Properties of Chlorinated Polyethylene Rubber/Ethylene Vinyl Acetate Copolymer Blend-Based Foam

Bao Sheng Zhang, Zhen Xiu Zhang, Xiu Feng Lv, Bing Xue Lu, Zhen Xiang Xin
Key Laboratory of Rubber-Plastics (Qingdao University of Science and Technology), Ministry of Education, Qingdao 266042, People's Republic of China

A series of chlorinated polyethylene rubber (CM)/ethylene vinyl acetate (EVA) blends were prepared at different blending ratio. The blends were foamed by compression molding and azodicarbonamide (AZDC) was used as chemical blowing agent. Cure characteristics were researched first, and then the morphology and physical properties were investigated. It was found that neat CM foams presented a series of problems such as low hardness and high shrinkage ratio. To solve the above problems, some EVA was added into CM matrix. And the results indicated that these aforementioned defects were improved after the addition of EVA component. Tensile strength increased first and then fell, and morphology properties of CM/EVA blends were also investigated. POLYM. ENG. SCI., 52:218–224, 2012. © 2011 Society of Plastics Engineers

INTRODUCTION

Many attractive properties such as light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction make elastomeric foam to be widely used in three major areas of thermal insulation, energy absorption, and structural usage [1]. Elastomeric foam or cellular rubber can be produced by utilizing one kind of either chemical or physical blowing agent with either open or closed cell structure. Azodicarbonamide (AZDC) is the most popular chemical blowing agent. When temperature increases, thermal decomposition occurs and gas, for example, Nitrogen (N_2), carbon monoxide (CO), or Carbon Dioxide (CO_2) are released. According to Tai et al. [2, 3] additives such as Zinc Oxide (ZnO) and/or Zinc Stearate (ZnSt) were employed as cell stabilizers or cell nucleation agents, as well as activators for chemical blowing agents. The decomposition behavior of AZDC was one function of particle size, heating rate, activator type, and concentration and uniformity of dispersion, which affect the total gas yields, and the rate of gas evolution of AZDC to eventually change the properties of foams [4–6].

Laakso et al. [7] reported that commercially available rubber-based polymeric foams were produced from synthetic polymers or rubbers such as ethylene vinyl acetate (EVA) copolymer, nature rubber (NR), ethylene propylene diene terpolymer (EPDM), acrylonitrile butadiene rubber (NBR), polychloroprene rubber (CR), and acrylonitrile butadiene-polyvinylchloride blends (NBR/PVC). As for chlorinated polyethylene, ASTM designation CM or commonly referred to as CPE, possesses high resistance to hydrocarbon oil, heat and weathering, which attributed to the addition of chlorine atoms, on the polyethylene backbone [8]. The random substitution of chlorine atoms gives rise to flexibility by suppressing crystallization of parent polymer, high-density polyethylene (HDPE). Chlorinated polyethylene rubber (CM) can provide performance and cost advantages over other elastomeric systems, such as CR, NBR, chlorosulfonated polyethylene (CSPE) etc. Furthermore, because CM consists of both non-polar groups (unmodified methylene units) and polar groups (chlorinated methylene co-units), it has considerable compatibility with either polar polymers or non-polar ones. Thus, it can be blended with many other materials for a desired set of properties, which have specific property advantages over those of the individual blend constituents [9].

Therefore, CM is arousing general attention in recent years. However, during the research on CM foams, it was found that the foaming sample presented some problems such as low hardness, high shrinkage ratio, and bad compression resistance. Because of the ability to combine the properties of each phase, polymer blends have gained an increasing popularity in the field of polymer science and industry. In recent years, substantial researches have concentrated on the preparation of microcellular foam of polymer blends [10, 11]. To solve these problems, we attempted to blend CM with EVA according to rubber-plastics blending theory, and the foaming temperature was 170°C.

In this study, the CM foams with different mixing ratio of the EVA were prepared by compression molding. The effect of mixing ratio of CM to EVA on cure characteristics, foam characteristics and mechanical properties of the CM/EVA foams were studied to enlarge the application field of sponge.

