

Radiation Effects on Poly(propylene) (PP)/Ethylene–Vinyl Acetate Copolymer (EVA) Blends

Siqin Dalai,* Chen Wenxiu

Department of Chemistry, Beijing Normal University, Beijing 100875, China

Received 22 March 2001; accepted 22 March 2002

ABSTRACT: Radiation effects on poly(propylene)/ethylene–vinyl acetate copolymer (PP/EVA) blends are discussed. Increasing the EVA content enhanced the crosslinking effect of radiation in PP/EVA blends. This effect was significant when the EVA content was $\geq 50\%$ in PP/EVA blends that were exposed to γ -ray irradiation in air. This phenomenon is discussed in relation to the compatibility, morphology, and thermal properties of PP/EVA blends. The results indicate that the effect is dependent on the compat-

ibility, the increase in the amorphous region content, and the EVA content in PP/EVA blends. The possible mechanism of radiation crosslinking or degradation in irradiated PP/EVA blends was studied quantitatively by a novel method, a “step analysis” process, and thermal gravimetric analysis. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3420–3424, 2002

Key words: radiation; poly(propylene); ethylene–vinyl acetate copolymer; blends; compatibility; amorphous

INTRODUCTION

High-energy irradiation (gamma or electron beam) is well known as a tool for modification of polymers. Radiation-modified blends of polyolefins have become commercially important because their properties are better than those of the parent homopolymers. Radiation crosslinked low-density polyethylene/ethylene–vinyl acetate copolymer (LDPE/EVA) blends are widely used in heat-shrinkable materials for wire and cable insulation¹ and foam materials.² The effects of electron beam irradiation and EVA content on the radiation crosslinking in LDPE/EVA blends have been studied by Gordiickuck et al.,³ Mateev and Karagegiev,⁴ and Jamaliah et al.⁵ In our previous papers,^{6,7} we investigated the γ -radiation effects of both LDPE/EVA and high-density polyethylene (HDPE)/EVA and found that the factors of good compatibility, higher amorphous region's content, and higher EVA content in the blends were favorable with regard to enhancing the radiation crosslinking of polyethylene (PE)/EVA blends. To date, only a few papers on the radiation effects of poly(propylene) (PP)/EVA blends have been published.

The mechanical and thermomechanical properties of γ -irradiated PP/EVA blends were studied by Thomas et al.⁸ and Minkova and Nikolova.⁹ In this work, the emphasis is on the effects of γ -radiation on

PP/EVA blends in air in relation to the compatibility, the amorphous region's content in the blend, and the EVA content in the blend. The possible mechanism of radiation crosslinking or degradation of PP/EVA blends was investigated by a novel method, “step analysis” process, and thermal gravimetric analysis (TGA).

EXPERIMENTAL

Materials

Industry grade poly(propylene) (PP; MFR, 2.0 g/10 min; product of No. 1 Chemical Factory of Yanshan Petrochemical Corporation, Beijing, China) and industry grade ethylene–vinyl acetate copolymer (EVA; MFR, 2.0 g/10 min; vinyl acetate content, 18%; EVA18-3, product of Beijing Organic Chemical Factory, Beijing, China) were used.

Sample preparation and irradiation

The PP and EVA were blended in the ratios 70/30, 50/50, and 30/70, with two roll mixing mills at 185–190°C, and pressed with a press machine at 190°C to form a sheet thickness of 1.0 ± 0.2 mm. Irradiation was carried out in air with a ⁶⁰Co γ -ray, and the dose rate was measured with a Fricke dosimeter. Irradiation doses were selected in the range 10–100 kGy.

Characterization

Gel content was measured with a simplified reflux instrument manufactured in our laboratory.¹⁰ Glass transition temperature (T_g) and melting properties were determined by differential scanning calorimetry

Correspondence to: S. Dalai (Sdalai@public.bta.net.cn).

