

# Preparation of Polyethylene–Octene Elastomer Foams by Compression Molding

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Received 29 September 2007; accepted 19 March 2008

DOI 10.1002/app.28415

Published online 23 May 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** To produce polyethylene–octene elastomer foams with compression molding, the influences of various activators on the thermal decomposition temperature of the chemical blowing agent azodicarbonamide were investigated with thermogravimetric analysis, which showed that the decomposition temperature of azodicarbonamide could be effectively reduced by the addition of zinc oxide/zinc stearate. The results of a moving die rheometer suggested that the vulcanization and blowing curves were influenced by the content of azodicarbonamide and tem-

perature, and the optimum temperature was about 170°C. The morphology and physical properties of the microcellular polyethylene–octene elastomer were studied. The results indicated that the amount of azodicarbonamide and the processing temperature played important roles in the cell morphology and physical properties of polyethylene–octene elastomer foams. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3249–3255, 2008

**Key words:** additives; blowing agents; polyolefins

## INTRODUCTION

Polymer foams are typical two-phase materials in which a gas is dispersed in a continuous macromolecular matrix.<sup>1–5</sup> Polymeric foam structures came into general practical use during the 1940s and 1950s. Now a wide variety of polymers can be formed into foams with widely varied structures. Polyolefin foams have many advantages, including light weight, a high strength-to-weight ratio, thermal insulation, chemical resistance, skin friendliness, no water absorption, cushioning performance, shock absorption, and buoyancy.<sup>5–7</sup>

In the last several years, some new materials have emerged as base materials for crosslinked polyolefin foams,<sup>8,9</sup> such as ethylene–styrene interpolymers,<sup>10</sup> metallocene polyethylenes,<sup>11–13</sup> polypropylene foams,<sup>14</sup> and blends of different polyolefin foams.<sup>15–18</sup> Currently, commercial polyolefin foams include low-density polyethylene, high-density polyethylene, linear low-density polyethylene, polypropylene, and ethylene/vinyl acetate copolymers. To satisfy the diversified market demands of crosslinked polyolefin foams, new foam materials are being developed.

Polyethylene–octene elastomer (POE), a metallocene-based polyolefin used as a novel polyolefin

elastomer, is widely used in applications such as sheets, automotive parts, durable goods, modifiers in engineering plastics, and wires and cables because of its good balance of mechanical properties and favorable processability.<sup>19–21</sup> However, POE foams have been seldom researched up to now.<sup>22–25</sup>

In this study, the influences of various activators on the thermal decomposition temperature of azodicarbonamide (AC) were investigated with thermogravimetric analysis (TGA). Furthermore, the relationship between the decomposition of the blowing agent (AC) and the cure characteristics of dicumyl peroxide (DCP) was studied on a moving die rheometer (MDR). A light-density POE foam was successfully obtained by compression molding. Scanning electron microscopy (SEM) results further proved that a closed-cell POE foam was formed. The most suitable temperature was confirmed to be about 170°C by theoretical calculations and experimental analysis.

## EXPERIMENTAL

### Materials

POE containing 24 wt % comonomer (Engage 8100) with a melt flow index of 1 g/10 min (190°C/2.16 kg), a density of 0.870 g/mL, and a Mooney viscosity of  $ML_{1+4}$  (121°C) = 35 was supplied by DuPont–Dow Elastomer (Shanghai, China). AC (a fine, yellow powder) was produced by Shanghai Xiangyang Chemical Co., Ltd. (Shanghai, China). DCP was

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Contract grant sponsor: Shanghai Leading Academic Discipline Project; contract grant number: B202.

TABLE I  
Elastomer Compound Formulations for Dynamic Vulcanization

Mix number	POE (phr wt)	AC (phr wt)	DCP (phr wt)	ZnO (phr wt)	ZnSt <sub>2</sub> (phr wt)	HSt (phr wt)	TiO <sub>2</sub> (phr wt)
A0 (blank)	100	0	1.5	4	1.5	1.5	5
A1	100	1	1.5	4	1.5	1.5	5
A3	100	3	1.5	4	1.5	1.5	5
A5	100	5	1.5	4	1.5	1.5	5
A7	100	7	1.5	4	1.5	1.5	5
A9	100	9	1.5	4	1.5	1.5	5
A11	100	11	1.5	4	1.5	1.5	5
A13	100	13	1.5	4	1.5	1.5	5

manufactured by Shanghai Fuzhe Chemical Co., Ltd. (Shanghai, China). All other additives and activators [zinc oxide (ZnO), zinc stearate (ZnSt<sub>2</sub>), and stearic acid (HSt)] were industrial-grade products purchased from Shanghai Yuanji Chemical Co., Ltd. (Shanghai, China).

