Effects of Foaming Variables on Density and Morphology of Expanded Ethylene–Propylene Terpolymers

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Synopsis

An experimental study of the relationships between foaming variables and foamed structures of expanded ethylene–propylene terpolymer (EPDM) is reported. The study was carried out using EPDM compositions containing azobisformamide blowing agent. The compositions were expanded and cured in hot air into a foamed structure consisting of dense skin and foamed core. The results showed that the foam density, skin thickness, average cell size, and number of cells of the expanded rubbers can be controlled closely by the foaming variables such as residence time, foaming temperature, and blowing agent concentration.

INTRODUCTION

High-quality expanded rubbers produced by continuous extrusion have received increased attention during recent years. The process is carried out by extruding and subsequently heating rubber compositions containing chemical blowing agents. The heating operation causes the extrudate to expand and cure into a foamed structure consisting of skin and core, as shown schematically in Figure 1. For future industrial and commercial applications, expanded rubbers with strong, smooth skin and uniform cell structure are required. Close control of the foamed structure depends on a better understanding of the foaming process.

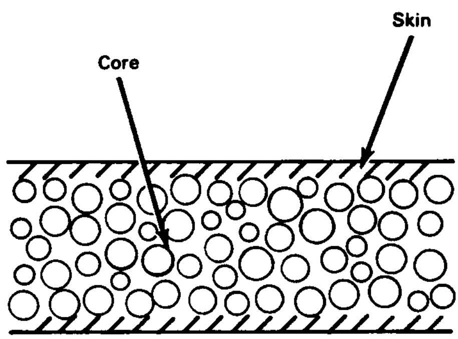

Fig. 1. Schematic representation of the skin and core structure of expanded rubbers.

 CCC 0021-8995/82/041205-11$02.10

In contrast to the thermoplastic foams, only a few articles on the expanding and curing behavior of rubbers have appeared in the literature. Previous studies on elastomer foams, as summarized by Benning[1] and Zimmerman and Bailey,[2] were primarily concerned with developing compounding techniques for various types of elastomers. It was suggested that elastomer foams of open or closed cells can be obtained by selecting proper blowing agents and curatives to achieve the correct balance between gas generation and degree of cure. For closed-cell expanded rubbers, for example, the correct balance requires the blowing agent to decompose after a considerable cure has been developed. However, it is not sufficient to describe the foamed structure only as being open-cell or closed-cell. Other aspects of the elastomer foamed structure such as density and skin and cell morphology are also critical. To date, information on controlling these structural variables is unfortunately very limited.

TABLE I
Compositions Used for Preparing Expanded EPDM

Materials	Parts
Fast-curing EPDM	50
Low-viscosity EPDM	50
FEF Black	25
SRF Black	35
Whiting	50
Mistron vapor talc	30
Paraffinic oil	40
Stearic acid	2
Factice vulcanized oil	5
Azobisformamide blowing agent	3–14
Zinc oxide	5
Sulfur	2
Zinc-*O*,*O*-di-*N*-butylphosphorodithioate, 62%	2.5
N,*N'*-Diphenylthiourea	3.0
Zinc dimethyl dithiocarbamate	3.0
Tellurium diethyl dithiocarbamate, 80%	1.0

In this study, the foaming process of expanded ethylene–propylene terpolymer (EPDM) is examined experimentally by determining the effects of foaming variables on the foamed structure. The foaming variables studied include residence time, foaming temperature, and blowing agent concentration.

TABLE II
Blowing and Curing Characteristics of EPDM Composition Containing 3.2% Blowing Agent

	Occurrence of blowing		Optimum Curing		Torque
Temp., °C	Time, min	Torque, dNm	Time, min	Torque, dNm	ratio[a]
200	1.2	42.9	1.8	55.6	0.77
190	1.9	52.0	3.0	61.4	0.85
180	3.3	58.0	4.7	65.9	0.88
172	7.5	67.8	11.0	72.2	0.94
165	—[b]	—	21.3	75.2	—

[a] Torque at blowing/torque at curing.
[b] No blowing detected.