EXPERIMENTAL

Materials

The chlorinated polyethylene (CM 135B), which contained 35% chlorine, was supplied by Qingdao Haijing Chemical Co., China. The EVA copolymer (ES 440) with VA content of 15% was obtained from Hyundai Co., Korea. The curing agent was dicumyl peroxide (DCP) supplied by Sinopec Shanghai Gaoqiao Petrochemical Corporation, China. The blowing agent used was Azodicarbonamide (AZDC, decomposition temperature 205°C), supplied by Qingdao HanbingChem CO., China. The Zinc Stearate (ZnSt) was supplied by LiYang XinWang Plastic CO., China. All other rubber ingredients, such as dioctyl phthalate (DOP) were commercial grade.

Composition and Foam Preparation

The CM compounds were mixed with ingredients according to the formulation in Table 1 at 70–80°C on a two-roll mill. CM and EVA were first masticated for 2 min at 100–110°C on a laboratory size open mill, and then other ingredients were added subsequently. The blowing agent was added along with the filler and activators for good dispersion. Finally, the curing agent DCP was added in case of scorch. At last, the compounds were taken out from the mill to form a sheet and stored at room temperature for 24 h before foaming. The cure characteristics of compounds were determined on a moving die Rheometer to determine the optimal curing time. Finally, the compounds were pressed in a closed mold, and the foams were obtained by compression molding at a pressure of 10 MPa and temperature of 170°C. After removal of the pressure, expansion took place immediately, and the obtained foams were left at room temperature to cool down.

Measurements

The cure characteristics of the compounds were measured on a moving die Rheometer (Model GT-M-2000-A,

TABLE 1. Formulations of the CM/EVA compounds.

Ingredients (phr)[a]	Sample[b]					
	F-1	F-2	F-3	F-4	F-5	F-6
CM/EVA	100/0	90/10	70/30	50/50	30/70	10/90
DCP	2	2	2	2	2	2
AZDC	8	8	8	8	8	8
ZnSt	8	8	8	8	8	8
SiO$_2$	2	2	2	2	2	2
DOP	20	20	20	20	20	20

[a] Parts per hundred of rubber.
[b] F-1, 2, 3, 4, 5, and 6. F refers to foam and 1–6 denote EVA content (0, 10, 30, 50, 70, 90, respectively).

Gotech, Taiwan). Tensile strength, modulus, and elongation at break were measured on five dumbbell specimens for each sample according to ASTM D 412 and the tear resistance was determined according to ASTM D 642 using computerized test instrument (Gotech, Taiwan) at a cross-head speed of 500 mm/min. The hardness of samples was measured according to ASTM D 2240 with a durometer and Shore C scale at room temperature.

The foam morphology was characterized by utilizing a scanning electron microscope (SEM, JSM6700). The foamed samples were cooled in liquid nitrogen and fractured to produce a clean and intact surface with minimum plastic deformation. They were then gold coated by using a sputter coater for enhanced conductivity. The cell sizes, cell densities, and relative densities were investigated. The cell diameter (D) was the average of all the cells on the SEM photo, usually >100 cells were measured.

$$D = \frac{\sum d_i n_i}{\sum n_i}, \tag{1}$$

where n_i was the number of cells with a perimeter-equivalent diameter of d_i.

The density of foam and unfoamed samples was determined from the sample weight in air and water, respectively, according to ASTM D 792 method A. Then the density of the foamed sample was divided by the density of the unfoamed sample to obtain the relative density (ρ_r). The volume fraction occupied by the microvoids (V_f) was calculated as:

$$V_f = 1 - \frac{\rho_f}{\rho_m}, \tag{2}$$

where ρ_m and ρ_f were the density of the unfoamed polymer and foamed polymer, respectively.

The cell density (N_f (number of cells per unit of volume) based on the foamed sample was calculated as:

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

so the cell density based on the unfoamed sample (number of cells per cm^3), N_0 can be calculated as:

$$N_0 = \frac{N_f}{1 - V_f} \tag{4}$$

where A was the area (cm^2) of the SEM image, M was the magnification factor and n was the number of cells in the SEM image, N_f was the cell density based on the foamed sample, N_0 was the cell density based on the unfoamed sample [12].

