Rheological Properties and Foam Processibility of Precured EPDM

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ABSTRACT: EPDM foam was prepared by dynamically vulcanizing EPDM compound in a HAAKE rheometer firstly, then mixing the partially precured EPDM compound with a blowing agent and a sulfur vulcanizing system on a two roll mill. The compound was extruded through a cold feed extruder, and the extrudate was foamed in a circulating hot air oven. EPDM compound was vulcanized partly in the HAAKE rheometer, the final torque increases with increasing sulfur content. Rheological measurement shows the dynamic storage modulus, the loss modulus, and the complex viscosity of precured EPDM compound increase with increasing sulfur content. Then the partially precured EPDM compound was compounded with a blowing agent and a sulfur vulcanizing systems, Rheometric measurement shows that the rate of vulcanization of partially precured EPDM compound is not affected by the precure. The blowing results show that the foam processibility could be improved and the expansion ratio increases in the same processing condition for optimum partially precured EPDM compound, which indicates the optimum crosslink density for EPDM could enhance the efficiency of blowing agent AC. SEM shows that the foam articles have a closed-cell structure with few open cells, and the large cells inlay among the small cells. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3387–3394, 2006

Key words: blowing agents; rheology; morphology; EPDM; rubber; procure; foam; crosslinking

INTRODUCTION

Polymeric foam structures came into general practical use during the 1940s and 1950s. Now a wide variety of polymers can be formed into foams having widely varied structures. Polymeric foam has several advantages over equivalent unexpanded materials, such as the lower density or light weight, good insulation and cushioning properties, and high strength to weight ratio, etc. These advantages lead to many applications, for example, thermal insulation, buoyancy, packaging, and gaskets. At the beginning of the 21st century, the world use of foamed products is estimated at [pound]23 billion/10.4 million tonnes and is projected to grow significantly.[1]

In general, two different processes for rubber blowing have to be taken into account, one is a continuous process,[2,3] which includes microwave, hot-air, liquid curing method (LCM or salt bath), and fluidized bed. The other is a discontinuous process,[4,5] which involves curing an unvulcanized rubber compound that contains a blowing agent in a mold under a high pressure and an elevated temperature. Regardless of the process employed, the successful production of foamed articles requires control of the entire cure–expansion operation,[6,7] which depends on a very delicate balance of two simultaneously occurring reactions—the vulcanization of the rubber and the decomposition of the blowing agent. In fact, to balance the reaction rate of decomposition and vulcanization, previous studies have shown the compound[8–10] of various blowing agents and cure accelerators is extremely important to the production of sponges with desired morphology. Because of the very complex systems and that various reactions interfere with each other strongly, it is very difficult to understand the two kinds of chemical reactions which take place simultaneously in the blowing process. The production of cellular elastomeric products is still more of an art than a science.[6]

It is well known that EPDM has chemical stability, good ageing resistance, high load capacity, and high resistance to breakdown during mechanical operations. Now EPDM finds increasing acceptance for producing cellular sections[3,11,12] The effects of the EPDM grade, blowing agent type, composition of EPDM blend, and processing conditions on the cell structure and the physical properties of the resultant EPDM foams were investigated.[9,10,13–15] However for EPDM, which is a slow vulcanizing rubber, the choice of type of vulcanization systems in combination with the

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TABLE I
Rubber Compound Formulations for Dynamic Vulcanization

	Mix number					
	G0	G1	G2	G3	G4	G5
EP35	100	100	100	100	100	100
Sulfur	0	0.025	0.05	0.075	0.1	0.15
Mercaptobenzothiazole (MBT)	0.5	0.5	0.5	0.5	0.5	0.5
Stearic acid	3	3	3	3	3	3
Zinc oxide	5	5	5	5	5	5
Calcium oxide	3	3	3	3	3	3
Carbon black (N330)	60	60	60	60	60	60
Talc	50	50	50	50	50	50
Sunpar 2280	50	50	50	50	50	50

