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Preparation of Radiation Crosslinked Foams from Low-Density Polyethylene/Ethylene-Vinyl Acetate (LDPE/EVA) Copolymer Blend with a Supercritical Carbon Dioxide Approach

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ABSTRACT: Low-density polyethylene/ethylene-vinyl acetate copolymer (LDPE/EVA) blend foams were prepared by a combination of radiation and supercritical carbon dioxide ($ScCO_2$) approach. The radiation effects on LDPE/EVA foams in different ratios were investigated in detail. For the LDPE/EVA blend in a w/w ratio of 70/30, the cell size decreased and the cell density increased with an increase of absorbed dose. The optimal dose and EVA content for the foaming of LDPE/EVA blend in $ScCO_2$ was found to be 50 kGy and 30%, respectively. It was also found that the radiation crosslinked LDPE/EVA blends had a wider foaming temperature range than uncrosslinked samples. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: LDPE/EVA blend; radiation; supercritical carbon dioxide; foam

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INTRODUCTION

Polymeric foams are lightweight materials and applied in various fields including construction materials, thermal and/or sound insulators, packing and transportation industries. The application of polymeric foam is determined by its structure, e.g., cell type, cell size, cell size distribution, and cell density. The polymeric foam structure is strongly dependent on the component[1,2] and foaming condition[3,4] of the polymer. Low-density polyethylene (LDPE) and ethylene-vinyl acetate copolymer (EVA) are popularly used in the manufacture of polymeric foams; in particular, the LDPE/EVA foam possesses higher flexibility and impact resistance.

Crosslinked polyethylene foams reveal an evident improvement on heat resistance compared with uncrosslinked ones. Crosslinked EVA usually shows a better control of nucleation and formation of cells with uniform size in the foaming of EVA.[5] Several studies have shown that the radiation-crosslinked polyethylene, EVA and their blend foams have more regular and homogeneous cells.[6–9] The previous studies adopted chemical foaming reagent and mainly concentrated on the processing, properties and cell structure of the foams. There is no report on foaming LDPE/EVA blends by a combination of radiation and supercritical CO_2 ($scCO_2$) approach.

The $scCO_2$ is an ideal replacement of traditional foaming agents because of its cheapness and environment friendly property as a physical foaming agent. The $scCO_2$ foaming approach has many advantages, e.g., adjustable solvent strength, plasticization, enhanced diffusion rates and high solubility in polymers.[1,2] We previously studied the preparation of the crosslinked LDPE foams by a radiation and $scCO_2$ approach.[7] The cell structures of two series of radiation-crosslinked LDPE foams were compared in detail, and the effects of radiation on cell size, cell density, and volume expansion ratio were also investigated. In the present study, the LDPE/EVA blends were irradiated by γ-rays and foamed by $scCO_2$. The effects of absorbed dose and EVA content on the foam morphology were investigated. The effect of EVA content on the expansion ratio of the crosslinked LDPE/EVA foams was also discussed.

EXPERIMENTAL

Materials

Low-density polyethylene (pellet) was purchased from Sinopec Beijing Yanshan Chemical Corporation, with a density of 0.92 g cm^{-3} and a melt index of 2.0 g/10 min. Ethylene-vinyl acetate copolymer, supplied by Samsung Total Petrochemicals, has a vinyl acetate content of 18%. Carbon dioxide (>99.5% purity) was obtained from Lou Tang Special Gases of Shanghai.

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Sample Preparation and Irradiation

LDPE/EVA Blends of various compositions (90:10, 80:20, 70:30, 60:40 and 50:50) were mixed at 140 °C in a two-screw mixer (Thermo Haake PolyDrive, Germany), and then hot pressed for 5 min at 140°C under a pressure of 12 MPa into thin sheets (1.0 mm in thickness) using a plate vulcanizing machine. The γ-irradiation was carried out in the ^{60}Co source of Shanghai Institute of Applied Physics. The LDPE/EVA sheets were irradiated in a nitrogen atmosphere at room temperature and a dose rate of 0.9 kGy h^{-1}. The accumulated absorbed doses were 25, 50, 75, and 100 kGy, respectively.

