

Radiation Effects on LDPE/EVA Blends

Siqin Dalai, Chen Wenxiu

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

Received 26 February 2001; accepted 15 February 2002

ABSTRACT: Radiation effects of low-density polyethylene/ethylene-vinyl acetate copolymer (LDPE/EVA) blends were discussed. EVA content in the LDPE/EVA blends was an enhancement effect on radiation crosslinking of LDPE/EVA blends, and the highest radiation crosslinking was obtained when the EVA content was reached at 30% when irradiated by γ -ray in air. The phenomenon was discussed with the compatibility, morphology, and thermal properties of LDPE/EVA blends and found that the enhanced radiation crosslinking of the LDPE/EVA blends was proportional to the good compatibility, the increasing degree of the amorphous region's content of the LDPE/EVA blends, and the

vinyl acetate content of EVA. We also found that the vinyl acetate of EVA in the blends is easily oxidized by γ -ray irradiation in air. The possible radiation crosslinking and degradation mechanism of LDPE/EVA blends was discussed quantitatively with a novel method "step-analysis" process of irradiated LDPE/EVA blends in the thermal gravimetric analysis (TGA) technique. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1296–1302, 2002

Key words: radiation effects; LDPE/EVA blends; compatibility; amorphous region's content; vinyl acetate content

INTRODUCTION

High-energy irradiation (gamma or electron beam) is a well-known tool used for modification of polymers. Radiation-modified blends of polyolefins have become commercially important, with the properties of the blends 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 To our knowledge so far, only a few articles on the radiation effects of LDPE/EVA blends have been published. The effects of electron beam irradiation and EVA content on the radiation crosslinking in LDPE/EVA blends have been studied by Gordiichuk and Gordineko,³ Mateev and Karageogiev,⁴ and Jamaliah et al.⁵ This article studies the emphasis on the γ -radiation effects of LDPE/EVA blends in air with the compatibility, the amorphous region's content, and the vinyl acetate content. The possible radiation crosslinking and degradation mechanism of LDPE/EVA blends are discussed by using a novel method "step-analysis" of irradiated LDPE/EVA blends in the thermal gravimetric analysis (TGA) technique.

Correspondence to: S. Dalai at Beijing Gamma Chemical Technology Development Center, Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, China (sdalai@public.bta.net.cn).

Journal of Applied Polymer Science, Vol. 86, 1296–1302 (2002)
© 2002 Wiley Periodicals, Inc.

EXPERIMENTAL

Materials

LDPE, industry-grade MFR 2.0 g/10 min, product of No. 1 Chemical Factory of Yanshan Petrochemical Corp., Beijing, China, was used. EVA, industry-grade MFR 2.0 g/10 min, vinyl acetate content 18 and 14%, EVA18-3 and EVA14-2, product of Beijing Organic Chemical Factory, Beijing, China, was used.

Sample preparation and irradiation

The LDPE and EVA were blended together at ratios of 70/30, 50/50, and 30/70 by using two roll mixing mills at 115–120°C and pressed by a press machine at 120°C to form a sheet thickness of 1.0 ± 0.2 mm. Irradiation was carried out in air by a ⁶⁰Co γ -ray, and the dose rate was measured by Fricke dosimeter. Irradiation dose was selected in the range of 10–1000 kGy.

Characterization

Gel content was measured by a simplified reflux instrument manufactured in our laboratory.⁶ Glass transition temperature (T_g) and melting properties were examined by a TA 3000 Model DSC30 differential scanning calorimeter (DSC), produced by Mettler Co., Switzerland, in nitrogen atmosphere at a heating rate of 10°C/min, and the scanning temperature was examined in a range of –170–25 and 25–250°C. The crystallinities were calculated from the enthalpy of fusion, obtained by DSC of the melting behavior of