blowing agents to produce the optimization of the cell structure and surface appearance is difficult aspect of the compounding technology for EPDM expansion. To overcome the difficulty, in general, foam processibility could be improved by adjusting the technological process, which contains three stages—precure, expansion, and final cure.[16] The first is the precure, namely nature cure,[17] which refers to the slow curing process in which no blowing agent decomposition occurs in lower temperature. This is a very important stage, which makes the modulus of matrix is strong enough to withstand the gas pressure and confine the released gas. In this article, we firstly partially precured the EPDM compound in the HAAKE rheometer, then studied the rheological properties of partially precured EPDM compound, and finally investigated the effects of partially precured EPDM compounds and blowing agent content on cell structure of the resultant EPDM foam. The results show that an optimum precure for EPDM compound could improve its foam processibility and obtain the higher expansion ratio in the same condition, which could improve the efficiency of blowing agent AC.

MATERIALS AND METHODS

Materials

EPDM (EP 35, containing ENB, iodine value 26) manufactured by JSR Corp. (Japan) was used. Carbon black (N330) was used as filler, supplied by Cabot Corp. Azodicarbonamide (AC) was produced by Shanghai Xiangyang Chemical Co., Ltd., China. All the other additives were rubber industrial grade products.

Compounding and sample preparation

EPDM was vulcanized partially with the ingredients according to the formulations listed in Table I in a HAAKE rheometer at 80 rpm for 10 min at 170°C. Then the precured EPDM compounds were compounded with the ingredients according to the formulations listed in Table II and Table III on a two-roll mill. Finally, the compounds were taken off the mill and stored at room temperature for 24 h prior to extrusion.

A cold-feed laboratory-scale extruder, equipped with a 5-mm cylindrical die and a 3 cm diameter single screw with a length to diameter ratio (L/D) of 12 : 1, was used for an extrusion. The rubber compound was extruded through a cylindrical die at processing temperatures of 20, 60, and 50°C for feeding, barrel, and die zones respectively. Using a screw speed of 20 rpm, the extrudate was immediately placed in a circulating hot air oven for foaming and vulcanizing at 190°C for 10 min.

Rheological properties

The rheological measurement for precured EPDM compound was conducted using a moving die processibility tester (Model rheo TECH MDPT, Tech-Pro). In the dynamic frequency sweep mode, G', G'', and η^* were measured as functions of frequency in the range from 0.03 to 20 Hz at a constant strain 10% at 190°C.

Vulcanization and blowing measurements

The vulcanization and blowing characteristics of the rubber compounds were measured on a moving die rheometer (MDR, Model UCAN-2030, U-can Dynatex,

TABLE II
Rubber Compound Formulations for Foaming Process

	Precured EP					
	G0	G1	G2	G3	G4	G5
AC	6	6	6	6	6	6
Diphenylguanidine (DPG)	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5

TABLE III
Rubber Compound Formulations for Foaming Process

	Precured EP				
	G2	G2	G2	G2	G2
AC	0	3	6	9	12
Diphenylguanidine (DPG)	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5

Inc., Taiwan) at 1 arc degree, according to ASTM D-5289 method. The MDR was equipped with a pressure sensor at the upper die. It can detect the pressure of the rubber compound during the rubber vulcanization in the mold. The torque difference shows shear dynamic modulus that indirectly relates to the crosslink density of the compounds. However, because of the decomposition of blowing agent which releases gas, the cure characteristics of rubber including blowing agent obtained on MDR are interfered with by gas dissolving under high pressure and/or forming microbubbles in the rubber phase.[15,18–20] To eliminate the false appearance, rubber compounds measured for vulcanization parameters excluded the blowing agents.

Density measurements

Density was calculated from the mass and volume of cylinder specimens with surfaces skin according to ISO 845-1988.

SEM observations

The cellular morphologies of the foam samples were observed by scanning electron microscopy (SEM, Model *S*-2150, HITACHI). Samples were razor-cut and the razor-cut surface was sputter-coated with gold before observation.

RESULTS AND DISCUSSION

EPDM precure

Precure of EPDM compound is carried out in the HAAKE rheometer according to the formulations listed in Table I. Figure 1 shows the torque variations during mixing for EPDM compounds with different sulfur content. In the case of the blends, the torque decreases to a minimum quickly after the initial loading peak, after about 4 min, the torque has a slow increase, which is due to the lightly crosslinking reaction of EPDM in the compound. The final torque increases with increasing sulfur content in the compound, which shows the final crosslink density of compound is closely related with sulfur content. The partial precrosslink degree of EPDM compound could be effectively controlled by adding sulfur content in dynamic vulcanizing process.