Foaming Process

The LDPE/EVA sheets were cut into 15 × 20 mm^2 rectangle pieces for the foaming process. A pressure quenching batch method was employed for the foaming of LDPE/EVA sheets. The supercritical experimental setup and foaming process were described in the previous paper.[10] The specimens sealed into a high-pressure vessel had been preheated to a desired temperature after air was expelled from the vessel by CO_2 gas. The specimen was saturated by $scCO_2$ after they were kept at the desired temperature and the pressure of 23 MPa for 8 h. The values of 105, 110, 120, and 130°C were adopted as the desired temperatures. Subsequently, to supersaturate the specimen with CO_2, the autoclave was quickly depressurized to the atmospheric pressure at the rate of 0.7 MPa s^{-1}. Eventually, the specimens were removed from the vessel and cooled to ambient temperature.

Characterization

The gel content was determined by a 72 h Soxhlet extraction cycle using xylene as the solvent. Approximately 1 g of the irradiated LDPE/EVA was placed in a preweighed stainless steel fine wire mash. After extraction, the solid portion was dried to a constant weight in a vacuum oven at 60°C and then weighed again. The gel fraction was sequentially obtained.

The morphology of the foamed sample was observed using SEM (JSM-5600LV and LEO 1530 VP). The samples were immersed in liquid nitrogen and fractured, then mounted on stubs. The fractured surfaces were sputter-coated with gold for observation. The foams with uniform cell morphologies were also characterized in terms of cell density and average cell size. The average cell size was obtained through the analysis of the SEM photographs by the software Image Pro-plus. The cell density N_f, was defined as the number of cells per unit volume of the foam, was calculated by

$$N_f = \left(\frac{nM^2}{A}\right)^{3/2} \quad (1)$$

where n, M, and A are the number of cells in the micrograph, the magnification number of the micrograph, and the area of micrograph (cm^2), respectively.

The volume expansion ratio of the foamed LDPE/EVA blends, R_v, was defined as the ratio of the bulk density of the virgin LDPE/EVA blend (ρ_s) to that of the foamed one (ρ_f):

$$R_v = \frac{\rho_s}{\rho_f} \quad (2)$$

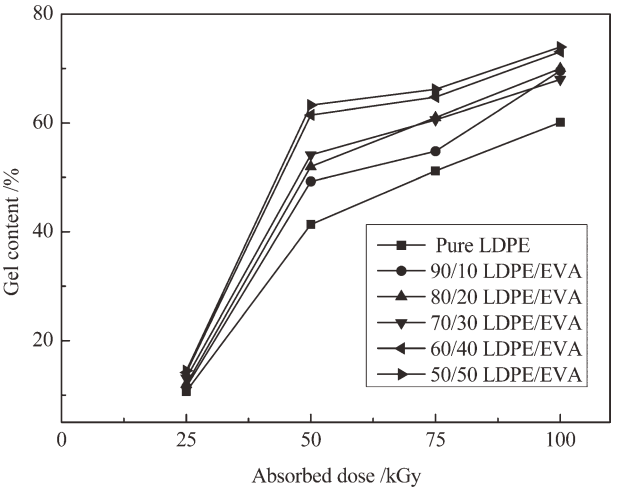

Figure 1. Effect of absorbed dose on the gel content of the LDPE/EVA blends.

The mass density of foamed LDPE/EVA blend sample (ρ_f) was measured according to ASTM D 792-00 involving the weighing polymer foam in water using a sinker.

RESULTS AND DISCUSSION

Radiation Crosslinking of LDPE/EVA Blends

All the original LDPE/EVA blend samples can dissolve in boiling xylene. After irradiation by γ-rays, the solubility decreased significantly and gels were retained after removing the soluble fraction. Figure 1 shows the dose dependence of the gel content of the LDPE/EVA blends. For all the cases, the gel content increased significantly with the dose up to 50 kGy, and then increased slightly beyond 50 kGy. The results implied that the crosslinking degree of the LDPE/EVA blends seemed to be saturated beyond 50 kGy. In particular, the gel content of LDPE/EVA blend was higher than that of LDPE under similar conditions. At the same dose, the gel content increased with the increasing of EVA content. This indicated that the presence of EVA was favorable to the crosslinking of polymer blend.