A 2×2 cm sample was cut from foam material and its thickness t_1 (cm) and weight W_2 (g) were measured. The expansion ratio was calculated from the following equation [13]:

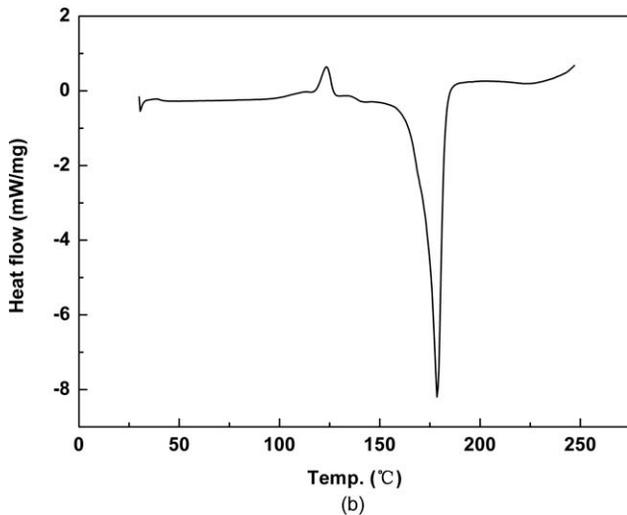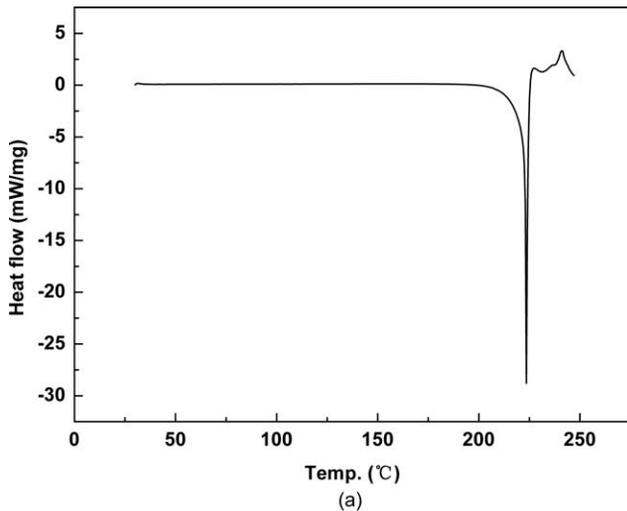$$\text{Expansion Ratio} = [(2 \times 2 \times t_1)/W_2] \tag{5}$$

FIG. 1. DSC curves of (a) pure AZDC and (b) AZDC/ZnSt.

FIG. 3. Cure characteristic of t_{s2} and t_{90} at various blend composition.

Differential scanning calorimeter was carried out on a DSC-204 (NETZSCH) (DSC) to study the decomposition temperature of th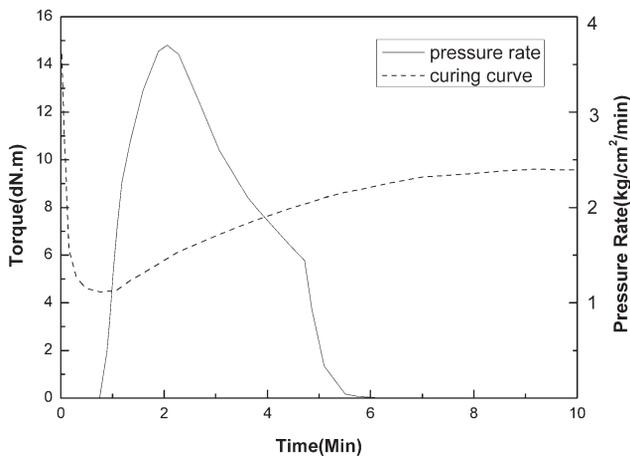e AZDC. Small samples (about 8–9 mg) were encapsulated in aluminum pans and analyzed in a temperature range from 30°C to 250°C at the heating rate of 10°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSION