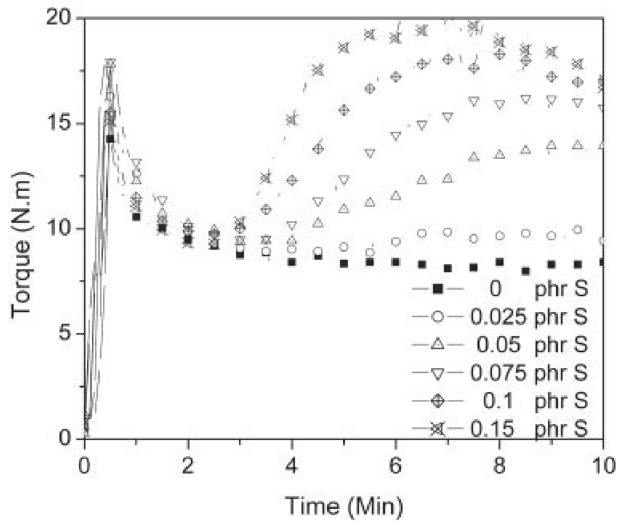

Figure 1 Torque–time relationship for EPDM compounds with various sulfur content.

Rhological properties of precured EPDM

The effect of frequency on the rheological properties of compounds was studied. The dynamic storage modulus (G′) and the loss modulus (G″) are plotted in Figures 2 and 3 as functions of frequency, respectively. The results clearly reveal that G′ and G″ increase with increasing the sulfur content, which is owing to the chemical crosslink that could increase the modulus for the unvulcanized rubber. This is similar to the Aranguren's results.[21] It also be seen that G′ and G″ in-

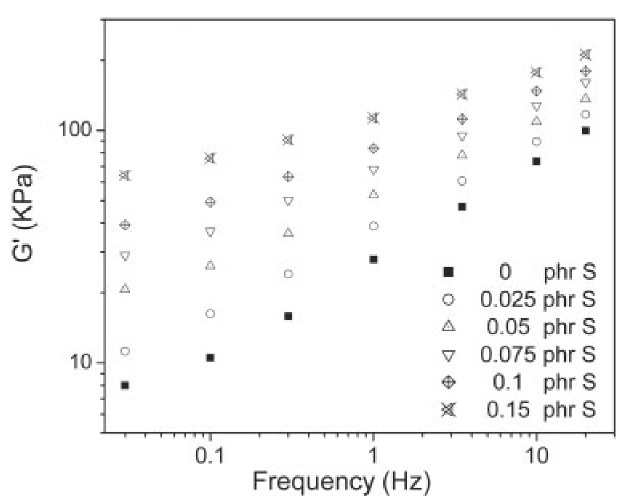

Figure 2 Storage modulus (G′) as a function of frequency of precured EPDM compounds with various crosslink densities.

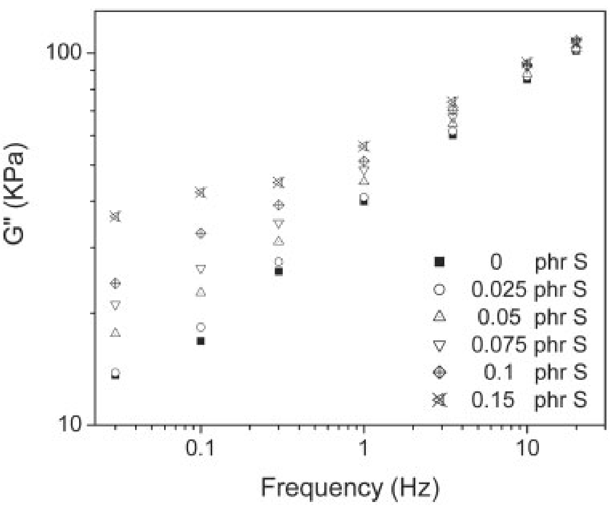

Figure 3 Loss modulus (G″) as a function of frequency of precured EPDM compounds with various crosslink densities.

