Radiation Effects on HDPE/EVA Blends

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ABSTRACT: In this article, we discuss the radiation effects of high-density polyethylene (HDPE)/ethylene–vinyl acetate (EVA) copolymer blends. In comparison with the low-density polyethylene/EVA blends, the EVA content in the HDPE/EVA blends had a lower enhancement effect on radiation crosslinking by γ-ray irradiation in air. The phenomenon is discussed with the compatibility, morphology, and thermal properties of HDPE/EVA blends. The HDPE/EVA blends were partly compatible in the amorphous region, and radiation crosslinking of the HDPE/EVA blend was less significant, although increasing the amorphous region's content of the HDPE/EVA blends and the vinyl acetate content of EVA were beneficial to radiation crosslinking. The good compatibility was a prerequisite for the enhancement effect of EVA on the radiation crosslinking of the polyethylene/EVA copolymer. The radiation crosslinking and the degradation mechanism of HDPE/EVA blends were examined quantitatively by a novel method, the step analysis process of irradiated HDPE/EVA blends with a thermal gravimetric analysis technique. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 553–558, 2002

Key words: radiation; HDPE/EVA blends; compatibility; amorphous; vinyl acetate contents

INTRODUCTION

High-energy [γ or electron beam (EB)] irradiation is a well-known tool for the 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 (LDPE)/ethylene–vinyl acetate (EVA) copolymer blends are widely used in heat-shrinkable materials for wire and cable insulation[1] and foam materials.[2] The effects of EB irradiation and EVA content on the radiation crosslinking in LDPE/EVA blends have been studied by Gordiichuck and Gordineko,[3] Mateev and Karagegeorgiev,[4] and Jamaliah et al.[5] In a previous study,[6] we investigated the γ-radiation effects of LDPE/EVA blends in air and found that EVA had an enhancement effect on the radiation crosslinking of LDPE/EVA blends. To our knowledge, so far, no article on the radiation effects of high-density polyethylene (HDPE)/EVA blends has been published.

In this study, we focused on the γ-radiation effects of HDPE/EVA blends in air with compatibility, amorphous region's content, and vinyl acetate content. The radiation crosslinking and degradation mechanism of HDPE/EVA blends was examined with a novel method, step analysis of the irradiated HDPE/EVA blends with a thermal gravimetric analysis (TGA) technique.

EXPERIMENTAL

Materials

We used HDPE, an industry-grade MFR (085 g/10 min; No. 1 Chemical Factory, Yanshan Petrochemical Corporation, Beijing, China). We also used EVA, an industry-grade MFR (2.0 g/10 min, vinyl acetate content = 18 wt %, EVA18-3; Beijing Organic Chemical Factory, Beijing, China).

Sample preparation and irradiation

HDPE and EVA were blended together at ratios of 70/30, 50/50, and 30/70 with two-roll mixing mills at 135–140°C and pressed by a press machine at 140°C to form a sheet with a thickness of 1.0 ± 0.2 mm. Irradiation was carried out by a ⁶⁰Co γ-ray in air, and the dose rate was measured by a Fricke dosimeter. The irradiation dose was selected in the range 10–1000 kGy.

Characterization

Gel content was measured by a simplified reflux instrument manufactured in our laboratory.[7] Glass-transition temperatures (T_g's) and melting properties were examined by a TA3000 model DSC30 differential scanning calorimeter (Mettler Company, Switzerland) in a nitrogen atmosphere at a heating rate of 10°C/min and with scanning temperature ranges of −170 to