### Sample preparation

The precured POE compounds were mixed with the ingredients according to the formulation in Table I at 80°C on a two-roll mill. Engage was first melted for 2 min, after which other ingredients were added. The blowing agent was added along with the filler and activators for good dispersion. Mixing was continued for another 3 min to ensure the homogeneous distribution of the ingredients. Finally, the curative DCP was added. Then, the compounds were taken out of the mill to form a sheet and stored at room temperature for 24 h before foaming. The cure characteristics of the vulcanizates were determined on an MDR. Finally, the compounds were pressed in a closed mold, and the foams were obtained by compression molding at a pressure of 10 MPa for 10 min. POE foams with different contents of the blowing agent were prepared at 170°C. For sample A5 in Table I, the effect of the temperature on the physical and mechanical properties of POE foams was further investigated.

### TGA

The decomposition behavior of the crosslinking agent DCP and chemical blowing agent AC was analyzed with a TGA7 thermogravimetric analyzer (PerkinElmer, Inc., USA). About 5 mg of a sample was placed on a microbalance and heated from room temperature to either 400°C (powders without the POE matrix were blended with a high-speed mixer to ensure a good dispersion) or 800°C (the samples including the POE matrix had to be blended on a two-roll mill) at a heating rate of 20°C/min. A stream of dry N<sub>2</sub> was used for the purging of oxygen.

### Rheological properties

The rheological measurements (the vulcanization and blowing characteristics) for the precured POE compounds were conducted with a moving die processability tester (i.e., an MDR; model UCAN-2030, U-Can Dynatex, Inc., Nantou, Taiwan) according to ASTM method D 5289. The MDR was equipped with a pressure sensor at the upper die. It could detect the pressure of the POE compound during the POE vulcanization in the mold.

### SEM observations

The cellular morphological analysis was carried out on freeze-fractured samples, and the corresponding cross sections with a sputtered gold coating were observed by SEM (model S-2150, Hitachi, Chi City, Japan).

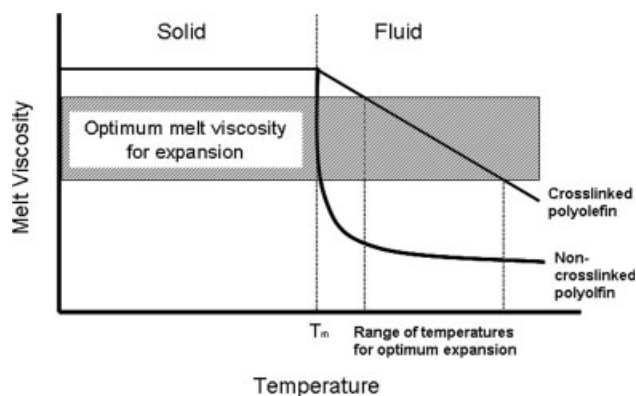
### Physical properties

The density was calculated from the mass and volume of cylinder specimens with a surface skin according to ISO 845-1988. The hardness was measured with a Shore C durometer according to ISO 2439-1980 (Cany Precision Instruments Co., Ltd., Shanghai, China). Stress-strain properties (tensile strength and elongation at break) were determined on a Universal electro-mechanical tester (Instron 4465, Instron Corp., Grove City, PA) at room temperature (25 ± 2°C) according to ASTM D 3574-86. The split tear strength and angle tear strength of cellular POE were also measured on the same tester according to ASTM D 3574-77. At least five sample replicates were tested to obtain the average values of different properties.

