

Investigation of Radiation-Crosslinked Foam of LDPE/EVA Blends

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SYNOPSIS

Low-density polyethylene/ethylene–vinyl acetate copolymer (LDPE/EVA) blend was irradiated by γ -ray and then expanded by heat as a foamed material. The EVA content in the LDPE/EVA blend was benefited to form a gel. The gel fraction of the irradiated LDPE/EVA blend increased with the increasing of its EVA content in a given dose. The gel fraction values of LDPE/EVA blend with 30% EVA content were higher than those of other blends in a same given dose; its gel fraction value was 1.7 times as those values of the LDPE without EVA. The gel fractions of the LDPE/EVA blend were increased with radiation dose in oxygen, in air, and in nitrogen, and the formation of gel was limited by oxygen. The oxidation products of the foam of the LDPE/EVA blend were observed in nitrogen, in air, and in oxygen by Fourier transform IR spectra. The LDPE/EVA blend system has no protection effect from oxidation in comparison with the LDPE system without EVA, which has less oxidation product than those without EVA in a same given gel fraction. The gel fraction of the LDPE/EVA blend around 25–35%, radiation dose 25 ± 5 kGy, irradiated by γ -ray in air or in nitrogen, with higher expansion ratio (19), smaller cell diameter (0.175 mm), lower apparent density (0.042 g/cm^3), higher tensile strength (0.40 MPa), and longer elongation at break (290–360%) foam of the LDPE/EVA blend were selected. These were optimum conditions for application in this system. The relations among gel fraction of the LDPE/EVA blend, expansion ratio, apparent density, average cell diameter, and mechanical properties of the foam were discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The application of crosslinked polyethylene (PE) foam has expanded due to its insulation from heat and resistance to shock. The traditional manufacture of PE containing the foaming agent and the peroxide crosslinking agent was foamed by heating.¹ PE containing the foaming agent was crosslinked by irradiation without the crosslinking agent and then foamed by heating,³ compared with the traditional, which had smooth surface due to the uniform of crosslinking.² Radiation crosslinked PE foam was also induced by an electron beam (EB).^{4,5} High energy was required due to the limitation of penetration by the EB because of the thickness of the sheet.²

This paper examines emphasis to irradiated dose, mechanical properties, and the benefit of ethylene–vinyl acetate copolymer (EVA) content on low-density PE (LDPE)/EVA blend. The influence of atmospheres and the effect of dose rate are studied. The Fourier transform infrared (FTIR) spectra of foam revealed the oxidation level. The relations among gel fraction of LDPE/EVA blend, expansion ratio, apparent density, average cell diameter, and tensile properties of foam are discussed.

EXPERIMENTAL

Materials

LDPE, industry grade MFR 2.0 g/10 min, product of No. 1 Chemical Factory of Yanshan Petrochemical Corporation, Beijing, China, was used. EVA, industry grade MFR 2.0 g/10 min, vinyl acetate con-

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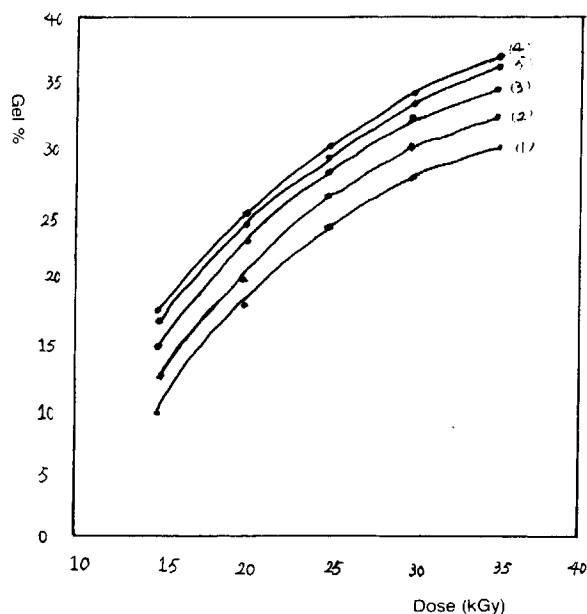


Figure 1 Gel % in the LDPE/EVA blend with different EVA content versus dose, irradiated by γ -ray in air, dose rate 16.2 kGy/h with EVA content 0 (curve 1), 20% (curve 2), 25% (curve 3), 30% (curve 4), 50% (curve 5), respectively.

tent 18%, product of Beijing Organic Chemical Factory, Beijing, China, was used. Azodicarbonamide (industry grade, decomposition point 190°C) was from Tianjin Organic Chemical Factory. Xylene AP and absolute alcohol AP were from Beijing Chemical Factory.