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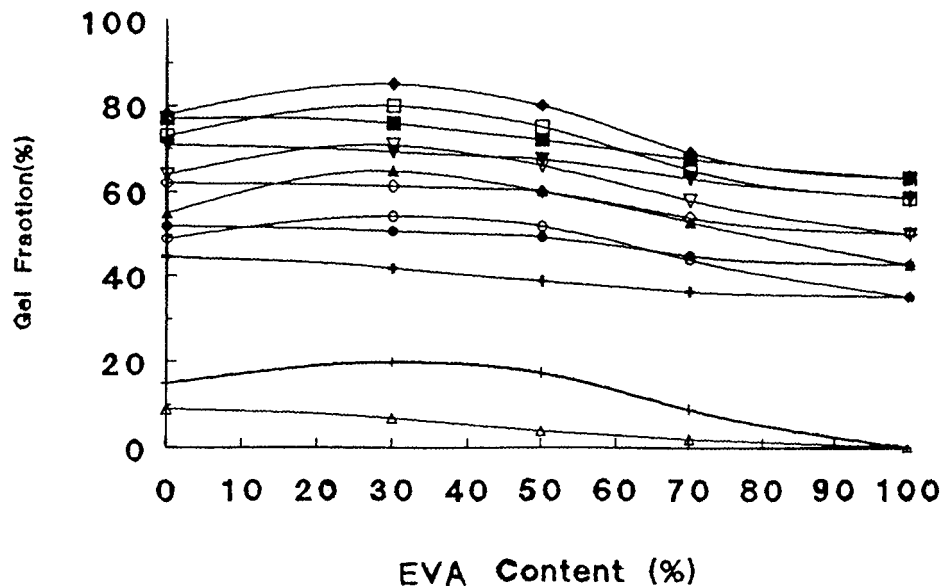
Figure 1 Gel fraction in the HDPE/EVA blend with different radiation doses versus the EVA content compared with the LDPE/EVA blend. LDPE/EVA: (+) 10, (○) 50, (▲) 100, (▽) 200, (◇) 500, and (♦) 1,000 kGy. HDPE/EVA: (△) 10, (+) 50, (●) 100, (□) 200, (▼) 500, and (■) 1,000 kGy.

25°C and 25–250°C. The crystallinities were calculated from the enthalpy of fusion, obtained by differential scanning calorimetry (DSC) of the melting behavior of samples and with a value of 290J/g[8] as the enthalpy of fusion for completely crystalline polyethylene (PE). TGA was carried out in a TA3000 model TG50 in a nitrogen atmosphere at a heating rate of 10°C/min, and the step analysis process was employed to determine the decomposition behavior.

RESULTS AND DISUSSION

Gel content

The gel content of the irradiated samples was determined to evaluate the content of crosslinking induced by irradiation. The comparison of a series curve on HDPE/EVA blends with a series curve on LDPE/EVA blends in Figure 1 indicates that the gel fractions of HDPE/EVA blends decreased with increasing EVA content, but the gel fractions of LDPE/EVA blends increased with increasing EVA content until its contents were less than or equal to 30 wt % and then decreased with EVA content from 30 to 100 wt %. The gel fractions of HDPE/EVA were lower than those of

LDPE/EVA with the same EVA content of blends in each given irradiation dose. This indicates that the EVA content caused less of an enhancement effect on the radiation crosslinking of HDPE/EVA blends. In our previous article,[6] we found that the EVA content had an enhancement effect on the crosslinking of LDPE/EVA blends. The facts identify that the effects of the EVA content on radiation crosslinking between LDPE/EVA and HDPE/EVA blends were different, and we explain the phenomenon with the different of the compatibility and morphology of both blends.

Compatibility

The gel fractions induced by irradiation on the polymer blends were not in conformity to the simple adding principle, which indicates that the radiation crosslinking reaction of components in the polymer blends did not occur independently. Various components affected each other, and it was dependent on the compatibility.[9] The DSC technique has been widely used to study of polymer–polymer compatibility and the amount of crystallinity present in semicrystalline polymer blends. The Gordon–Taylor relation was ap-