## RESULTS AND DISCUSSION

### Accelerating effect of activators

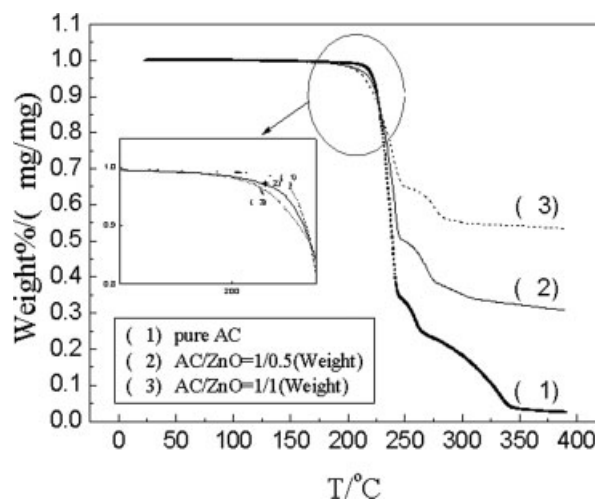
Temperature is very critical for producing a POE foam because it can affect the decomposition of the chemical blowing agent (AC) or crosslinking agent (DCP) and the melt viscosity of the polymer, which influences cell nucleation, growth, stabilization, and



**Figure 1** Melt viscosity sketch of the polymer before and after crosslinking ( $T_m$  = melting temperature).

retention of the foam (Fig. 1). It is good for the production of the foam that the chemical blowing agent can start to decompose, whereas the melting and crosslinking of POE occur through the control of the temperature. In general, the temperature at which a large amount of decomposition starts for DCP is about  $100^\circ\text{C}$  (the half-lives at 101, 150, and  $171^\circ\text{C}$  are ca. 100 h, 9 min, and 1 min, respectively), whereas AC starts to decompose around  $205^\circ\text{C}$ ; this means that the decomposition of AC does not start when the crosslinking processing of POE is completed. The decomposition reaction of AC must take place when the polymer is at the proper melt viscosity or degree of cure.<sup>26</sup> Activators can lower the decomposition temperatures of blowing agents. Tai and Wang<sup>27</sup> found that the addition of ZnO to the foaming agent AC not only lowered the decomposition temperature but also accelerated its decomposition. Therefore, ZnO could be considered an activator for AC.

It can be seen from Figure 2 that the decomposition temperature of AC decreased to around  $175^\circ\text{C}$  when AC/ZnO (1/0.5) was added. However, there was plenty of gas released by AC up to  $200^\circ\text{C}$ , which was not effective at reducing the decomposition temperature of AC. Some studies<sup>5,14,27</sup> have found that the decomposition temperature of AC decreases with an increase in the amount of ZnO. In our work, to a certain extent, adding more ZnO had little effect on the decomposition temperature of the foaming agent. The results in Figure 2 indicate that the decomposition temperature of AC did not decrease significantly with the amount of ZnO increasing from 0.5 to 1 phr. Some foaming experiments were also carried out at 160, 170, and  $180^\circ\text{C}$  through compression molding. The results showed that AC could not decompose completely with the addition of various amounts of ZnO only, and a low-density POE foam failed to be produced; that is, it was difficult to get the needed decomposition temperature by the addition of ZnO only. Therefore, another activator, ZnSt<sub>2</sub>, was added to AC/ZnO to

