluminescence investigation was accomplished on LUMIPOL 3 (Slovakia) in air under isothermal regime at 170°C.

FTIR spectra were recorded using ATR unit of JASCO 4000 spectrometer. Applied scanning number was 50.

3. Results and discussion

The oxidation of polyamides starts on the amide groups, which are the most vulnerable units. According to the generally accepted radical chain mechanism, the initiation step is a hydrogen abstraction from the most susceptible hydrogen, which is the hydrogen on the N-vicinal methylene group.



On its reaction with oxygen this radical will form a peroxy intermediate.

The molecular weight distribution as the consequence of scissions is slightly ascendant [4], which demonstrates the remarkable resistance of this kind of structure upon the action of ionizing radiation. The appearance of free radicals allows the promotion of structural branching, which diminishes the radical availability to the reaction with oxygen.

The addition of inorganic filler has two effects: the first is the decrease in the oxygen diffusion rate due to the difference in the material compacting. The second surface consequence is the interaction of intermediates with filler particles that controls the reactivity and migration of radical units.

In Fig. 1 the evolution of characteristic bands in pristine polyamide 6 is presented, while Fig. 2 illustrates the modifications on the same spectral regions occurred in rice husk ash modified polyamide 6. The neat material exhibits larger differences in the absorbance values for amide and ketonic vibrations. Meanwhile, the presence of rice husk ash induces not only a higher stability, but also the absence of ketonic groups. The progress in the received doses causes the consumption of amide group, which is transformed into oxygenated structures by its reaction with dissolved oxygen. This feature was observed in the pristine polyamide 6, where there is not barrier for oxidative degradation. The presence of filler (rice husk ash) hinders the subsequent process of oxidation (Fig. 2). In addition, the pseudosuperposition of FTIR spectra recorded on ash-modified polyamide 6 reveals the efficient contribution of filler, in particular amorphous silica, which may scavenge free radicals generated from basis polymer.

The accelerated degradation induced by electron beam irradiation takes place only in the organic phase. The inorganic filler which is added in increasing concentration induces a preservation of initial polymer structure. This behavior is explained by the interaction of unpaired electron placed on radical position and free orbitals existing in oxygen atoms of SiO₂ filler. The amorphous state of filler allows the diffusion of small radicals into these particles. Consequently, the abstraction of reactive intermediates contributes to the diminution of degradation rate, which means that this kind of filler is suitable for the manufacture of long term materials destined to several applications foreseen for hard service conditions.

The chemiluminescence measurements performed on PA 6/rice husk ash composites reveal the interference of filler on the oxidation process of polyamide 6 under electron beam radiation exposure (accelerated degradation).

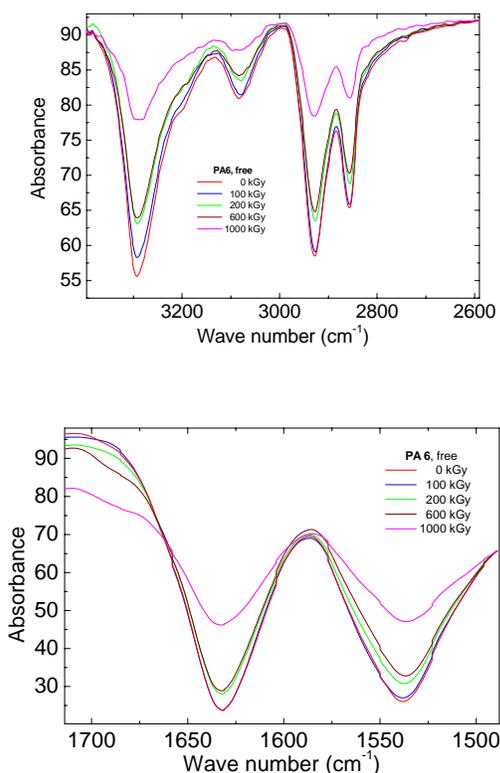


Fig. 1. Spectral modifications in PA 6 recorded after electron beam irradiation at various doses.

From Fig. 3 an evident difference between neat polyamide 6 and its composites with rice husk ash is revealed. The CL emission intensity of pristine polymer is with an order of magnitude higher than any studied composite. The beneficial effect on stabilization promoted by rice husk ash filler is efficient on the first 5 minutes after the heating of samples. It means that the filler particles homogeneously distributed in polymer matrix acts immediately after the start of thermal treatment. In the contrast with pristine sample, where the process of oxidation happens on the same period, the modified polyamide 6 emits CL quanta on the decreasing regime. A plateau is attained soon after the adsorption becomes effective. The distance that separates the CL curves registered for composite samples becomes more and shorter, which demonstrates the adsorption efficiency of filler particles dispersed in the volume of polyamide 6.

The presence of filler in these composites modifies the manner of radical decay. In Fig. 4 the chemiluminescence curves depicting the variation in the emission intensity are presented. The unmodified polyamide 6 presents an initial increase in the CL intensity caused by the accumulation of radicals generated during radiolysis.