Acceleration Effect of Activators

Temperature is very critical for producing rubber foam because it can affect the decomposition of the chemical blowing agent (AZDC) or curing agent (DCP) and melt viscosity of the polymer, which influences cell nucleation, growth, stabilization, and retention of the foam [14]. In general, the temperature at which a large amount of decomposition starts for DCP is about 120°C, whereas AZDC starts to decompose around 205°C. The decomposition of AZDC must take place when the polymer is at the proper melt viscosity or degree of cure [15]. Activators can lower the decomposition temperatures of blowing agents. Some studies [5, 14, 16] have found that the addi-
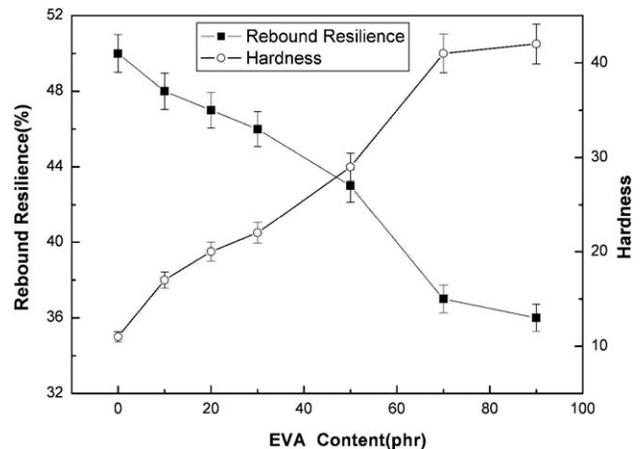

FIG. 2. Rheograph of CM/EVA blend composition at 50/50.

FIG. 4. Variation of rebound resilence and hardness of CM/EVA foam.
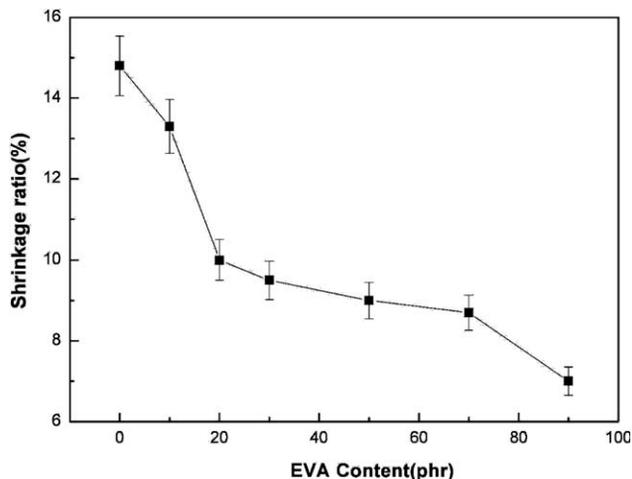
FIG. 5. The change of shrinkage ratio of CM/EVA foam.

FIG. 7. Stretching stress variation of foam with CM/EVA composition.

tion of ZnO or ZnSt to the chemical foaming agent AZDC not only lowered the decomposition temperature but also accelerated its decomposition. Our previous study found that the optimal curing temperature of CM/EVA was about 170°C. So to make the curing temperature of CM/EVA and decomposition of AZDC match well, in this study, ZnSt was used as the activator to decrease the decomposition temperature of AZDC [2]. It can be seen from Fig. 1a that the decomposition of pure AZDC took place at about 200°C. In comparison with the pure sample, when 8 phr of ZnSt was added (Fig. 1b), the initial decomposition temperature of AZDC was lowered to about 160°C, which was about 40°C lower than that of pure AZDC, and the decomposition temperature peak changed from 223.4°C to 178.6°C.

The cure characteristics of the compounds at various compositions (100/0, 90/10, 80/20, 70/30, 50/50, 70/30, 90/10) were measured on a moving die Rheometer.