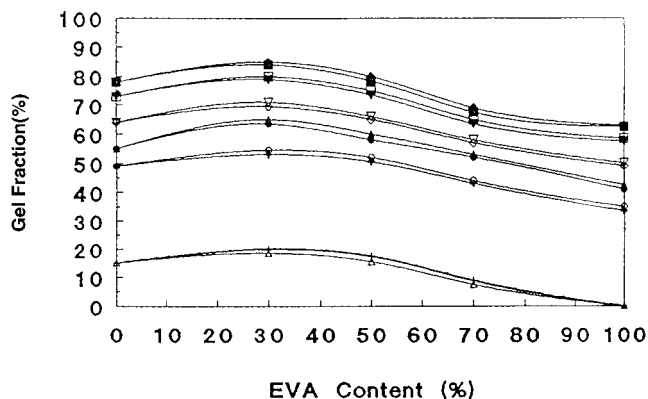


Figure 1 The gel fraction in the LDPE/EVA blend with different radiation doses versus the EVA content.

	10 kGy	50 kGy	100 kGy	200 kGy	500 kGy	1000 kGy
LDPE/EVA18-3:	+	○	▲	▽	◇	◆
LDPE/EVA14-2:	△	+	●	□	▼	■

samples and by using a value of 290 J/g⁷ as the enthalpy of fusion for completely crystalline polyethylene. TGA was carried out on a TA 3000 Model TG50 in nitrogen atmosphere at a heating rate of 10°C/min, and the step-analysis process was employed to determine the decomposition behavior.

RESULTS AND DISCUSSION

Gel content

The gel content of irradiated samples was determined to evaluate the content of crosslinking produced by irradiation. The results are shown in Figure 1 as gel fraction versus EVA content in the LDPE/EVA blends. The gel content of LDPE, EVA, and LDPE/EVA blends increase with increasing irradiation doses. The gel content of LDPE/EVA blends increases with increasing EVA content and the highest gel content is observed when LDPE, EVA, and LDPE/EVA blends increase with increasing irradiation doses. The gel content of LDPE/EVA blends increase with increasing EVA content and the highest gel content is observed when EVA content reaches 30%. The above results show that the EVA content had an enhancement effect on the crosslinking of LDPE/EVA blends, and it was

significant when the EVA content was 30% in the blends.

Figure 1 also shows the effect of EVA in different vinyl acetate (VA) contents on the gel content of LDPE/EVA blends. The radiation effects of EVA content on the gel contents of LDPE/EVA14-2 blends were similar to that of LDPE/EVA18-3 (i.e., the gel content of the two types of LDPE/EVA blends increased by increasing the EVA content), and the highest gel content of both LDPE/EVA blends was obtained when the EVA content was 30%. The gel content of LDPE/EVA blends was higher when EVA had a higher VA content, indicating that the higher VA content in the EVA was beneficial to the crosslinking of LDPE/EVA blends. Gordiichuk and Gordineko,³ examined the radiation effects of LDPE/EVA (EVA ≤ 30%) blends in EB irradiation and found that the EVA had a sensitive effect on the radiation crosslinking of LDPE/EVA blends. EVA had superior crosslinking to LDPE in EB irradiation⁸ and it was predictable and reasonable that the higher radiation crosslinkable EVA had a sensitive effect on the lower radiation crosslinkable LDPE. In our experimental condition, irradiated by γ -ray in air, the lower crosslinkable EVA has an enhancement effect of the radiation crosslinking on the higher crosslinkable LDPE. It is an interesting phenomenon and also our expecting result.

Compatibility

The gel contents of the polymer blend do not conform to the principle of simple adding. It is indicated that the radiation crosslinking reaction of each polymer in the blends does not occur independently and affects each other. The degree of this effect depends on the compatibility of the polymer blends.⁹ The DSC technique has been widely used in the study of polymer-polymer compatibility and the amount of crystallinity present in semicrystalline polymer blends. The Gordon-Taylor relation is applied to predict the compatibility of two polymers:

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

where T_{ga} and T_{gb} are the glass transition temperatures of polymer a and b , T_g is the glass transition temper-

TABLE I
The Values of the Glass Transition Temperature (T_g) (°C) of LDPE, EVA, and LDPE/EVA Blends