Sample Preparation, Irradiation, and Expansion

One hundred parts (wt) of the LDPE/EVA blend and 15 parts (wt) of the azodicarbonamide were mixed by two roll mixing mills at 115–120°C and pressed by press machine at 120°C to form a sheet thickness of 2.0 ± 0.2 mm. Sheets were irradiated by EB (dose rate 360 kGy/h) or by γ -ray (dose rate 16.2 kGy/h). The irradiated sheets were expanded by hot air at 200°C to obtain a formed sheet.

Examination

Gel fraction was measured by a simplified reflux instrument manufactured in our laboratory.⁶ Apparent density was measured by National Standards GB 6343-86. Tensile strength and elongation at break were measured by National Standards GB6344-86. Average cell diameter was determined by TX-1 optical microscope with a magnification of $\times 100$. IR

spectra was recorded with a Nicolt 60 XB-FTIR Spectrophotometer.

RESULTS AND DISCUSSION

Gel Fraction of the Foam of the LDPE/EVA Blend

Benefit of EVA Content

Figure 1 shows the relation of gel % versus dose in that the gel fraction in the irradiated LDPE/EVA blend increased with the increasing of its EVA content in a given dose. The gel fraction values of LDPE/EVA blend with 30% EVA content were higher than those of other blends in a same given dose, and its gel fraction values were 1.7 times as those values of LDPE without EVA. If the EVA content in the blend was increased up to 50%, the gel fractions of LDPE/EVA blend have not increased further; there was a maximum value of gel fraction in the LDPE/EVA blend with 30% EVA content in each given dose, i.e., the gel fraction value of blend was not composed by each component of blend additionally. That means the EVA content in the irradiated LDPE/EVA blend system possessed sensitive effects on the gel fraction; this effect was favorable to decrease the required dose for gel formation.

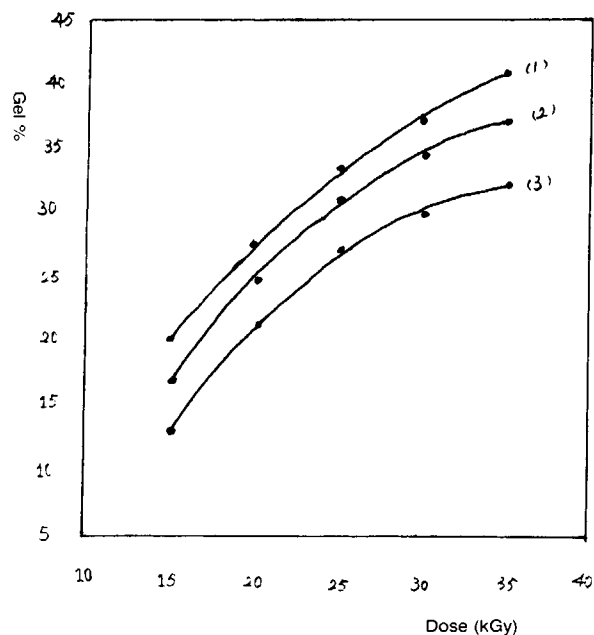


Figure 2 Gel % in the LDPE/EVA (70/30) blend versus dose in nitrogen (curve 1), in air (curve 2), and in oxygen (curve 3), irradiated by γ -ray, dose rate 16.2 kGy/h.

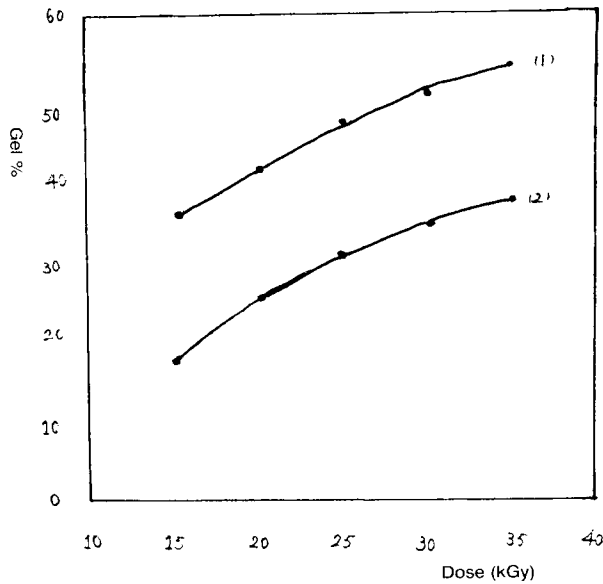


Figure 3 Gel % in the LDPE/EVA (70/30) blend versus dose, irradiated by EB (curve 1) and γ -ray (curve 2) in air, dose rate 360 and 16.2 kGy/h, respectively.