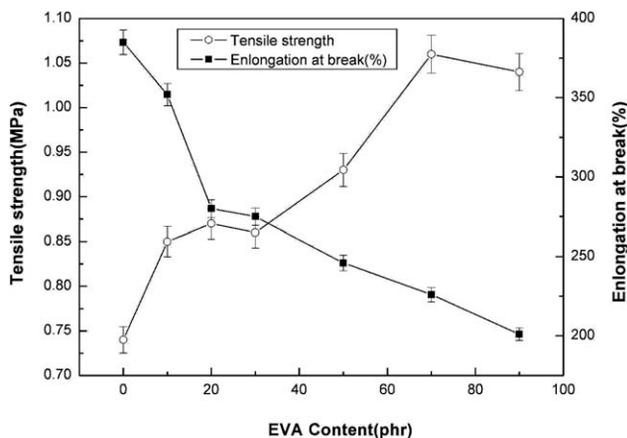Figure 2 shows the rheograph obtained for CM/EVA blend at 50/50 as an example. AZDC starts to decompose at the beginning of cure and when cure finished decomposition also finished. What is more, the decomposition rate peak occurred at the metaphase of vulcanization. According to classic principle of foaming, we can get the conclusion that curing rate of CM/EVA and decomposing rate of AZDC can match well.

The cure characteristics of the foamed CM/EVA with different blending ratio were presented in Fig. 3. Scorch time (t_{s2}) is a measure of time when the premature vulcanization of the material occurs. It is the time taken for the minimum torque value to increase by two units. As illustrated in the curves of Fig. 3, at the beginning, t_{s2} increased significantly with the addition of EVA content, and scorch time reached its peak when 10 phr EVA was added, which demonstrated that the compound at this ratio possessed the best processing safety. However, with the further increase of EVA content, scorch time of different blend ratio showed little change. The change of the optimum cure time, t_{90} with increasing EVA content was also observed. It can be seen that the

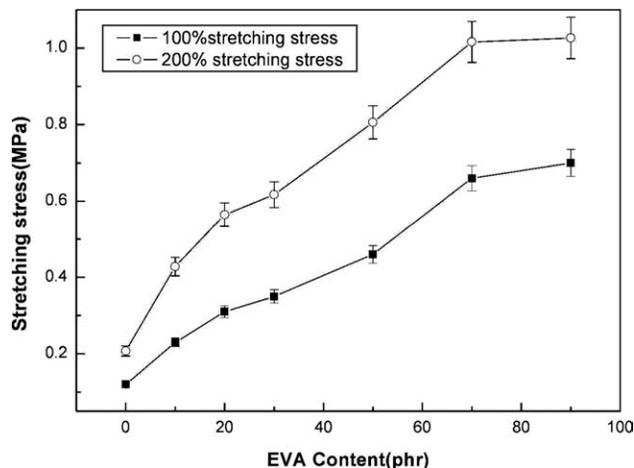FIG. 6. Variation of tensile strength and elongation at break of CM/EVA foams with various blend ratio.
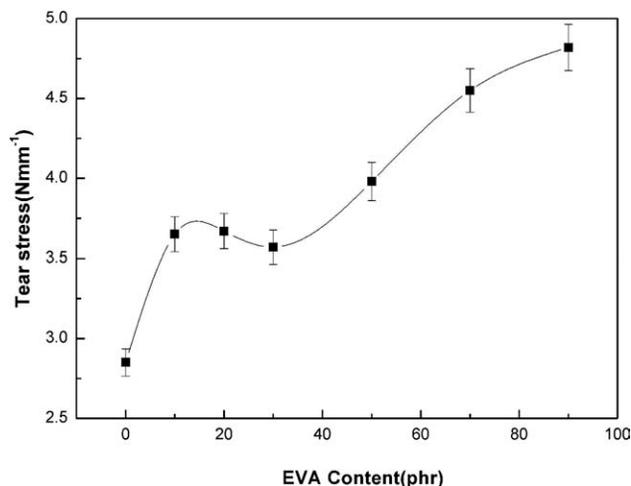