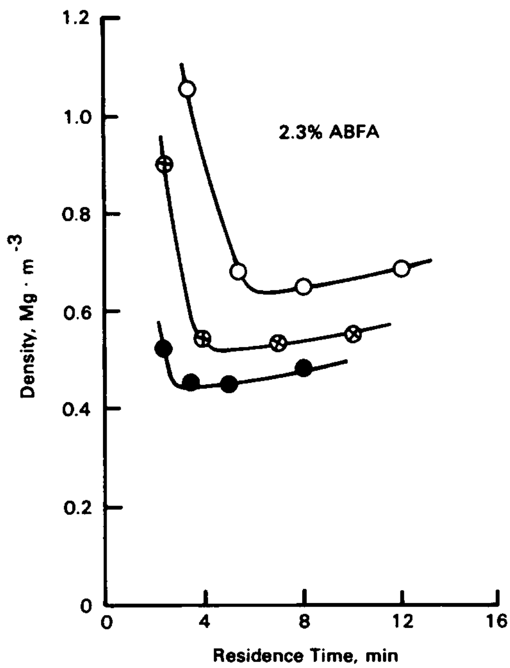

Fig. 2. Effect of residence time on density of expanded EPDM prepared from composition containing 2.3% blowing agent: (O) 193.3°C; (⊕) 204.4°C; (●) 215.6°C.

EXPERIMENTAL

Materials

The expanded EPDM rubbers used in this study were prepared from the compositions described in Table I. The compositions were developed by modifying a formulation given by Filburn and Spenadel.[3] A low-structure furnace black was used to replace the thermal black in the original composition. The compositions are based on a 50/50 blend of a fast-curing and low-viscosity EPDM for providing appropriate cure rate and flow properties. The blowing agent was azobisformamide (ABFA) in the concentration range of 1.0–4.4 wt %.

The expanding and curing characteristics of the EPDM compositions were determined from cure curves, expressed as torque vs. time, using a Monsanto Rheometer. For the rubber composition containing blowing agent, its cure curve shows a distortion when blowing takes place in addition to the regular cure progression. Table II summarizes the results obtained at various temperatures for the EPDM composition containing 3.2% ABFA. It is evident that blowing of this composition always occurs after a considerable cure has been developed, as seen by the ratios of torque at onset of blowing to that at the optimum cure.

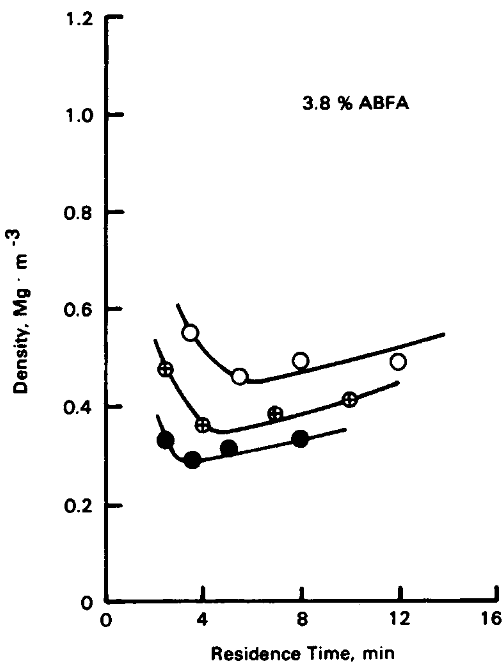

Fig. 3. Effect of residence time on density of expanded EPDM prepared from composition containing 3.8% blowing agent: (O) 193.3°C; (⊕) 204.4°C; (●) 215.6°C.

Procedures

In preparing EPDM compositions, the ingredients given in Table I were mixed in a model B Banbury mixer. The compositions were then molded at 75°C into 2-mm-thick slabs and foamed in a hot air oven at 193.3, 204.4, and 215.6°C for residence times ranging from 2.5 to 12.0 min depending on the temperature. The densities of the expanded EPDM rubbers were determined by measuring the weights of samples of known dimensions. The evaluation of skin and cell morphology of the samples was carried out using a Leitz optical microscope at 45× magnification.