*Present address: Beijing Gamma Hi-tech Company Ltd., Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, China

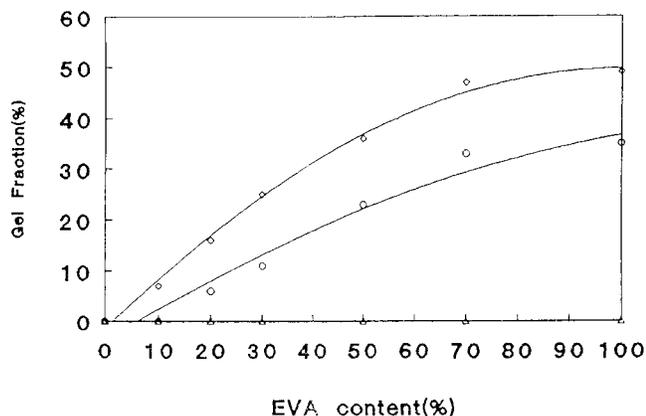


Figure 1 Gel fraction versus EVA content in PP/EVA blends in different radiation doses. Key: (Δ) 10 kGy; (\circ) 50 kGy; (\diamond) 100 kGy.

(DSC; TA 3000 model DSC30 calorimeter; Mettler Company, Switzerland) in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}$ and within the scanning temperature ranges -170 – 25 and 25 – 250°C . The crystallinities were calculated from the values of the enthalpy of fusion, which were obtained by DSC using values of 290 and 190 J/g^{11} as the enthalpy of fusion for completely crystalline PE and PP, respectively. TGA was carried out in a TA 3000 model TG50 apparatus in a nitrogen atmosphere at a heating rate of $10^{\circ}\text{C}/\text{min}$. The “step analysis” process was employed to determine the decomposition behavior.

RESULTS AND DISCUSSION

Gel fraction

The gel fraction of irradiated samples was determined to evaluate the content of crosslinking induced by irradiation, and the results are shown in Figure 1 as gel fraction versus EVA content in PP/EVA blends. No gel was obtained in pure PP (i.e., EVA content of zero) from 10 to 100 kGy, and no gel was formed following low-dose irradiation (10 kGy) in PP/EVA blends (i.e., EVA content of 10–70%) and pure EVA (i.e., EVA content of 100%), as shown in curve 1 of Figure 1. These results indicate that there is no radiation crosslinking (no gel fraction) following irradiation at 10 kGy in PP/EVA blends, in EVA, or in PP. PP is susceptible to oxidation, initiated by heat or ultraviolet (UV) or γ -irradiation,^{12–16} and is easily degraded at a high dose. At irradiation doses of 50 or 100 kGy, the gel fraction increased with increasing EVA content in PP/EVA blends (see curves 2 and 3, Figure 1). These results indicate that the higher EVA content enhanced the radiation-induced crosslinking in PP/EVA blends and prevented the PP component in PP/EVA blends to degrade at high dose.

Compatibility

The gel contents in a polymer blend are not in conformity with the additives of the components fraction in

TABLE I
Values of the Glass Transition Temperature (T_g) in PP, EVA, and PP/EVA Blends

T_g	pp	PP/EVA (70/30)	PP/EVA (50/50)	PP/EVA (30/70)	EVA
Experimental	-18	-37	-61	-72	-98
Calculated		-35	-58	-74	

the blend. This phenomenon indicates that the radiation crosslinking reaction of each component polymer in a blend does not occur independently, but the polymers affect each other, depending on their compatibility in the polymer blends.¹⁷ The DSC technique has been widely used to study polymer–polymer compatibility and to detect the amount of crystallinity present in semicrystalline polymer blends. The Gordon–Taylor relation is applied to predict the compatibility between two polymer components in blend:

$$T_g = W_a T_{ga} + W_b T_{gb} \quad (1)$$

where T_g is the glass transition temperature of the blend, T_{ga} and T_{gb} are the glass transition temperatures of polymers a and b in the blend, respectively, and W_a and W_b are the weight fractions of polymers a and b in the blend, respectively.

