Accelerated Electron Effects on EVA Based Compound

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ABSTRACT: The major effects induced by accelerated electron irradiation on EVA based polymeric compound were evaluated for various doses up to 240 kGy. Some main characteristics (gel fraction, density, elongation at break, and tensile strength) were investigated. Oxygen uptake and thermal analysis methods (TG, DTG, and DTA) were applied for determination of oxidation resistance of radiation processed EVA samples. It was established that a 30 kGy exposure dose promotes maximum crosslinking. At this dose the den- sity and tensile strength reach maximum values, which are maintained for higher doses up to 240 kGy. On the other hand, the thermooxidative stability exhibits a sharp de- crease as the absorbed dose rises from 0 to 30 kGy and has a constant value for the absorbed dose range 30–240 kGy. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 613–617, 2005

Key words: radiation processing; EVA; mechanical proper- ties; crosslinking; oxidative degradation

INTRODUCTION

At any temperature ionizing radiation induces chem- ical reactions in polymers. In the first step of high energy irradiation, excited molecules, ions, and radi- cals are formed in polymers. These reactive interme- diates initiate chain reactions causing macroscopic processes: scission, crosslinking or grafting, oxidative degradation, or depolymerization. The balance be- tween crosslinking and scission, in polymers exposed to ionizing radiation, determines the controllable be- havior of materials.[1] Taking into account the main reaction (scission or crosslinking) that occurs at a higher rate, one has to differentiate whether a plastic belongs to the "crosslinkable" or the "degradable" group of plastics.[2] Favorable changes in material properties of crosslinkable polymers can be achieved by irradiation, namely, mechanical properties (elastic- ity modulus, tensile strength, elongation at break, hardness, etc.); thermal properties (dimensional stabil- ity under heat, aging resistance, etc.); and chemical properties (solubility, swelling resistance, stress crack- ing resistance, etc.). Radiation processing is widely used to improve product quality, to raise technologi- cal efficiency, and to manufacture items with con- trolled properties.[1,3]

The aim of the present work is the investigation of radiation effects on polymeric EVA based compound, exposed to accelerated electron, by assessment of gel fraction, density, mechanical properties (elongation at break and tensile strength), and thermooxidative re- sistance.

EXPERIMENTAL

Materials

The present investigation was carried out on "FRANGOM P/1" a compound based on EVA con- taining magnesium hydroxide, antioxidants, and an- tiagers (age resisters), provided by SACOM, Parma, Italy. This polymeric material exhibits the following initial characteristics: density: 1.50 g·cm^{-3}; melt flow index (21.8 kg at 190°C): 20 g/10 min; tensile strength: 9 N·mm^{-2}; elongation at break: 500%; temperature index (21% O_2): 360°C. This polymeric material was not subjected to any purification to obtain reliable data for industrial applications.

Sample plaques were obtained starting from mate- rial pellets, which were pressed in electrical equip- ment for 10 min, at 180°C and 150 bars.

Irradiation

Compound samples were irradiated in air, at room temperature, with accelerated electron beams ob- tained by means of the accelerator ILU 6M (Budker, Institute of Nuclear Physics, Novosibirsk, Russia). The absorbed doses of 12, 30, 60, 90, 120, 150, 180, and 240 kGy were selected. Unirradiated samples (control) were also investigated.

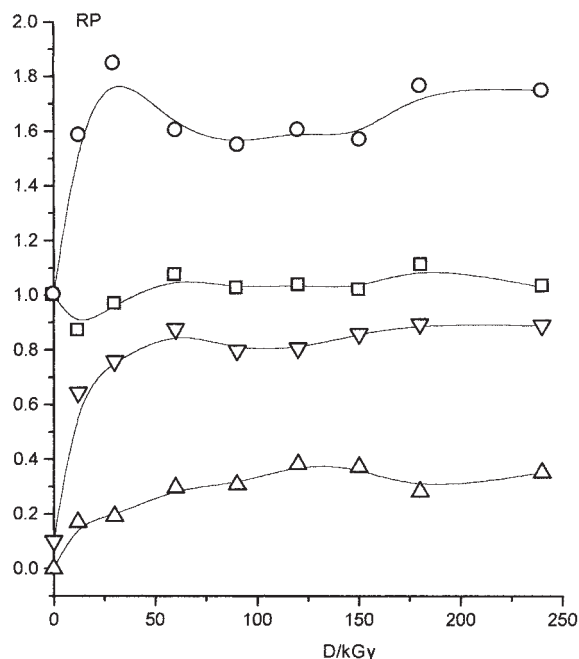*Correspondence to:* T. Zaharescu (traian_zaharescu@yahoo. com).