RESULTS AND DISCUSSION

The foaming behavior of EPDM rubbers is shown in Figures 2 and 3, in which the sample density is plotted versus residence time for EPDM compositions containing 2.3 and 3.8% of the blowing agent. For all the foaming temperatures studied, the results show that the compositions expand to a maximum volume at the initial heating stage and then shrink slightly. The effects of foaming temperature and blowing agent concentration on the density of expanded rubbers are shown in Figure 4 for EPDM compositions foamed for 8 min. The density is found to decrease by increasing either of the two or both variables.

The foaming process therefore is characterized by an expansion of the EPDM compositions followed by slight shrinkage. The initial expansion results from thermal decomposition of the blowing agent, while the shrinkage takes place when the decomposition is complete. Using differential scanning calorimetry

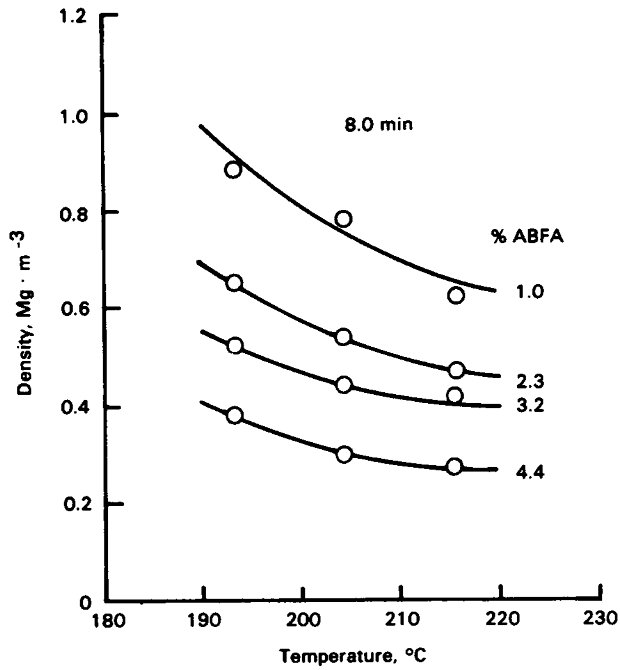

Fig. 4. Effects of foaming temperature and blowing agent concentration on density of expanded EPDM.

(DSC) analysis, the amounts of residual blowing agent in expanded EPDM samples foamed at 193.3°C for 3.5 and 5.5 min are compared in Figure 5 based on the area under the ABFA decomposition peak. It is seen that the decomposition peak at 195°C in the DSC scan for the 3.5-min residence time sample disappears when the EPDM composition is foamed for 5.5 min. This result suggests the completion of decomposition at 5.5 min of residence time, which is close to the end of the expansion stage as shown in Figure 2. The shrinkage phenomenon, which occurs in the system with increased curing but no more blowing, might be explained by a gas diffusion mechanism similar to the one proposed by Rubens[4] for describing collapse of polystyrene foams. It is recognized, though, that the foaming processes are different for the two materials.

A summary of the foaming behavior at maximum expansion of EPDM rubbers is presented in Table III. It is evident that the maximum expansion or the lowest density of expanded EPDM is obtained at a residence time dependent upon the foaming temperature but not the blowing agent concentration. The residence time for maximum expansion is decreased from 6 to 3 min by increasing the foaming temperature from 193.3 to 215.6°C. In addition, the lowest density values decrease when the foaming process is carried out at higher temperature or higher blowing agent concentration.

As described in Figure 1, the structure of expanded EPDM rubbers is a sandwiched construction of dense skin and foamed core which consists of relatively uniform spherical cells. Figure 6 shows representative photomicrographs of the morphology of expanded EPDM samples foamed under various conditions. These morphological data are analyzed in terms of skin thickness, average cell size or diameter, and number of cells per unit volume of rubber.