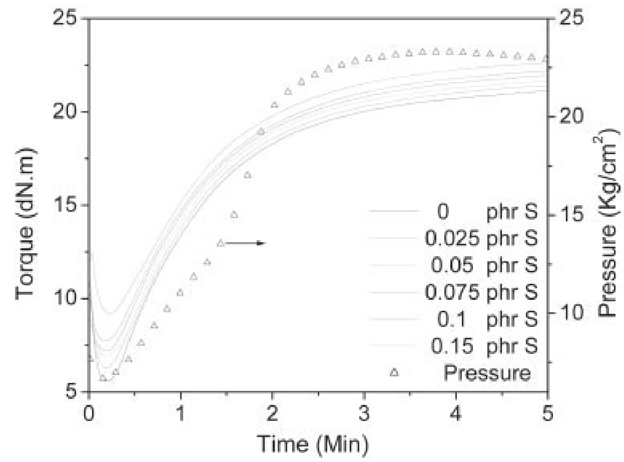

Figure 5 Blowing and vulcanization curves of precured EPDM foaming compounds with different crosslink densities at 190°C.

crease with increasing the frequency for all the precured EPDM compounds. This behavior is typical for polymers[22]—in lower frequency, there is sufficient time to allow the chains to reorganize themselves, and the polymer appears soft, and the modulus is lower. Nevertheless, the increase of G′ and G″ with increasing frequency for precured EPDM compound with higher crosslink density reveals a shallower slope than those with the lower crosslink density, which shows that the increase of G′ and G″ with increasing the sulfur content was more sensible at lower frequency.

Figure 4 reveals the complex viscosity (η^*) as a function of frequency. It is clear the η^* of precured compounds increases with increasing sulfur content, which shows the chemical crosslink restrict the chain

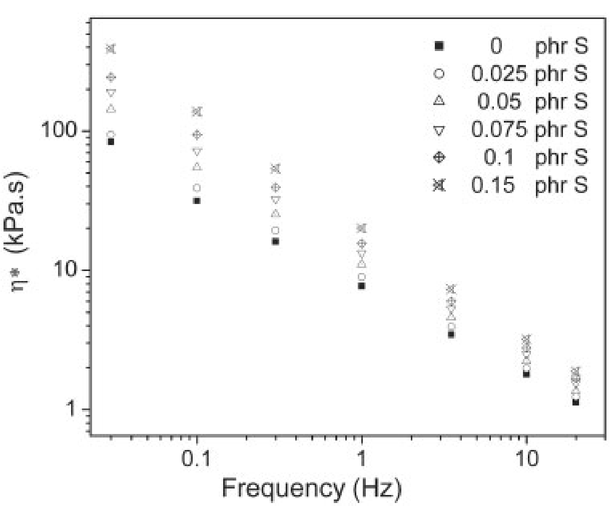

Figure 4 Complex viscosity (η^*) as a function of frequency of precured EPDM compounds with various crosslink densities.

movement. It could also be seen that η^* decreases with increasing frequency, which is not unusual,[23] indicating the pseudoplastic behavior of the compounds. However the complex viscosity plot of compound with higher crosslink density reveals steeper slopes than those with lower crosslink density, which shows that the increase of η^* with increasing sulfur content was less sensible at higher frequency.

Foam preparation

The effect of precured EPDM

The precured EPDM compounds were compounded with the ingredients according to the formulations listed in Table II for blowing process, as can be seen only the crosslink density of compound was changed. Figure 5 depicts the characteristics of the rubber vulcanization and blowing agent decomposition at 190°C. The experiments show that the curves of the blowing agent AC decomposition are superposition for different compounds, which shows the decomposition rate of blowing agent in compound is similar to each other. This might be owing to the quite similar chemical environment and the same blowing agent AC content. So we listed only one curve of blowing agent decomposition. It is apparent that the minimum torque (M_L) and maximum torque (M_H) increase with increasing crosslink density of the precured EPDM compound. It seems that the torque curve is shifted upward to some degree with increasing the crosslink density of precured EPDM compound, which means the rate of rubber vulcanization is not affected by previous dynamic vulcanization process in the HAAKE rheometer. Thus for different precured EPDM compound, the matrix has a different viscosity and elastic modulus when the blowing agent decomposes and releases gas.