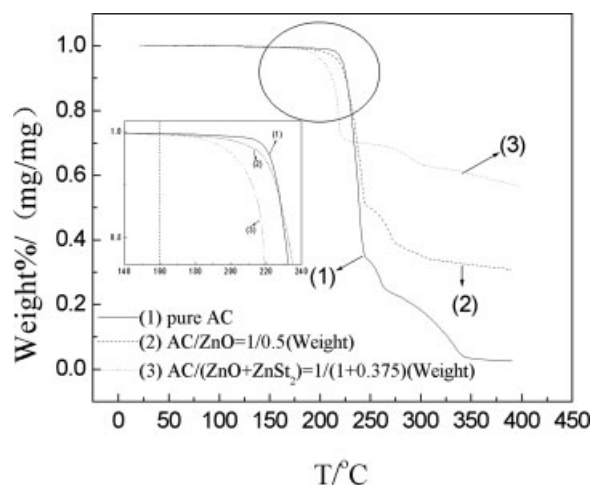


**Figure 2** TGA curves of AC and AC/ZnO ( $T$  = temperature).

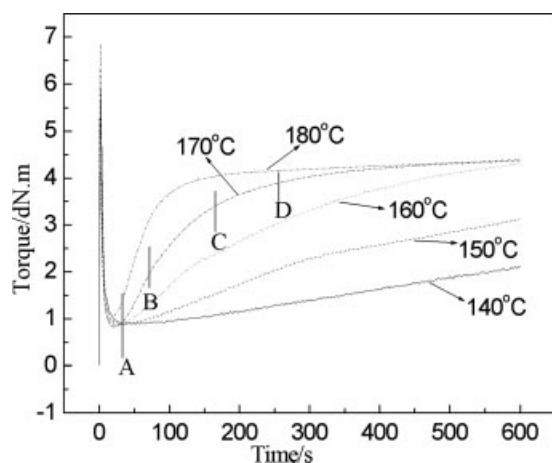
decrease the decomposition temperature of AC to the appropriate value. For instance, when 0.375 phr ZnSt<sub>2</sub> was added, the decomposition temperature of AC was lowered to around  $160^\circ\text{C}$  (Fig. 3), which was lower than that with the addition of ZnO alone. There was much gas released from the AC composite around  $175^\circ\text{C}$ . Therefore, the decomposition temperature of AC could be decreased to an appropriate value for foaming by the addition of the compound activators ZnO and ZnSt<sub>2</sub>.

#### Relationship of the rate of POE vulcanization and blowing agent decomposition: the effect of temperature

In foaming processes in which foam expansion is accomplished by heating, bubbles need to be stabilized by the crosslinking of the polymer.<sup>26</sup> Generally,



**Figure 3** TGA curves of AC, AC/ZnO, and AC/ZnO/ZnSt<sub>2</sub> ( $T$  = temperature).



**Figure 4** Representative rheographs of POE foaming compound A3 at different temperatures.

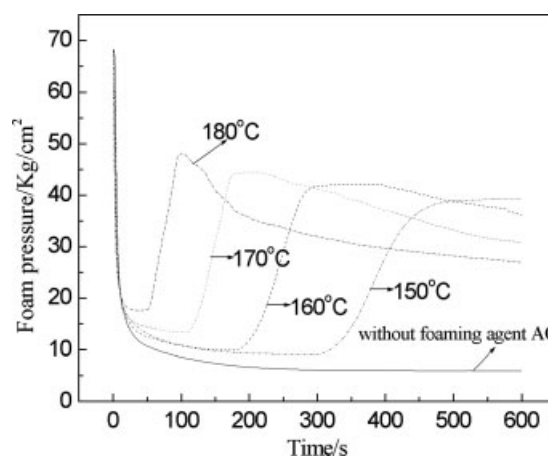
a change in the rheometric torque is basically consistent with the decomposition process of DCP. The effect of temperature on the curing characteristics of the compounds is shown in a representative Monsanto rheograph (Fig. 4). It can be seen from the slopes of these curves that the velocities of the POE crosslinking process were different at different temperatures, and the torque-varying rate increased with increasing temperature because of the increase in the decomposition speed of DCP. However, DCP is difficult to decompose completely in 10 min below 160°C, and this means that the temperature should be over 160°C if the POE crosslinking process is to be completed in 10 min.

To comprehend the relationship of the rate of POE vulcanization and blowing agent decomposition, the torque curves of POE compounds at 170°C in Figure 4 are used as an example. In the beginning of heating, the viscosity of the elastomer compounds decreases, and this results from the melting of POE compounds; then, the torque starts to increase because of crosslinking. If the foaming process starts before point A, the rubber compounds have low viscosity; gas released from the foaming agent can easily escape from melted POE. Therefore, foam materials cannot be produced at this stage. When the foaming process occurs at stage AB, it is easy to produce a cellular structure with interconnected cells because of the low cell strength and plastic deformation of the polymeric matrix. When the foaming agent decomposes in the range of BC, the system has an appropriate viscosity for foaming, the blends have compatible fluidity and high cell strength, and a closed cell will be obtained. If the vulcanization of POE is finished (after point D), it will be difficult to produce a foam because the viscosity of POE is too high to dissolve gas into the POE matrix. Figure 4 shows that it is detrimental to the growth of cells at 180°C because the rate of the curing curve is rapid

enough to compete the vulcanization. Therefore, the relationship of the rate of POE vulcanization and blowing agent decomposition is a key factor in producing foam materials, and this is similar to the results of some reports.<sup>28–30</sup> According to integrated factors, 170°C is the most appropriate temperature for foaming.

