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Radiation thermoluminescence investigation of structural modifications of polymers

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The high energy irradiation causes significant structural modifications on the backbones of polymers. The radiation thermoluminescence method of investigation reveals the types of defects that are formed as electron traps. The recombination of released electrons with positive defects expels a quantum. The RTL intensity varies with temperature and distribution of gap depths. The difference between various sorts of polyolefins may be demonstrated by the position of maxima on the recorded glow curves.

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1. Introduction

The irradiation of polymers induces several modifications in the structure because of the deposited energy on macromolecules. The investigations on radiation thermoluminescence (RTL) on polymers have received a constant attention due to its potential in the description of major changes induced during the action of ionizing radiation [1-3]. The application of polymers in economic areas requires detailed information, with which the manufacturers can directed the technological processing to the quality product. From emission RTL records (glow curves), the estimation of degradation level is possible.

Radiation thermoluminescence being defined as the emission of light from solid state materials caused by thermal recombination of previously trapped electrons and holes is a suitable methods for characterization of the alterations in polymer materials. Electrons and holes formed by exposure to radiation may become separated and trapped in energy wells at defect or impurity sites such that the probability of recombination by either radiative or nonradiative processes is very low. If the temperature is raised thermal energy may become sufficient to allow the electrons and holes to escape from the traps and recombine. When this occurs by a radiative process then, as the temperature is increased, the sample will begin to emit light and continue to emit until all of the traps are emptied. Glow curves of emission intensity as a function of temperature give information on trap energies, which are directly related to the material structure [4, 5].

2. Experimental

This study was performed on various sorts of polymers (polyethylene, polypropylene, polytetrafluorethylene), whose characteristics illustrate the initial differences between the studied materials and they were reported in earlier papers [6, 7].

The exposure to γ-radiation of studied materials was performed in air, at room temperature in a ^{137}Cs irradiator (GAMMATOR – USA) at a dose rate of 0.46 kGy/h. The RTL measurements were done after the elapse of exposure period. The irradiation dose was calculated after the exposure of Fricke dosimeter together with polymer samples.

The recording of RTL signals was done using a cryostat coupled with a photomultiplier EMI-9558 QA and a recorder ORION-EMG. The increase in temperature was measured with a thermocouple iron/constantan at a heating rate of 90 ^{o}C/min.

3. Results and discussion

The RTL emission spectra from irradiated specimens are presented in Figs. 1 and 2. The glow curves present characteristic shape in connection with the induced modifications.

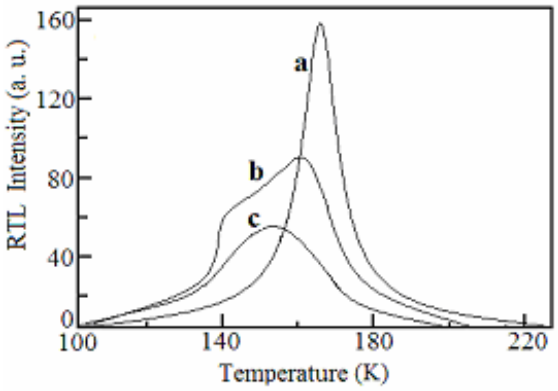

Fig. 1. Glow curves for (a) low density polyethylene, (b) high density polyethylene and (c) polypropylene.

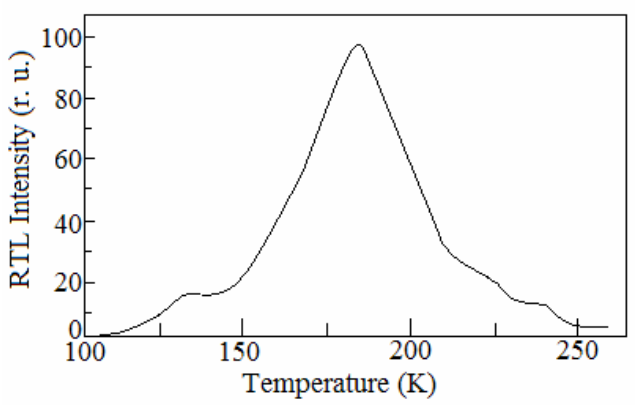

Fig. 2. Glow curve for polytetrafluorethylene.

