Radiation Processing of Polyolefin Blends. I. Crosslinking of EPDM–PP Blends

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ABSTRACT: Radiation crosslinking of polymer blends containing the ethylene–propylene terpolymer (EPDM) and polypropylene (PP) was studied. Four binary systems with mixing ratios of 80/20, 60/40, 40/60, and 20/80 w/w and the individual components were γ-processed. The development of the gel content formed in irradiated blends proved that the increase in PP concentration generated an increasing insoluble fraction. A linear dependence of the gel fraction on PP concentration was found. The optimal dose range for the efficient crosslinking of all EPDM/PP blends was 40–180 kGy. The use of PP customer waste was also examined. The thermal stability of the studied mixtures was assessed in order to state the contribution of the components to the radiation compatibilization of investigated polymers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 982–987, 2000

Key words: ethylene–propylene terpolymer; polypropylene; radiation crosslinking

INTRODUCTION

The radiation compatibilization of binary systems has been a topic of interest for many years. Ethylene–propylene rubbers (EPDM) and polypropylene (PP) are widely used in various economical areas. They show a high thermal or radiation stability (EPDM) or remarkable mechanical properties (both materials). Particular applications, like gaskets, electrical insulators, or medical supplies, require certain characteristics that can be easily obtained by radiation processing at suitable irradiation conditions and certain material composition.

Many investigators have focused on the degradation aspects of irradiation[1–3] or on the stabilization efficiency of antioxidants.[4–8] The radiation compatibilization of polymers has been rather rarely investigated.[9,10] 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. Large-scale applications of radiation-crosslinked compounds sustain extensive evaluation of radiation-induced vulcanization. The resistance to the damaging action of various agents like oxygen, water, ozone, or chemical reagents and significant energy transfer (heat, ionizing radiation) becomes the main problems of long-term service. To avoid a fast 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 properties of processed mixtures.

As previously stated,[11] organic polymers can be divided into two different categories: One of them consists of radiation-crosslinkable polymers. EPDM elastomers belong to this material category. The second class of materials includes the

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radiation-degradable polymers like PP. This polyolefin is crosslinked in an inert atmosphere, but it is degraded when irradiation is carried out in air.[12] This behavior may be considered a valid criterion of radiation-processed blends.

This article presents the development of a gel fraction created by the action of γ-radiation on binary EPDM/PP mixtures. An estimation of optimal irradiation conditions for blended polymers represents a profitable start point for radiochemical technologies.

EXPERIMENTAL

This investigation was carried out on two polymers provided by ARPECHIM Piteşti (Romania): ethylene–propylene–diene (EPDM, Terpit C®) and PP (injection kind F 401®). The main characteristics of the EPDM elastomer were presented in a previous article.[13] Fresh PP presents the following parameters: melt point: 3–3.5 g/10 min (230°C and 2.12 kg) and Mooney viscosity [ML(4) 125°C] 58–59°M; waste parallelly tested PP (carbonyl index 0.02) showed a melt index of 16 g/10 min (230°C and 2.16 kg). Sheet formulations with compositions 100/0, 80/20, 40/60, 60/40, 80/20, and 0/100 (w/w) were prepared. The blending was performed in a laboratory roll unit at 175°C. Plate pressing was performed under the following conditions: temperature 180–185°C; pressure 150 atm.

Irradiation was performed in air inside a ^{137}Cs (GAMMACELL, USA) facility to various absorbed doses up to 370 kGy at room temperature, dose rate being 0.54 kGy/h. The γ-exposed specimens were processed after 10 min after the end of irradiation.

The gel content of radiation-modified EPDM/PP blends was calculated from the solubility measurements of irradiated samples. The sol extraction (Soxhlet procedure) in boiling *o*-xylene for 24 h was applied for characterization of radiation-induced chain scission and crosslink reactions. Duplicate samples were used to assess the gel fraction.