Effect of Absorbed Dose on the Morphology of LDPE/EVA Blend Foams

The crosslinked LDPE/EVA blends were foamed during the rapid depressurization of CO_2 from an enormous pressure to atmosphere. Figure 2 shows the cell morphology of the LDPE/EVA blend foams with the different absorbed doses. At the dose of 25 kGy [Figure 2(a)], most of the cells were polyhedron and walls of some cells got wrinkling. The best uniform cell morphology was observed in a nice spherical shape at 50 kGy [Figure 2(b)]. At doses of 75 and 100 kGy [Figure 2(c,d)], evident nonuniform of cell size was found.

Scission and crosslinking of polyethylene molecular chains can simultaneously take place when it is subject to irradiation by γ-ray. The chain scission occurs mainly at a low dose and the chain crosslinking prevails at a higher dose.[11–13] On the one hand, the crosslinking results in the formation of a three-dimensional network in the LDPE/EVA blends, leading to an increase of the melt viscosity and strength of the LDPE/EVA.

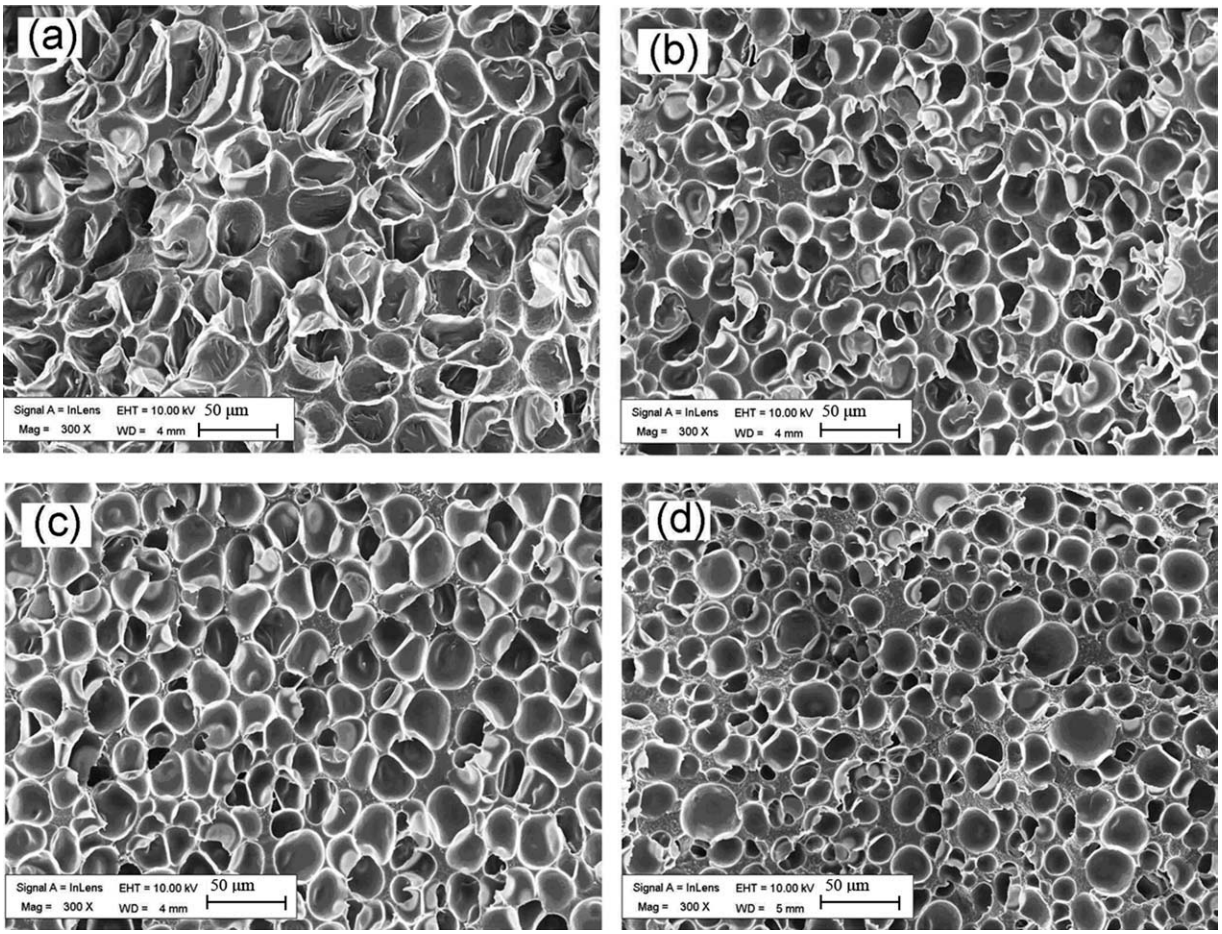