Figure 1 Variation with irradiation dose of the mechanical properties, density, and crosslinking degree of the investigated material. The index 0 corresponds to the initial sample. $\square$ $\varepsilon/\varepsilon_0$; o σ/σ_0; $\Delta 10 \times \rho - \rho_0/\rho_0$; ∇ $0.1 \times CD/CD_0$.

Density

Density was determined by successive weighing in heptane and in air. This value was calculated using Archimede's law.

Crosslinking degree

Crosslinking degree was evaluated as the ratio between weight loss obtained after boiling in xylene for 12 h and initial weight (gel fraction).

Mechanical properties

The elongation at break and tensile strength of the initial and radiation processed specimens were determined using a tensile tester: ZMGi-500-Veb Thusinger Industriewerk, Germany. Crosshead speed was 200 mm/min, test specimens being prepared according to ASTM D-412 requirements.

Oxygen uptake

Small chips were removed from initial and irradiated specimens and located on aluminum trays. Polymer samples were weighed about 20 mg and introduced in the oxygen uptake equipment. The flow sheet, the experimental procedure, and the competence of method were previously reported.[4] All determinations

were performed in air, under isothermal (195°C) and isobaric (normal pressure) conditions.

Thermal analysis

The heating curves (TG, DTG, and DTA) of the initial and irradiated samples were recorded with a Q-1500D Derivatograph (MOM, Budapest, Hungary) in static air atmosphere, in the temperature range 20–500°C, at a heating rate of 2.5 K·min^{-1}. The masses of the analyzed samples were in the range 19.9–21.0 mg. The heating of each sample was performed in a cylinder-shaped platinum crucible and α-Al$_2$O$_3$ was used as reference material.

RESULTS AND DISCUSSION

Changes in mechanical properties, density, and crosslinking

The changes in mechanical properties [elongation at break (ε), tensile strength (σ)], density (ρ), and crosslinking degree (CD), as the result of irradiation of the investigated material, are shown in Figure 1. Each point from the curves given in figure corresponds to the average value of the property determined for a minimum of three samples.

Except for the curve ($\varepsilon/\varepsilon_0$) versus dose ($D$), each curve from Figure 1 exhibits an initial portion for which the property increases with the absorbed dose, followed by another region where the property is practically constant. The dependence ($\varepsilon/\varepsilon_0$) on D shows an initial small decrease, followed by a rapid increase to a constant value exceeding unity. The increase in the relative properties can be assigned to the initial crosslinking of the EVA compound, and prop-
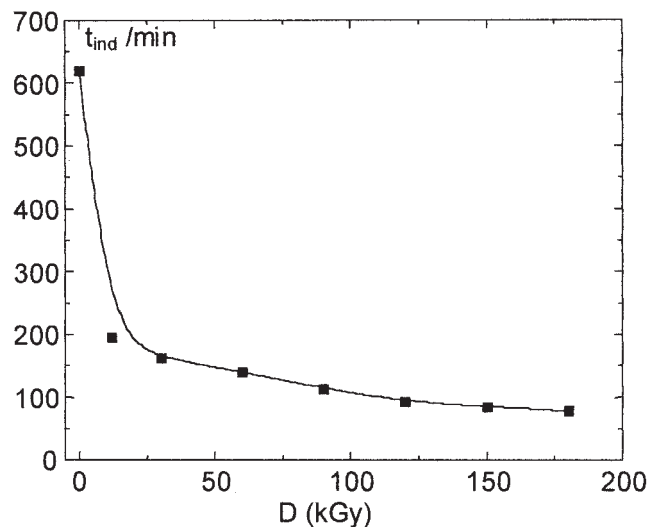