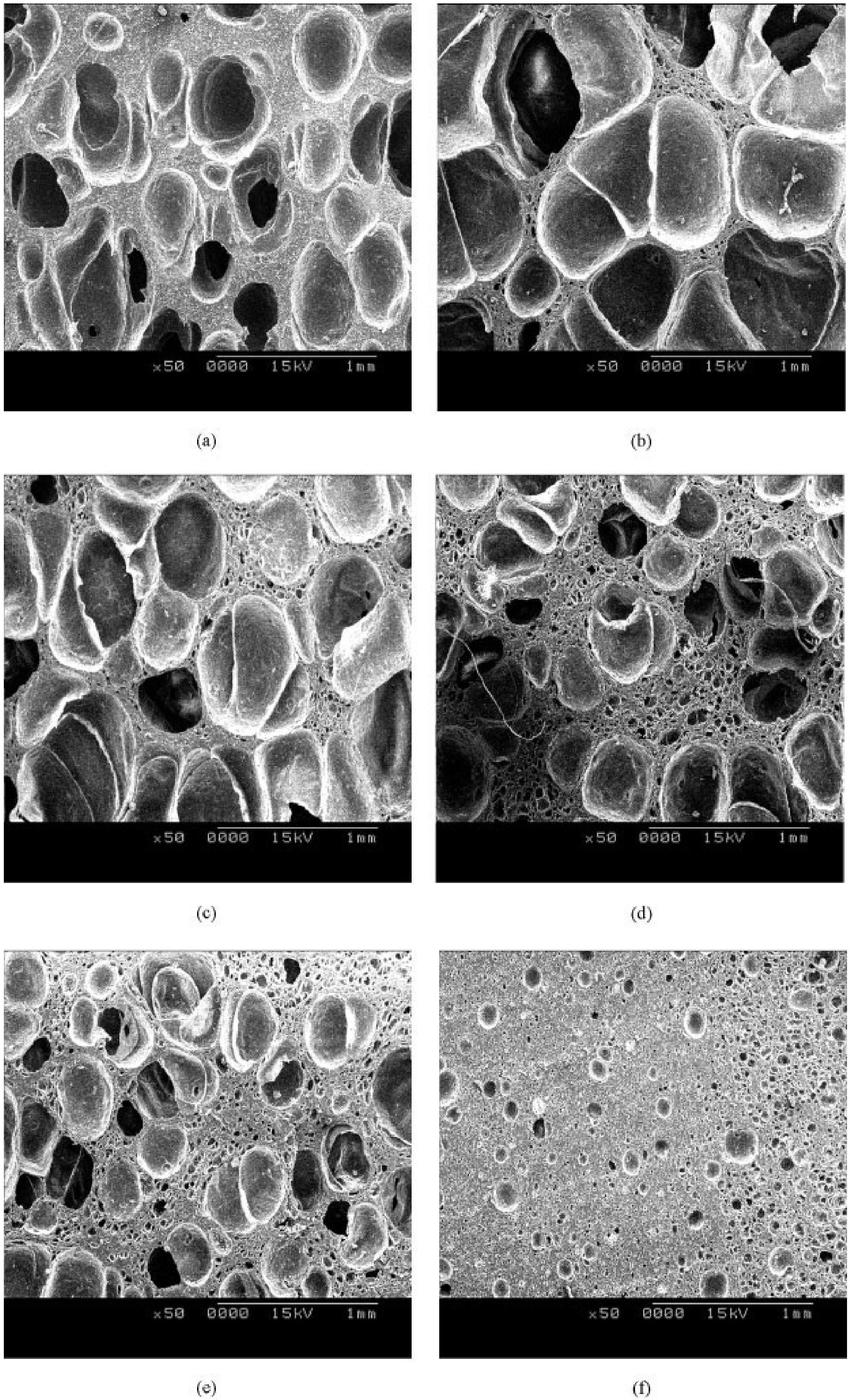

Figure 6 SEM photomicrograph of razor cut surfaces of EPDM foam. (a) 0 phr sulfur; (b) 0.025 phr sulfur; (c) 0.05 phr sulfur; (d) 0.075 phr sulfur; (e) 0.1 phr sulfur; (f) 0.15 phr sulfur.

