Radiation Processing of Ethylene-Propylene Rubber

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ABSTRACT: The effects of ionizing radiation on ethylene-propylene copolymer were evaluated over the range of total γ doses up to 500 kGy. The influence of the irradiation dose was investigated by oxygen uptake and thermal analysis. Four testing temperatures (170, 180, 190, and 200°C) and two heating rates between 2.9 and 5.9 K/min were selected for oxygen uptake measurements and thermal analysis, respectively. The competition between crosslinking and scission was examined on the basis of kinetic parameters of postirradiation oxidation. The influence of the momentary concentration of hydrocarbon free radicals is discussed in regard to the contribution of the antagonistic processes of crosslinking and oxidative degradation. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 298–303, 2000

Key words: radiation processing; ethylene-propylene rubber; crosslinking; oxidative degradation

INTRODUCTION

The important changes in polymers resulting from radiation-induced reactions have to be studied for any application in nuclear power stations. Therefore, fast degradation is certainly the main origin in more or less accidental events in the radiation field. The resistence radiation range is sufficiently large[1,2] for polyolefins but the start of material damage occurs very early. Free radicals generated by energy transfer from incidental radiation onto polymers may react with oxygen molecules or recombine to cause degradation or crosslinking in irradiated material.

Ionizing radiation can profoundly modify the macroscopic properties of irradiated polymers. Polymers are used in various areas, for example, cable insulation, seals, gaskets, pipes, hoses, coatings, electrical housings, structural components, and many others. Their lifetime depends intrinsically on the oxidation rate. A lower degradation rate can be obtained by the addition of stabilizers[3–5] or by hardening with peroxide[6] or high energy radiation.[7] Furthermore, in recent years a great deal of work has been carried out on binary blends containing synthetic elastomers as a practical alternative for the increase in material stability.[8–10]

During exposure to ionizing radiation, homolytical bond rupture occurs in polymers and free radicals are produced in sufficient amounts. These intermediates provide oxidative degradation in the presence of oxygen that may limit the durability of the materials. The results of the competition between crosslinking and degradation are reflected in the mechanical and chemical resistance of a processed system. However, good management of irradiation, especially under accelerated electron beams, proved to be a suitable procedure for the improvement of polymer properties.[11]

This article discusses the effects induced in ethylene-propylene (EP) elastomer exposed to γ radiation by the assessment of oxidation resistance and the competitive aspects of crosslinking and degradation of this material.

EXPERIMENTAL

This investigation was carried out on EP copolymer provided by ARPECHIM Piteşti (Romania). This polymer presents a C_2/C_3 ratio of 1.6 (w/w). Its other main characteristics were presented in an earlier article.[12] The polymer material was not subjected to any purification in order to obtain proper data for industrial applications.

Irradiation

The irradiation was performed in air in a ^{137}Cs facility to absorbed doses of 40, 80, 120, 150, 200, and 500 kGy. The dose rate selected for this study was 5.4 kGy/h. The exposed samples were thin films obtained by solvent (CHCl$_3$) removal from polymer solution. The foreseen determinations were promptly performed after the end of irradiation.

Oxygen Uptake Determinations

The resistance to oxidation of processed polymer samples was determined by measurement of the oxygen uptake. The equipment was a laboratory made device presented in a previous article.[13] The EP rubber (EPR) samples were placed on round and thin aluminum plates. All oxygen uptake determinations were performed in isobaric conditions (air at normal pressure). Four testing temperatures (170, 180, 190, and 200°C) were utilized to obtain proper oxidation rates.

The derivatives of the oxygen uptake dependencies on time were obtained according to the procedure presented earlier.[14]

Thermal Analysis

The thermal analysis curves (TG, DTG, and DTA) for the polymer samples were recorded with a Q-1500D (MOM, Budapest) Paulik–Paulik–Erdey derivatograph in a static atmosphere in a temperature range of 20–500°C. The heating rates were selected between 2.9 and 5.9 K/min.