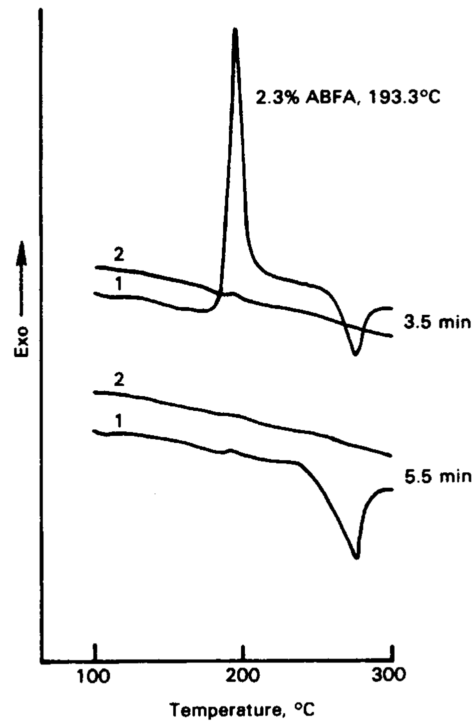

Fig. 5. First (1) and second (2) DSC scans of expanded EPDM prepared with 3.5 and 5.5 min of residence time.

Figure 7 shows typical results of the effects of residence time and blowing agent concentration on the skin thickness of expanded EPDM. Evidently, the skin thickness is affected more strongly by the blowing agent concentration than by the residence time. A significant decrease in the skin thickness of expanded EPDM foamed at 204.4°C is observed when the ABFA concentration is increased from 1.0 to 4.4%.

TABLE III
Foaming Behavior of Expanded EPDM at Maximum Expansion

Blowing agent, wt %	Foaming temp., °C	Density, (Mg/m³)	Residence time for maximum expansion, min
1.0	193.3	0.87	6
	204.4	0.78	5
	215.6	0.60	4
2.3	193.3	0.64	6
	204.4	0.52	5
	215.6	0.45	3
3.2	193.3	0.51	6
	204.4	0.43	5
	215.6	0.38	3
3.8	193.3	0.45	6
	204.4	0.35	5
	215.6	0.29	3
4.4	193.3	0.37	6
	204.4	0.29	5
	215.6	0.24	3