Figure 2. SEM micrographs for the LDPE/EVA blend (70/30) foams produced at 105°C and 23 MPa. (a) 25 kGy, (b) 50 kGy, (c) 75 kGy, (d) 100 kGy.

The crosslinking takes place in the amorphous region and the surface of crystalline region of the semicrystalline part. On the other hand, the chain scission leads to a decrease in melt viscosity and strength, happening over the whole domain of the LDPE/EVA during the irradiation.[14] At a lower absorbed dose, e.g., 25 kGy, the chain scission can take place in the whole matrix of the LDPE/EVA. At a higher absorbed dose, e.g., 100 kGy, the prevailing crosslinking reaction only takes place in the

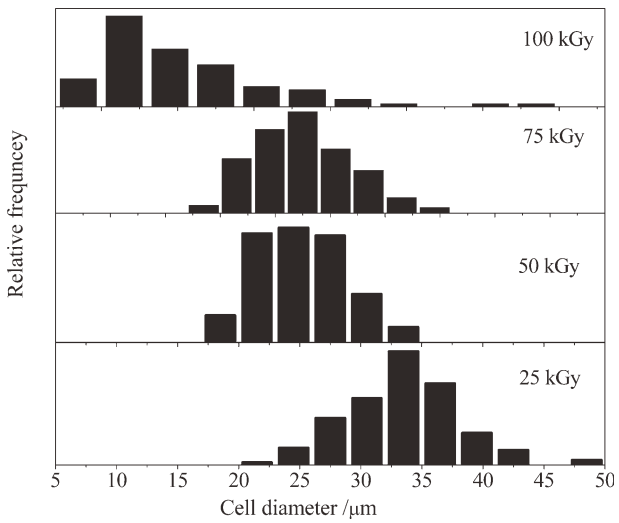

Figure 3. Effect of absorbed dose on the cell size distribution of the LDPE/EVA blend (70/30) foams produced at the same condition in Figure 2.

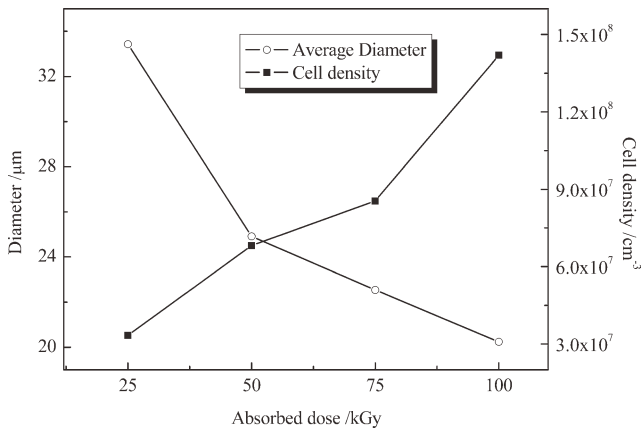

Figure 4. Effect of absorbed dose on the average cell diameter and cell density of the crosslinked LDPE/EVA blend (70/30) foams produced at 105°C and 23 MPa and at different doses.