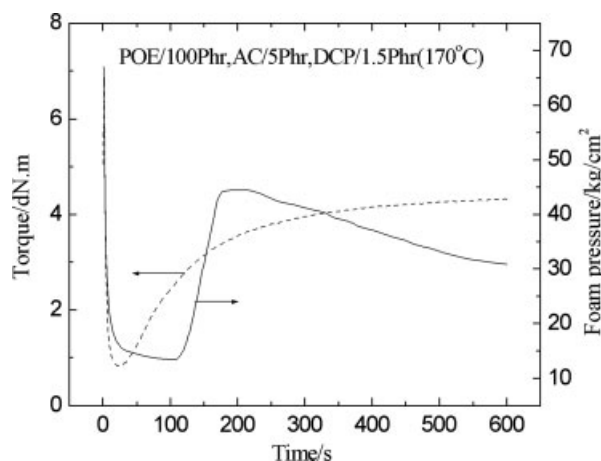
The blowing characteristics of the POE compounds were measured with an MDR through the detection of the pressure of the rubber compound during the rubber vulcanization in the mold. However, gas from AC easily escapes from the cavity, so air is not completely locked; therefore, the values of the foam pressure tested are not accurate, and they are used only to reflect the decomposition conditions of foaming agent AC. Figure 5 depicts the characteristics of blowing agent decomposition at various temperatures from 150 to 180°C. The decomposition rate of foaming agent AC accelerated with increasing temperature. The foaming agent gradually decomposed with an increase in time, and this led to the foam pressure increasing and finally reaching a balance. However, in our experiment, the foam pressure initially increased with the prolongation of time, reached a maximum, and then slightly decreased with time because the cavity in which air was not completely locked led to more gas escaping from the POE matrix with the increase in temperature. This method can limit the evaluation of the real decomposition process of AC.

In Figure 6, the relationship of the rate of rubber vulcanization and blowing agent decomposition is quite perfect. In theory, a POE foam with a closed cell can be produced at 170°C with the formulations in Table I. Therefore, the relationship between the POE vulcanization rate and the blowing agent decomposition can be improved by the addition of foaming agent activators and the adjustment of the decomposition temperature of AC and DCP.



**Figure 5** Blowing curves of POE foaming compound A3 at different temperatures.



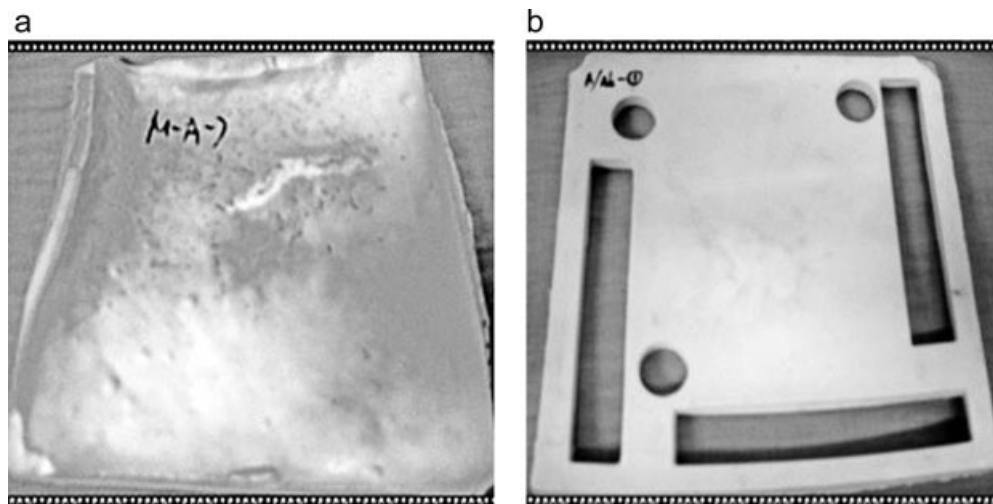


**Figure 6** Rheographs and blowing curves of A5 at 170°C.

POE compounds were foamed at different temperatures via compression molding, and the results are shown in Figure 7. When the molding temperature was 180°C [Fig. 7(a)], chaps and a little rigidity occurred on the surface of the foam because the decomposition of DCP was finished in 2 min (Fig. 4); therefore, it was difficult to produce foam materials. When POE compounds were foamed at 170°C, POE foam was successfully produced with a good surface and soft feeling [Fig. 7(b)]. POE foams with lower expanding multiples were produced below 170°C. Eventually, experiments demonstrated that the optimal temperature for foaming was 170°C. The results agreed with the academic analysis by TGA and MDR.