RESULTS

Oxidatability

The most representative dependencies of oxygen uptake on time and their derivatives for radiation processed EP copolymer are presented in Figures
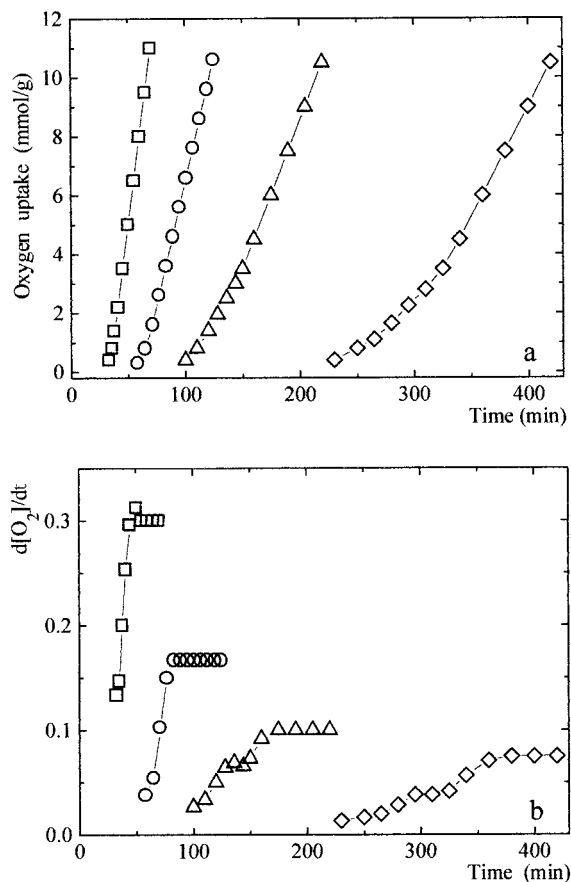

Figure 1 The (a) change of the oxygen uptake and (b) progress in the oxidation rate vs. time for unirradiated EPR at (□) 200°C, (○) 190°C, (△) 180°C, and (◇) 170°C.

1–3. The shape of these curves prove the chain characteristics of polymer oxidation due to free-radical generation. The γ irradiation of elastomer samples modifies the oxidation induction time (OIT). If the unirradiated specimens of EPR exhibit curve distribution according to the thermal resistance (induction and rate of oxidation) at the used temperatures, the increase in free-radical amount diminishes the differences in OIT for the first doses. In Figure 2 small discrepancies between the induction times measured at 170, 180, and 190°C on the exposed samples at 40 kGy can be seen. Similar results were obtained in the irradiation carried out at 80 kGy. At the higher dose (150 kGy) that involves a large energy transfer onto polymer samples a regular increase in the degradation progress accompanied by advanced crosslinking can be noted from Figure 3. The derivatives of the oxygen uptake curves [Figs. 1(b), 2(b), and 3(b)] prove the occurrence of simultaneous processes by the modification in the height
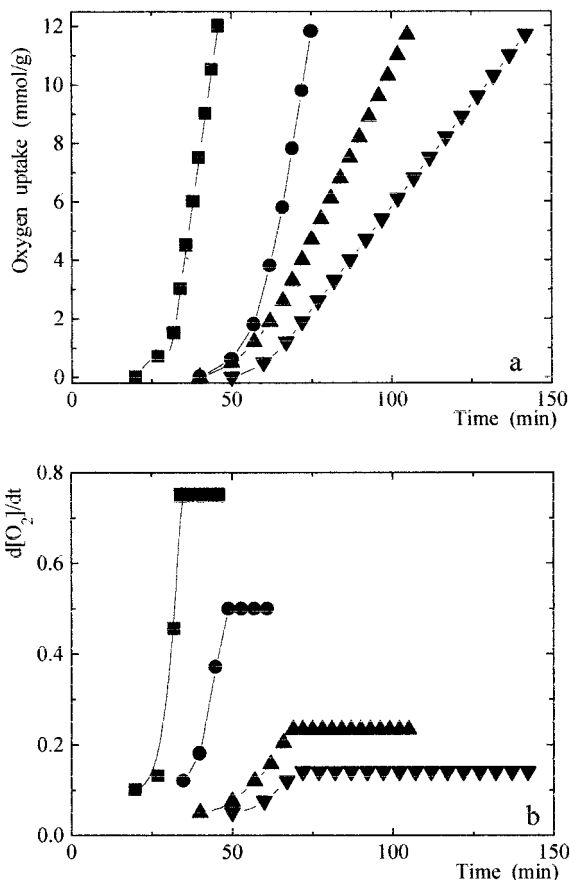
Figure 2 The (a) change of oxygen uptake and (b) progress in the oxidation rate vs. time for EPR irradiated at 40 kGy and (■) 200°C, (●) 190°C, (▲) 180°C, and (▼) 170°C.