The oxygen-uptake measurement of the gel fraction were carried out under isothermal and isobaric conditions. A laboratory tight equipment was used to determine the amount of consumed oxygen.[14] The normal air pressure and the temperature of 180°C were chosen in order to obtain a significant oxidation rate. The polymer samples destined to oxygen-uptake measurements were obtained by the removal of $CHCl_3$ (solvent) from the polymer solution properly adjusted. Thin films (50 μm) were prepared on round aluminum trays.

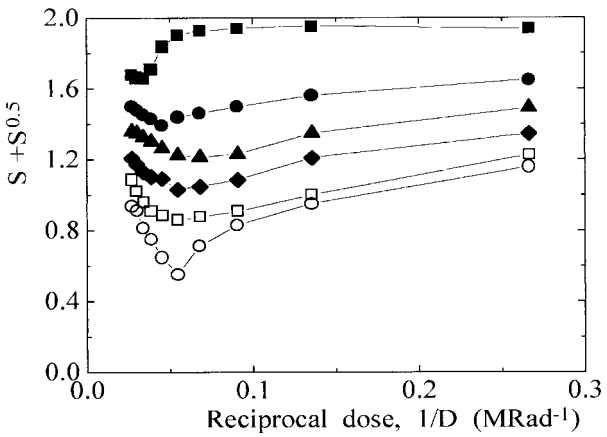

Figure 1 Charlesby–Pinner representation for the tested EPDM/PP blends: (■) PP 100%; (●) PP/EPDM = 20/80; (▲) PP/EPDM = 40/60; (◆) PP/EPDM = 60/40; (□) PP/EPDM = 20/80; (○) EPDM 100%.

The spectral records over the 2000–400 cm^{-1} range were performed with a Carl Zeiss Specord IR 75 spectrometer. The carbonyl index was calculated according to the method proposed by Papet et al.[15]

RESULTS

Changes in the Gel Content of Irradiated EPDM/PP Blends

Polymers can be characterized by their behavior under the action of ionizing radiation.[11,12] The competition between the main processes occurring in γ-irradiated polymers, scission and crosslinking, determines the level of gel content and the state of degradation, if the exposure is carried out in an oxidative environment.

Figure 1 shows a Charlesby–Pinner representation[16] drawn for γ-irradiated EPDM/PP blends. Minimum values in $S + \sqrt{S} = f(1/D)$, where S is the sole amount at dose D, can be noticed. The dose range selected for this study is divided into two areas: in the left region, the rate of scission exceeds the rate of crosslinking, while in the right region, the gel development is the dominant feature of high-energy irradiation. The change in component concentrations induces a shift of opti-