	LDPE	LDPE/EVA (70/30)	LDPE/EVA (50/50)	LDPE/EVA (30/70)	EVA
Experimental	-73	-79	-84	-89	-98
Calculated	—	-81	-86	-91	—

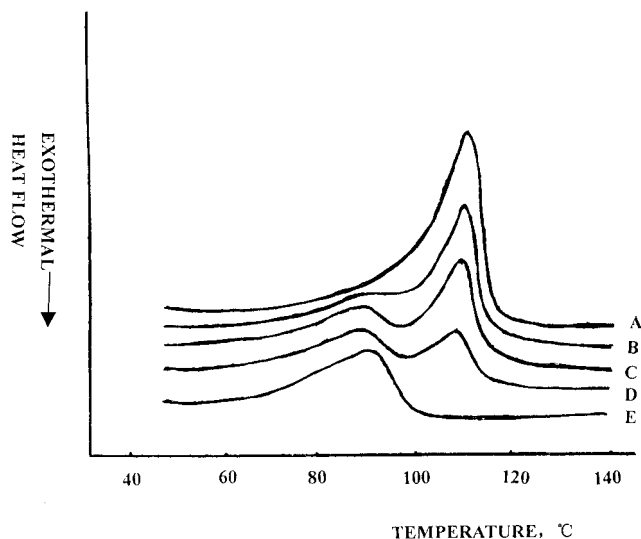


Figure 2 DSC thermograms of different LDPE/EVA blends, LDPE/EVA18-3: (A) 100/0; (B) 70/30; (C) 50/50; (D) 30/70; (E) 0/100, respectively.

ature of blend, and W_a and W_b are the weight fractions of a and b in the blends.

It was found that the validity of eq. (1) was well established for glass transition temperatures for all LDPE/EVA blends. Theoretical glass transition temperatures, as predicted for compatible blends, were in close agreement with experimental glass transition temperatures for all LDPE/EVA blends as shown in Table I and also in good agreement with Ray and Khastgir's DMA (dynamic mechanical analysis) result.¹⁰ This signifies that there is good compatibility in the amorphous region of the two polymers. LDPE and EVA exhibit two distinct endothermic peaks corresponding to the melting of two different crystallites present in the LDPE/EVA blend, as shown in Figure 2. The existence of two melting peaks for each blend, which coincide exactly with peaks corresponding to two pure components, indicates no probability of the compatibility of the crystalline phases of the two polymers. The polymers may be intimately mixed in the molten state, but as the blends are cooled from the melt, the crystallization of different components occurs separately, leading to two distinctly different crystalline phases.¹⁰

It is known that LDPE and EVA are compatible in the amorphous region for all the LDPE/EVA blends, and good compatibility of LDPE/EVA blends is favorable to an enhancement effect of EVA on the radiation crosslinking of LDPE/EVA blend, as observed in Figure 1.

Morphology

The crystallinities of LDPE/EVA blends are examined by the DSC technique. Table II shows that the crystallinity of EVA is lower than that of LDPE, that is to say, the amorphous region's content of EVA is higher than that of LDPE. The radiation crosslinking and degradation reactions mainly occurred in the amorphous regions of semicrystalline polymers during the irradiation.¹¹ Higher amorphous content is favorable to the radiation crosslinking of polymer, especially for high dose rate irradiation, such as electron beam (EB).⁸ The radiation crosslinking is lowered by oxidation of polymer during the irradiation in the air, especially for irradiation by low dose rate, such as γ -ray, as shown in Figure 1.

Table II also shows that the crystallinity of LDPE/EVA blends was decreased by increasing the EVA content in the blends, that is to say, the amorphous region's content increased by increasing the EVA content in the blends. The increasing degree of the gel content was significant when the amorphous region's content of LDPE/EVA blend was about 70% (EVA content is 30% in the blend), and no further increase was observed, although the amorphous region's content continued to increase in the blends, as shown in Figure 3. The results confirmed that radiation oxidation was also accelerated by increasing the amorphous region's content in the LDPE/EVA blends when irradiated by γ -ray in air. As a result, the radiation crosslinking of the blends was reduced, although the good compatibility and the higher amorphous region's content in the blends were beneficial to the radiation crosslinking of the blends.