Influence of the Atmospheres

Figure 2 shows that gel fractions of the irradiated LDPE/EVA blend versus dose in oxygen, in air, and in nitrogen and the gel fractions irradiated in oxygen were less than those in air and in nitrogen due to oxygen as a scavenger of radicals inhibiting the crosslinking of blend by diffusion. So, the effect of radiation atmospheres must be considered in LDPE/EVA blend system.

Effect of Dose Rate

Figure 3 shows the gel fraction versus dose in various dose rates. In higher dose rates, irradiated by EB, the gel fraction of LDPE/EVA blend was higher than those in the lower dose rates, irradiated by γ -ray, because the reaction rate of radicals was accelerated in higher dose rate compared with the diffusion control of oxygen.

Oxidation Product in Irradiated Sheet of the LDPE/EVA Blend

For comparison, the FTIR spectra of the irradiated LDPE samples without EVA in air is shown in Figure 4. The spectra in the 1700-cm^{-1} region with three bands were observed, i.e., 1710, 1730, and 1745 cm^{-1} , indicated various ketonic groups were formed by oxidation during irradiation.⁷ The absorbance of the $\text{C}=\text{O}$ band at 1730 cm^{-1} in different atmospheres

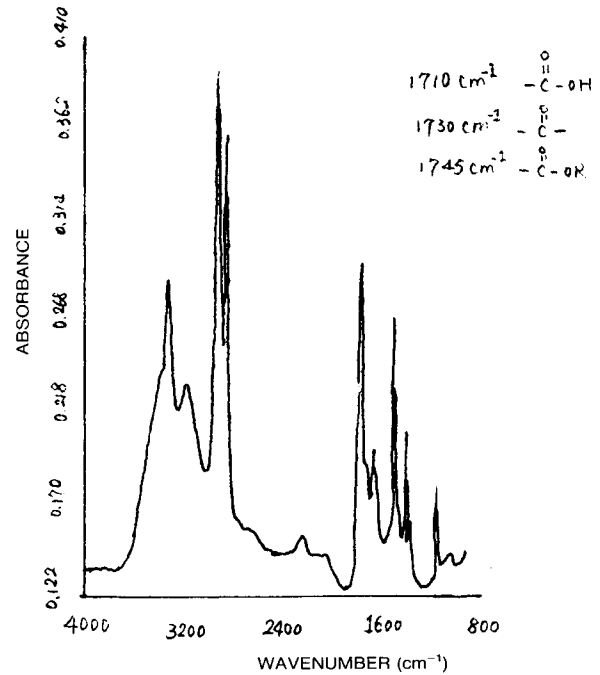


Figure 4 FTIR spectra of the LDPE without EVA, irradiated by γ -ray in air.

versus irradiated dose is shown in Figure 5. The absorbance in the 1730 cm^{-1} increased with the increasing of radiation doses in oxygen, in air and also in nitrogen. The absorbance of ketonic groups in oxygen was stronger than those in air and in nitro-

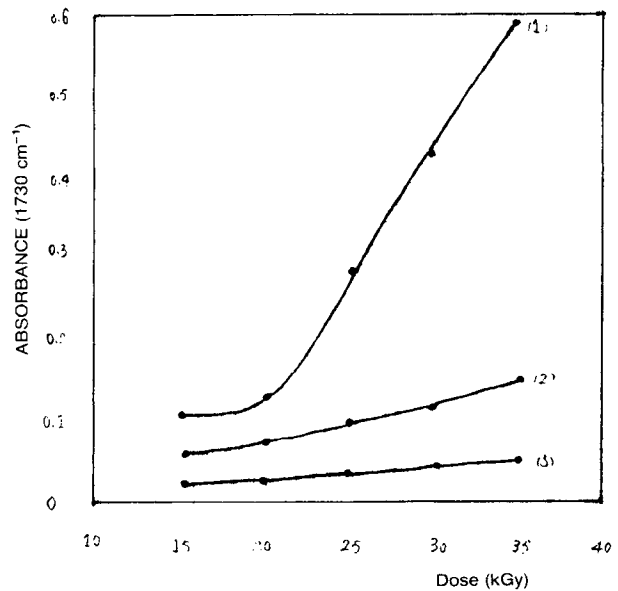


Figure 5 Absorbance in the 1730 cm^{-1} of the LDPE without EVA versus dose in oxygen (curve 1), in air (curve 2), and in nitrogen (curve 3), irradiated by γ -ray.