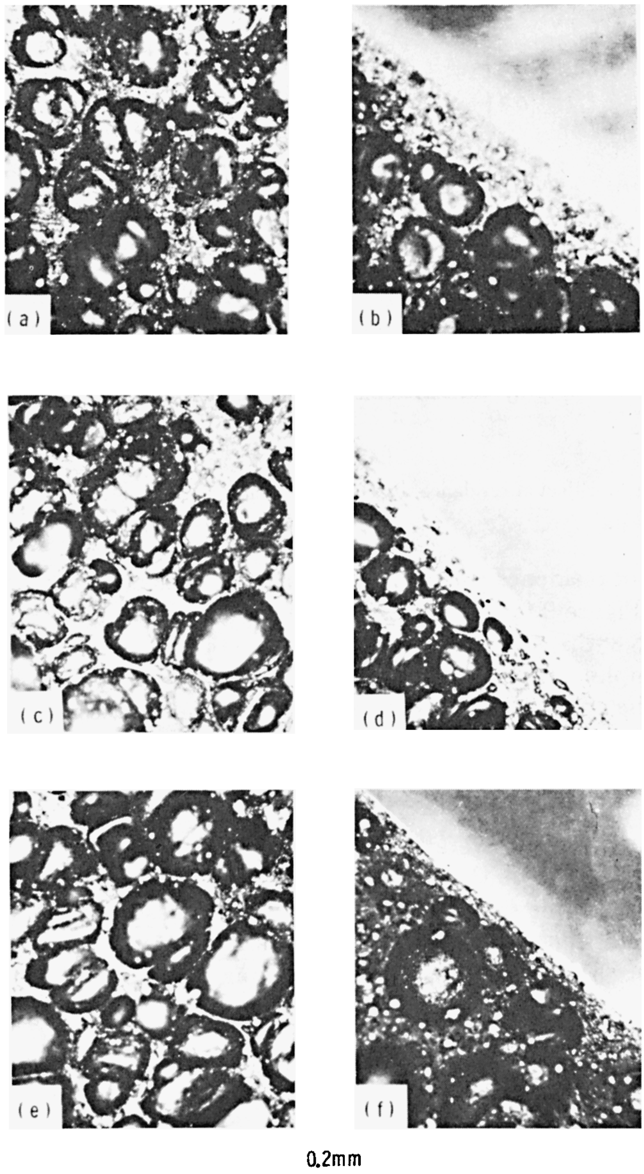

Fig. 6. Photographs showing skin and core morphology of expanded EPDM prepared from compositions containing 3.2% ABFA. Foaming conditions are 193.3°C, 8.0 min for (a) and (b); 204.4°C, 7.0 min for (c) and (d); and 215.6°C, 5.0 min for (e) and (f).

The relationships between skin thickness and blowing agent concentration at various foaming temperatures are shown in Figure 8. It is seen that the rate of decrease of skin thickness with increasing blowing agent concentration is greater at lower foaming temperatures. The results also demonstrate that the skin thickness of expanded EPDM decreases at higher foaming temperature. These findings explain partly the effects of foaming temperature and blowing agent concentration on the sample density as observed in Figure 4.

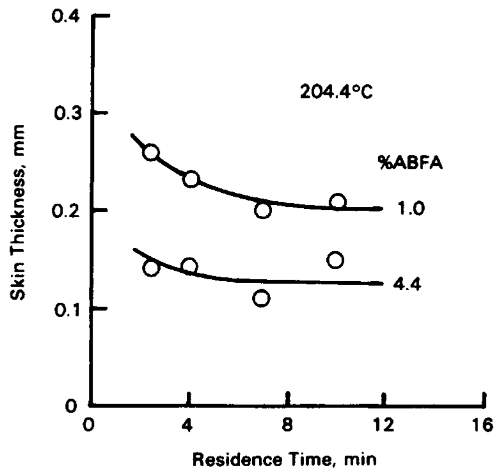

Fig. 7. Effect of residence time on skin thickness of expanded EPDM.

The effect of residence time on the average cell size of expanded rubbers is described in Figure 9 for the EPDM composition containing 2.3% ABFA and foamed at 193.3°C. Also shown in this figure is the calculated core density for respective samples. Based on the schematic structure of expanded EPDM given in Figure 1, the core density ρ_c was calculated by the expression

$$\rho_c = \frac{1}{t_0 - 2t_s} (t_0\rho_0 - 2t_s\rho_s) \tag{1}$$

where ρ_0 is the measured overall density of an expanded rubber with thickness t_0, and ρ_s is the density of the skin with thickness t_s. To simplify the analysis, ρ_s is assumed to be the same as the density of solid elastomer composition.

Since the skin thickness is essentially not affected by residence time in the working range, as shown in Figure 7, the foaming behavior described in Figure

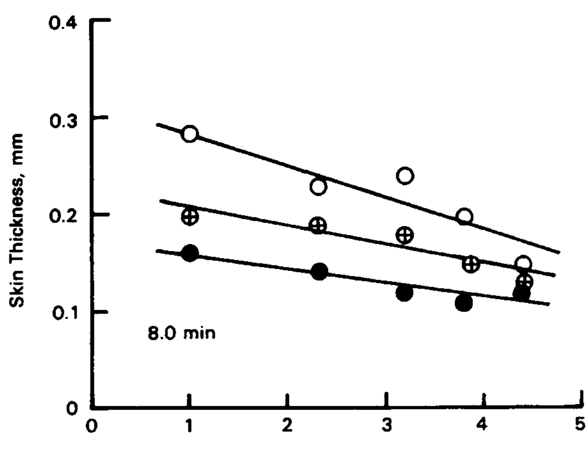

Fig. 8. Effect of blowing agent concentration on skin thickness of expanded EPDM at varying foaming temperatures: (○) 193.3°C; (⊕) 204.4°C; (●) 215.6°C.