As it may be noticed from figure 1, the low density polyethylene specimen exhibits two peaks at 145 and 173 K, while high density polyethylene shows the glow peaks at 131 and 158 K. Polypropylene has one peak placed at 143 K. These maxima can be ascribed to various categories of phenomena. The peaks situated at low temperatures appeared due to the relaxation of macromolecular chains, when the scavenged charges are easy released. In the cases of LDPE and HDPE, these maxima are determined by γ transitions caused by the rotation of the 4 four methylene groups from the main backbone and for PP, maximum is appeared after the transition δ resulting from the rotation of methyl moieties around the axis, which is perpendicular on the chain.

For polytetrafluorethylene, four maxima are recorded at 139K, 173 K, 205 K and 253 K. Their relative intensities are 50:200:30:1. The maxima placed at 139 K and 173K presented an increase with dose up to 30 kGy, followed by a sharp decrease (Fig. 3). The maximum at 205 K, a continuous increase in the RTL intensity could be observed followed by a pseudoplateau (Fig. 3). Due to the light intensity of maximum at 253 K, its variation was not taken into consideration.

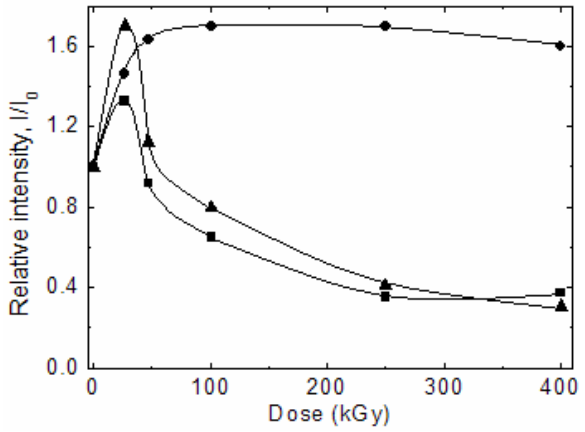

Fig. 3. Change in the maximum intensities for irradiated PTFE (■) 139 K, (▲)173 K, (●) 205 K.

For the two types of polyethylene, the maximum intensities at 173 K (LDPE) and 158 K (HDPE) decrease as the irradiation dose is higher (Fig. 4).