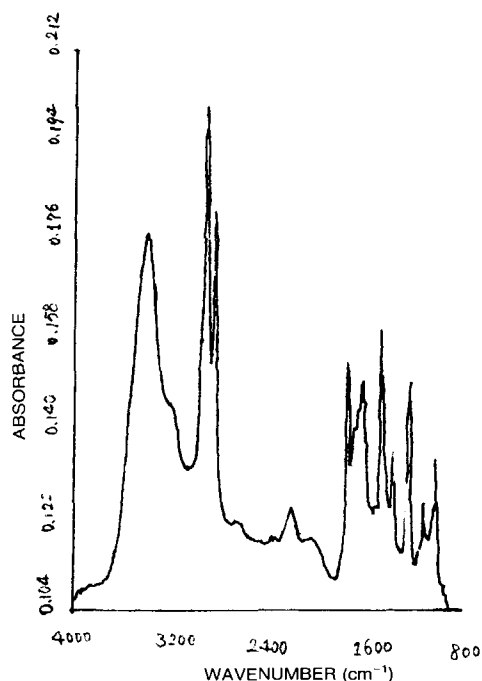


Figure 6 FTIR spectra of the LDPE/EVA (70/30) blend, irradiated by γ -ray in air.

gen, especially a sharp slope was observed above 20 kGy in oxygen. The reaction mechanism has been explained by Torikai et al.⁸

The oxidation product of the LDPE/EVA blend (70/30) was also examined by a high-resolution FTIR spectrometer, as shown in Figure 6. The absorbance in the 1730 cm^{-1} in different atmospheres, at a dose of 25 kGy, is listed in Table I.

The absorbance of the LDPE/EVA blend (70/30) (Table I) compared with that of the LDPE without EVA (Fig. 5) was similar in a given dose. The absorbance of the LDPE/EVA blend in different atmospheres was slightly higher than that of the LDPE without EVA; it means there was no protection from oxidation in the blend system with EVA. In accordance with Figure 1, the required radiation dose for gel formation of LDPE/EVA blend (curve 4) was lower than that of LDPE without EVA (curve 1) in a given gel fraction, indicating that the blend system has less oxidation in comparison with the LDPE system without EVA in a same gel fraction.

Physical and Mechanical Properties of the Foam of the LDPE/EVA Blend

Apparent Density and Expansion Ratio

Figure 7 shows that the apparent density of the foam of the LDPE/EVA blend increased with the increase

Table I Absorbance in the 1730 cm^{-1} on LDPE/EVA (70/30) Blend, Irradiated by γ -Ray in Different Atmospheres, Dose 25 kGy

	Atmospheres		
	Oxygen	Air	Nitrogen
Absorbance	0.3012	0.1042	0.0467

of the gel fraction in the LDPE/EVA blend. The apparent density of the foam of the LDPE/EVA blend irradiated in oxygen was smaller than those in air and in nitrogen.

Figure 8 shows that the expansion ratio of the foam of the LDPE/EVA blend decreased with the increase of the gel fraction in the LDPE/EVA blend. The expansion ratio of the foam of the LDPE/EVA blend irradiated in oxygen was the highest among them, and the expansion ratio of the foam of the LDPE/EVA blend in air was close to that in nitrogen with a higher expansion ratio value of 19, when the gel fraction in the LDPE/EVA blend was around 25–35%. The apparent density of foam was a value of 0.042 g/cm^3 in the same gel fraction as shown in Figure 7.

Average Cell Diameter

Figure 9 shows that the average cell diameter of the foam of the LDPE/EVA blend versus the gel fraction