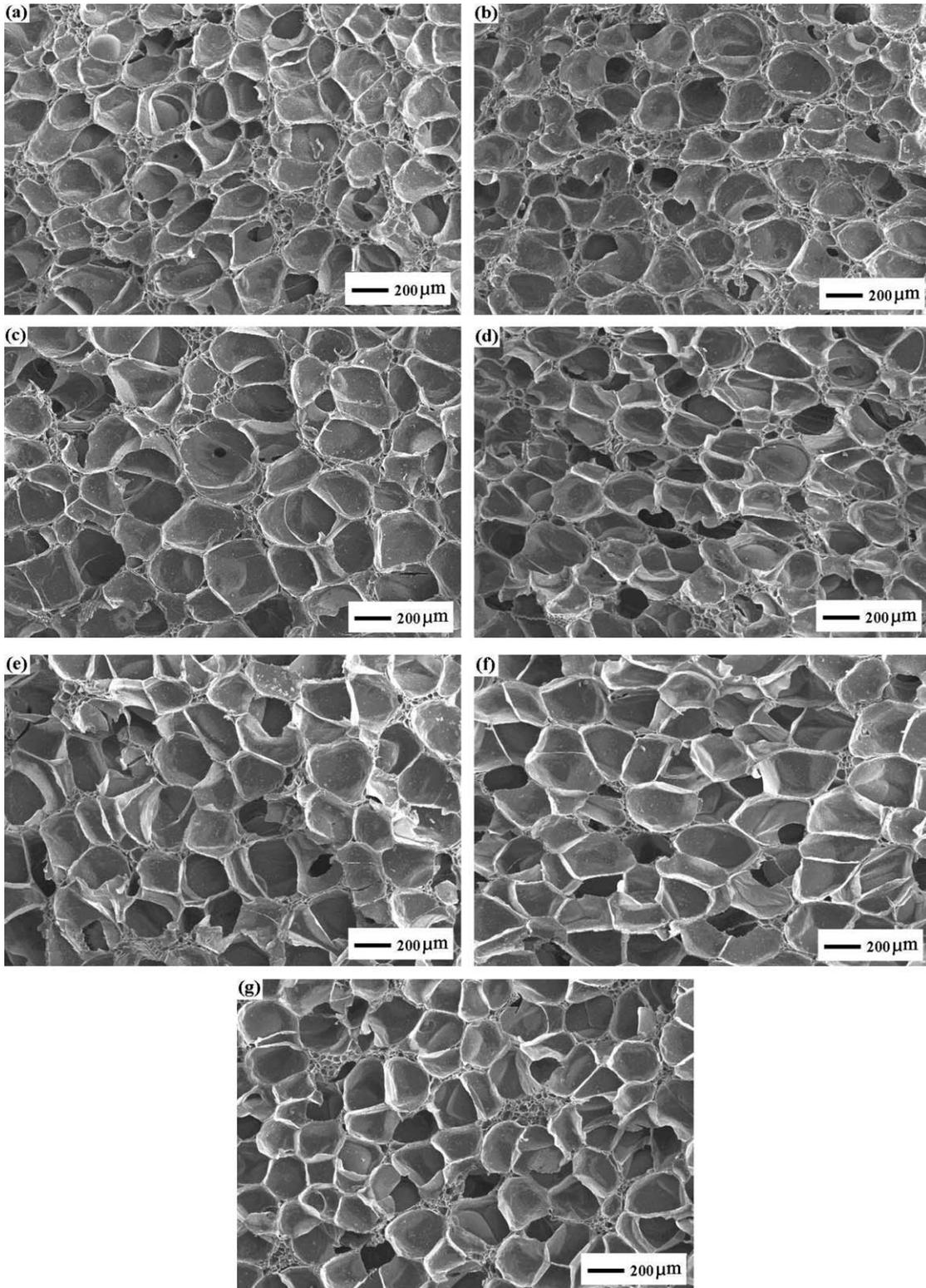FIG. 8. The effect of EVA content on tear strength of CM/EVA foam.

FIG. 9.   SEM images of CM/EVA foam with various composition: (a) F-1; (b) F-2; (c) F-3; (d) F-4; (e) F-5; (f) F-6; (g) F-7.

change trend of t_{90} was consistent with that of t_{s2}. This result shows that changing blend ratio has little effect on t_{s2} or/and t_{90} after EVA content reaches 10 phr.