The crystallinities of LDPE, EVA, and LDPE/EVA blends are slightly decreased by irradiation, as shown in Table II. These results indicate that the surfaces of crystalline, whether pure polymer or blends, are also oxidized when irradiated by γ -ray in air.

TABLE II
The Crystallinities (%) of LDPE, EVA, and LDPE/EVA Blends

	LDPE	LDPE/EVA (70/30)	LDPE/EVA (50/50)	LDPE/EVA (30/70)	EVA
Unirrad	38.7	30.4	24.6	19.3	10.8
10 kGy	38.5	30.4	24.4	19.2	10.7
100 kGy	38.3	30.3	23.8	18.8	9.8
500 kGy	37.9	29.3	23.0	17.8	9.0

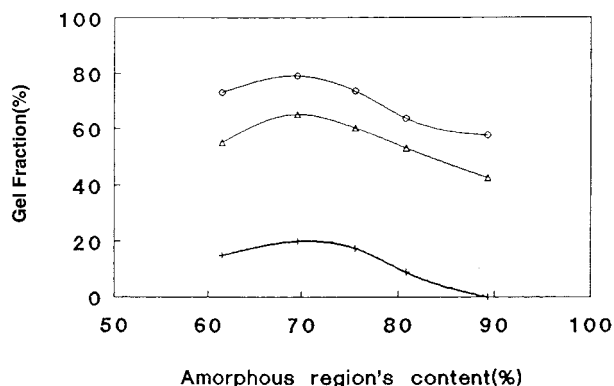


Figure 3 The gel fraction in the LDPE/EVA18-3 blend versus the amorphous region's content of the blend; (+) 10 kGy; (Δ) 100 kGy; (O) 500 kGy; respectively.

Reaction mechanism

EVA is a block copolymer consisting of the chains of PE and PVA, and the PVA content can be examined by TGA method.¹² The step analysis process in the TGA technique was employed to study the thermal degradation behavior of irradiated LDPE/EVA blends to evaluate the radiation crosslinking and degradation mechanism of LDPE/EVA blends.

Table 3 shows the TGA results of irradiated and unirradiated EVA and LDPE/EVA blends. Both EVA and LDPE/EVA blends show a two-step decomposition (i.e., the PVA chain in the EVA and LDPE/EVA blends decomposed first, and the PE chain decomposed in following step. We supposed that the decomposition temperature is increased when polymers are crosslinked by irradiation, and the decomposition temperature is decreased when polymers are degraded by irradiation. The decomposition temperatures of both EVA18-3 and EVA14-2 in the first step (T_1) decreased with increasing radiation dose, and the values of T_1 were lowered 2.3 and 1.7°C when the radiation dose reached 500 kGy. The values of Δm_1 in both EVAs were also lowered 1.60 and 0.99%, respectively, in the same given dose. These results indicate that the decomposition products of EVA in the first step are also included in the decomposed product of

PE chain of EVA. We characterized the decomposition temperature in the second step (T_2) as radiation crosslinking of EVA and LDPE/EVA blends. The rising degree of decomposition temperature of EVA18-3 in the second step, T_2 , was higher than that of EVA14-2, and the values of T_2 increased 6.4 and 4.3°C, when the radiation dose reached 500 kGy, as shown in Table III. These results illustrated that the decomposition temperatures were raised because the radiation crosslinking increased with increasing radiation dose and also explained that the higher PVA content in the EVA18-3 had more contribution to the radiation crosslinking than that of EVA14-2 (i.e., the PVA content is an enhancement effect on the radiation crosslinking of pure EVA). The enhancement effect of PVA content on the radiation crosslinking is also significant in the LDPE/EVA blends. The rising degree of T_2 in the LDPE/EVA18-3, 6.9°C, is higher than that of LDPE/EVA14-2, 4.5°C, as observed in table III. These results illustrate why the gel contents of all LDPE/EVA18-3 blends are always higher than that of all LDPE/EVA14-2 blends in the given dose, as observed in Figure 1.