The validity of eq. 1 was well established for T_g s for PP/EVA blends. Calculated T_g s are in close agreement with experimental T_g s for PP/EVA blends, as shown in Table I. This result signifies that there is compatibility between the two component polymers in the amorphous region.

Two distinct endothermic peaks are present in the DSC thermogram of the PP/EVA blend shown in Figure 2. These peaks correspond to the melting of PP and EVA crystallites that are present in the PP/EVA blend, as evidenced by their coincidence with the melting peaks of two pure components. Because the blends were cooled from their melting state, the crys-

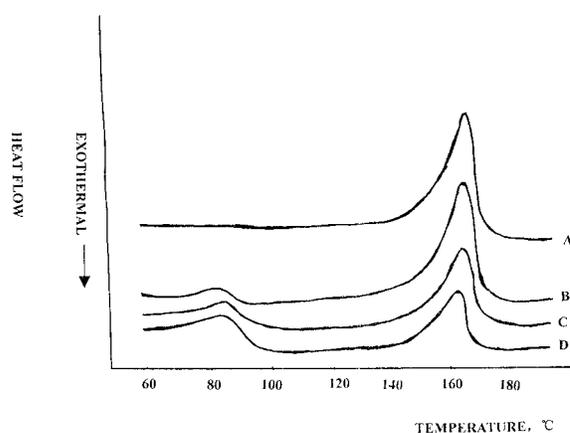


Figure 2 DSC thermograms of different PP/EVA blends: (A) 100/0; (B) 70/30; (C) 50/50; and (D) 30/70.

TABLE II
Crystallinities of PP, EVA, and PP/EVA Blends

Radiation	PP	PP/EVA (70/30)	PP/EVA (50/50)	PP/EVA (30/70)	EVA
Unirrad	44.8	36.9	28.4	18.8	10.8
10 kGy	44.0	36.2	28.0	18.2	10.7
100 kGy	43.6	35.8	27.4	17.6	9.8

tallization of different components occurred separately, leading to the formation of distinctly different crystalline phases. This phenomenon has no effect on the compatibility in the amorphous region in the PP/EVA blend, because the compatibility took place in the amorphous region in the blend.

In our previous papers,^{6,7} we found that good compatibility was a prerequisite to enhancing the radiation crosslinking of PE/EVA copolymer blends. PP and EVA are compatible in PP/EVA blends in the amorphous region, which is favorable for enhancing the radiation crosslinking and preventing PP degradation in PP/EVA blends, as shown in the Figure 1.

Morphology

The crystallinities of PP/EVA blends were examined by the DSC technique, and the results (Table II) indicate that the crystallinity of EVA is lower than that of PP; that is, the content of EVA in the amorphous region is higher than that of PP. The radiation crosslinking and degradation reactions mainly occur in the amorphous regions of semicrystalline polymers during irradiation.¹⁸ The radiation crosslinking is reduced by oxidation of polymer during irradiation in air, especially by a low dose rate of γ -ray irradiation.

The results in Table II also show that the crystallinity of PP/EVA blends decreased (i.e., the amorphous region's content increased) with the increasing of EVA content in blends. The gel content increased significantly if the amorphous region's content was >72% in the PP/EVA blend (i.e., EVA content \geq 50% in blend), as shown in the Figure 3. These results indicate that

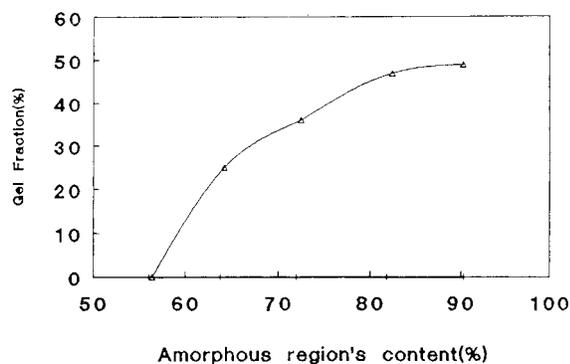


Figure 3 Gel fraction in PP/EVA blend versus the amorphous region's content of the blends. Key: (+) 10 kGy; (Δ) 50 kGy.