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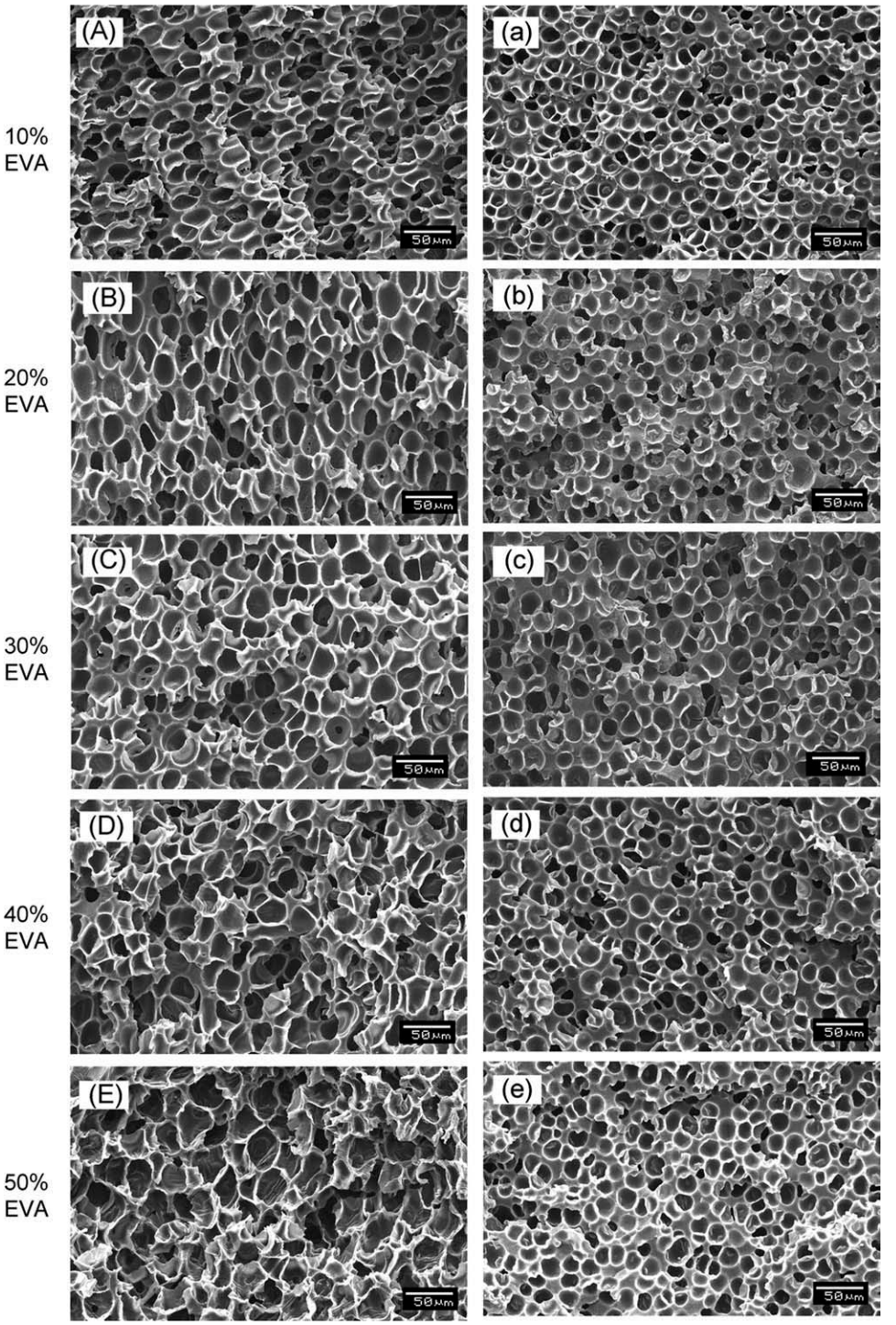

Figure 5. SEM micrographs for the noncrosslinked (A, B, C, D, and E) and crosslinked (a, b, c, d, and e) LDPE/EVA foams produced at 105°C and 23 MPa with various EVA contents: (A) and (a) 10%; (B) and (b) 20%; (C) and (c) 30%; (D); and (d) 40%; (E) and (e) 50%.