From the technical point of view, it indicated that CM/EVA blend foam had technological feasibility with peroxide curing system.

Mechanical Properties

Figure 4 shows the rebound resilence and hardness of CM/EVA foam. According to the two curves, we can see that the rebound resilience of CM/EVA foam decreased with increasing EVA content. While the hardness of the CM/EVA foam showed reverse trend. And the result was consistent with the anticipation.

The shrinkage ratio of CM/EVA foam declined all the time with the increase of EVA as shown in Fig. 5. Especially when the EVA content beyond 20 phr, the shrinkage ratio of the blend based foam declined drastically. So we can draw a conclusion that the addition of EVA was favorable for the dimensional stability of CM foam.

The effects of EVA content on the tensile properties and elongation at break of the foamed CM/EVA were shown in Fig. 6. It was found that the tensile strength first increased and then decreased with the increase of EVA composition, and the maximum tensile strength can be up to 1.06 MPa at 30/70 blend ratio. The elongation at break dropped continuously with increasing EVA composition.

Figure 7 shows the 100% and 200% stretching stress of CM/EVA foams. With increasing EVA composition, both 100% stretching stress and 200% stretching stress increased linearly.

Tear strength is the force per unit thickness used to initiate a rupture or tear of the materials. Tear strength of the samples increased continuously with the addition of EVA composition and the maximum tear strength can be up to 4.8 N·mm^{-1} as shown in Fig. 8, which was similar to the trend of tensile strength.

Foam Characteristics

The influence of EVA content on the cell morphology and foam characteristics of CM foams were presented in Figs. 9–11. Statistical analysis and SEM were used to test the foam characteristics, for example, cell diameter was determined with the help of software image tool, and at least 100 cells were measured. The process of cell growth
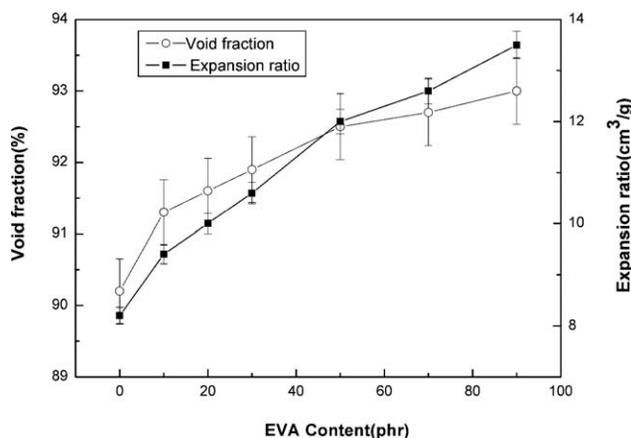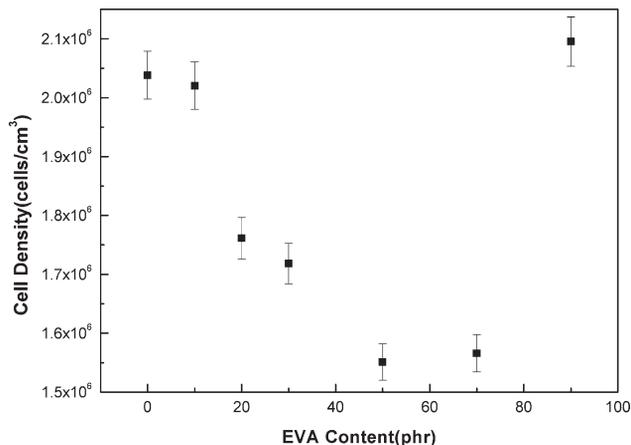

FIG. 11. The change of cell density with composition of CM/EVA foam.

and incorporation determined the final foam morphology. The cell size and shape changed unobviously with increasing EVA composition. Foams made from compounds of all range of blending ratios exhibited a closed cell structure and well-separated spherical cells were formed. This point can be illuminated by the electronic microscope photograph from Fig. 9. The expansion ratio and void fraction of CM/EVA vulcanizates were shown in Fig. 10. It was observed that both expansion ratio and void fraction increased with increasing EVA composition, and this phenomenon can attribute to the reason that the nucleation rate whose increment was of benefit to more nucleus increased with increasing EVA composition. So the conclusion that EVA composition can induce V_f to increase was obtained. Cell density decreased with increasing EVA composition, but it increased significantly when EVA content was >70 phr as shown in Fig. 11.