TABLE I
T_g of HDPE, EVA, and HDPE/EVA Blends

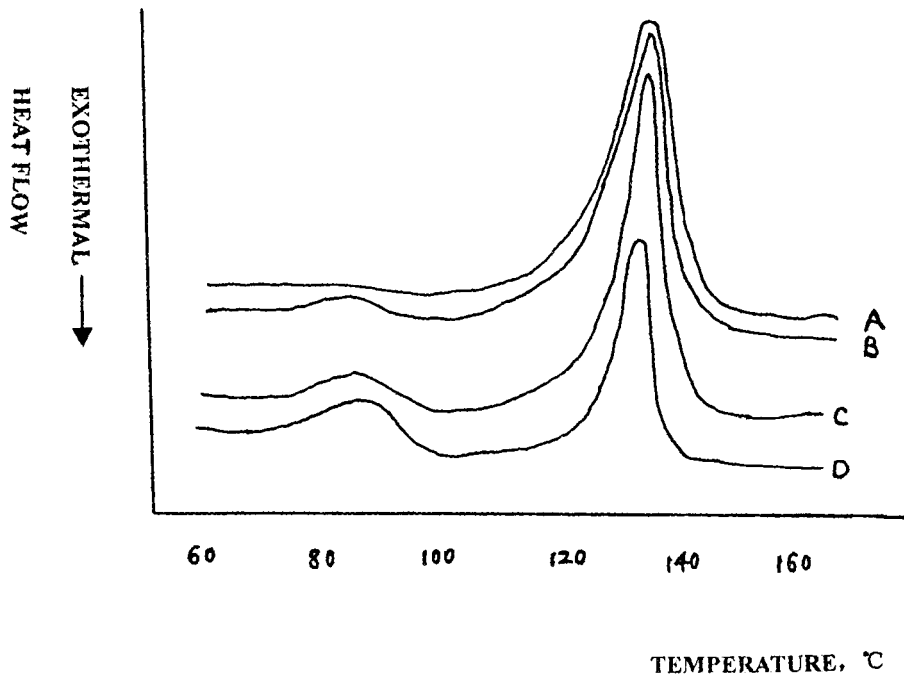|	HDPE	HDPE/EVA (70/30)	HDPE/EVA (50/50)	HDPE/EVA (30/70)	EVA
		−69	−75	−80	−84	−98
Experimental T_g (°C)			−88	−92	−95	
Calculated T_g (°C)	−78	−84	−89			

Figure 2 DSC thermograms in different HDPE/EVA blends. HDPE/EVA ratio: (A) 100/0, (B) 70/30, (C) 50/50, and (D) 30/70.

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

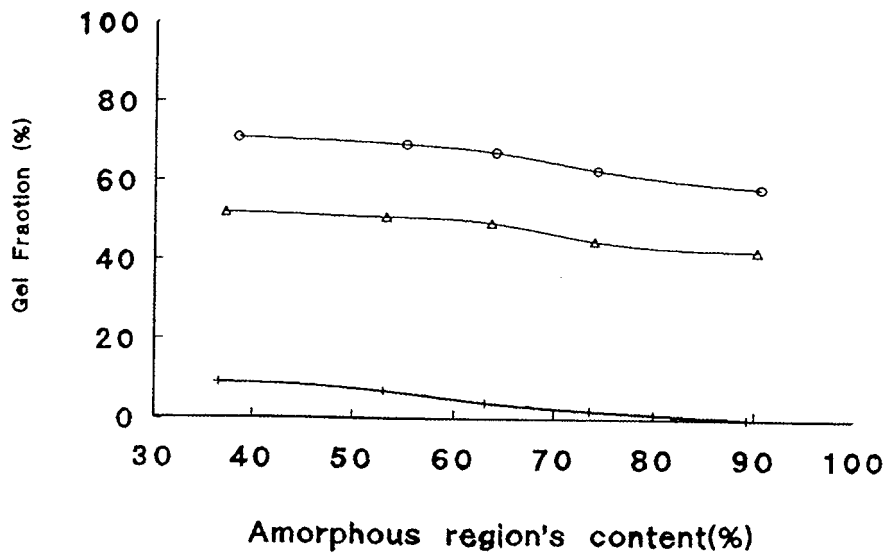|	HDPE	HDPE/EVA (70/30)	HDPE/EVA (50/50)	HDPE/EVA (30/70)	EVA
Unirradiated	63.2	47.5	37.3	26.4	10.8
10 kGy	63.4	46.9	36.9	26.2	10.7
100 kGy	62.8	46.8	36.4	25.8	9.8
500 kGy	61.6	45.9	36.0	25.4	9.0

Figure 3 Gel fraction in the HDPE/EVA blend versus the amorphous region's content in the blend: (+) 10, (△) 100, and (○) 500 kGy.

plied to predict the compatibility of polymer blends with two components:

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

where T_{ga} and T_{gb} are the respective T_g's of components a and b, T_g is the glass-transition temperature of the blend, and W_a and W_b are the respective weight fractions of a and b in the blends.

