Structure and Properties of Closed-Cell Foam Prepared from Irradiation Crosslinked Silicone Rubber

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Received 9 January 2008; accepted 25 February 2009
DOI 10.1002/app.30341
Published online 8 May 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Silicone rubber foam was prepared through crosslinking with electron beam irradiation and foaming by the decomposing of blowing agent azobisformamide (AC) in hot air. The crosslinking and foaming of silicone rubber was carried out separately, which was different from the conventional method of chemical crosslinking and foaming. After foaming, the silicone rubber foam was irradiated again to stabilize the foam structure and further improve its mechanical properties. The effects of irradiation dose before and after foaming, and the amount of blowing agents on the structure and properties of silicone rubber foam were studied. The experimental results show that with the increase of AC content, the average cell diameter of silicone rubber foam increases a little, the foam density decreases to a minimum value when AC content is 10 phr. With the increase of irradiation dose before foaming from 10 to 17.5 kGy, the cell nucleation density of silicone rubber foam increases, the average cell diameter decreases, and the foam density increases. With the increase of irradiation before foaming, the tensile strength, tensile modulus, and the elongation at break of the silicone rubber foam increase. Through irradiation crosslinking again after foaming, the foam density is decreased and the mechanical properties of silicone foam are further improved. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3590–3595, 2009

Key words: silicone rubber; foam; electron beam; irradiation crosslinking

INTRODUCTION

Silicone rubbers are compounds based on polydiorganosiloxanes with high molecular weight. Its basic building block is the silicon—oxygen (Si—O) bond and organic groups attached directly to the silicon atom via silicon—carbon (Si—C) bonds.[1] Because of the unique structure, silicone rubbers exhibit a wish list of characteristics including superb chemical resistance, high- and low-temperature performance, good thermal and electrical resistance, excellent ultraviolet and ozone resistance, etc. Silicone rubber foam combines the virtues of silicone rubber and foam material and has been widely used in many areas such as high performance gasketing, thermal shielding, vibration mounts, and press pads.

Rubbers are usually foamed through expansion process, which relies on the expansion of gaseous phase dispersed throughout the rubber melt. In closed-cell foam, the gas is dispersed as discrete gas bubbles and the polymer matrix forms a continuous phase.[2,3]

During the foaming process, silicone rubbers are usually crosslinked by conventional chemical methods and expanded through the decomposition of chemical blowing agent.[4–9] The crosslinking and foaming progress simultaneously in this process. The crosslinking rate of the rubber melt should be synchronous with the decomposing rate of the blowing agent. The matching of these two processes is crucial to obtain rubber foams with excellent properties.

Electron beam or gamma ray irradiation-induced crosslinking is proposed as successful alternative to conventional, chemical methods of crosslinking of elastomers. Compared with conventional chemical crosslinking, irradiation crosslinking of rubbers or elastomers has many advantages such as low operation cost, absence of various noxious chemical additives, high speed of crosslinking process, effective penetration of electron beam or gamma ray inside the sample, and uniformity of crosslinking.[10,11] Owing to these advantages, irradiation vulcanization has recently received a great deal of attentions.[3,10–14]

Silicone rubber could be crosslinked effectively by electron beam irradiation or gamma ray irradiation.[15–18] In this work, we aim to produce silicone rubber foam through vulcanizing with electron beam irradiation. The vulcanizing and foaming process were operated separately, which is different from the conventional method of chemical crosslinking.[19–22] The effects of irradiation dose, the amount of blowing agents on the structure, and properties of silicone rubber foam were studied to control and optimize the physical and mechanical properties of the foam.

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EXPERIMENTAL

Materials

The methyl vinyl silicone rubber (MVQ) used in this study was 110-2vt having 0.15 mol % vinyl group, its viscosity average molecular weight was 560,000, was supplied by Chenguang Institute of Chemical Engineering of China. The hydroxyl silicone oil containing 8% hydroxyl group used as constitution controller was also obtained from Chenguang Institute of Chemical Engineering. Its viscosity was 50 Pa S. Fumed silica (Cabot EH-5) of Cabot Corporation (USA) was used as fillers of silicone rubber. Its specific surface area was 380 m^2/g and specific gravity is 2.2 g/cm^3. Azobisformamide (AC) was used as foaming agent, which was produced by Tianyuan Company of Yinbin of China. Zinc oxide (ZnO), supplied by Chengdu Kelong Factory of Chemical Engineering Reagent of China, was used to accelerate the decomposition of AC.

Preparation of silicone rubber and foam

The MVQ, fumed silica, hydroxyl silicone oil were mixed by a twin roller mixing mills at ambient temperature (about 25°C) for a period of 10 min. After bin aging, the reinforced rubber was formulated with the addition of AC and ZnO and mixed again for 10 min, and then compression molded to a sheet of 2 mm thickness. Afterward, the sheet was crosslinked through electron beam irradiation. The irradiation was performed in air at ambient temperature (about 25°C) by a JJ-2 static electron accelerator at a voltage of 1.5 MeV. The conveyer on which the sheet was placed was reciprocated at a speed of 2.38 cm/min. After crosslinked by electron beam irradiation, the sheet was expanded by hot air at 200°C for 5 min to prepare silicone rubber foam. The foamed sheet was crosslinked again through electron beam irradiation with a dose of 30 kGy.