Figure 2 Dependence of the oxidation induction time on the irradiation dose.
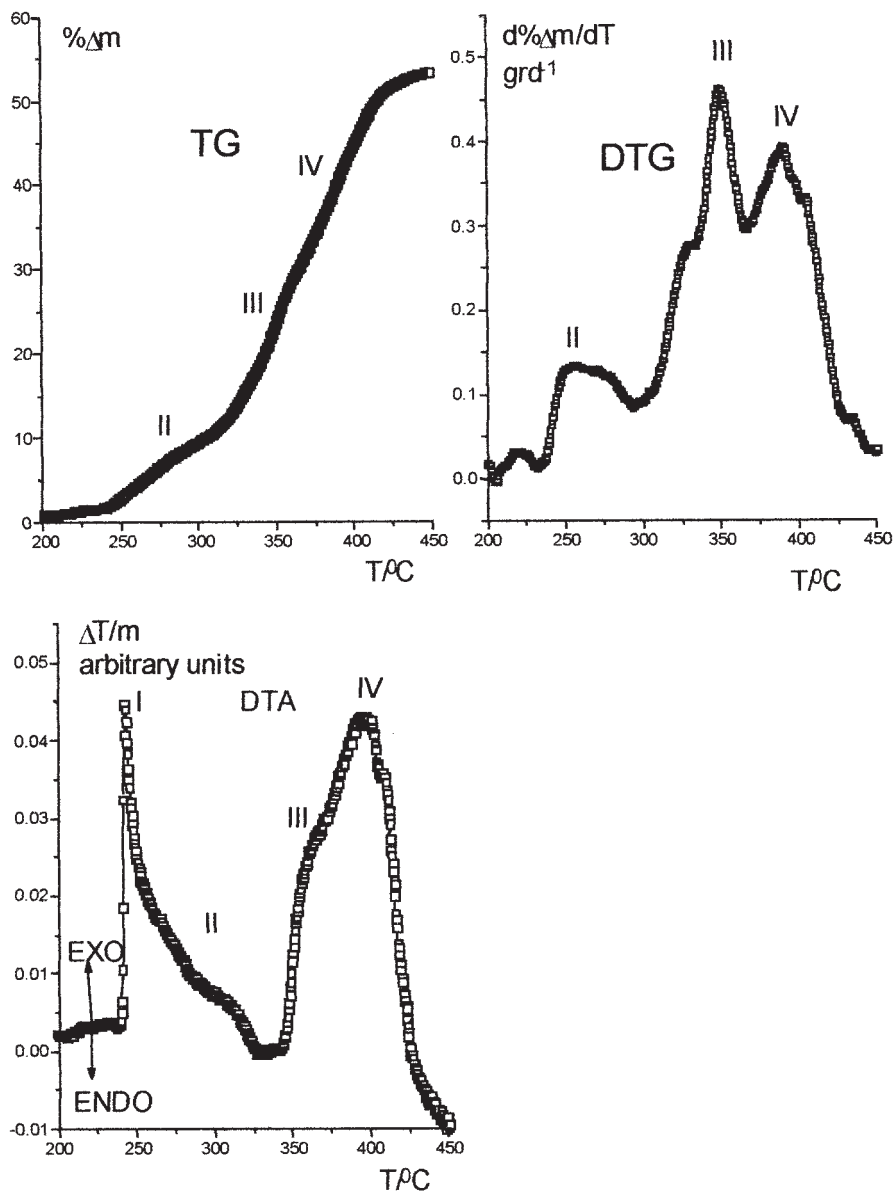
Figure 3 TG, DTG, and DTA curves of the initial polymeric material, in static air atmosphere, at a heating rate of 2.5 K·min^{-1}.

erties reach a constant value for the higher dose range (30–240 kGy). These results suggest that accelerated electron irradiation of EVA compound yields a maximum crosslinking level at the dose of 30 kGy.

Oxygen uptake

Figure 2 displays the influence of the absorbed dose on the induction time of the irradiated samples. The first stage of high-energy treatment consists of bond scission and formation of peroxy radicals as the precursors of degradation. The accumulation of these intermediates will bring a severe decrease of thermal stability for the first 12 kGy. A dose exceeding this value would raise the concentration of oxygenated

reactive entities, but they are simultaneously depleted by other reactions. The pseudoplateau, starting from about 30 kGy, proves that a steady state is achieved as the degradation advances. Similar results were obtained on the radiation degradation of ethylene–propylene terpolymer blends.[5]

TG, DTG, and DTA data

Figure 3 depicts TG, DTG, and DTA curves for the initial polymeric material. Similar curves were obtained for the irradiated samples.