Table IV shows that the TGA results of irradiated and unirradiated LDPE/EVA18-3 blends. The T_2 in the blends was raised with increasing radiation dose, and the rising degree of the values in the LDPE/EVA (70/30), 6.9°C, was higher than that of both LDPE/EVA (50/50) and LDPE/EVA (30/70), 3.0 and 1.5°C [i.e., the decomposition temperature of LDPE/EVA (70/30) was significantly higher than the other two blends]. These results illustrate that higher radiation crosslinking of LDPE/EVA (70/30) made T_2 of LDPE/EVA (70/30) higher than that of the other two blends, and they were consistent with the results of the gel content, as shown in Figure 1.

We compare the weight loss in the first step, observed in experimental, $(\Delta m_1)_{\text{exp}}$, with the weight loss in the first step calculated, $(\Delta m_1)_{\text{cal}}$, obtained by the weight loss of pure EVA in first step multiplying the ratio of EVA in the LDPE/EVA blends to evaluate the radiation degradation of LDPE/EVA blends, as shown in Table V. The values of $(\Delta m_1)_{\text{exp}}$ in the

TABLE III
The TGA Results of EVA and LDPE/EVA Blends

	EVA18-3				LDPE/EVA18-3 (70/30)				LDPE/EVA14-2 (70/30)				EVA14-2			
	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)
Unirrad	358.3	15.40	463.7	84.70	358.3	4.61	474.1	95.35	356.3	3.58	472.0	96.42	357.0	11.29	464.3	89.61
10 kGy	356.0	15.60	467.2	84.30	349.4	4.78	471.0	95.20	357.1	3.70	470.0	96.30	355.0	11.40	465.7	88.60
100 kGy	355.7	15.90	469.7	84.10	361.0	4.70	478.0	95.30	358.8	3.81	474.2	96.19	354.5	11.68	467.0	88.30
500 kGy	356.0	16.00	470.1	84.0	363.0	4.48	481.0	95.10	360.2	4.06	476.5	95.94	355.3	12.08	468.5	87.90

T_1 and T_2 are the peak decomposition temperature in the first and second step, respectively; Δm_1 and Δm_2 are the weight loss in the first and second step, respectively.

TABLE IV
The TGA Results of LDPE/EVA Blends

	LDPE			LDPE/EVA (70/30)			LDPE/EVA (50/50)			LDPE/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	471.3	99.86	474.1	357.7	8.31	468.0	357.8	11.09	468.0	91.69	357.8	468.0	358.3	15.4	463.7	84.70
10 kGy	469.0	99.86	471.0	357.0	8.70	466.3	359.4	11.20	463.0	91.30	359.4	463.0	356.0	15.60	467.2	84.30
100 kGy	474.0	99.80	478.0	361.0	8.60	468.3	359.7	11.80	468.3	91.40	359.7	468.3	355.7	15.90	469.7	84.10
500 kGy	476.0	99.82	481.0	363.0	8.70	471.0	358.0	11.90	469.5	91.30	358.0	469.5	356.0	16.00	470.1	84.0

The abbreviations are the same as table III.

LDPE/EVA (70/30) were extremely close to $(\Delta m_1)_{\text{cal}}$, whereas the values of $(\Delta m_1)_{\text{exp}}$ in the other two blends (50/50 and 30/70) were larger than that of $(\Delta m_1)_{\text{cal}}$. It was indicated that the radiation degradation also increased with the EVA content in the blends and identified that EVA is more easily oxidized than LDPE by irradiation in air. These facts quantitatively explained why the enhancement effect of EVA on the radiation crosslinking of LDPE/EVA blends is reduced by increasing the EVA content in the blends; the relationship is well expressed in Table VI.