SEM photomicrographs (Fig. 6) show foam morphology of compounds with their blowing taken place at 190°C. It is apparent that for the compound G0 without sulfur in precure process, the foam articles have quite a few open cells and thicker cell walls with few small cells. However for the compound containing sulfur in precure process, the foam articles have a closed-cell structure and the cell walls with many smaller cells. With increasing crosslink density of precured EPDM compound, the size of the larger cells has a maximum value. This might be explained from two ways—the viscosity and modulus of the matrix. When the blowing agent begins to release gas, if the crosslink density of EPDM compound is quite low, the modulus of the matrix are relatively weak, so that gas pressure is easy to break the cell walls and the gas would be drained out in lower viscosity, then form a few open cells with thicker cell walls. If the crosslink density of EPDM compound increases to optimum level, the modulus of cell membrane is high enough to prevent cell walls from rupture, and in low viscosity the chains reorganize and the bubbles grow, which leads to the pressure decrease and the bubble being stable. At the same time, there exists cell-to-cell diffusion for small cell having higher gas pressure,[24] which leads to the structure that the large cells inlay among the small cells. If the crosslink density of EPDM compound continues to increase, the viscosity is high enough to dampen the cell growth, the gas pressure of bubble rise swiftly and exceed the film strength, then gas pressure break the cell walls, and form a higher density end product with an interconnecting cell structure. This is similar to Strecker's explanation about foaming,[6] in which they prepared rubber foam by adjusting the rate of rubber vulcanization and blowing agent decomposition simultaneously. Although the ways are different from each other, both show the initial crosslink density of compound is the very key factor for foaming when blowing agent begins decomposition. Figure 7 shows the relationship between the crosslink density of precured EPDM compound and the foam density, it is clearly shown that the foam density of EPDM compound begins to decrease then to increase with increasing the crosslink density of precured EPDM compound, which further favors the previous explanation about foaming. The results show the optimum precrosslink degree for EPDM compound could improve its foam processibility and enhance the efficiency of blowing agent AC.

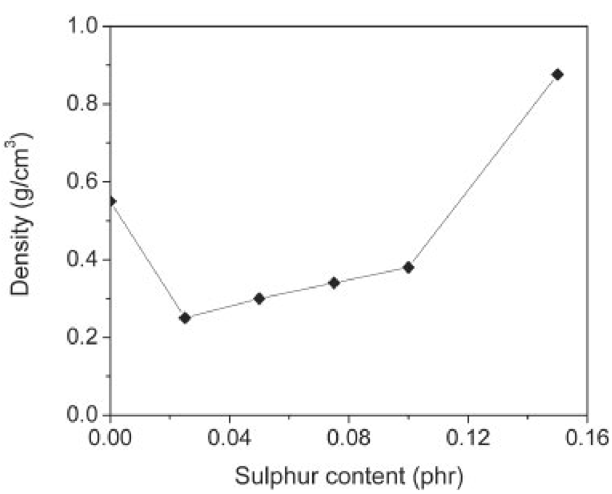

Figure 7 The effect of the crosslink density of precured EPDM on foam density at 190°C.

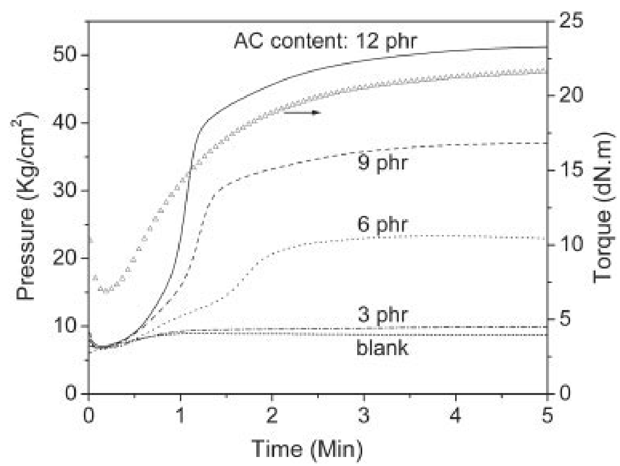

Figure 8 Blowing and vulcanization curves of the optimum precured EPDM (G2) foaming compound with different AC contents at 190°C.