The thermooxidative degradation occurs through four main processes, denoted by I, II, III, and IV regions.
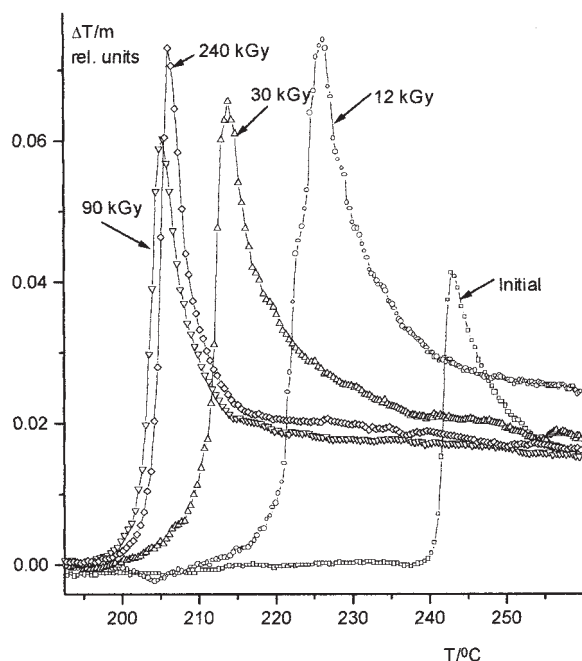
Figure 4 The DTA curves characteristic for the process I and corresponding to initial and irradiated samples.

The exothermic change I, evidenced in the DTA curve, occurs without a detectable weight change in the TG curve. The real modification consists of polymeric material thermooxidation that generates solid products, probably hydroperoxides,[6] via peroxyl radicals. In the investigated cases the corresponding increases of the sample weight were not detected because the change I is immediately followed by the change II in which some volatile compounds are generated.

At higher temperatures, three thermooxidative degradation steps (II, III, and IV) accompanied by volatile product generation occur. The DTG peaks, corresponding to processes II and IV, are well separated only for the initial sample. For each irradiated sample, the process IV is characterized in the DTG curve by a "shoulder" of the main peak corresponding to process III.

Thermooxidative behavior, characterized by two kinds of oxidation processes (one with formation of solid compounds and the others by releases of volatile compounds), has also been reported for other polymers subjected to thermooxidative degradation.[5–16]

As can be seen in Figures 4 and 5, high energy irradiation of the EVA compound determines certain modifications in the following characteristic parameters: (a) the height of the DTA curve, which is proportional to the reaction rate and (b) the temperature of initiation of oxidation (T_i) and the temperature corresponding to the maximum of the DTA peak (T_{max}). The minimum height of the DTA curve belongs to initial sample, and both T_i and T_{max} display a sharp

decrease over the dose range of $0 \approx 60$ kGy. If the dose exceeds ≈ 60 kGy, T_i and T_{max} are practically constant. Consequently, the main structural modifications of the material occur during the first 30 kGy.

The main parameters, identifying the processes II, II, and IV, are listed in Table I. This table shows the following differences in the behavior of the initial sample with respect to the irradiated ones:

- the mass loss in process II has a minimum value (7.2%) for the initial sample and practically the same value (12.1 $\pm$ 1.1%) for the irradiated samples;
- the mass loss in process III has also a minimum value (21.2%) for the initial sample and similar values (24.5 $\pm$ 1.9%) for the irradiated samples;
- the mass loss in process IV has a maximum value for the initial sample.

The characteristic temperatures of the processes II, III, and IV are not significantly influenced by the irradiation dose.

The reaction rates for process II at 258°C [the mean value of T_{max}^{DTG} (II)] and the process III at 354°C [the mean value of T_{max}^{DTG} (III)] were evaluated using DTG curves. Figure 6 displays the dependencies of these rates on the irradiation dose. It can be observed that both reaction rates display a sharp increase in the range 0–30 kGy. If the dose exceeds 30 kGy, the rates corresponding to both temperatures are practically
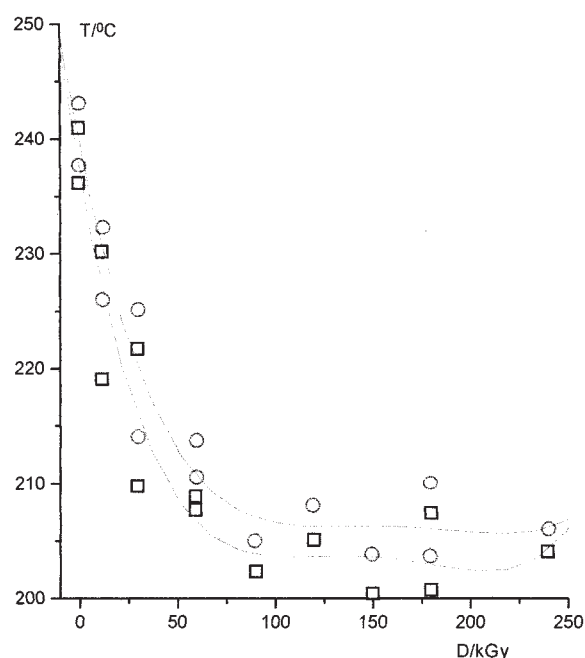

Figure 5 The changes in the characteristic temperatures of the process I ($\square$ $T_{i[infi]}$; $\bigcirc$ T_{max}) with the irradiation dose for thermal oxidation of the investigated material at a heating rate of 2.5 K·min^{-1}.