There were two experimental T_g's that appear in the HDPE/EVA blends as shown in Table I. The values (-88, -92, and -95) in the second line of Table I were related with the components of EVA in the HDPE/EVA blends with ratios of 70/30, 50/50, and 30/70 separately. The T_g values (-75, -80, and -84) in the upper line of Table I were related with the components of HDPE in the blends, and those values were close to the calculating values (-78, -84, and -89) from eq. (1) in the bottom line of Table I. It is illustrated that the compatibility of the HDPE/EVA blends rich in HDPE content was better than that of those rich in EVA content. The more compatible the blend was, the higher the gel fraction was, as shown in the Figure 1. The gel factions are from higher to lower orders on the HDPE/EVA blend with ratios of 70/30, 50/50, and 30/70.

Two distinct endothermic peaks corresponding to the melting of two different crystallites were present in the HDPE/EVA blend as shown in Figure 2. This indicates that HDPE and EVA were incompatible in the crystalline region. It was known that HDPE and EVA were partly compatible in the amorphous region for HDPE/EVA blends, that the interactions between the two components in the partly compatible blends were weaker than that of fully compatible blends, and that this was unfavorable to the enhancement effect of the EVA content on the radiation crosslinking of HDPE/EVA blends. So, there was less of an enhancement effect of EVA on the radiation crosslinking of the HDPE/EVA blend, as shown in Figure 1.

Morphology

The crystallinities of HDPE/EVA blends were examined by the DSC technique. Table II shows that the crystallinity of EVA was lower than that of HDPE; the amorphous region's content in EVA was higher than that of HDPE. The radiation crosslinking and degradation reactions mainly occurred in the amorphous regions of the semicrystalline polymers.[10] Higher amorphous content is favorable to the radiation crosslinking on the polymer, especially under high dose-rate irradiation, such as EB irradiation.[11] The radiation crosslinking is low if it irradiates in the air, especially in low dose-rate irradiation, such as γ-ray irradiation.

TABLE III
TGA Results for HDPE/EVA Blends

	HDPE				HDPE/EVA (70/30)				HDPE/EVA (50/50)				HDPE/EVA (30/70)				EVA			
	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 (%)	T_1 (°C)	Δm_1 (%)	T_2 (°C)	Δm_2 (%)
Unirradiated			478.0	99.70	358.2	4.56	479.0	95.43	358.0	8.36	478.1	91.60	358.3	10.94	476.3	89.00	358.3	15.4	463.7	84.70
10 kGy			478.3	99.80	358.4	4.61	479.4	95.35	358.2	8.55	478.5	91.41	358.5	11.02	476.5	88.95	356.0	15.60	467.2	84.30
100 kGy			480.6	99.70	359.3	4.70	480.1	95.26	359.2	8.70	479.2	91.25	358.9	11.65	477.1	88.35	355.7	15.90	469.7	84.10
500 kGy			483.0	99.90	360.5	4.82	484.5	95.14	359.8	9.10	480.9	90.86	360.0	12.00	477.7	87.95	356.0	16.00	470.1	84.0

T_1 and T_2 are the peak decomposition temperatures in the first and second step, respectively.

TABLE IV
Comparison $(\Delta m_1)_{\text{exp}}$ with $(\Delta m_1)_{\text{cal}}$ for the HDPE/EVA Blends

	HDPE/EVA (70/30)		HDPE/EVA (50/50)		HDPE/EVA (30/70)	
	$(\Delta m_1)_{\text{exp}}$ (%)	$(\Delta m_1)_{\text{cal}}$ (%)	$(\Delta m_1)_{\text{exp}}$ (%)	$(\Delta m_1)_{\text{cal}}$ %	$(\Delta m_1)_{\text{exp}}$ %	$(\Delta m_1)_{\text{cal}}$ %
Unirradiated	4.56	4.62	8.36	7.70	10.94	10.78
10 kGy	4.61	4.68	8.55	7.80	11.02	10.92
100 kGy	4.70	4.77	8.70	7.95	11.65	11.13
500 kGy	4.82	4.80	9.10	8.00	12.00	11.20

Table II also shows that the crystallinity of HDPE/EVA blends decreased with increasing EVA content in the blends; the amorphous region's content increased with increasing EVA content in the blends. The gel content of the HDEP/EVA blends decreased with increasing amorphous region content in the HDPE/EVA blends, as shown in Figure 3. The results were confirmed that radiation oxidation was accelerated significantly in the partly compatible HDPE/EVA blends under γ-ray irradiation in air. As a result, the radiation crosslinking of the HDPE/EVA blends was reduced, despite the higher amorphous region content in the blends.