The effect of blowing agent content

The optimum precured EPDM compound G2 was compounded with other ingredients according to the formulations listed in Table III for blowing process. Figure 8 depicts the characteristics of blowing agent decomposition and the vulcanization of rubber at 190°C. It could be seen that there are no obviously pressure increase for the rubber compound with 3 phr AC. This might be owing to the gas that blowing agent AC release could dissolve into the rubber matrix and form a homogeneous phase. When AC content is more than 6 phr, the gas pressure increases obviously with increasing AC content, which might be too much gas that blowing agent AC release to make the matrix be supersaturated.

SEM photomicrographs (Fig. 9) shows the foam articles have a closed-cell structure with few open cells. It is apparent that the rubber compound without blowing agent vulcanized in circular hot air has a few small cells formed, which might be owing to preexisting microvoids on the matrix or volatiles attached to the ingredients volatilize at high temperature. When the blowing agent content is up to 3 phr, there is no

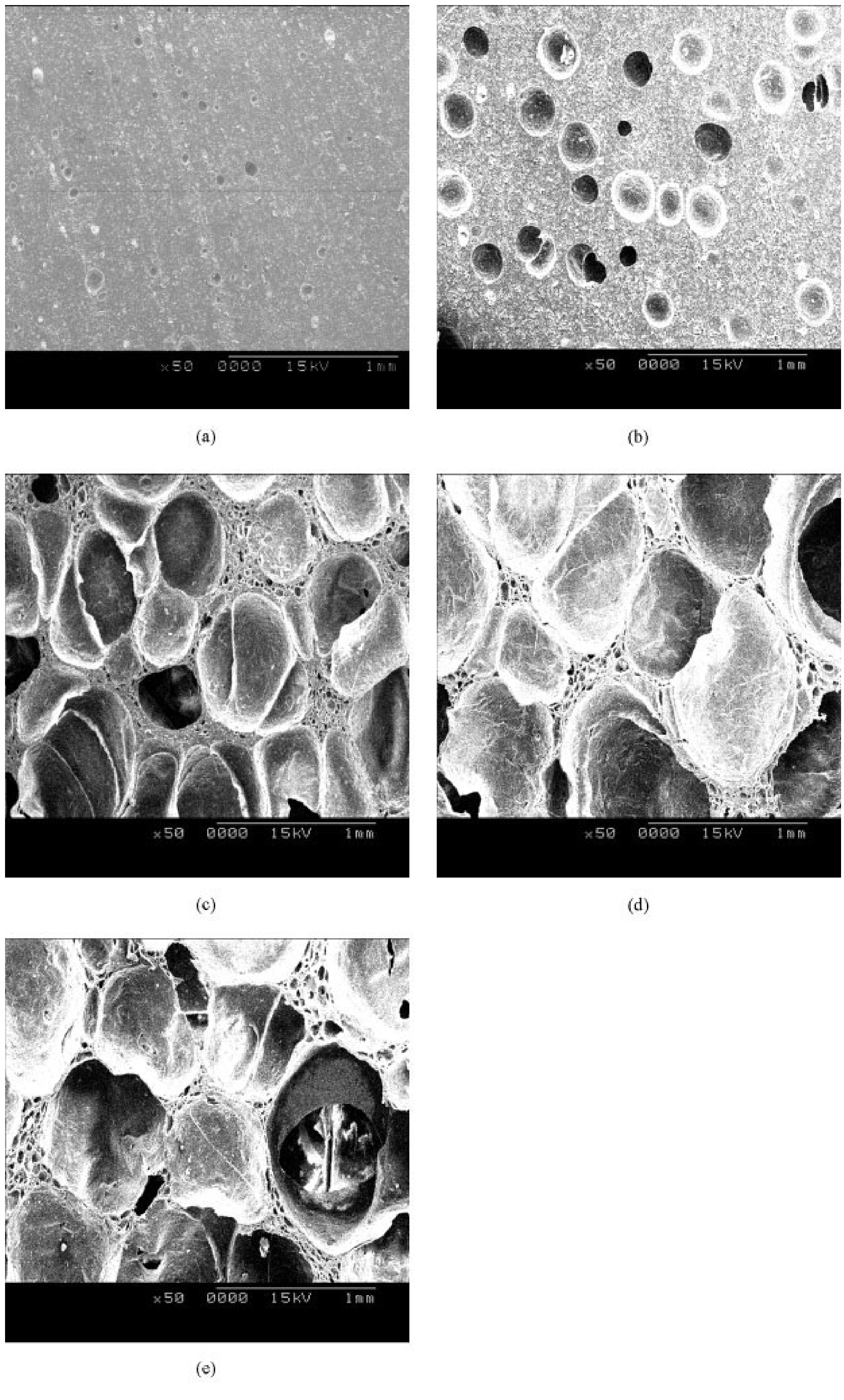

Figure 9 SEM photomicrograph of razor cut surfaces of EPDM foam. (a) blank; (b) 3 phr AC; (c)6 phr AC; (d)9 phr AC; (e)12 phr AC.

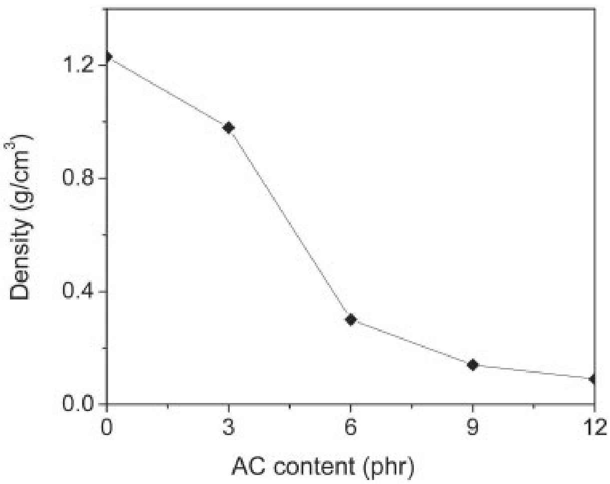

Figure 10 The effect of blowing agent content on foam density at 190°C.

obvious increase for cell number in the matrix vulcanized, but the size of cell increases obviously. This might be explained by that blowing agent releases the gas too little to make the matrix be supersaturated with gas and the nucleation could not be formed. Consequently the released gas dissolves into the matrix and diffuses into the preexisting microvoids, which leads to bubble growth. When the blowing agent content is more than 6 phr, both cell size and cell number increase obviously. However, when the blowing agent content is 12 phr, the SEM photograph shows the foam designed to be a closed-cell structure has a few open cells, which