and disposition of the maximum oxidation rates for various doses. The competition between crosslinking and oxidation is the main factor that determines the chemical state on every exposure time. It can be remarked that oxidation takes place more slowly at 150 kGy (Fig. 3) than at 40 kGy (Fig. 2). Over this irradiation dose range the crosslinking rate exceeds the rate of degradation because the diffusion of oxygen cannot provide enough O_2 to cause the oxidative damage to progress.[10,12]

Figure 4 displays the influence of the absorbed dose on the thermal behavior of γ-irradiated elastomer samples. The time corresponding to the achievement of the maximum oxidation rate ($t_{inflection}$) was obtained by second-order derivation of the experimental function $[O_2] = f(t)$ according to the method presented in an earlier article.[15] It represents the time when the generation rate of the peroxy radical is equal to the

depletion rate of these main oxidation intermediates. This value provides practical information on the contribution of crosslinking and oxidation to the aging state of materials. Over the first dose range (up to 120 kGy) the decrease in $t_{inflection}$ can be explained by a small contribution of crosslinking to the material stability. The higher the dose, the lower the differences between the thermal instability of the irradiated polymer samples. For the doses exceeding 150 kGy the crosslinking improves the thermal resistance and the $t_{inflection}$ increases smoothly. It can be assumed that at higher doses this pseudoplateau will disappear and a sharp diminishing of $t_{inflection}$ would follow because of the advanced degradation.

The history of polymer samples can be easy cleared up by oxygen uptake measurements that allow the assessment of the evolution of the radical concentration during crosslinking, grafting, or degradation. The availability of free radicals to
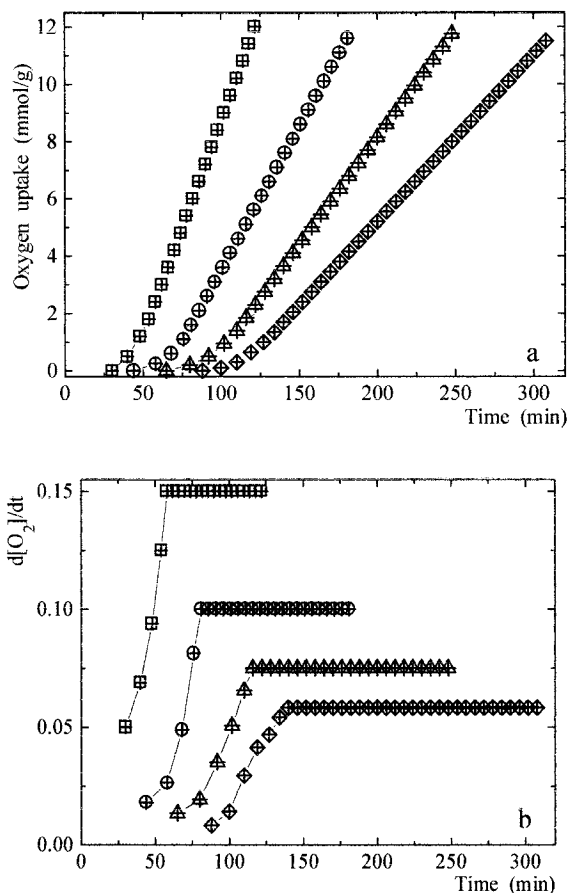

Figure 3 The (a) change of oxygen uptake and (b) progress in the oxidation rate vs. time for irradiated EPR at 150 kGy and (□) 200°C, (○) 190°C, (△) 180°C, and (◇) 170°C.
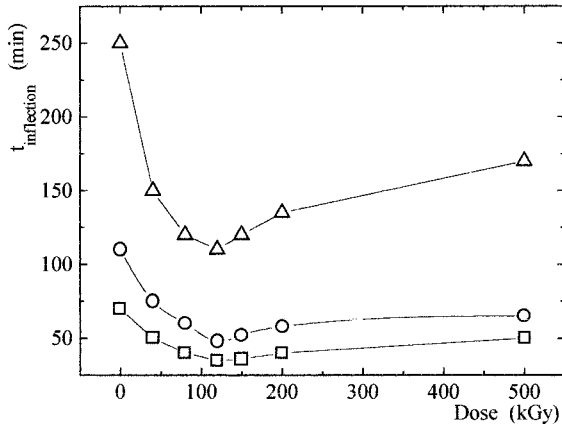
Figure 4 The dependencies of the time corresponding to the maximum oxidation rate on the irradiation dose at ($\square$) 190°C, ($\bigcirc$) 180°C, and ($\triangle$) 170°C.