TABLE III
TGA Results for the PP/EVA Blend^a

Radiation	PP			PP/EVA (70/30)			PP/EVA (50/50)			PP/EVA (30/70)			EVA			
	T_1 (°C)	Δm_1 (%)	T_2 (°C)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)
Unirrad	458.0	100.0	458.0	356.0	4.47	457.0	356.0	8.31	462.0	356.0	10.71	463.0	358.3	15.4	463.7	84.70
10 kGy	457.0	99.89	457.2	356.0	4.21	457.2	356.0	8.58	462.4	356.0	11.10	464.3	356.0	15.60	467.2	84.30
50 kGy	455.0	99.92	458.0	356.0	6.68	458.0	356.0	10.65	463.2	356.0	11.98	464.6	355.7	15.90	469.7	84.10
100 kGy	451.0	99.95	458.0	356.0	9.98	458.0	356.2	11.20	463.8	357.1	12.01	466.0	356.0	16.00	470.1	84.0

^a Where T_1 and T_2 are the peak decomposition temperatures in the first and second step, respectively; and Δm_1 and Δm_2 are the weight losses in the first and second step, respectively.

TABLE IV
Comparison of $(\Delta m_1)_{\text{exp}}$ with $(\Delta m_1)_{\text{cal}}$ in PP/EVA Blends

Radiation	PP/EVA (70/30)		PP/EVA (50/50)		PP/EVA (30/70)	
	$(\Delta m_1)_{\text{exp}}$, %	$(\Delta m_1)_{\text{cal}}$, %	$(\Delta m_1)_{\text{exp}}$, %	$(\Delta m_1)_{\text{cal}}$, %	$(\Delta m_1)_{\text{exp}}$, %	$(\Delta m_1)_{\text{cal}}$, %
Unirrad	4.47	4.62	8.31	7.70	10.71	10.78
10 kGy	4.21	4.68	8.58	7.80	11.10	10.92
50 kGy	6.68	4.77	10.65	7.95	11.98	11.13
100 kGy	9.98	4.80	11.20	8.00	12.01	11.20

radiation crosslinking was accelerated by increasing of the amorphous region's content in PP/EVA blends, although PP was degraded by γ -ray irradiation in air. The results confirm that higher amorphous region's content is also favorable to prevent the effect of radiation degradation and enhancement of radiation crosslinking in compatible PP/EVA blends.

The crystallinities of PP, EVA, and PP/EVA blends slightly decreased by irradiation, as shown in the Table II. These results indicate that a little part of crystallite, whether in pure polymer or in blends, is destroyed (primarily oxidized) by γ -ray irradiation in air.

Reaction mechanism

EVA is a block copolymer consists of the chains in PE and PVA. The step analysis process in the TGA technique was employed to detect the thermal degradation behavior in irradiated PP/EVA blends to evaluate its radiation crosslinking or degradation mechanism.

The TGA results of irradiated and unirradiated PP, EVA, and PP/EVA blends are shown in Table III. Both EVA and PP/EVA blends show a two-step decomposition; that is, the PVA chain in EVA and PP/EVA blends was decomposed first and the PE and PP chains were decomposed second. We suppose that the decomposition temperature was increased by radiation crosslinking, and therefore the radiation degradation was decreased. The decomposition temperatures (T_2) in PP was decreased by 7°C (i.e., the ΔT_2 was decreased by 7°C until 100 kGy), whereas the ΔT_2 in 70/30, 50/50, and 30/70 PP/EVA blends was increased by 1.0, 1.8, and 3.0°C , respectively. The ΔT_2 in PP/EVA at 50/50 and 30/70) was higher than that in PP/EVA at 70/30 until the radiation dose reached 100 kGy, as shown in the Table III. These results illustrate that the decomposition temperature of PP decreased with increasing radiation dose because PP degraded at a high dose. The decomposition temperatures in PP/EVA increased with increasing radiation dose because the crosslinking of PP/EVA increased with radiation dose so that the radiation crosslinking in PP/EVA blends of 50/50 and 30/70 was higher than that in PP/EVA blends of 70/30. Enhancement of the crosslinking effect was significant if the EVA content

in PP/EVA blends was $\geq 50\%$, which could prevent the degradation of PP in the PP/EVA blend.