As the concentration of filler is enhanced, the descendent part on the early oxidation stage becomes sharper. The scavenging activity of filler is pointed out by the acute diminishing in the CL emission intensity. The

chemiluminescence curves are gathered at higher concentration, which highlights the availability of filler for the abstraction of radicals in the favor of material stability. The further analysis of radiation stability of PA 6/rice husk ash composites allows characterizing the conducive effect of increasing the filler proportion in polymer composites. Thus, the decrease in the CL intensity level caused by the hindering oxidation is the major consequence got in on the background of the competition between the degradation of polymer and the recombination the free radical.

4. Conclusions

The addition of rice husk ash into polyamide 6 composites leads to the increase in the material stabilization during the exposure to electron beam radiation. The applied procedures (FTIR analysis and CL investigation) emphasized that the presence of rice husk ash, in fact – silica, promotes scavenging of free radicals in the detriment of their reaction with available oxygen molecules. The stability tests accomplished by the exposure of PA 6/ rice husk ash composites have demonstrated the increasing capacity of rice husk ash (amorphous silica) to the preservation of initial structures even at high irradiation dose (1000 kGy).

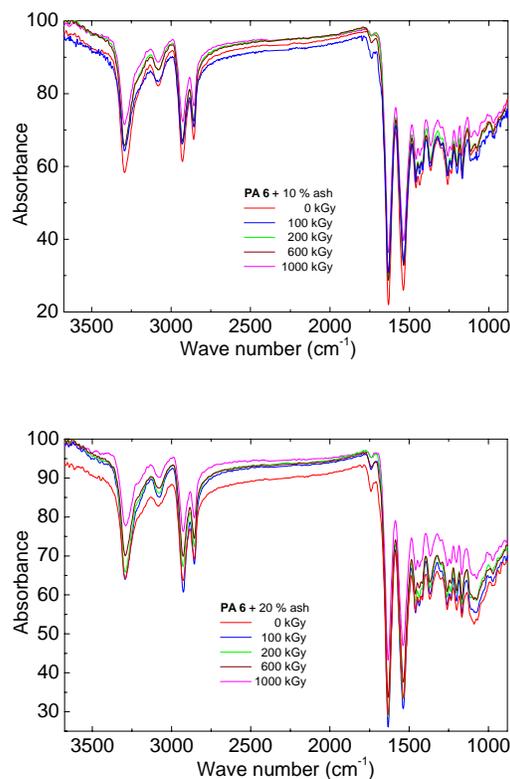


Fig. 2. Spectral modifications in PA 6 modified with rice husk ash in two concentrations after electron beam irradiation at various doses.

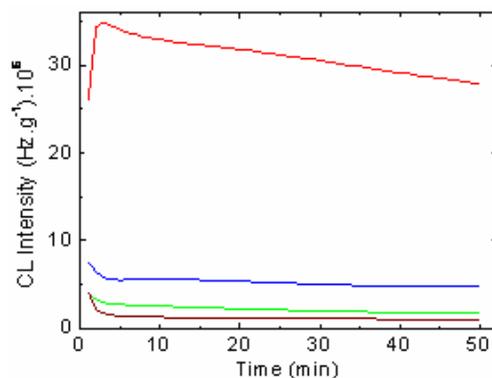


Fig. 3. Chemiluminescence curves recorded for PA 6/rice husk ash composites at different filler concentrations subjected to electron beam dose of 100 kGy. (red) 0%;(blue) 10%; (green) 20 %; (brown) 30 %.