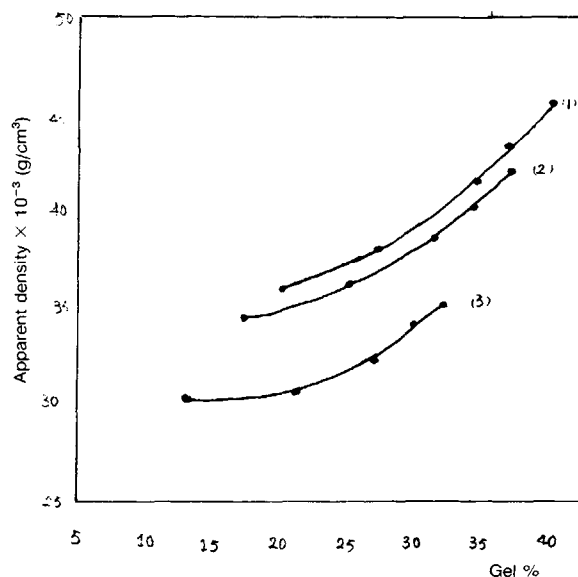


Figure 7 Apparent density of the foam of the LDPE/EVA (70/30) blend versus gel fraction, irradiated by γ -ray in nitrogen (curve 1), in air (curve 2), and in oxygen (curve 3).

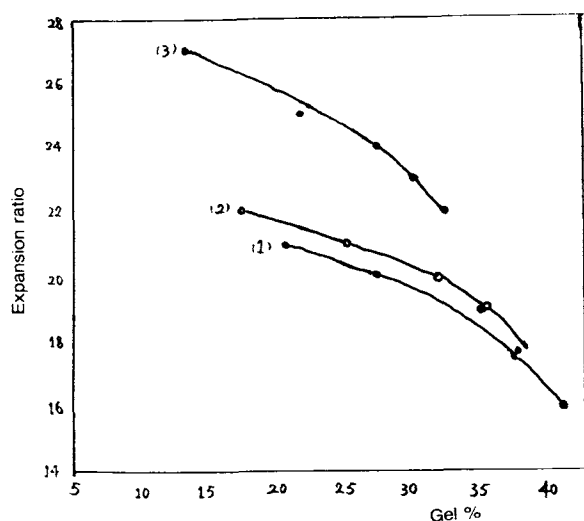


Figure 8 Expansion ratio of the foam of the LDPE/EVA (70/30) blend versus gel fraction, irradiated by γ -ray in nitrogen (curve 1), in air (curve 2), and in oxygen (curve 3).

that decreased with the increase of gel % in the LDPE/EVA blend. The average cell diameter of the foam of the LDPE/EVA blend irradiated in air was close to the value in nitrogen. The smaller the average cell diameter of foam was, the higher the tensile strength (Fig. 10), the longer elongation at break (Fig. 11), and the smoother the surface was.

Tensile Strength and Elongation at Break

Figure 10 shows that the tensile strength of the foam of the LDPE/EVA blend increased with the increase of the gel fraction in the LDPE/EVA blend. Tensile strength of the foam irradiated in nitrogen was extremely close to the tensile strength in air. Tensile strength in oxygen was the lowest among them, because the peroxide ($-\text{O}-\text{O}-$) chain was easily formed during irradiation in oxygen, so that the tensile strength was decreased by the weak peroxide chain, which coincided with the results of FTIR spectra as shown Figure 5. In comparison with Figure 10, if the gel fraction is around 25–35%, besides the higher expansion ratio (19), the smaller cell diameter (0.175 mm), and the lower apparent density (0.042 g/cm^3), the tensile strength value of foam was 0.40 MPa during irradiation in nitrogen or in air. So, the physical properties of the foam in above conditions irradiated in air were similar as in nitrogen.

Figure 11 shows the elongation at break of the foam of the LDPE/EVA blend versus the gel fraction. There was a maximum value of elongation at

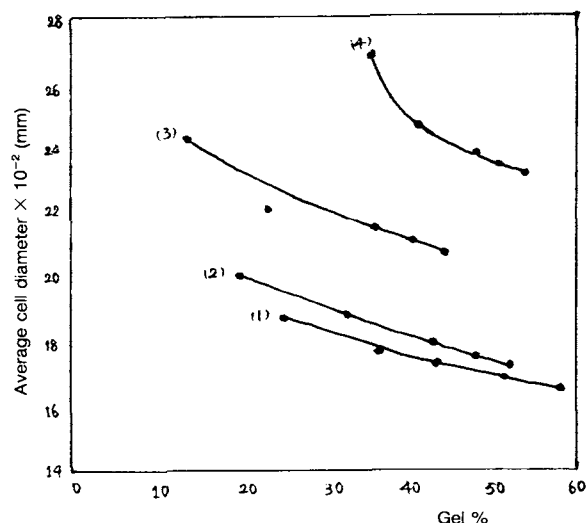


Figure 9 Average cell diameter of the foam of the LDPE/EVA (70/30) blend versus gel fraction, irradiated by γ -ray in nitrogen (curve 1), in air (curve 2), and in oxygen (curve 3) and irradiated by EB in air (curve 4).

break on the curves 1, 2, 3, and 4, whether irradiated in various atmospheres or in different radiation technology. If the radiation dose was fixed around $25 \pm 5 \text{ kGy}$, the values of elongation at break were 200–300% with reproducibility, but it would be less reproducible beyond the above dose range. The tensile strength of the foam in 25 kGy was similar as the result of EB, so the crosslinking of LDPE/EVA blend can be irradiated by γ -ray or EB.