amorphous region; therefore the LDPE/EVA has distinct melt properties in the amorphous and crystalline region. At a moderate dose of 50 kGy, the LDPE/EVA has a homogenous and modest crosslinking of molecular chain. After the foaming process, the LDPE/EVA foams with 25 kGy possess large polygonal cells due to its low melt viscosity and strength. The LDPE/EVA foams with 100 kGy have nonuniform cells due to a heterogeneous distribution of crosslinking sites in the matrix of LDPE/EVA blends. The LDPE/EVA foams with 50 kGy have the most uniform cell morphology. It is implied that the optimal absorbed dose was 50 kGy for the foaming of crosslinked LDPE/EVA blend.

Figures 3 and 4 show the effects of absorbed dose on cell size distribution, average cell diameter, and cell density of the

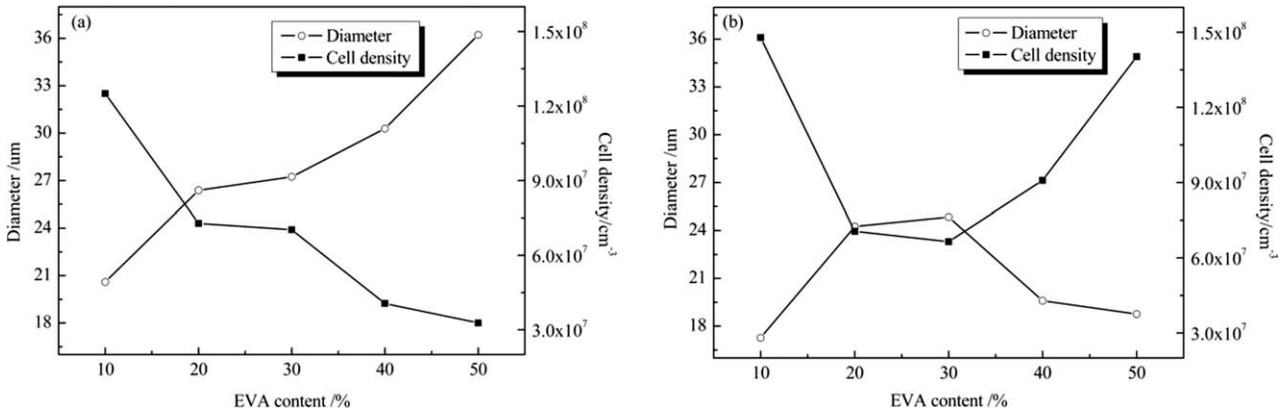

Figure 6. Cell diameters and cell density of the LDPE/EVA blends foamed at 105°C and 23 MPa: (a) noncrosslinked foams (b) crosslinked foams with a dose of 50 kGy.

LDPE/EVA (70 : 30) samples foamed at 105°C. The cell size distribution, average cell diameter, and cell density are dependent on the absorbed dose. The width of the cell size distribution, which indicates the uniformity of the cell size, first decreases with the enhanced dose until 50 kGy, and then increases to the widest cell size distribution at 100 kGy. These results indicate that the uniformity of the cell size is the best at a dose of 50 kGy. The average cell diameter decreases from 33 to 20 μm, and the cell density increases by nearly five times. The crosslinking in the LDPE/EVA matrix improves the melt viscosity and strength,[6,15] leading to a higher resistance to bubble expansion and an obstacle to coalescence of the neighboring cells, hence we can obtain a smaller cell size and a higher cell density of the foams. When the absorbed dose is below or beyond 50 kGy, the cell size becomes either too large or too dispersive. Therefore, the moderate dose of 50 kGy is optimal for obtaining microporous LDPE/EVA foam with a narrow cell size distribution.