CONCLUSIONS

CM/EVA foams with different blending ratios were successfully prepared using compression molding. The important results were as follows:

Adding 8 phr ZnSt as activator could lower the decomposition temperature of AZDC from 223.4°C to 178.6°C. With the increase of EVA content, little effect on curing characteristics such as t_{s2} or/and t_{90} was observed. So CM/EVA blending foams with peroxide curing system was technological feasible. The hardness, 100% and 200% stretching stress of the compounds increased while the elongation at break, rebound resilience, and shrinkage ratio decreased with the increase of EVA addition. Tensile strength of CM/EVA foams presented the trend of rise first and then fell when EVA content was >70phr, and tear strength increased consistently. Closed-cell structures of CM/EVA compounds with all range of blending ratios were sufficiently confirmed by characterization of SEM. The expansion ratio and void fraction increased with the increase of EVA composition while cell density

FIG. 10. Variation of void fraction and expansion ration of CM/EVA foam.

decreased which presented a significant increase after EVA composition reached 70 phr.

NOMENCLATURE

AZDC	Azodicarbonamide
CM	Chlorinated Polyethylene rubber
CO	Carbon monoxide
CR	Polychloroprene rubber
CSPE	Chlorosulfonated polyethylene
DCP	Dicumyl peroxide
DOP	Dioctyl phthalate
DSC	Differential scanning calorimeter
EPDM	Ethylene propylene diene terpolymer
EVA	Ethylene Vinyl Acetate Copolymer
HDPE	High-density polyethylene
NBR	Acrylonitrile butadiene rubber
NR	Nature rubber
PVC	Polyvinlchloride

REFERENCES

1. N. Sombatsompop, *Cellular Polymers*., **17**, 63 (1998).
2. H.J. Tai and J.B. Wang, *J. Cell. Plast*., **33**, 304 (1997).
3. R. Pop-lliev, F. Liu, G. Liu, and C.B. Park, *Adv. Polym. Technol*., **22**, 280 (2003).
4. D.A. Trageser, *Radiat Phys Chem*., **9**, 261 (1997).
5. G.L.A. Sims and H.A.S. Jaafar, *J. Cell. Plast*., **30**, 175 (1994).
6. H.H. Yang and C. D. Han, *J. Appl. Polym. Sci*., **29**, 4465 (1984).
7. R. Laakso, V. Guffey, and V. Rajan, *Rubber World*., **238**, 23 (2008).
8. A.M. Ariff, Z. Zakaria, L.H. Tay, and S.Y. Lee. *J. Appl. Polym. Sci*., **107**, 2351 (2008).
9. J.A. Balatoni, S.N. Khanna, W.S. Mills, U.S. Patent 3,882,191 (1975).
10. W.T. Zhai, H.Y. Wang, J. Yu, J.Y. Dong, and J.S. He, *J. Polym. Sci. Polym. Phys*., **46**, 1641 (2008).
11. C.Z. Sahagun, R. Gonzalez-Nunez, and D. Rodrigue, *J. Cell. Plast*., **42**, 469 (2006).
12. S.K Goel and E.J. Beckman, *Polym. Eng. Sci*., **34**, 1148 (1994).
13. N. Uejyukkoku and Y. Nakatsu, U.S. Patent 786,406 (1996).
14. Y. Mao and R. Qi, *J. Appl. Polym. Sci*., **109**, 3249 (2008).
15. D.J. Kim, S.W. Kim, H.J. Kang, and K.H. Seo, *J. Appl. Polym. Sci*., **81**, 2443 (2001).
16. R. Gendrony and C. Vachon, *J. Cell. Plast*., **39**, 71 (2003).