react with molecular oxygen at various temperatures is described in Figure 5. The movement of free radicals increases with temperature but a proportionality is not followed because of the hindering due to the network buildup. An exponential dependence of the oxygen uptake attained at the maximum oxidation rate on temperature seems to be an appropriate interpretation of the progress in polymer radiochemical oxidation.

Thermal Stability

Figure 6 presents the derivatogram of the unirradiated elastomer. Similar curves were recorded for the other EPR specimens that were exposed to various doses. The EP copolymer displays an exotermic oxidative degradation process with a slight
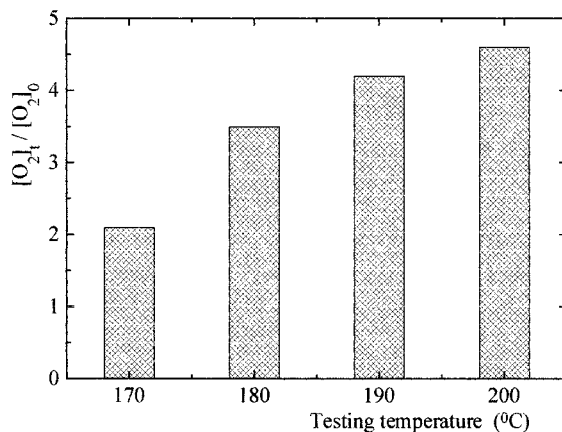

Figure 5 The relative oxygen uptake at the maximum oxidation rate for various testing temperatures. Control, unirradiated specimen; dose, 80 kGy.
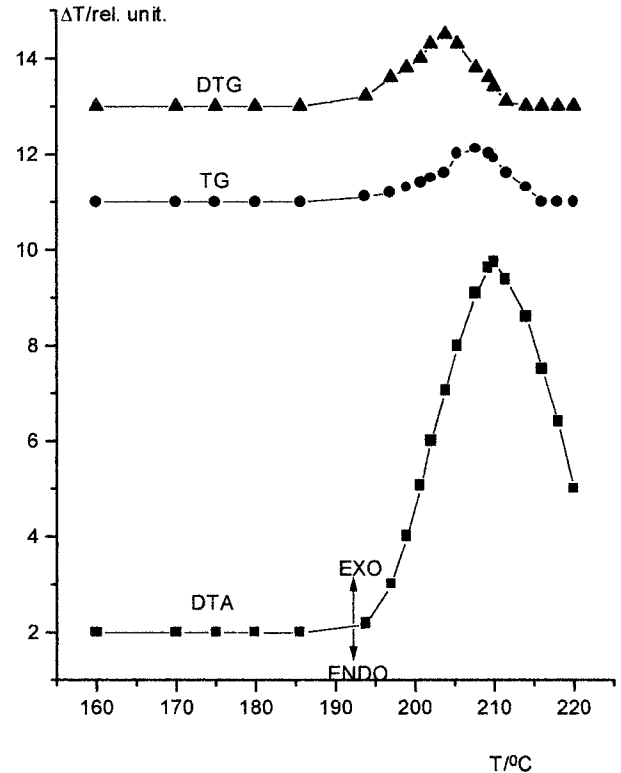

Figure 6 The TG, DTG, and DTA curves of unirradiated EPR obtained in a static air atmosphere at a 2.9 K/min heating rate.

increase in weight. An analogous thermal oxidative process was previously reported in connection with the degradation of various polymers.[16–23] During this process oxygenated products, principally hydroperoxides, are produced that are due to the attack of singlet oxygen ($^1O_2$, $^1\Delta_2$) on the methylene groups.[18]