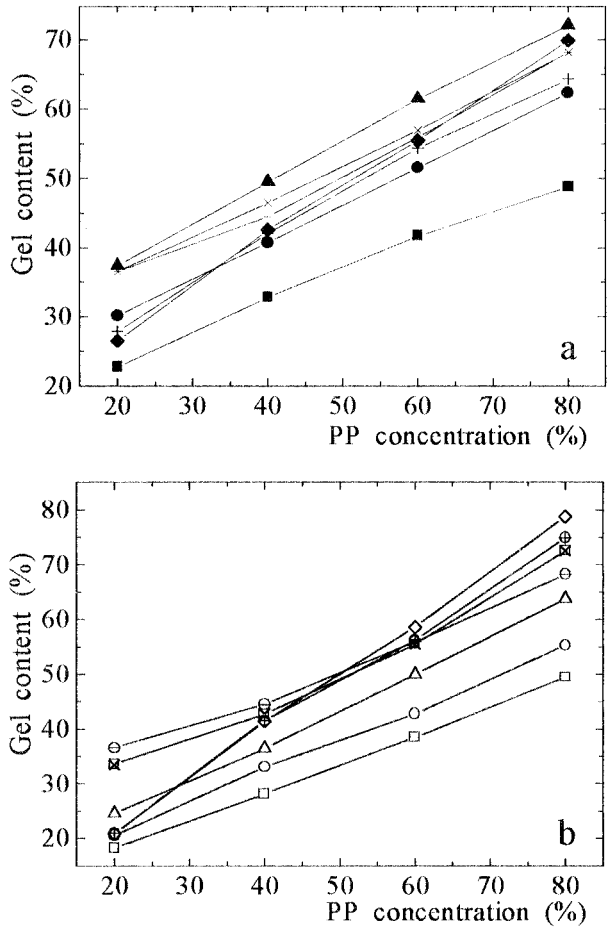

Figure 2 Gel content change versus the concentration of PP in irradiated EPDM/PP blends at various doses: (a) mixtures containing fresh PP; (b) mixtures containing waste PP. (□,■) 37.5 kGy; (○,●) 73.7 kGy; (▲,△) 110.2 kGy; (◆,◇) 146.8 kGy; (*,⊕) 183.1 kGy; (x,⊠) 221.5 kGy; (−,⊖) 258.3 kGy.

mal crosslinking dose from 40 kGy (PP) to 180 kGy (EPDM).

Similar plots were obtained for the blends containing waste PP. However, a difference between the two kinds of analogous mixtures was remarked. The maximum level of crosslinking was obtained at a somewhat lower irradiation dose in the case of waste-containing blends.

The presence of PP causes an increase in gel content because its radiation stability is low. It can be considered as the main source of free radicals for initiating crosslinking. The mechanism involving radicals[17] is appropriate for the explanation of gel development.

Figure 2(a,b) present the development of a gel fraction on constituent concentrations for rested blends containing fresh PP and waste PP, respectively. The linear relationships proving the influence of the blending composition on the insoluble content at various doses are listed in Table I. The general eq. (1) empirically derived from the present data describes the mathematical correlation between the insoluble fraction (Y) and the PP concentration (X) in the studied blends:

Table I Dependencies of Gel Content (Y) on Component Concentration (X) at Various Irradiation Doses

Dose (kGy)	Relationship	Correlation Factor
35.5	$Y = 0.874 - 0.0044\,X$	0.990
73.7	$Y = 0.898 - 0.0065\,X$	0.980
110.2	$Y = 0.844 - 0.0068\,X$	0.947
146.8	$Y = 0.895 - 0.0075\,X$	0.990
183.1	$Y = 0.888 - 0.0069\,X$	0.992
221.5	$Y = 0.853 - 0.0067\,X$	0.993
258.3	$Y = 0.883 - 0.0063\,X$	0.998
295.5	$Y = 0.759 - 0.0049\,X$	0.977
332.1	$Y = 0.760 - 0.0045\,X$	0.996
370.8	$Y = 0.772 - 0.0043\,X$	0.997

$$Y = (0.837 \pm 0.055) - (0.0059 \pm 0.0012)X \quad (1)$$

Changes in Oxidation Stability of EPDM/PP Blends

The presence of oxygen in the irradiation environment generate oxygen-containing products. Figure 3 presents the changes in the carbonyl index induced by modification in the irradiation dose and in the polymer sample formulation. The diffusion of oxygen and ozone into the polymer bulk

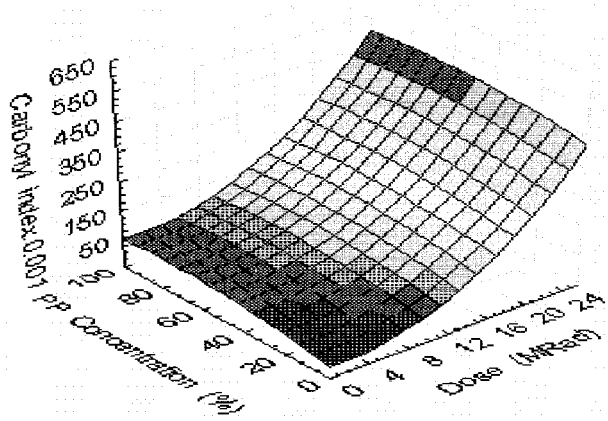

Figure 3 Changes in carbonyl index versus irradiation dose and blend composition for EPDM/(fresh)PP.

represents a continuous source for peroxy radical formation and, later, the final product accumulation. The higher the radiation dose and the concentration of PP, the greater the carbonyl index.