TABLE I
Thermoanalytical Data Characteristic for Processes II, III, and IV, Which Occur at the Progressive Heating of Initial and Irradiated Samples

	Process II			Process III				Process IV			
D (kGy)	ΔT (II) (°C)	Δm (II) (%)	T_{max}^{DTG} (II) (°C)	ΔT (III) (°C)	Δm (III) (%)	T_{max}^{DTG} (III) (°C)	T_{max}^{DTA} (III) (°C)	ΔT (IV) (°C)	Δm (IV) (%)	T_{max}^{DTG} (IV) (°C)	T_{max}^{DTA} (IV) (°C)
0	230–293	7.2	256	293–364	21.2	349	361[a]	364–420	21.0	390	397
12	216–297	11.6	258	297–373	27.0	352	358	373–420	7.9	377[a]	380[a]
30	207–303	11.8	253	303–369	25.6	352	360	369–420	12.0	373[a]	—
60	204–307	12.9	262	307–373	27.3	356	366	373–420	12.7	377[a]	379[a]
90	199–315	13.8	257	315–370	24.5	356	367	370–420	14.7	373[a]	377[a]
120	200–309	10.6	261	309–370	23.1	356	368	370–420	14.1	378[a]	381[a]
150	194–304	11.0	262	304–369	23.2	353	370	369–420	16.6	378	378[a]
180	203–310	12.7	257	310–370	22.3	358	370	370–420	13.4	378[a]	—
240	199–305	12.7	258	305–367	23.1	354	366	367–420	14.4	369[a]; 388[a]	—

ΔT, the temperature range where the process occurs; Δm, the mass loss; T_{max}^{DTG}, the temperature corresponding to DTG maximum; T_{max}^{DTA}, the temperature corresponding to DTA maximum.
*The temperature corresponds to a "shoulder" of the DTG or DTA peak.

constant. The increase in these rates, as well as the decreases in the characteristic temperatures of the process I (Fig. 5) over the mentioned dose range can be assigned to the crosslinking of the investigated material due to tertiary carbon atoms. It is well known that, in the oxidation reaction, the chemical reactivity of the carbon atoms increases with their degree of substitution.[6,9]

CONCLUSIONS

The experimental results presented in this paper depict the effects of irradiation with accelerated electron beams on the following properties of the investigated polymeric material (compound based on EVA): mechanical properties (elongation at break and traction resistance), density, gel fraction, and thermal oxidative stability. The 30 kGy irradiation level determines the maximum crosslinking of EVA compound. This crosslinking degree is not affected by further irradiation until the dose of 240 kGy. The increase in crosslinking degree determines the increase in the tensile strength and density, accompanied by the decrease in thermooxidative stability.

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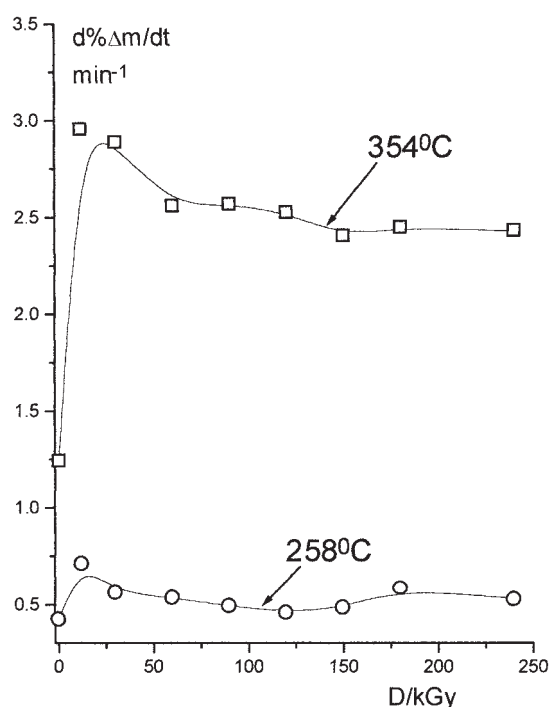16. Budrugeac, P. J Mater Sci 2001, 36, 2999.

Figure 6 The changes in the reaction rates at 258 and 354°C with irradiation dose.