We compared the weight loss in the first step observed experimentally, $(\Delta m_1)_{\text{exp}}$, with that calculated, $(\Delta m_1)_{\text{cal}}$, to evaluate the radiation degradation of PP/EVA blends. As shown in the Table IV, $(\Delta m_1)_{\text{cal}}$ was obtained by multiplying the weight loss of pure EVA in the first step by the ratio of EVA in PP/EVA blends. After irradiation, the values of $(\Delta m_1)_{\text{exp}}$ in PP/EVA blends increased with the increasing dose by 5.51, 2.89, and 1.30 in 70/30, 50/50, and 30/70 PP/EVA blends, respectively, and the values of $(\Delta m_1)_{\text{cal}}$ increased with dose by 0.18, 0.30, and 0.42 in 70/30, 50/50, and 30/70 PP/EVA blends, respectively. The increase in $(\Delta m_1)_{\text{exp}}$ was significantly higher than that of $(\Delta m_1)_{\text{cal}}$ in the 70/30 PP/EVA blend. This result indicates that the radiation degradation was accelerated in 70/30 PP/EVA blends. If the EVA in the PP/EVA blend increased, the degradation of PP in PP/EVA blends would be reduced, as in the 50/50 and 30/70 PP/EVA blends. These results indicate that the content of EVA can sufficiently prevent the radiation degradation in PP/EVA blends, although EVA was oxidized by γ -irradiation in air.^{6,7} These facts quantitatively explain the increased enhancement effect of radiation crosslinking in PP/EVA blends with the increase of EVA content in blends; these relationships are expressed in the Table V.

Radiation crosslinking in PP is due to combination of alkyl radicals by the free radical mechanism, similar to the crosslinking of PE.^{19, 20} However, the radiation

TABLE V
Relationship of Thermal Decomposition Properties Between Radiation Crosslinking and Degradation in PP/EVA Blends^a

Parameter	PP/EVA		
	70/30	50/50	30/70
ΔT_2 , $^\circ\text{C}$	1.0	1.80	3.0
Δm_1 , %	5.51	2.89	1.30
Gel content, %	lowest	middle	highest

^a Where ΔT_2 is change of thermal decomposition temperature with dose in the second step, and Δm_1 is the change of the weight loss in the first step, in PP/EVA blends at 100 kGy.

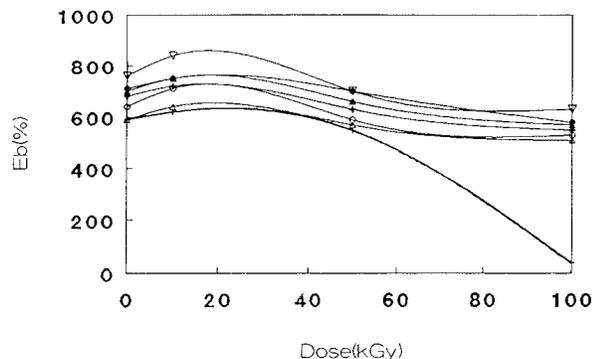


Figure 4 Elongation at break (E_b) versus the radiation dose in various PP/EVA blends. Key: (+) 100/0; (Δ) 90/10; (\circ) 80/20; (+) 70/30; (\blacktriangle) 50/50; (\bullet) 30/70; (∇) 0/100.

crosslinking efficiency of PP is lowered because of its tendency to undergo chain-scission and easy oxidation by irradiation in air. We confirmed in our previous paper⁶ that both alkyl radicals in PE chains and methyl radicals in PVA chains participate in the radiation crosslinking of EVA. The radiation crosslinking reactions of PP/EVA blends are related to those of PE and EVA chains. The higher mobile methyl radicals in PVA chains combined with alkyl radicals in PP chains can enhance crosslinking in PP/EVA blend so that the crosslinking in PP/EVA blend was enhanced by alkyl radicals in PP chains and methyl radicals in EVA chains. This result means that PP contributes to the crosslinking in PP/EVA blends and that PP degradation is prevented in PP/EVA blends; that is, methyl radicals in EVA chains are active sites for enhancement of radiation crosslinking in PP/EVA (50/50, 30/70) blends.