might be explain that when the blowing agent content increases to a certain value, the bubble pressure is high enough to exceed the cell walls strength. Thus the bubble breaks its walls and the gas escapes out of the matrix into the environment, which decreases the amount of gas available for the growth of cells. As a result, continuing to enhance the blowing agent content could not make the density decrease obviously, which be observed in Figure 10. The density of EPDM foam obviously decrease with AC content increase at the beginning, the foam density could reach 0.14 g/cm^3 at 9 phr AC content. If AC content is more than 9 phr, the foam density only has a slight decrease.

CONCLUSIONS

Partially precuring of EPDM compound in the HAAKE rheometer has been demonstrated as an effective technique for controlling the crosslink density of EPDM compound. The rheological properties for precured EPDM compound were studied, the results reveal that G′, G″ and η^* of compounds increase with increasing the crosslink density. With increasing the frequency, G′ and G″ of compounds increase, however η^* of compounds decrease.

Furthermore, the characteristics of vulcanization and foam processibility were investigated for the precured EPDM compounds, the vulcanization rate of EPDM is not affected by partially precure in the HAAKE rheometer. With increasing the crosslink density of precured EPDM compound, the density of foam article has a minimum value, while the size of large cells has a maximum value. The optimum precured EPDM compound could improve the foam processibility and enhance expansion ratios in the same condition, which shows the optimum crosslink density for EPDM could improve the efficiency of blowing agent AC. SEM shows the foam designed to be a closed-cell structure has very few open cells and the large cells inlay the small cells. For optimum precured compound, the density of foam EPDM decreases with increasing the blowing agent, and the density of foam EPDM could attain about 0.09 g/cm^3.

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