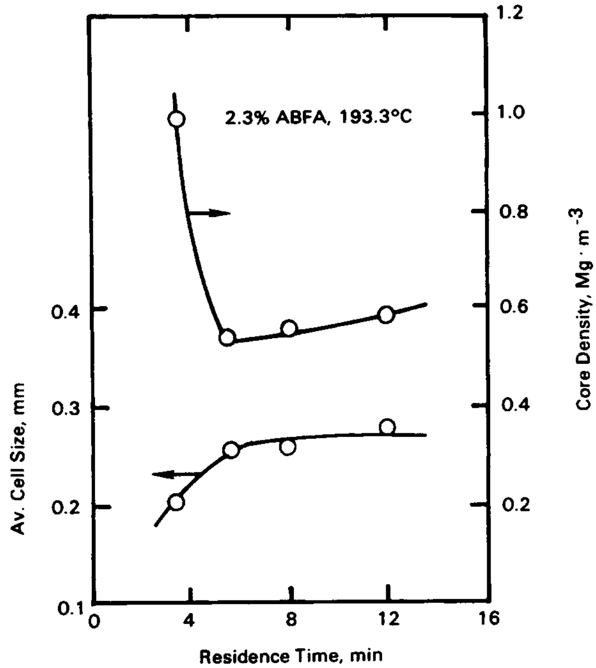

Fig. 9. Effect of residence time on average cell size and core density of expanded EPDM.

9 in terms of calculated core density is, as expected, very similar to the results given in Figures 2 and 3 which show plots of the overall density ρ_0 vs. residence time. Both results indicate that the foaming process of expanded EPDM consists of an expansion and a shrinkage stage. Corresponding to the expansion stage, Figure 9 shows an increase in the average cell size of expanded EPDM samples. The small amount of shrinkage observed from the core density data, however, is not observed from the results of cell size because of the averaging process employed to calculate cell size values.

The effects of the blowing agent concentration and foaming temperature on the average cell size and core density at the maximum expansion are summarized in Figure 10. The data shows an increase in the average cell size and, correspondingly, a decrease in the core density with increasing blowing agent concentration or foaming temperature. The results of average cell size measurements are therefore also consistent with the density change caused by the two foaming variables, i.e., blowing agent concentration and foaming temperature.

Moreover, previous studies[5,6] have shown that the number of cells formed in a foaming process is useful for describing the cell formation mechanism and foam quality. The number of cells of expanded EPDM at the maximum expansion is calculated and shown in Figure 11 based on the data of cell size and core density given in Figure 10. The relation used for the calculation is given by