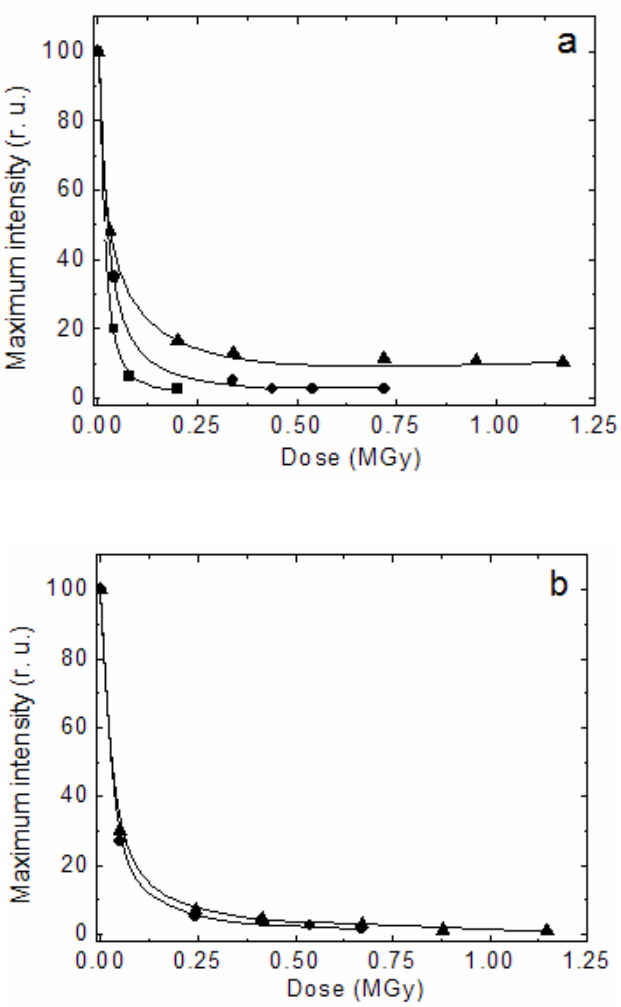

Fig. 4. Changes in the maximum intensities for irradiated polyolefins (a) (▲) 145 K for LDPE; (●) 131 K for HDPE; (■) 143 K for PP; (b) (●) 173 K for LDPE; (▲) 158 K for HDPE.

The radiothermoluminescence mechanism follows several stages: the ionizing of polymer, the trapping of charges at low temperature into different depth gaps and their recombination during the hating of samples; the traps that are formed along the radiation exposure will be emptied in the order of increased depth. For polyolefins, the nature of electron traps that are involved in the RTL emission at low temperatures would be the unsaturated entities placed on macromolecular backbone [8]. Our results contradict this assessment and the correlation between the concentration of unsaturation and the RTL maximum intensities is presented in Fig. 5.

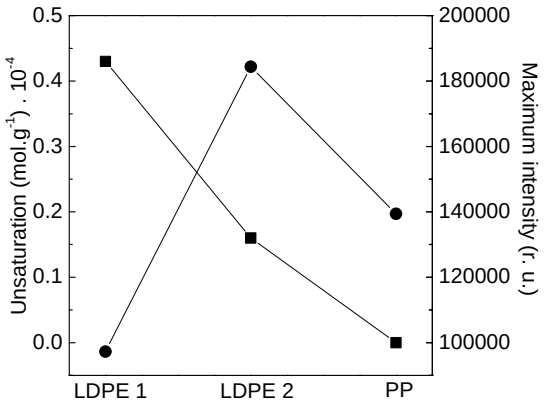

Fig. 5. The values of unsaturation and maximum intensities at low temperatures for some polyolefins.

The RTL maxima in the emission spectrum of polytetrafluorethylene at 139 K and 173 K appear from the same type of traps: the peroxyl radicals that are formed during radiochemical oxidation of substrate, due to the positive electron affinity [9, 10]. The γ relaxation of polymer matrix takes place on the temperature range between 140 and 180 K [11] and the remote of electrons from traps is promoted by the rotation of the four CF_2 groups placed in the amorphous zone, where molecular movement is more probable than in the crystalline regions. Similar evaluation of RTL emission can be remarked for polypropylene, where the high content of CH_3 groups is associated with a great value of RTL intensity.

The structure of polymer influences the molecular motion, which is involved in the emission of radiationthermoluminescence. In Fig. 6 the activation energies required for molecular motion in studied polymers are presented.

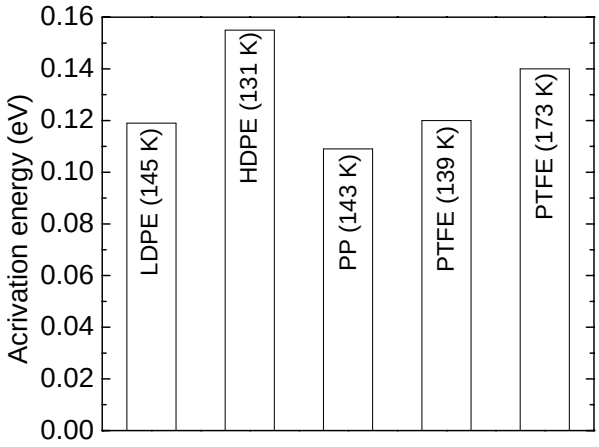

Fig. 6. The activation energies for RTL emissions from some γ-irradiated polymers

For γ-exposed polyolefin samples, the RTL intensity decrease sharply after irradiation at low doses (50 kGy). This dose does not exceed the gel dose. It means that the problem of movement hindering is not real one, because polyethylene does not start to be crosslinked. It may be assumed that the oxidative degradation must be responsible for this decrease in the emission intensity. The main oxidation product that can be involved in radiothermoluminescence emission is carbonyl-containing molecules. Fig. 7 demonstrated the severe modification in RTL intensity at higher temperature caused by oxidative degradation of material.

