

# Chemiluminescence study on $\gamma$ -irradiated EPDM/IIR blends

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The oxidation degradation of gamma exposure on various compositions of ethylene-propylene diene terpolymer/isoprene rubber (EPDM/IIR) is presented. The polymer samples consisting of both elastomers (mixing ratios 25:75, 50:50, 75:50) were subjected to radiochemical modification in air, in water and in salt solution (5 % NaCl) at various absorbed doses (10, 20 and 50 KGy), in order to investigate the progressive radiation damage of materials in function of radiation resistance of components. The thermal stability of blends was tested by isothermal chemiluminescence method. From the dependences of CL intensities on investigation time the kinetic parameters for thermal oxidation of irradiated samples were calculated and discussed. The contribution of each component to the progress of radiooxidative degradation is evaluated.

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## 1. Introduction

Butyl and EPDM rubbers are often used in several applications among which are various types of membranes, joint connections, automotive sealants. The problem which must be solved is the long life of items in the safety condition of usage. The inconsistency in properties can be attributed to a different degree of compatibilization in the blend system. A heterogeneous blend usually results when two chemically dissimilar rubbers are mixed. Several investigators have examined the stability of blends [1-4]. Many papers have been established the level of effects which are important in determining the endurance properties of such kind of blends [5]; other reports have presented detailed investigations on the compatibility of rubber blends [6-8].

The radiochemical compatibilization of binary systems has been a topic of interest for practical purposes. They show a high thermal or radiation stability (EPDM) or remarkable mechanical properties (both materials). Particular applications like gaskets, electrical insulators require certain characteristics that can be easily obtained by radiation processing at suitable irradiation conditions and appropriate material composition.

The current trends in the development of polymers exhibiting high characteristics are obviously illustrated by the increasing number of specific studies on radiation-processed materials. Practical support for these kinds of studies is provided by the operation of polymers under various hard conditions. The resistance to the damaging action of degrading agents like oxygen, water, salt solution, or chemical reagents and significant energy transfer (heat, ionizing radiation) becomes the main problem of long-term service. To avoid an advanced degradation of polymer products, the crosslinking of macromolecular compounds can be adopted. The competition between scission and crosslinking, the

blending formulation, the dose rate, and the total dose will influence the final properties of processed mixtures.

Crosslinking radiation processing of polymers due to the ionizing ray exposure provides increased stability and improved mechanical resistance [9-10]. Under the action of high energy radiation, ethylene-propylene elastomers are able to form intermolecular links, especially in the presence of polyfunctional compounds, giving a proper crosslinking level with a minimum degree of oxidation [11-13].

In this paper the main radiochemical effects of  $\gamma$  - exposure of ethylene-propylene diene terpolymer/ isoprene rubber (EPDM/IIR) blends are presented. The experimental conditions simulate the long term operation of this kind of products.

## 2. Experimental

Ethylene-propylene-diene terpolymer (EPDM) containing 29 % propylene and 3.5 % ethylidene norbornene was supplied by ARPECHIM Pitesti (Romania). Isoprene rubber was BK 2045 (Russia) type initially containing 2 % unsaturation.

These three compositions, EPDM/IIR = 25/75, 50/50 and 75/25, were prepared by intimate mixture in a roll mill. After homogenous blends were obtained, the plaques of all samples were pressed in an adequate equipment by heated-plates unit at 150°C for 10 minutes.

The irradiation was performed at room temperature, under various conditions (air, water and salt solution), in an irradiator Gammator with <sup>137</sup>Cs source. The dose rate was 0.4 kGy/h.

Isothermal chemiluminescence measurements were performed in air at 200 °C in a Chemiluminograph CL-934 M, made in our laboratory. Details on equipment and procedure were previously presented [14]. The EPDM/IIR blends samples were placed in the oven of CL equipment.

### 3. Results

The chemiluminescence dependencies of emitted intensity on thermal degradation time are presented in Figs. 1-3. From these records, the main kinetic parameters, oxidation induction time and oxidation rate on the propagation step of thermal degradation are presented in Table 1.

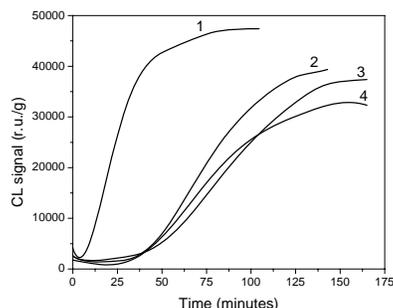


Fig. 1. CL curves recorded at 200 °C from EPDM/IIR blends  $\gamma$ -irradiated (10KGy) in air, for various ratios EPDM:IIR: 1- 100:0; 2- 25:75; 3-50:50; 4-75:25.

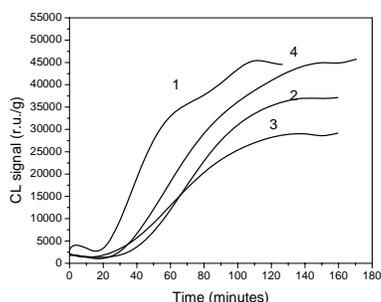


Fig. 2. CL curves recorded at 200 °C from EPDM/IIR blends  $\gamma$ -irradiated (10KGy) in water, for various ratios EPDM:IIR: 1- 100:0; 2- 25:75; 3-50:50; 4-75:25.