$$N = \frac{6}{\pi d^3}\left(\frac{\rho_s}{\rho_c} - 1\right) \tag{2}$$

where N is the number of cells per unit volume of rubber and d is the average

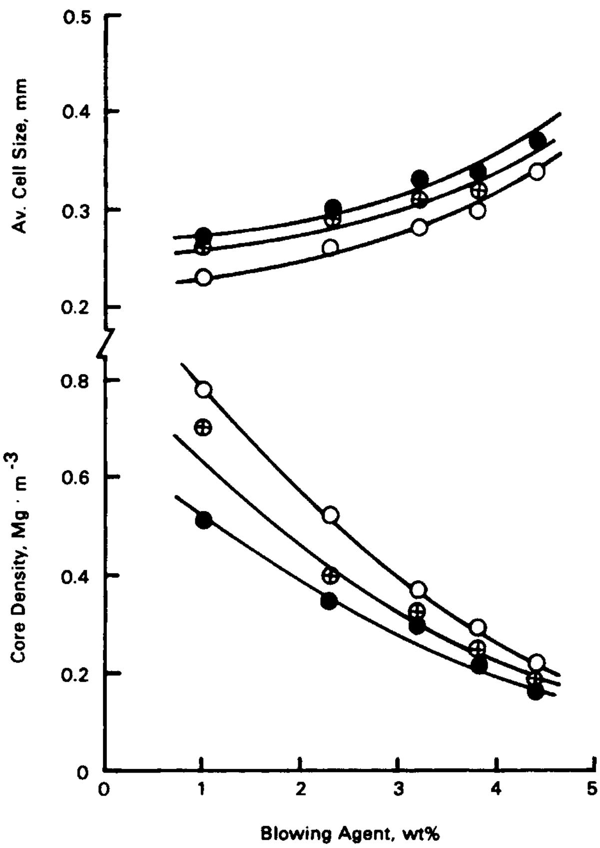

Fig. 10. Effects of blowing agent concentration and foaming temperature on average cell size and core density at maximum expansion in the foaming process: (○) 193.3°C; (⊕) 204.4°C; (●) 215.6°C.

cell diameter. It is seen that N is affected apparently by the blowing agent concentration but not by the foaming temperature. The number of cells is increased from 1.0×10^{11} to 2.3×10^{11} per m^3 rubber by increasing the blowing agent concentration from 1.0 to 4.4% in the EPDM compositions. The results therefore suggest that foaming temperature and blowing agent concentration play different roles in the foaming process of expanded EPDM, although they both affect sample density, skin thickness, and average cell size in a similar manner.

SUMMARY AND CONCLUSION

The foaming process of expanded EPDM has been studied based on relationships between various foaming variables and the foamed structure. The density data show that the process is characterized by an expansion of EPDM compositions followed by slight shrinkage. The density of the expanded rubber is decreased by increasing the foaming temperature and/or blowing agent concentration. The skin thickness decreases with increased foaming temperature or blowing agent concentration and depends only weakly upon the residence time.

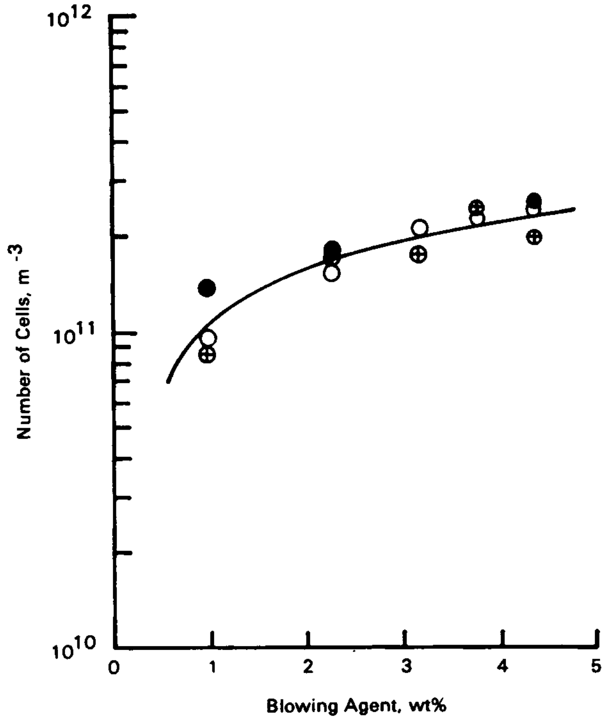

Fig. 11. Effect of blowing agent concentration on number of cells of EPDM at maximum expansion: (O) 193.3°C; (⊕) 204.4°C; (●) 215.6°C.

On the other hand, the average cell size of the foamed core increases with increasing foaming temperature and blowing agent concentration. The number of cells in a unit volume of rubber, however, primarily is not affected by the foaming temperature. It increases only with increasing blowing agent concentration. The results, therefore, indicate that the density and skin and core morphology of expanded EPDM can be controlled closely by residence time, foaming temperature, and blowing agent concentration.

The author wishes to acknowledge the technical assistance of Mr. G. Rorie in the experimental work. Thanks are also due to Drs. I. A. Abu-Isa and M. C. H. Lee for helpful discussions.

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Received July 15, 1981
Accepted August 17, 1981