Gamma rays act as a powerful energy source for free radicals because they penetrate the whole of the irradiated materials, bringing about scission of the weaker bonds of the macromolecules. An additional contribution to the bonds cleavage is brought by Compton scattering that creates supplementary amounts of free radicals. All these alkyl intermediates participate in the reactions according to their affinity, the local concentration of the various entities, and the diffusion characteristics of each kind of radical. The molecular oxygen preexisting in the initial polymers or those diffused into the material reacts with alkyl radicals and forms peroxy radicals. They become the start intermediates for autocatalytic degradation. The next scheme presents the general reactions involved in the degradation mechanism of polyolefins:

$$\text{R—R}' \rightarrow \text{R}^{\bullet} + \text{R}'^{\bullet}\ (\text{H}^{\bullet}) \qquad \text{(a)}$$

$$\text{R}^{\bullet} + \text{O}_2 \rightarrow \text{RO}_2^{\bullet} \qquad \text{(b)}$$

$$\text{RO}_2^{\bullet} + \text{RH} \rightarrow \text{ROOH} + \text{R}^{\bullet} \qquad \text{(c)}$$

$$\text{RO}_2^{\bullet} + \text{R}^{\bullet} \rightarrow \text{ROOR} \qquad \text{(d)}$$

$$\text{RO}_2^{\bullet} + \text{RO}_2^{\bullet} \rightarrow \text{ROOR} + \text{O}_2 \qquad \text{(e)}$$

$$\text{R}^{\bullet} + \text{R}^{\bullet} \rightarrow \text{R—R} \qquad \text{(f)}$$

The oxygen-uptake measurements performed on the irradiated EPDM/PP blends revealed the influence of the PP content on the oxidation strength of these systems. Figure 4(A) shows the changes in the oxygen amount reacted with various polyolefin mixtures at 180°C. These diagrams emphasize the increased thermal stability of the mixtures containing a high concentration of EPDM. Moreover, the application of the derivative method for the stability assessment[18] [Fig. 4(B)] allows us to characterize the thermal behavior by the maximum oxidation rate. Table II lists the dependence of $(d[\text{O}_2]/dt)_{\max}$ on the PP concentration for all tested EPDM/PP blends. The time presented in the second column represents the moments when the concentration of peroxy radicals becomes constant (the propagation stage of the oxidative degradation). The analytical relationship that describes the dependence of the maximum oxidation rate on the PP concentration is fitted to a first-order function (2):