Mechanical properties

Radiation influences the properties of polymer materials. Suitable crosslinking of polymer materials is favorable to improving the properties of polymer materials, whereas excessive crosslinking makes polymer materials brittle and lose the value of their industrial application. We characterized the elongation at break (E_b) of irradiated PP/EVA blends as the radiation-resistant properties in the blends.

The E_b of PP decreased with the increasing radiation dose: the E_b value dropped to 40% at 100 kGy, whereas the E_b values in PP/EVA blends were \sim 550% at a radiation dose 100 kGy, as shown in the Figure 4.

This result explains why the radiation resistant properties of PP/EVA are superior to those of pure PP.

CONCLUSION

The EVA content in the PP/EVA blends can enhance radiation crosslinking in PP/EVA blends irradiated by γ -ray in air, especially in 50/50 and 30/70 PP/EVA blends.

The PP/EVA blends are compatible in the amorphous region. Good compatibility of the blends in higher amorphous region's content favorably enhances the radiation crosslinking in PP/EVA blends while preventing radiation degradation.

A novel method, a "step analysis" process in the TGA technique, was employed to study quantitatively the radiation crosslinking or degradation of PP/EVA blends. The methyl radicals in EVA chains have an enhancing effect on the radiation crosslinking and a preventative effect on radiation degradation in PP/EVA blends.

The radiation-resistant properties of PP/EVA blends are superior to that of pure PP.

References

- Li, S. Z. *Radiat Res Radiat Processing (China)* 19990, 8(2), 65.
- Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 1996, 62, 75.
- Gordiichuk, T. N.; Gordineko, V. P. *Kompoz Polim Mater* 1988, 38, 33.
- Mateev, M.; Karageogiev, S. *Radiat Phys Chem* 1998, 51, 205.
- Jamaliah, S.; Sharifah, H. S. S. A. A.; Kamaruddin, H. *Radiat Phys Chem* 2000, 58, 191.
- Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 2002, 86, 1296.
- Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 2002, 86, 553.
- Chen, W. X.; Bao, H. Y.; Jia, H. X.; Liu, D. Y.; Lu, X. D. *J Beijing Normal Univ* 1979, 2, 58.
- Thomas, S.; Gupta, B. R.; De, S. K. *Polym Degrad Stab* 1987, 18, 189.
- Minkova, L.; Nikolova, M. *Polym Degrad Stab* 1989, 23, 217.
- Mandelkern, L. *Crystallization of polymers*; McGraw-Hill: New York, 1964.
- Adams, J. H. *J Polym Sci, A-1* 1970, 8, 1279.
- Carlsson, D. J.; Wiles, D. M. *J Macromol Sci Rev Macromol Chem* 1976, C14, 65.
- Decker, C.; Mayo, F.R. *J Polym Sci, Polym Chem Ed* 1973, 11, 2847.
- Ginhac, J. M.; Gardette, J. L.; Arnaud, R.; Lemaire, J. *Makromol Chem* 1981, 182, 1017.
- Severini, F.; Gallo, R.; Ipsale, S. *Polym Degrad Stab* 1988, 22, 185.
- Zhang, Y. F. *Radiat Res Radiat Processing (China)* 1985, 3, 40.
- Spadaro, G. *Acta Polym* 1989, 40(11), 702.
- Charlesby, S. *Atomic Radiation and Polymers*; Pergamon Press: Elmsford, NY, 1960.
- Lacoste, J.; Vaillant, D.; Carlsson, D. J. *J Polym Sci, Part A: Polym Chem* 1993, 31, 715.