The analysis of the thermograms recorded for initial and γ-irradiated samples provided characteristic temperatures of the process of thermal degradation (T_i, the temperature for the start of oxidation, and T_{max}, the maximum temperature on the DTA peak). The dependencies of these parameters on the irradiation dose (D) are shown in Figure 7 where T_i versus D and T_{max} versus D for the heating rate of 5.9 K/min are drawn. A similar curve aspect was obtained for the heating rate of 2.9 K/min. It can be observed that T_i and T_{max} both display a sharp decrease over the dose range of 0–200 kGy. If the dose exceeds 200 kGy and T_i and T_{max} are practically constant, the main structural modifications occur on the first 200 kGy.
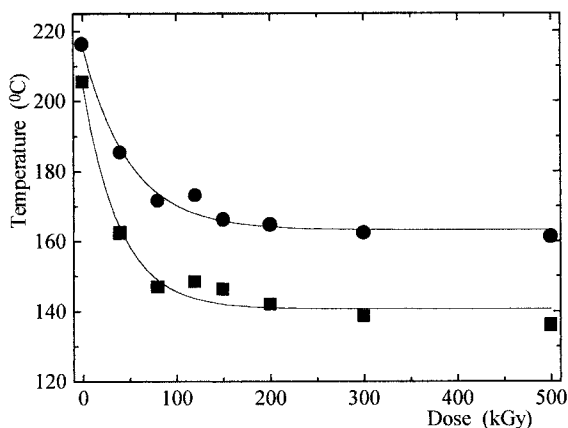
Figure 7   The changes in (■) T_i and (●) T_{max} with the irradiation dose for thermal oxidation of EPR at a heating rate of 5.9 K/min.

DISCUSSION

The experimental data reflect the difference between the irradiated samples at various doses. The decrease of oxidation times and the rise of oxidation rates are caused by the formation of hydroperoxides and partially peroxyl radicals because of their short lifetime (2.5 h).[24] They represent the entities that participate in the propagation of the oxidation process. Simultaneously, hydrocarbon free radicals are subjected to a recombination process with a direct result in the increase of crosslinking.[25] The competition between crosslinking and oxidation determines the thermal behavior of irradiated polymer samples. At low irradiation doses free radicals react mainly by growing a 3-dimensional network, because hydroperoxides are spread over the whole of the material in a small amount. When the transferred energy causes enough bond breaks, accumulated hydroperoxides initiate more and more fast oxidation and the thermal degradation studied by oxygen uptake starts earlier. Thermal analysis proves the lowering of the time of the start of oxidation. On the other hand, the gel dose for γ-irradiated EPR was stated as 75 kGy.[12] This means that the rate of crosslinking exceeds the rate of scission over this dose. The oxidation process occurring simultaneously with crosslinking becomes the main process after 200 kGy, when the reactions involving molecular oxygen and peroxy radicals deplete alkyl free radicals.

The competition between crosslinking and oxidative degradation can be depicted by the evolution of free-radical concentration. The kinetics of postirradiation oxidation depend on the decline in the concentration of hydrocarbon free radicals according to the relationship proposed by Neudörfl[26]:

$$[O_2] = \rho^{-1} a^{-3} \ln \frac{[R^\bullet]_0}{[R^\bullet]}$$

where $[O_2]$ represents the oxygen uptake measured at the free-radical concentration $[R^\bullet]$, ρ is the density of the polymer, a is a constant (36.8 Å), and $[R^\bullet]_0$ is the initial radical concentration. This expression may be written for two different moments of degradation. By dividing each we can obtain the following:

$$\frac{[O_2]_1}{[O_2]_2} = \ln \frac{[R^\bullet]_2}{[R^\bullet]_1}$$

This expression proves that the increase in the amount of consumed oxygen is the main origin of free-radical depletion. Figures 1(b), 2(b), 3(b), and 5 illustrate the involvement of hydrocarbon radicals in the processes occurring during irradiation and thermal degradation. If it is taken into account that alkyl radicals react not only with oxygen but are also involved in recombination reactions or other additional processes, the oxidation induction time and the rate of oxidation are substantially influenced by radiation and thermal aging conditions.[27]

CONCLUSION

The experimental results presented in this article demonstrate the effects of competition between crosslinking and degradation during radiation exposure. The irradiation with γ rays at a low dose rate causes oxidative degradation to prevail. If accelerated electron beams are employed the results are favorable to crosslinking. Under these circumstances the lifetime of irradiated products (via manufacture technologies or accidentally) is decided by the dose received.

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