The thermal regime of experiments was selected to obtain significant values for oxidation rate, the parameter which depicts the thermal strength under all service conditions. Depending on the type of environment, these values characterize the ability of materials to resist on the simultaneous attack of heat, ionizing radiation and oxidants (oxygen, water radiolysis products).

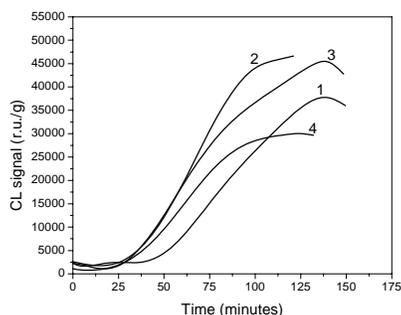


Fig. 3. CL curves recorded at 200 °C from EPDM/IIR blends  $\gamma$ -irradiated (10KGy) in salt solution, for various ratios EPDM:IIR: 1- 100:0; 2- 25:75; 3-50:50; 4-75:25.

Table 1. CL parameters of irradiation of EPDM/IIR blends in various irradiation environments.

Ratios EPDM:IIR	Air	Distilled water	5%NaCl aqueous solution
10 KGy of $\gamma$ -dose			
<b>Oxidation induction time (min)</b>			
100:0	9	34	50
25:75	42	32	38
50:50	46	41	33
75:25	39	24	23
<b>Rate of oxidation (r.u./g.min)</b>			
100:0	1639	984	516
25:75	584	558	815
50:50	430	406	407
75:25	281	602	399

In Fig. 4, the initial values of CL intensities are figured, because it demonstrates the existence of long life free radicals after  $\gamma$ -irradiation.

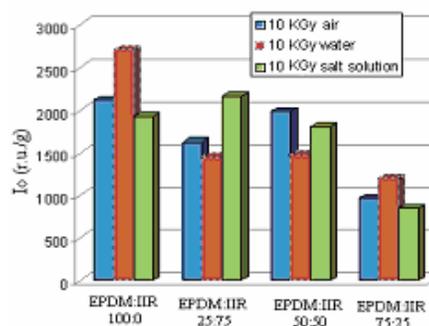


Fig. 4. Values of initial CL intensities for all studied types of samples.

### 4. Discussion

The radiation stability of studied polymer blends depends on the molecular structure of component.

However, the stability of ethylene-propylene terpolymer is higher than the similar feature of butyl rubber because it contains higher proportion of tertiary carbon atoms in the chain of macromolecules. The unsaturation (residual double bond) contained in this last material promotes oxidation, which will be accompanied by the attack of peroxy radicals (the precursors in the oxidative degradation) on the ethylene-propylene terpolymer chains, the most reactive component. The suggested steps in the main reactions involving studied polymers are depicted in Fig. 5.

Butyl and EPDM rubbers participate to several reactions through which the oxidation products are generated. The samples which were irradiated in air present the trend of oxidation by bond scission as the content of butyl rubber in increasing (Fig. 1). The similar oxidation induction periods for the polymer specimens that were irradiated in distilled water illustrate the contribution of butyl component for the initiation of oxidation. The oxidation rates are different depending on the blend

formulations, due to the specific contribution of each blending components.

The  $\gamma$ -exposure of EPDM/IIR blends in aqueous salt solution gathers the CL curves on the initial period of thermal degradation because the chloride ions promotes crosslinking in the ethylene-propylene phase [15].

During irradiation, the free radicals that are formed according with the scheme presented in Fig. 5, are in a competition for the reaction with molecular oxygen, by which the degradation progresses. The different contents of components determine different rates of oxidation for each type of macromolecules. The thermal degradation of unirradiated or  $\gamma$ -processed EPDM/IIR blends follows the Bolland and Gee mechanism [16], proving that this process takes place as radical one.

The interaction between the components of these blends is reflected in the differences in the kinetic parameters. The susceptibility of components to oxidation is increased either due the increased doses, or due to the irradiation environment.

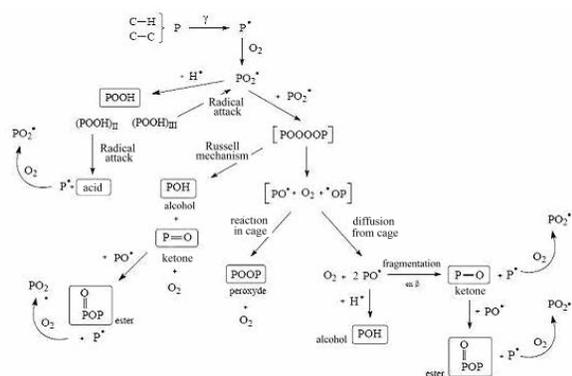


Fig. 5. Main steps in the mechanism of polymer radiooxidation.

## 5. Conclusions

Irradiation of polymer blends consisting of ethylene-propylene-diene terpolymer and butyl rubber has pointed out a new material with improved thermal and radiation stability can be obtained at a relatively low dose. By derivation of time dependence of chemiluminescence it is possible to evaluate the oxidation resistance. Gained properties suggest the availability of radiochemical processing for large industrial application.

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