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RADIOCHEMICAL PROCESSING OF EPDM/NR BLENDS

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ABSTRACT

Radiochemical crosslinking of polymer systems consisting of ethylene-propylene terpolymer (EPDM) and natural rubber (NR) is studied. Three binary blends (3:1, 1:1 and 1:3 w/w) were exposed to γ–rays (^{137}Cs) at various doses (up to 300 kGy). The gel content of irradiated mixtures were determined. Oxidation stability was evaluated by isothermal oxygen uptake in air at normal pressure. The contribution of each component to the oxidation stability of stud-ied blends is discussed. The application of first derivative of $[O_2]= f(t)$ to the estimation of stability under oxidation is presented.

INTRODUCTION

Polymeric materials are widely used as cable insulation and jacketing in electrical cables of nuclear power plants. In such units, the cables and seals may be exposed to low rate irradiation at room temperature. Their durability is estimated at about 30 years [1]. Particular service illustrated by accidental events requires suitable behavior under hard operation conditions. Long time duty is based on certain properties that guaranty the high performances of units. In spite of low risk of

nuclear equipment for power transmission and instrumentation, evaluation of chemical stability of polymers must gain appropriate attention. Various polymer like mono-component systems or blends have been checked by means of accelerated tests in order to found satisfactory formulas for products [for example, 2-5].

Many polymer blends that are used in degrading environments have been studied. Some of them present the benefit of multicomponent mixtures on mechanical [6], electrical [7] or radiochemical [8] properties. These systems are of growing industrial importance. Crosslinking and degradation are the main processes that are intensively investigated because they are involved in the prediction of material durability.

The present work intends to provide information regarding changes in chemical structure provided by γ-irradiation of EPDM/NR blends.

EXPERIMENTAL

Ethylene-propylene-diene terpolymer (EPDM) containing 3.5% ethylidene norbornene and 29% propylene was supplied by ARPECHIM Pitesti (Romania). Natural rubber (RSS_1, Malaysia) contained 96% unsaturation. These polymers were not subjected to any purification prior mixing and irradiation, because it was intended to work under industrial conditions. Samples were prepared by solvent ($CHCl_3$) removal from mixed polymer solutions. Gel content was determined by reflux boiling for 24 hours in o-xylene. Oxygen uptake evaluation was performed as isothermal and isobaric measurements, according to the procedure published earlier [10]. All experiments were carried out a few minutes after the end of irradiation.

Exposure to γ-radiation was managed in a GAMMACELL facility provided with ^{137}Cs source in air at room temperature. The dose rate was 0.54 kGy/h. Round aluminum trays supported the thin films (~0.025g) of blended polymers during irradiation and oxygen uptake measurements.

RESULTS AND DISCUSSION

Polymers can be characterized by means of their behavior under the action of ionizing radiation [2, 10]. Some polymers, like polyethylene, ethylene-propylene elastomers can be crosslinked by exposure to high energy radiation. Polymers belonging to the degrading class materials, for example natural rubber, never increase their insoluble fraction. This means that the competition between scission and crosslinking will change the average number of crosslinks per molecule.

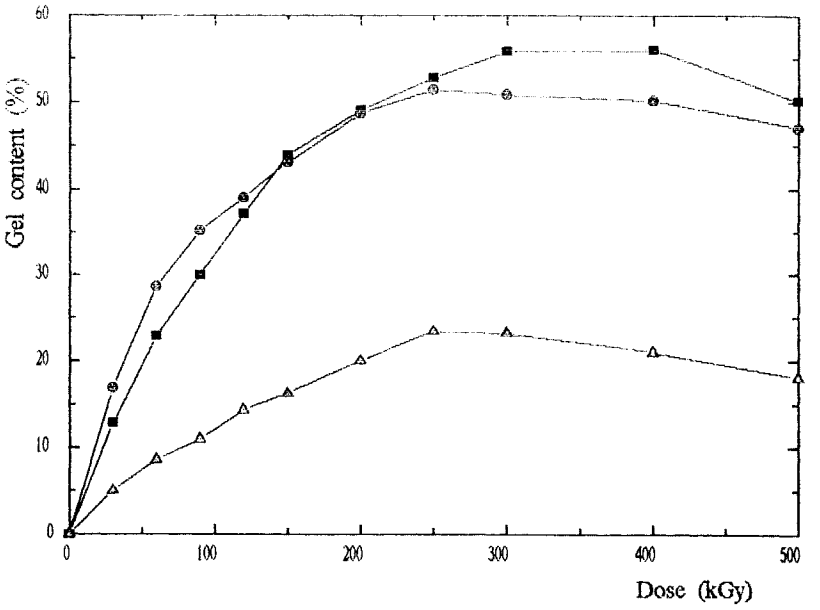

Figure 1. Dependence of gel content on irradiation dose for three blending ratios