Effects of EVA Content on the Morphology of LDPE/EVA Blend Foams

The SEM pictures in Figure 5 show the cell morphology of the noncrosslinked and crosslinked LDPE/EVA foams with various EVA content from 10 to 50%. For the noncrosslinked foams, it can be observed that the samples with higher EVA content have larger cells and thinner cell wall. In Figure 5(c–e), some cells of the samples even have wrinkles and holes on the wall. However, all the crosslinked samples present an improved cellular structure in terms of continuous spherical cell shape and uniform cell size. The cell-growth of the polymeric foam primarily depends on temperature of the system, hydrostatic pressure (or stress applied on the polymer matrix), length of cell growth period, degree of supersaturation of blowing reagent, and viscoelastic properties of the polymer matrix.[16] Wang et al.[17] and Yuan et al.[18] have suggested that the polymer blends with a higher complex viscosity can be shaped into smaller cellular foam, and vice versa. An increase of EVA content results in the decrease of the melt viscoelasticity of the LDPE/EVA blend.[19,20] Therefore, the cell expansion of the LDPE/EVA foams becomes easier due to lower resistance to cells expanding at higher EVA content. Moreover, the cell can fuse and break due to poor melt strength. After the LDPE/EVA blends are irradiated, the melt viscosity and strength of the blends are enhanced by the crosslinking network in the polymer blends. The fusion and break of the cells can be restrained, and the cells can also become smaller.

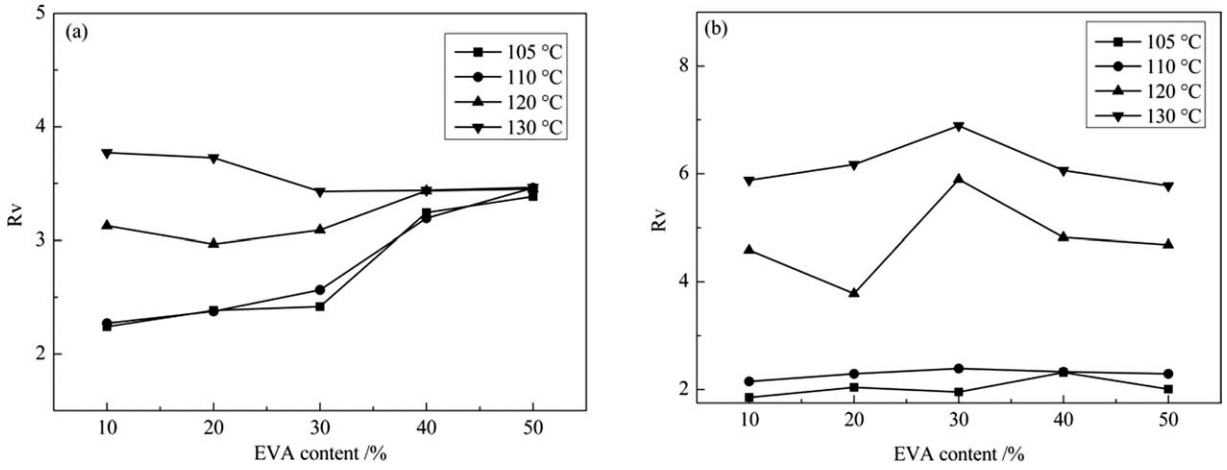

Figure 7. Effect of the EVA content on the volume expansion ratio (R_v) for the LDPE/EVA blends produced at 105–130°C and the LDPE/EVA blends was first crosslinked at 50 kGy: (a) noncrosslinked; (b) crosslinked.