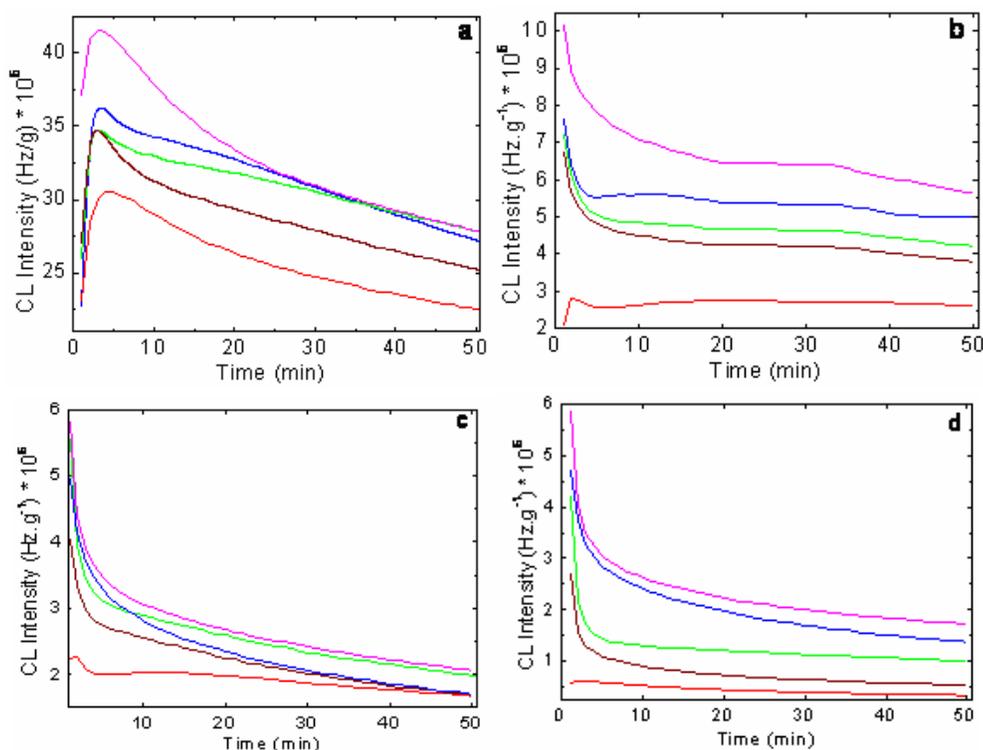


Fig. 4. CL curves drawn for PA 6/rice husk ash composites at different doses for filler concentrations: (a) free; (b) 10 %, (c) 20 %; (d) 30 % (-) 0 kGy; (-) 100 kGy; (-) 200 kGy; (-) 600 kGy; (-) 1000 kGy.

References

- [1] T. Karstens, V. Rossbach, Makromol. Chem., **190**, 3033 (1989).
- [2] K. Johanson, PhD thesis, Royal Institute of Technology, Stockholm, 1999.
- [3] Z. Wang, P. Y. Deng, J. H. Sun, M. X. Ding, Radiat. Phys. Chem., **65**, 87 (2002).
- [4] S. Dadbin, M. Frounchi, D. Goudarzi, Polym. Degrad. Stab. **89**, 436 (2005).
- [5] R. Sengupta, S. Sabharwal, A. K. Bhowmick, T. K. Chaki, Polym. Degrad. Stab., **91**, 1311 (2006).
- [6] C. Rosales, S. López-Quintana, I. Gobernado-Mitre, J. C. Merino, J. M. Pastor, Nucl. Instrum. Meth. in Phys. Res., **B 265**, 156 (2007).
- [7] T. Zaharescu, L. G. A. Silva, S. Jipa, W. Kappel, Radiat. Phys. Chem., **79**, 388 (2010).
- [8] R. D. Davis, J. W. Gilman, D. L. VanderHart, Polym. Degrad. Stab., **79**, 111 (2003).
- [9] C. Rosales, S. López-Quintana, I. Gobernado-Mitre, J.

- C. Merino, J. M. Pastor, Nucl. Instrum. Meth. in Phys. Res., **B 265**, 156 (2007).
- [10] H. Cartledge, C. A. Baillie, J. Mater. Sci., **34**, 5099 (1999).
- [11] R. Sengupta, S. Sabharwal, A. K. Bhowmick, T. K. Chaki, Polym. Degrad. Stab., **91**, p. 1311 (2006).
- [12] P. van Rijswijk, K. S. Lindstedt, D. P. N. Vlasveld, H. E. N., Bersee, Polym. Testing, **25**, 873 (2006).
- [13] A. Ulrich, A. Handge, Hedicke-Höchstötter, V. Altstädt, Polymer, **51**, 2690 (2010).
- [14] A. Grozdanov, G. Bogoeva-Gaceva, J. Thermoplast. Composite Mater., **23**, 99 (2010).
- [15] D. Bhattacharyya, P. Maitrot, S. Fakirov, eXPRESS Polym. Lett., **3**, 525 (2009).
- [16] L. Lánská, L., Matisová-Rychlá, J. Rychlý, Polym. Degrad. Stab., **72**, 249 (2001).
- [17] P. Cerruti, C. Carfagna, J. Rychlý, L. Matisová-Rychlá, Polym. Degrad. Stab., **82**, 477 (2003).
- [18] B. J. Lyons, L.C. Glover Jr., Radiat. Phys. Chem. **37**, 93 (1991).
- [19] B. Mizusawa, T. Baba, Nucl. Instrum. and Meth. in Phys. Res., **B 208**, 106 (2003).
- [20] L. Mészáros, T. Czvikovszky, Radiat. Phys. Chem., **76**, 1329 (2007).
- [21] M. C. Evora, L. D. B. Machado, V. L. Lourenço, O. L. Gonçalez, H. Wiebeck, L.G. de Andrade e Silva, Thermochim. Acta, **67**, 337 (2002).
- [22] T. Zaharescu, L. G. A. Silva, S. Jipa, W. Kappel, Radiat. Phys. Chem., **79**, 388 (2010).
- [23] D. J. Houston, Rice – Chemistry and Technology; American Association of Cereal Chemists, Minnesota, USA, Cap **12**, 301 (2000).
- [24] M. F. Souza, W. L. E. Magalhães, M. C. Persegil, Mater. Res. **5**, 467 (2002).
- [25] S. Jipa, T. Zaharescu, R. Setnescu, I. V. Popescu, C. Oros, Optoelectr. Adv. Mater., Rapid Commun., **3**, 845 (2009).

*Corresponding author: traian_zaharescu@yahoo.com