LDPE, EVA, and LDPE/EVA blends are crosslinked by irradiation. Radiation crosslinking reaction of polyethylene is produced by the combination of alkyl radicals with the free-radical mechanism.^{13,14} EVA is a block copolymer consisting of PE and PVA chains, and both its alkyl radicals in the PE chain and methyl radicals on the acetoxy group in the PVA chains participated with the radiation crosslinking reaction, as discussed above. For additional assistance in identifying the above mechanism of radiation crosslinking of EVA, consider the work of Barth and Peter,¹⁵ Loan,¹⁶ and Sato,¹⁷ who have investigated the peroxide crosslinking of the EVA copolymer. Although peroxide crosslinking takes place at higher temperatures, presumably both radiation and peroxide crosslinking occur in amorphous polymer through a free-radical mechanism and similarities can be expected. These authors point out the active hydrogen at the PE chains and also identify the methyl hydrogens on the acetoxy group as a likely crosslinking site. To support a major contribution of the acetoxy group to crosslinking, they have all shown that peroxide-crosslinked EVA copolymer is converted to an alcohol copolymer and crosslinking is reduced. In addition, radiation crosslinking of poly(vinyl acetate) through the acetoxy group is suggested by Charlesby and Pinner.¹⁸ The results of gel content and decomposition behavior discussed above identify that the PVA content in the EVA is favorable to radiation crosslinking of EVA. Thus, there is ample evidence to implicate the acetoxy group as a potential crosslinking site and to confirm that both alkyl radicals in the PE chains and methyl radicals on the acetoxy group in the PVA chains participated with the radiation crosslinking of EVA.

The radiation crosslinking reactions of LDPE/EVA blends are carried on with the mechanisms of PE and EVA. LDPE/EVA blends are compatible in the amorphous region, and both PE and PVA chains have high mobility in the amorphous region, especially for flexible PVA chains. The higher mobile methyl radicals on the acetoxy group in the PVA chains are more easily combined with both alkyl radicals in the PE chains and themselves to crosslinking than that of alkyl radicals in the PE chains. It is the reason EVA has an enhancement effect on radiation crosslinking in the

TABLE V
Comparison $(\Delta m_1)_{\text{exp}}$ with $(\Delta m_1)_{\text{cal}}$ in the LDPE/EVA Blends

	LDPE/EVA (70/30)		LDPE/EVA (50/50)		LDPE/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	4.61	4.62	8.31	7.70	11.09	10.78
10 kGy	4.78	4.68	8.70	7.80	11.20	10.92
100 kGy	4.70	4.77	8.60	7.95	11.80	11.13
500 kGy	4.48	4.80	8.70	8.00	11.90	11.20

LDPE/EVA (70/30) blend. Radiation crosslinking in the LDPE/EVA blends is reduced by the combination of easily mobile methyl radicals on the acetoxy group in the PVA chains and oxygen molecules irradiated in the air, as obtained in the LDPE/EVA (50/50, 30/70) blends. The facts illustrate that PVA chains in the EVA have an enhancement effect on both radiation crosslinking and radiation oxidation, and the contradictory elements are reached to optimum equilibrium for radiation crosslinking in the LDPE/EVA (70/30) blend.

Mechanical properties

Radiation influences the properties of polymer materials. Suitable crosslinking of polymer materials is favorable to improving the properties of polymer materials, while excessive crosslinking made polymer materials brittle and lost the value of industrial application. We characterized the elongation at break of irradiated LDPE/EVA blends as the radiation-resistant properties in the blends.

The elongation at break of LDPE/EVA blends was longer than that of pure LDPE in a given dose (i.e., the elongation at break of LDPE/EVA blends was maintained around in 560%, whereas the value of pure LDPE was lowered to 410% in the radiation dose of 200 kGy), as shown in Figure 4. These results identify that the radiation-resistant properties of LDPE/EVA blends are superior to that of pure LDPE.

TABLE VI
The Relationship of Thermal Decomposition Properties Between Radiation Crosslinking and Degradation in the LDPE/EVA Blends

LDPE/EVA	70/30	50/50	30/70
$\Delta T_2, ^\circ\text{C}$	6.9	3.0	1.5
$\Delta m, \%$	-0.31	0.39	0.81
Gel content, %	highest	middle	lowest

ΔT_2 is the raising degree of thermal decomposition temperature in the second step, and Δm is the increasing degree of the thermal degraded product in the first step, of LDPE/EVA blends, in 500 kGy.