### Morphology of POE foams

SEM micrographs of microcellular POE foam materials with various formulations and processing temperatures



**Figure 7** Photographs of microcellular Engage produced by compression molding: (a) A5 (180°C) and (b) A5 (170°C).

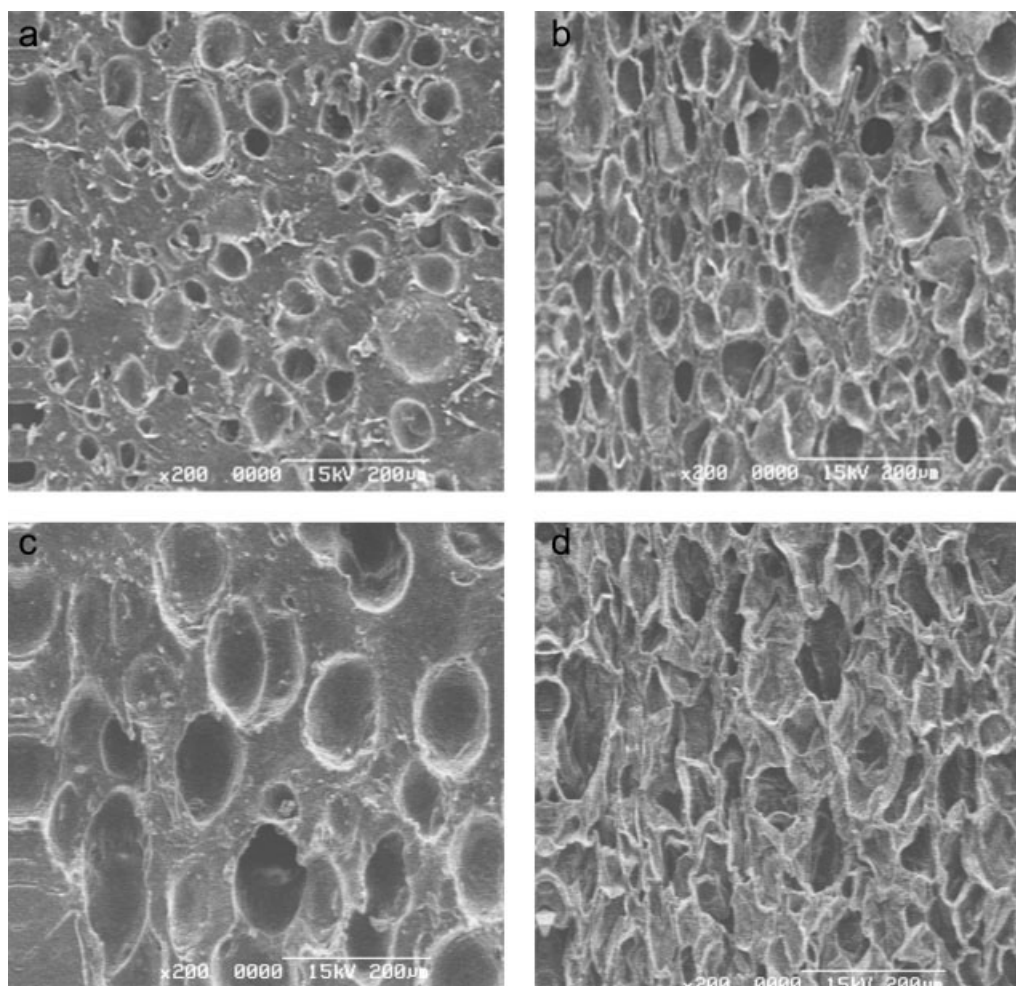
are shown in Figure 8. All foams exhibited a closed-cell structure. It was also noted from the SEM images that the cells were not very homogeneous.