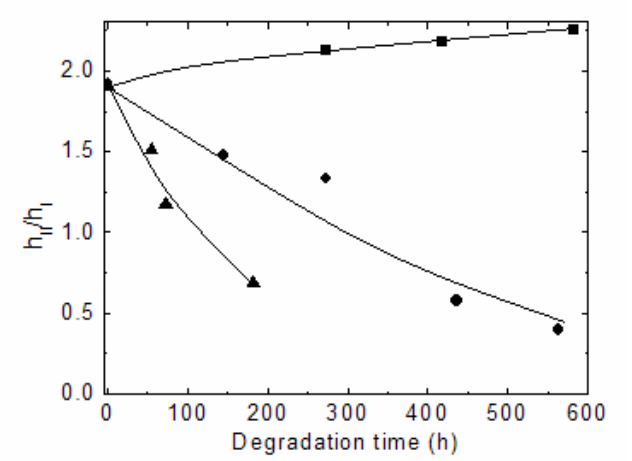

Fig. 7. The modification of maximum height ratio for LDPE at various degradation temperatures (■) 80 ^{0}C; (●) 95^{0}C; (▲) 104 ^{0}C.

The proof for the involvement of peroxyl radicals in the radiative RTL emission of PTFE samples is illustrated in Fig. 8, where the increase of temperature is accompanied by the significant diminishing in the concentration of $RO_2^{\cdot}$ radicals. These oxygenated entities act as electron traps because of their high electronegativity. The recombination centers emitting RTL quanta appear by the reaction of primary radicals, hydrocarbon or fluorocarbon moieties, with molecular oxygen that exists or penetrates material during irradiation.

4. Conclusions

The radiolysis of polymers contributes to the generation of new structures (oxygenated products and double bonds), which act as efficient traps for expelled electrons. The recombination of defects being proportional with the measured emission can be designated as the process through which the intermediates may be counted. The RTL method is able to get distinctions between the different radiochemical comportments of polymers in relation with their stability. Various trap depths depict the capture strength of intermediates that are formed during irradiation, especially oxygenated and unsaturated structures.

References

[1] D. R. Vij, Thermoluminescent Materials, PTR Prentice Hall, Englewood Cliffs NJ (1993).
[2] K. Mahesh, P. S. Weng, C. Furetta, Thermoluminescence in Solids and its Applications, Nuclear Technology Publishing, Ashford UK (1989).
[3] L. Zladkevich, Radiothermoluminescence and Transitions in Polymers, Springer, New York, 1987.
[4] A. E. Blake, A. Charelsby, K. J. Randle, J. Polym Sci., Polym. Lett. Ed., **11**, 165 (1973).
[5] A. Markiewicz, R. J. Fleming, J. Polym. Sci., Part B, Polym. Phys. **24**, 1713 (1986).
[6] S. Jipa, T. Zaharescu, W. Kappel, R. Setnescu, C. Oros, Proc. 14 World Forum on Advanced Materials, Nara, Nara University Press, 2006, p. 224.
[7] S. Jipa et al., Materiale Plastice (Bucharest), **25**, 27 (1988).
[8] L. Boustead, A. Charlesby, Proc. Royal Soc. (London), A315, 271 (1970).
[9] N. S. Hush, Y. Holpe, Trans. Faraday Soc. **51**, 600 (1955).
[10] Y. R. Hoyland, L. Goodman, J. Chem. Soc. **36**, 21 (1962).
[11] V. G. Nikolski, V. V. Kuakov, Vysokomol. Soed., **B26**, 118 (1984).

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