The crystallinities of HDPE, EVA, and the HDPE/EVA blends were slightly decreased by irradiation, as shown in Table II.

Reaction mechanism

EVA is a block copolymer that consists of the chains of PE and poly(vinyl acetate) (PVA), and the PVA content can be examined by the TGA method.[12] We employed the step analysis process in the TGA technique to study the thermal degradation of irradiated HDPE/EVA blends to evaluate its radiation crosslinking and degradation mechanism.

Table III shows the TGA results on irradiated and unirradiated HDPE/EVA blends. The HDPE/EVA blends showed a two-step decomposition; that is, the PVA chain in the HDPE/EVA blends decomposed first, and the PE chain decomposed in the second step. We suppose that after irradiation, the decomposition temperature of polymers increased with crosslinking and decreased with degradation. We characterized the decomposition temperature in the second step (T_2) as the radiation crosslinking of HDPE/EVA blends. T_2 (484.5°C) of HDPE/EVA (70/30) at 500 kGy was compared with T_2 (479.0°C) before irradiation; the raising temperature was 5.5°C, and this raising value was higher than those raising values of 2.8°C for HDPE/EVA (50/50) and 1.4°C for HDPE/EVA (30/70) as shown in Table III. These results illustrate that the decomposition temperatures (T_2) were raised with the crosslinking that was induced by irradiation; that is, T_2 also increased with dose. The radiation crosslinking of HDPE/EVA (70/30) was higher than that of

HDPE/EVA (50/50) and HDPE/EVA (30/70) because the compatibility of HDPE/EVA (70/30) was better than that of HDPE/EVA (50/50) and HDPE/EVA (30/70). This coincided with the results of gel content and compatibility in the HDPE/EVA blends as discussed previously. These facts quantitatively explain that the good compatibility of PE/EVA copolymer blends was a prerequisite for the enhancement effect of EVA on the radiation crosslinking of PE/EVA copolymer blends.

To evaluate the radiation degradation of HDPE/EVA blends, we obtained the weight loss in the first step, observed in the experiment [$(\Delta m_1)_{\text{exp}}$] in comparison with that calculated [$(\Delta m_1)_{\text{cal}}$] by the weight loss of pure EVA in the first step multiplied by the content ratio of EVA in the HDPE/EVA blends, as shown in Table IV. The values of $(\Delta m_1)_{\text{exp}}$ in HDPE/EVA (70/30) were 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 those of $(\Delta m_1)_{\text{cal}}$. The radiation degradation also increased with increasing EVA content in the blends, and EVA was more easily oxidized than HDPE in the HDPE/EVA blends by irradiation in air. The better compatibility was favorable to protect the oxidation of EVA in the blends. The relationships of radiation crosslinking and the degradation behavior of HDPE/EVA blends are shown in Table V.

Radiation crosslinking took place between PE and EVA components in HDPE/EVA blends. The PE and PVA chain components have high mobility in the amorphous region, especially for flexible PVA chains. The more highly mobile methyl radicals on the ace-

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

LDPE/EVA	70/30	50/50	30/70
ΔT_2 (°C)	5.5	2.8	1.4
Δm (%)	0.26	0.74	1.04
Gel content (%)	Highest	Middle	Lowest