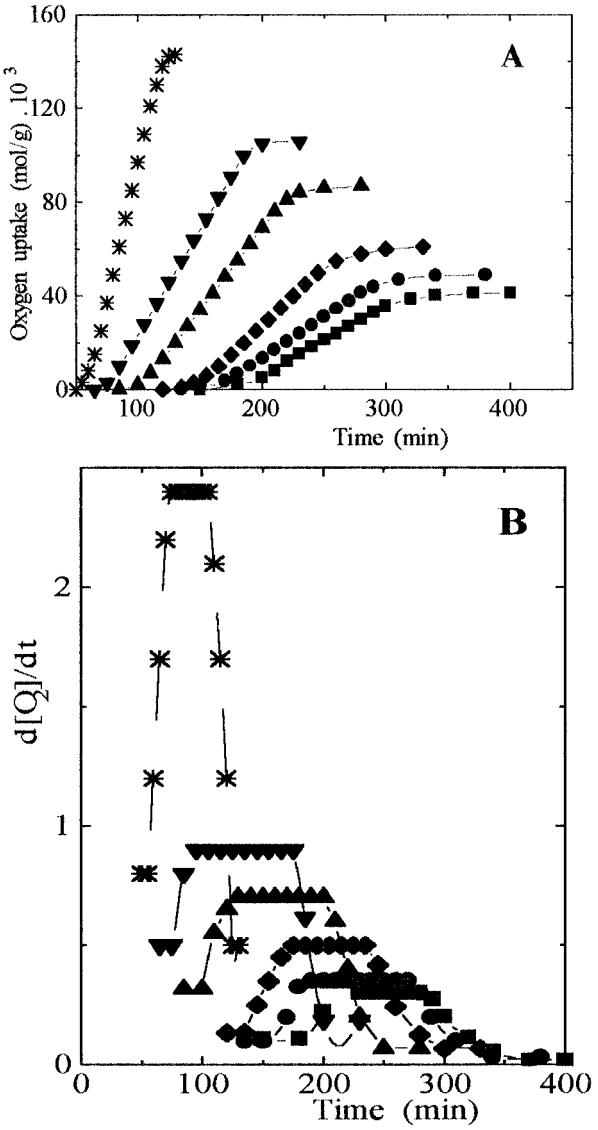

Figure 4 (A) Oxygen-uptake diagrams and (B) their first derivatives for unirradiated EPDM/PP blends: (■) EPDM 100%; (●) PP/EPDM = 20/80; (◆) PP/EPDM = 40/60; (▲) PP/EPDM = 60/40; (▼) PP/EPDM = 80/20; (✳) PP 100%.

$$Y = 263.7 - 1.7X \qquad (2)$$

where Y denotes $(d[\text{O}_2]/dt)_{\max}$ and X represents the PP concentration in the blends. The negative sign may be ascribed to the decreasing contribution to the thermal stability of PP.

Table II Dependence of $(d[O_2]/dt)_{max}$ on the PP Concentration

PP Concentration (%)	$(d[O_2]/dt)_{max}$
0	90
20	128
40	163
60	200
80	230
100	260

$$Y = 263.7 - 1.7\,X$$

DISCUSSION

The radiation chemistry of EPDM[13] and PP[19] has proved that their stability is very unlike. Their radiochemical yields for chain scission differ with one order of magnitude,[20] indicating that in the EPDM/PP blends the main source of free radicals are PP macromolecules. Similar behavior was reported earlier.[9] In addition, the fraction of the isotactic fraction from raw PP starts to be degraded first.[21]

The availability of free radicals produced by γ-exposure is shown in Figure 2. The optimal dose for maximum crosslinking is in the range from 40 to 180 kGy depending on PP concentration (Fig. 1). The gel dose of EPDM is about 60 kGy. The appropriate concentration of free radicals for an efficient crosslinking would be attained at doses higher than the gelation dose of EPDM.

Some remarks can be made on the characterization of radiation processing of the EPDM/PP systems:

- A higher content of PP decreases the optimal crosslinking dose.
- A short time exposure and a high dose rate are favorable conditions for the low content of oxidation products; over the first 80 kGy, oxidative degradation of crosslinked EPDM/PP systems occurs slowly.
- Thermal stability of radiation-processed materials decreases as the PP concentration increases and the irradiation dose exceeds 180–200 kGy.
- The compounded EPDM terpolymer can be regarded as proper material for the production of new products using high-energy radiation.

The mechanistic description of the radiation processing of polyolefins involves various reactions of free radicals: recombination, disproportionation, hydrogen abstraction, or branching apart from their reaction with molecular oxygen. Their proportion in the overall effects of γ-irradiation depends on the concentration of free radicals (the formulation of mixture), on the dose rate, and on the exposure time. The presence of an antioxidant will provide a higher stabilization effect on the radiation-processed materials.

It can be postulated that the ethylene–propylene copolymer (EPR) could be used instead of EPDM; the same results will be obtained at higher irradiation doses because of its remarkable radiation stability. In addition, the oxidative degradation would start earlier because the free radicals generated by PP will react more rapidly with oxygen. Future studies on the radiation processing of polyolefins will investigate the oxidation stability as well as the changes in mechanical and thermal properties of γ-irradiated EPDM/PP systems.

CONCLUSIONS

The EPDM/PP blends are efficiently crosslinked at low doses. The PP components of these mixtures provides the main amount of free radicals that can recombine to increase gel content. The EPDM elastomer acts as host component on which the second polymer can be grafted. Research on the radiation crosslinking of compounded EPDM must be considered as the start point of a new unconventional procedure of polymer product manufacture.

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