However, if the AC content had been superfluous [DCP was fixed; Fig. 8(d)], the shape of the cell would have changed from round or elliptical to anomalous, and cell coalescence would have occurred. The cells seemed to be elongated. Cell coalescence was not the only reason for cell density deterioration in the foaming polymer. The irregular cell structure was obtained because adjacent cells were united by the pressure difference. Because of the pressure difference, the gas in the smaller cell diffused to the larger cell.<sup>14,29</sup> Therefore, a low-density POE foam was obtained. On the other hand, the irregular cell structure could worsen the physical properties of foam materials.

The effect of the foam processing temperature on the cell morphology of the POE foam was also investigated. Figure 8(b,c) shows SEM images for POE foams at 150 and 170°C. Figure 8(c) shows that the cell number was low with a cell density of  $3.79 \times 10^9$  cells/cm<sup>3</sup> when the foaming temperature was 150°C, and this indicated that the foam materials had a low density. This was mainly because AC did not completely decompose at 150°C in 10 min, and the foam formed less cell nucleation. It was also noted that the foam processed at 170°C had a smaller average cell size of 50.5 μm and a higher cell density of  $6.29 \times 10^{10}$  cells cm<sup>-3</sup> in comparison with the foam processed at 150°C. The cell wall thickness decreased from 80.4 to 5.6 μm.

### Physical and mechanical properties

According to the aforementioned work, POE foams were obtained. The physical and mechanical properties of the POE foams were also studied.



**Figure 8** SEM photomicrographs of freeze-fractured cross sections of microcellular Engage vulcanizates: (a) A1 (170°C), (b) A5 (170°C), (c) A5 (150°C), and (d) A13 (170°C).

Table II list the effects of the foaming temperature and the AC content on the physical and mechanical properties of the POE foams. When the foaming temperature changed from 150 to 160°C, the foam density decreased from 0.638 to 0.171 g/cm<sup>3</sup> and then hardly changed as the processing temperature further increased; this could be attributed to some

collapse of cells during processing at a high temperature. The physical and mechanical properties decreased when the foaming temperature increased from 150 to 160°C and then changed little as the foaming temperature further increased; this was closely related to the POE foams. The foam prepared at 170°C had better integrative physical and

**TABLE II**  
Effects of the AC Content and Processing Temperature on the Physical and Mechanical Properties of POE Foams

Mix	Density (g/cm <sup>3</sup> )	Hardness (Shore C)	Resilience (%)	Tensile strength (MPa)	Elongation at break (%)	Split tear strength (N/mm)	Angle tear strength (N/mm)
A0 (blank)	0.896	84	87	7.63	657	33.6	38.5
A1	0.820	80	84	5.25	602	27.7	34.0
A3	0.290	51	58	2.88	272	6.15	10.3
A5/170°C	0.170	38	49	2.02	238	2.49	8.40
A5/150°C	0.638	74	54	1.69	307	17.0	6.84
A5/160°C	0.171	39	47	1.72	221	2.81	7.13
A5/175°C	0.181	41	48	1.40	222	2.23	6.20
A7	0.120	31	31	1.35	174	1.46	4.85
A9	0.085	23	28	1.03	147	1.16	3.76
A11	0.072	19	24	0.99	145	1.09	3.07
A13	0.057	15	23	0.82	127	0.95	2.67

mechanical properties, which agreed with the results of MDR and SEM. Therefore, 170°C as an optimal temperature was used in the following work. Table II also shows that the density of the POE foam decreased from 0.896 to 0.057 g/cm<sup>3</sup> with an increase in the AC content in the range of 0–13 phr, and this led to the physical and mechanical properties of the POE foams decreasing. It could be explained that the physical and mechanical properties of the POE foams mainly depended on their density.

### CONCLUSIONS

A POE foam was successfully prepared with compression molding. The important results were as follows:

1. Adding appropriate activators (ZnO and ZnSt<sub>2</sub>) could lower the decomposition temperature of AC, which could be consistent with that of DCP. AC/ZnO/ZnSt<sub>2</sub> was suitable for producing the POE foam.
2. The optimal temperature was 170°C.
3. SEM showed that the POE foam was a closed-cell structure.
4. The density and properties of the POE foam materials decreased with an increase in the amount of AC and the temperature.

The authors thank Shuangwu Huang (Micron Semiconductor Asia Pte., Ltd., Singapore) for enthusiastic discussion.

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