ΔT_2 is the raising value of thermal decomposition temperature in the second step, and Δm is the weight degree of the thermal degraded product in the first step of LDPE/EVA blends in 500 kGy.
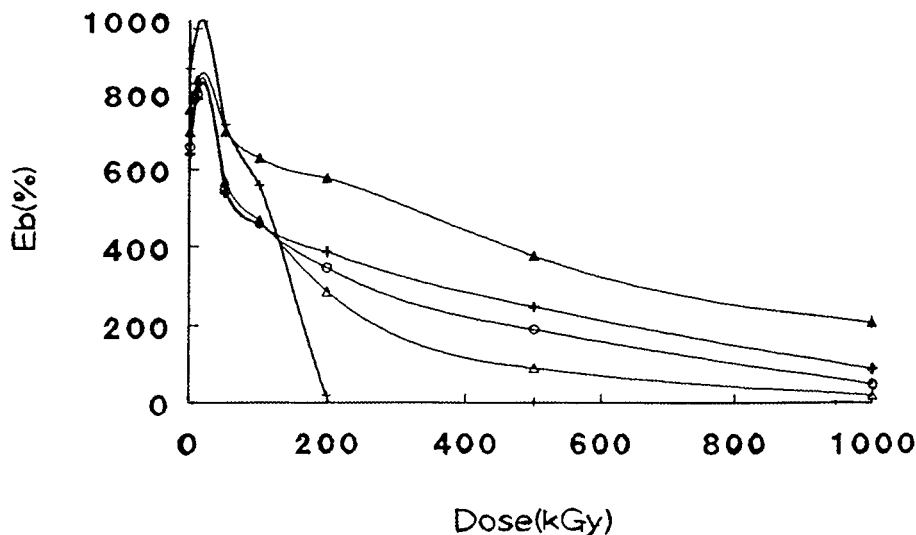
Figure 4 E_b in the HDPE/EVA versus the radiation dose. LDPE/EVA18-3 ratio: (+) 100/0, (△) 70/30, (○) 50/50, (+) 30/70, and (▲) 0/100.

toxy group in the PVA chains are more easily combined with alkyl radicals in the PE chains than with alkyl radicals combined each other within the PE chains. The HDPE/EVA blends were partly compatible in the amorphous regions, so the enhancement effect of EVA content on the radiation crosslinking of HDPE/EVA blends was less significant.

Mechanical properties

Radiation influences the properties of polymer materials. Suitable crosslinking of polymer materials was favorable for improving the properties of polymer materials, whereas excessive crosslinking made the polymer materials brittle, causing them to lose value for industrial application. We characterized the elongation at break (E_b) of irradiated HDPE/EVA blends as the radiation-resistant properties in the blends.

E_b of HDPE/EVA blends was less than that of pure HDPE in the range of radiation dose until 200 kGy was reached. Poor compatibility of HDPE/EVA blends was unfavorable for improving the radiation resistance of the blends. It had no practical value for industrial application, although the some improvement was observed in the radiation dose over 200 kGy, as shown in Figure 4.

CONCLUSIONS

The enhancement effect of EVA content on radiation crosslinking was not significant in the HDPE/EVA blends, compared with the LDPE/EVA blends.[6]

The HDPE/EVA blends were partly compatible in the amorphous region, and it was unfavorable for the enhancement effect of EVA on the radiation crosslinking of HDPE/EVA blends. The radiation oxidation also took place in the amorphous region under γ-ray irradiation in air. The good compatibility is a prerequisite for the enhancement effect of EVA on the radiation crosslinking of the PE/EVA copolymer.

We used a novel method, the step analysis process with a TGA technique, to study quantitatively the radiation crosslinking and degradation mechanism of HDPE/EVA blends and found that the PVA chains in the EVA had the effect of enhancing radiation crosslinking by γ-ray irradiation in air.

The radiation-resistant properties of HDPE/EVA blends were not better than those of pure HDPE.

References

1. Li, S. Z. Radiat Res Radiat Process (China) 1990, 8, 65.
2. Dalai, S.; Wenxiu, C. J Appl Polym Sci 1996, 62, 75.
3. Gordiichuk, T. N.; Gordineko, V. P. Kompoz Polim Mater 1998, 38, 33.
4. Mateev, M.; Karagegeogiev, 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. Dalai, S.; Wenxiu, C. J Appl Polym Sci, to appear.
7. Chen, W. X.; Bao, H. Y.; Jia, H. X.; Liu, D. Y.; Lu, X. D. J Beijing Normal University 1979, 2, 58.
8. Mandelkern, L. Crystallization of Polymers; McGraw-Hill, 1964.
9. Zhang, Y. F. Radiat Res Radiat Process (China) 1985, 3, 40.
10. Spadaro, G. Acta Polym 1989, 40, 702.
11. Burns, N. M. Radiat Phys Chem 1979, 14, 797.
12. Wenlandt, W. M. Thermal Methods of Analysis, Ind. ed.; Wiley, 1974.