(■) EPDM/NR = 3:1; (●) EPDM/NR = 1:1; (▲) EPDM/NR = 1:3.

An alternative way for the improvement in processability of ethylene-propylene elastomer can be achieved by γ-irradiation of EPDM/NR blends. During the first stage of interaction of radiation with polymer linear energy transfer generates excited molecules which are homolytically split to provide free radicals. They are involved in subsequent reactions, namely recombination or disproportionation. The rates determine the final characteristics of processed material.

As is well known, the amount of the insoluble fraction of polymer is formed by a three-dimensional network. The extent of gel depends on the irradiation dose and on mixture composition (Figure 1). The difference in the radiation stability of both components makes it possible to obtain three curves corresponding to various concentrations of natural rubber component. Thus, an increased quantity of natural rubber decreases the quantity of insoluble part of irradiated material. The contribution of crosslinking and scission simultaneously occurred in both polymers is revealed by the Charlesby-Pinner representation [11] (Figure 2). In spite of the similarity in curve shape, it may be noted that in the first step of exposure the rate of scission exceeds the overall crosslinking rate. This means that a greater part of the free radical quantity is accumulated and reactive

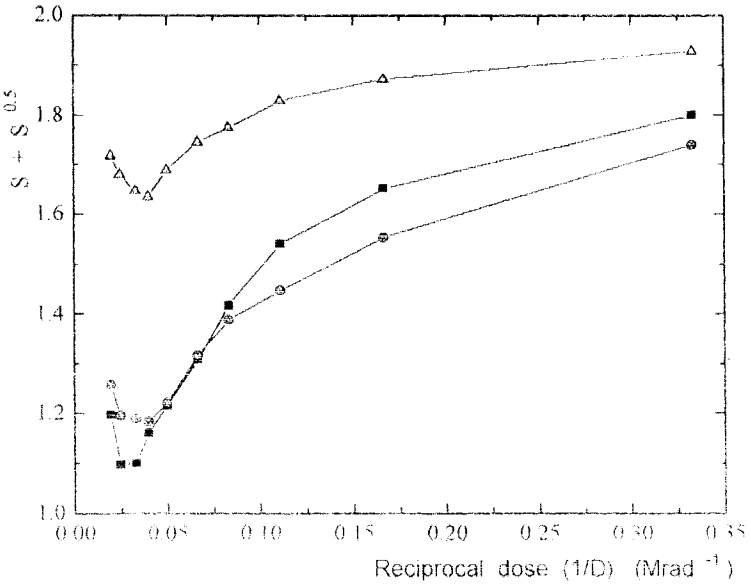

Figure 2. Charlesby–Pinner representation for irradiated EPDM/NR blends (■) EPDM/NR = 3:1; (●) EPDM/NR = 1:1; (▲) EPDM/NR = 1:3.

centers are still far enough from each other to enable fast interaction. The dose is 60 kGy which corresponds to 8.5J transferred energy per gram of polymer. This energy is quite sufficient for bond cleavage, but it is also transferred as kinetic energy to various free radicals. At higher irradiation doses, local concentration of radicals increases significantly so that they are placed closer and closer, enhancing reaction probability. It is reasonable to suppose that all kinds of radicals can be grafted of the most stable macromolecules (EPDM). Over the last stage of irradiation, tertiary and quaternary carbons are susceptible to provide new radicals as double bonds belonging to natural rubber do constantly.