CONCLUSIONS

The EVA content in the LDPE/EVA blends has an enhancement effect on radiation crosslinking of the blends irradiated by γ -ray in the air, and the highest radiation crosslinking of the blend is observed when the EVA content is 30%. The higher VA content in the EVA is used, the higher the radiation crosslinking of LDPE/EVA is obtained.

The LDPE/EVA blends are compatible in the amorphous region, and the compatibility and higher amorphous region's content of the blends are favorable to the enhancement effect of EVA on the radiation crosslinking of LDPE/EVA blends. The radiation oxidation is also accelerated by increasing the amorphous region's content when irradiated by γ -ray in the air.

A novel method, step-analysis process in the TGA technique, is employed to study quantitatively the radiation crosslinking and degradation mechanism of LDPE/EVA blends, and it was found that the acetoxy group in the PVA chains of EVA chains are active sites for both enhancing radiation crosslinking and accelerating radiation oxidation.

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

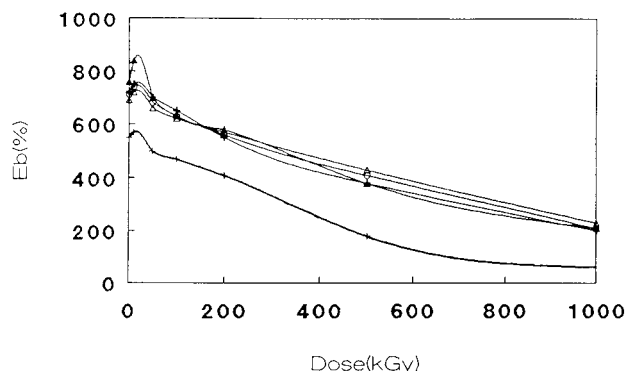


Figure 4 Elongation at break (Eb) in the LDPE/EVA versus the radiation dose. LDPE/EVA18-3: (+) 100/0; (Δ) 70/30; (\circ) 50/50; (+) 30/70; and (\blacktriangle) 0/100; respectively.

References

1. Li, S. Z. *Radiat Res Radiat Process (China)* 1990, 8 (2), 65.
2. Dalai, S.; Wenxiu, C. *J Appl Polym Sci* 1996, 62, 75.
3. Gordiichuk, T. N.; Gordineko, V. P. *Kompoz Polim Mater* 1988, 38, 33.
4. Mateev, M.; Karageogiev, S. *Radiat Phys Chem* 1998, 51, 205.
5. Jamaliah, S.; Sharifah, H. S. S. A. A.; Kamaruddin, H. *Radiat Phys Chem* 2000, 58, 191.
6. Chen, W. X.; Bao, H. Y.; Jia, H. X.; Liu, D. Y.; Lu, X. D.; Beijing J. Normal Univ 1979, 2, 58.
7. Mandelkern, L. *Crystallization of Polymers*; McGraw-Hill: New York, 1964.
8. Burns, N. M. *Radiat Phys Chem* 1979, 14, 797.
9. Zhang, Y. F. *Radiat Res Radiat Process (China)*, 1985, 3, 40.
10. Ray, I.; Khastgir, D. *Polymer* 1993, 34, 10, 2030.
11. Spadaro, G. *Acta Polym* 1989, 40, 11, 702.
12. Wendlandt, W. M. *Thermal Methods of Analysis*; 2nd. Ed.; Wiley: New York, 1974.
13. Charlesby, A. *Atomic Radiation and Polymers*; Pergamon Press: Tarrytown, NY, 1960.
14. Dole, M. *The Radiation Chemistry of Macromolecules*; Academic Press: San Diego, 1973.
15. Barth, H.; Peter, J. *Kautschuk Gummi Kunstst* 1961, 14.
16. Loan, L. D. *Rubber Chem Tech* 1967, 40, 1, 149.
17. Sato, M. *Nippon Gomu Kyohaishi* 1970, 43, 9, 753.
18. Charlesby, A.; Pinner, S. H. *Proc R Soc London, Ser. A* 1959, 249, 367.