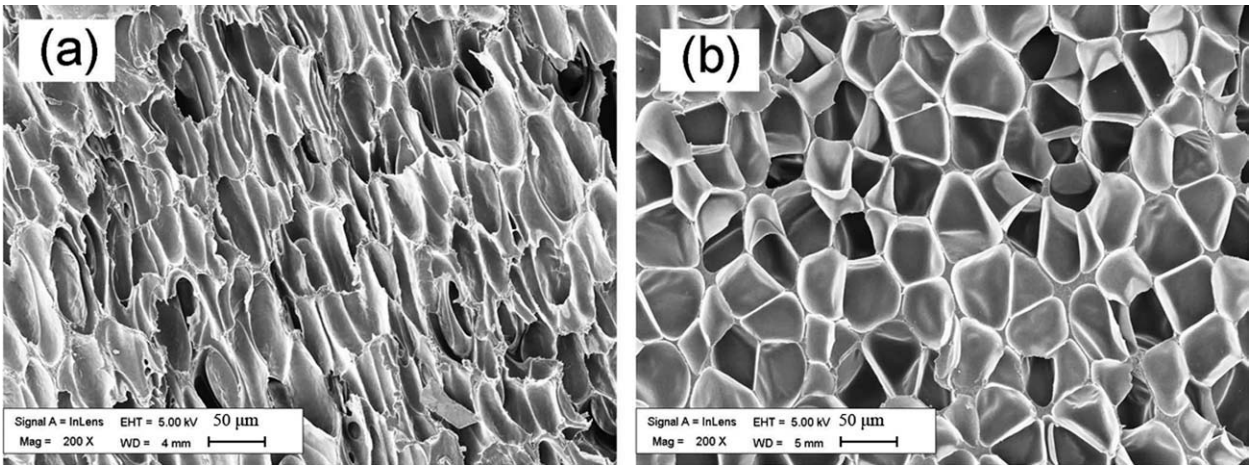

Figure 8. SEM micrographs of LDPE/EVA (70/30) foams produced at 130°C and 23 MPa: (a) noncrosslinked; (b) crosslinked.

Figure 6 shows the dependence of the foam structure parameter on the EVA content in the blends. It is clearly seen that the structure is different between noncrosslinked and crosslinked foams. For the noncrosslinked foams, as shown in Figure 6(a), the average cell diameter increases and the cell density decreases with the addition of EVA. For the crosslinked foams, as shown in Figure 6(b), the average cell diameter increases initially and then decreases with the increasing of EVA content. The difference between the noncrosslinked and crosslinked foams indicates a remarkable improvement to the cell structure of the foams with a higher EVA content. The main reason of the improvement is the increase of melt strength due to radiation crosslinking.

Effect of EVA Content on Volume Expansion Ratio of LDPE/EVA Blend Foams

Foam volume expansion ratio (R_v) and bulk density are important physical properties of the foam materials. High R_v and low bulk density are ideal for the foams due to its reduced cost. Figure 7 shows the effect of the EVA content on the R_v for both noncrosslinked and crosslinked samples foamed at different foaming temperatures. The R_v of the noncrosslinked foams increases with the increasing EVA content at a lower foaming temperature. However, the increment of R_v decreases at higher foaming temperatures. Particularly, the R_v has only a slight increase with increasing the EVA content at 130°C. For the crosslinked foams, the R_v has little change with the increasing of EVA content at a lower foaming temperature. However, at high temperatures, the R_v increases initially and then decreases with the increasing of EVA content. The maximum R_v is observed at the EVA content of 30%, implying an optimal EVA content of 30% for the foaming of crosslinked LDPE/EVA blends. Moreover, the R_v of the crosslinked foams is higher than that of the noncrosslinked foams at higher foaming temperatures.

For the noncrosslinked samples, the cell fusion and collapse of the cell wall appear clearly as shown in Figure 8(a). Because of the low melt strength of LDPE/EVA blends, the cell wall cannot bear the expansion force and breaks up at the foaming temperature of 130°C. In the case of crosslinked sample, as shown in Figure 8(b), the cells remain intact polygonal closed-cell structure because of the increased melt viscosity and strength of LDPE/EVA blends. This is the reason that why a higher R_v of the crosslinked foam can be obtained at a higher foaming temperature. It has been demonstrated that radiation crosslinking of LDPE/EVA blends results in remarkable extension of the foaming temperature range due to the improved melt viscosity and strength.

CONCLUSION

In this work, the LDPE/EVA blends were irradiated by γ-ray and then foamed by using supercritical CO_2 as a blowing agent under batch foaming conditions. The cell morphology of the LDPE/EVA foams was improved by radiation crosslinking. The crosslinked foams possessed more homogenous cell distribution, smaller cell size, higher cell density, and higher volume expansion ratio than the noncrosslinked foams. Radiation crosslinking led to a wider foaming temperature range of the LDPE/EVA blends. The dose of 50 kGy and the EVA content of 30% were found to be the optimal conditions for the foaming of LDPE/EVA blend.

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