Irradiation of mixed polymer systems is always accompanied by oxidation, if oxygen is present. Peroxyl radicals can be formed by reaction of free radicals and polymer macromolecules with molecular oxygen, according to the mechanism proposed by Bolland and Gee [12]. Initially, oxygen is supplied by the material itself as solved O_2. While irradiation takes place, gaseous oxygen diffuses into the material and oxidation is promoted. The competition between crosslinking and oxidation influences the behavior of the irradiated samples. Figure 3 presents changes in the oxygen uptake and oxidation induction time determined on

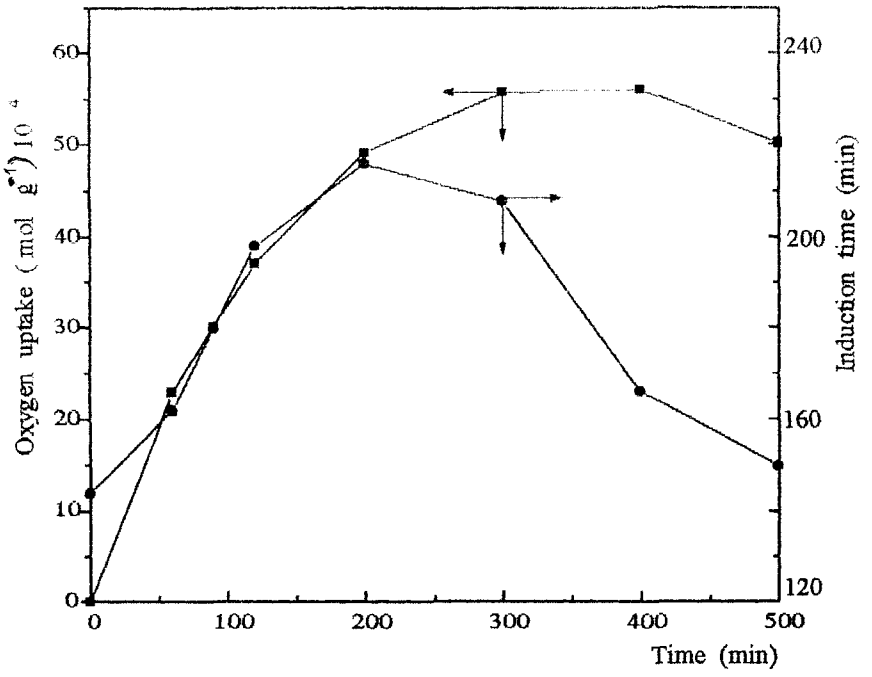

Figure 3. Changes in oxygen uptake and in oxidation induction time for irradiation of EPDM/CN=3:1 samples at various doses.

EPDM/NR=3:1 at various doses. It can be observed that gel content and oxidation induction time (OIT) increase over the first 200 kGy. Then, the insoluble fraction decreases more smoothly than OIT, because the lower molecular weight allows oxygen to penetrate more easily.

Unirradiated samples of EPDM/NR blends present similar sigmoidal shape, but the increase in consumed oxygen quantity is different. The oxidation rate of various compositions of tested blends decreases when the natural rubber content rises (Figure 4). Low diffusion coefficient of natural rubber explains this behavior. The greater content of natural rubber hinders new molecular oxygen to be provided into the inner layers of polymer film samples. The first derivative of oxygen consumption as a function of time points out that the most important period in oxidation of polymers is the time of peroxyl accumulation (Figure 5). It occurs at a different rate, depending on the composition of the material. It can be remarked that the same order in increase of the weight proportion of natural rubber is found in the se-