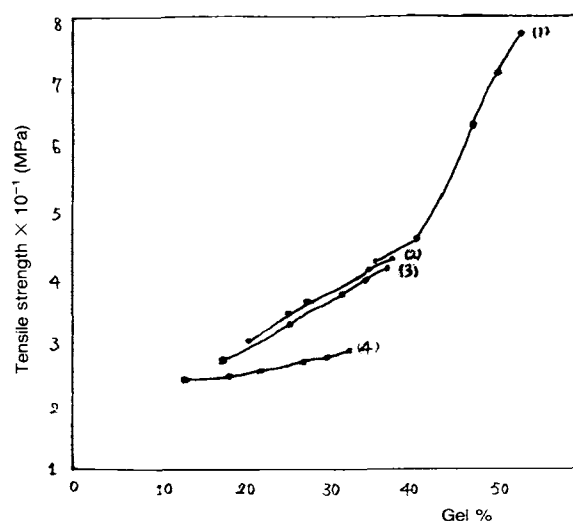


Figure 10 Tensile strength of the foam of the LDPE/EVA (70/30) blend versus gel fraction, irradiated by γ -ray in nitrogen (curve 2), in air (curve 3), and in oxygen (curve 4) and irradiated by EB in air (curve 1).

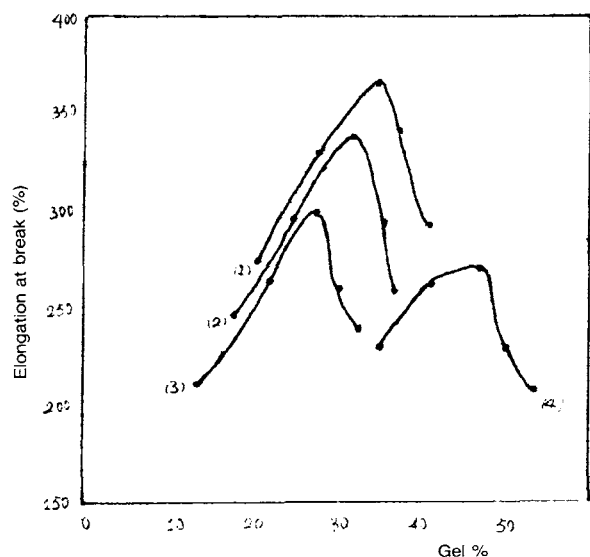


Figure 11 Elongation at break of the foam of the LDPE/EVA (70/30) blend versus gel fraction, irradiated by γ -ray in nitrogen (curve 1), in air (curve 2), and in oxygen (curve 3) and irradiated by EB in air (curve 4).

CONCLUSION

The gel fraction of the irradiated LDPE/EVA blend increased with the increase of its EVA content in a given dose. The gel fraction values of LDPE/EVA blend with the 30% EVA content were higher than those of other blends in a same given dose. The content of EVA in the blend was benefited to gel formation.

The gel fractions of the LDPE/EVA blend irradiated in oxygen were less than those in air and in nitrogen.

In higher dose rates irradiated by EB, the gel fractions of the LDPE/EVA blend were higher than those in lower dose rates irradiated by γ -ray due to the acceleration of the radicals' reaction compared with the diffusion controlled by oxygen.

The oxidation products of the foam of the LDPE/EVA blend were observed by FTIR spectra in nitrogen, in air, and in oxygen. The results indicate that the LDPE/EVA blend system had no protection from oxidation, but compared with the LDPE system without EVA, which had less oxidation in a same given gel fraction.

The gel fraction of the foam of the LDPE/EVA blend was around 25–35%, radiation dose 25 ± 5 kGy, irradiated by γ -ray in air or in nitrogen, the higher expansion ratio (19), the smaller cell diameter (0.175 mm), the lower apparent density (0.042 g/cm^3), the higher tensile strength (0.40 MPa), and the longer elongation at break (290–360%) of the foam of the LDPE/EVA blend were obtained. These were optimum conditions for application in this system.

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