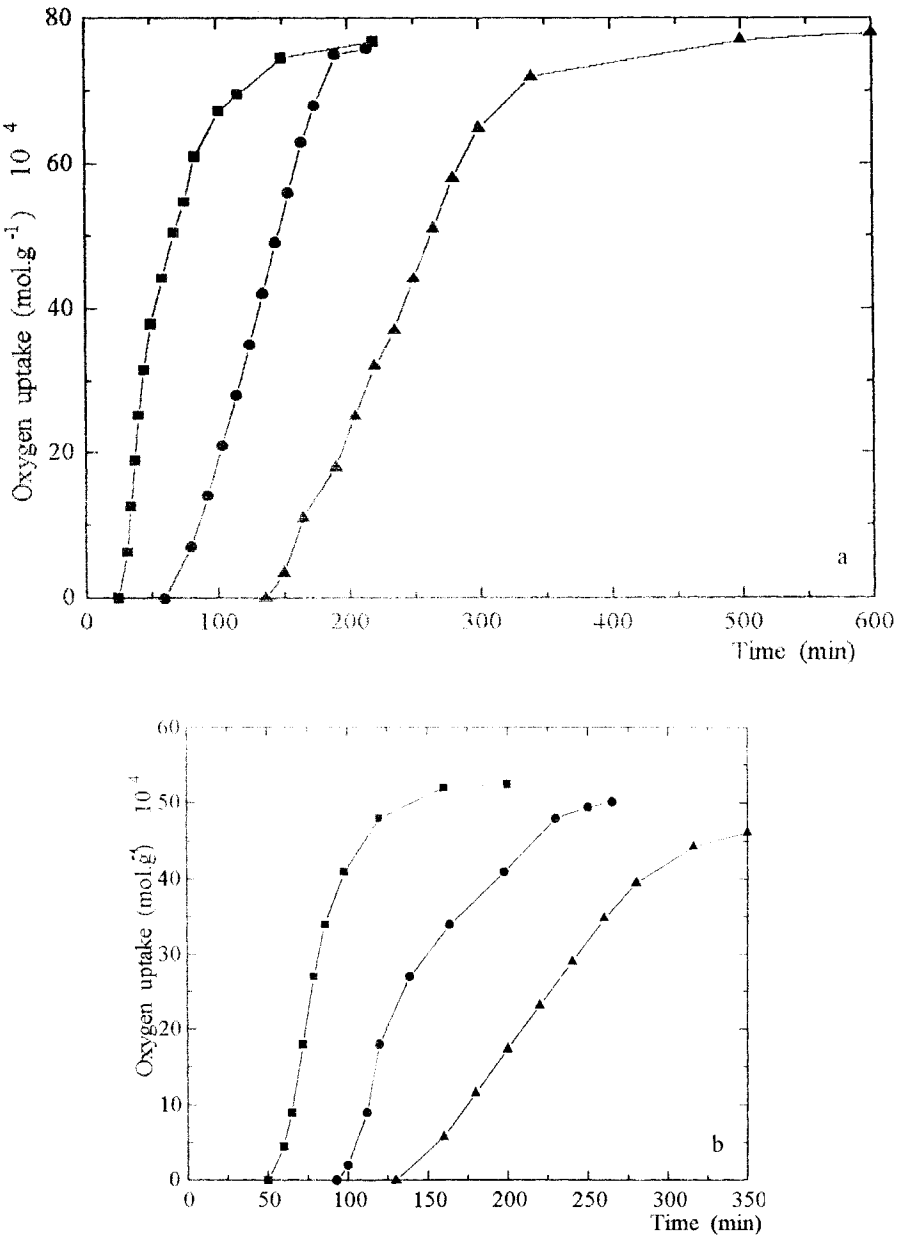

Figure 4. Time evolution of oxygen uptake for unirradiated EPDM/NR blends (a) EPDM/NR = 3:1; (b) EPDM/NR = 1:1; (c) EPDM/NR = 1:3. (■) 180°C; (●) 170°C; (▲) 160°C.

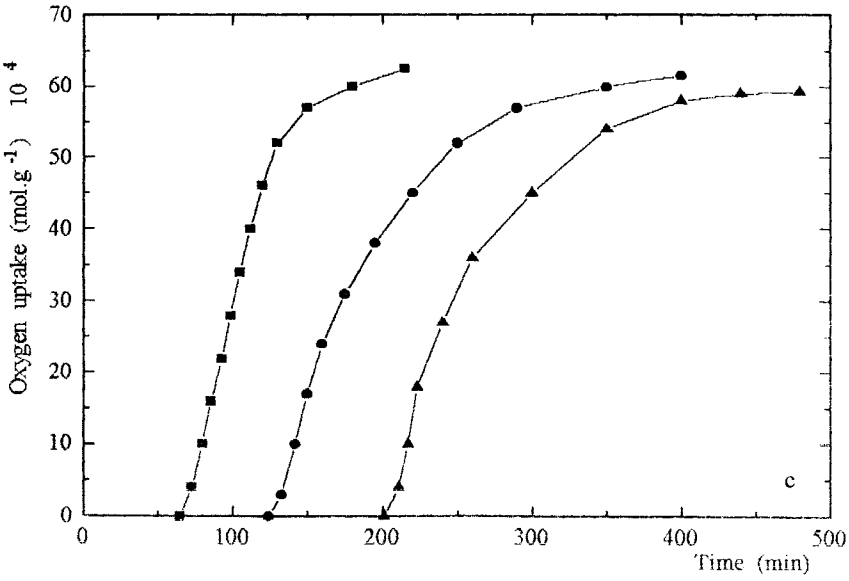

Figure 4. Continued

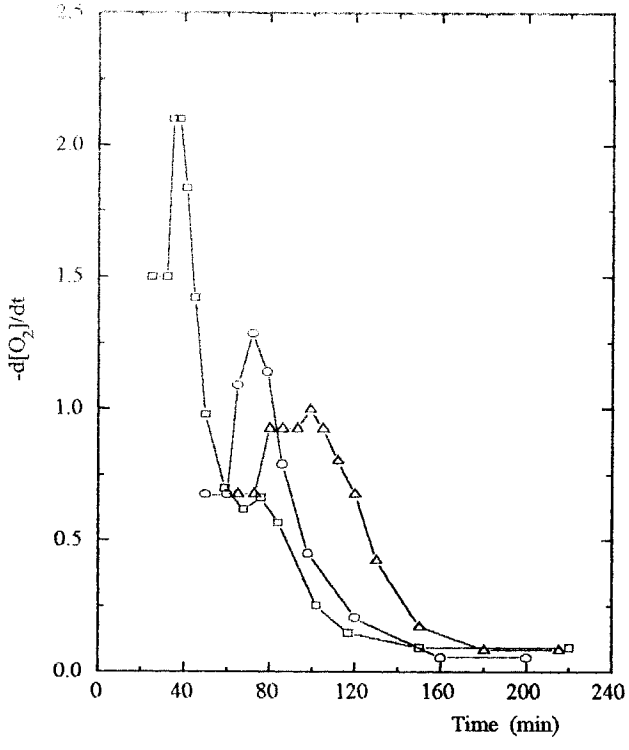

Figure 5. First derivative of time dependency of oxygen uptake for isothermal measurements at 180°C

(■) EPDM/NR = 3:1; (●) EPDM/NR = 1:1; (▲) EPDM/NR = 1:3.

Table 1. Some Kinetic Characteristics of γ-irradiated EPDM/NR Blends at 160°C

EPDM/NR sample	Dose (kGy)	v_{ox} (mol $O_2.g^{-1}.sec^{-1}$) $.10^7$	τ_{ox} (min)
3:1	0	6.8	136
	60	5.5	163
	150	4.9	220
	250	5.2	192
	400	5.6	166
1:1	0	7.7	150
	60	8.1	131
	150	8.6	118
	250	9.7	92
	400	10.1	78
1:3	0	10.2	201
	60	10.6	120
	150	11.8	76
	250	12.1	51
	400	12.3	32

quence of peaks belonging to $d[O_2]/dt$ curves. The periods corresponding to a high rate accumulation of $RO^{\bullet}_2$ radicals increase proportionally with natural rubber content. Then, the competition between generation and depletion of peroxyl radicals determines the rate of degradation over the propagation stage of oxidation. Larger and larger peaks on the first derivatives of oxygen uptake dependencies on time (Figure 5) emphasize the increase in the concentration of higher stability component. It means that the shape and the relative height of $RO^{\bullet}_2$ accumulation peak can be regarded as useful parameters in the evaluation of oxidation stability of polymers.

Exposure of EPDM/NR blends to γ-radiation proves that the ethylene-propylene component offers grafting possibility to the radicals formed by cleavage of natural rubber molecules (Figures 1 and 2). Both polymers contain double bonds, but natural rubber is more susceptible to be degraded. Table 1 points out that optimum composition for crosslinking is EPDM/NR = 3:1. The proper dose for radiochemical compatibilization of the two components of this blend seems to be

150 kGy, because the samples that received this dose show the lowest oxidation rate and the most extensive oxidation induction time. By contrary, higher natural rubber content promotes faster oxidation. Though irradiation generates increased gel content for the first 200 kGy, the accumulation of peroxyl radicals does not recommend the mixing compositions of EPDM/NR other than 3:1 for compatibilization with high energy radiation. However, if a higher dose rate is chosen, a low irradiation dose creates stable materials with quite moderate concentration of oxygenated products.

CONCLUSION

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

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