Measurements and characterization

Crosslink density

The crosslink density of the vulcanized silicone rubber was determined by the equilibrium swelling technique. The samples were swelled in toluene so that the equilibrium swelling volume reached. The crosslink density of samples was determined by using Flory–Rehner equation [eq. (1)] as follows[23]:

$$\nu = \frac{-[\ln(1-v_2) + v_2 + \chi v_2^2]}{\rho_r V_1 (v_0^{2/3} v_2^{1/3} - v_2/2)} \tag{1}$$

Where ν is the moles of crosslinks per unit mass (mol/g), v_2 is the volume fraction of rubber in the swollen sample, v_0 is the volume fraction of rubber in the unswollen sample, V_1 is the molar volume of the toluene, which is 106.3 cm^3/mol, ρ_r is the raw rubber density, χ is interaction parameter between rubber and toluene, which is 0.45.

Foam density

The apparent density of foam was measured according to ISO 845-1988. The dimensions of the samples were measured with a micrometer, and the weights were measured with a balance. The foam density is expressed as the weight of the sample over its volume (g/cm^3).

Cell structure observation and cell size distribution

The cell structure of silicone rubber foam was observed with scanning electron microscope (SEM, GSM-5900L, electronic Corp., Japan). The cell size and its distribution were statistically analyzed by the image analysis system attached to the SEM instrument.

Cell nucleation density (N_0), cell density (N_f), and average cell diameter

N_0 is defined as the number of cells nucleated per cubic centimeter of unfoamed polymer and is given by[24,25]:

$$N_0 = N_f/(1 - V_f) \tag{2}$$

Where N_f is the cell density (the number of bubbles per cubic centimeter of the foam), and V_f is volume fraction of voids in foam.

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

Where n is the number of bubbles in the SEM micrograph of the foam sample, A is the area of the micrograph, cm^2, and M is the magnification factor of the micrograph.

Let D be the average cell diameter as determined from the SEM micrograph. Then

$$V_f = (\pi/6)D^3 \cdot N_f \tag{4}$$

or

$$D = \sqrt[3]{\frac{Vf}{Nf(\pi/6)}} \tag{5}$$

The average cell diameter could be calculated with this formula.[24]

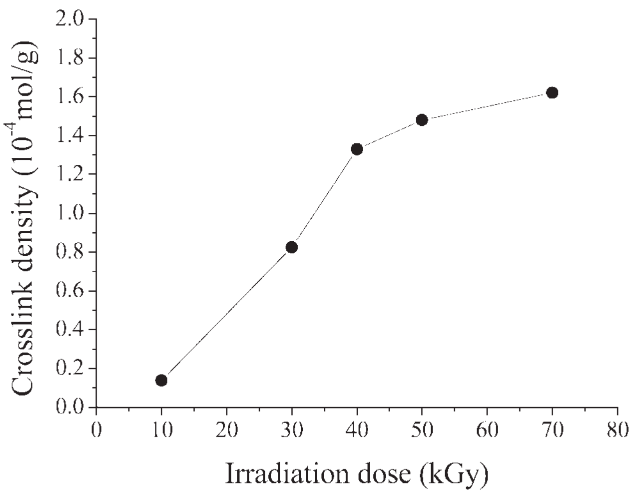

Figure 1 Crosslink density of silicone rubber (MVQ/fumed silica/hydroxyl silicone oil = 100/35/6) vs. irradiation dose.

Mechanical properties

Tensile strength, tensile modulus, and elongation at break of silicone rubbers and foams were measured on a tensile tester (Instron 4320, Instron Corp., USA) at a crosshead speed of 500 mm/min according to ISO 37-1994. The compression set of the foam specimens was measured according to ASTM D1056 procedures on a self-made instrument. The specimen of 12.5 mm thickness was piled up by 4–5 single sample of ϕ 28 mm × 3 mm. For each data of mechanical properties, five specimens were measured.

RESULTS AND DISCUSSION

Crosslinking of silicone rubber through electron beam irradiation

Different methods could be used for crosslinking a silicone elastomer. Compared with chemical curing,

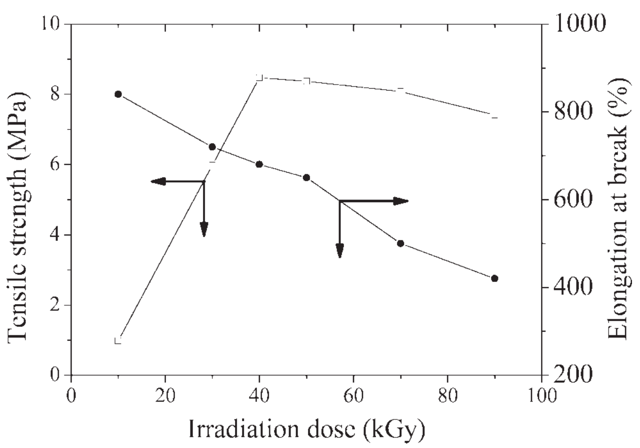

Figure 2 Tensile strength and elongation at break of silicone rubber (MVQ/fumed silica/hydroxyl silicone oil = 100/35/6) vs. irradiation dose.

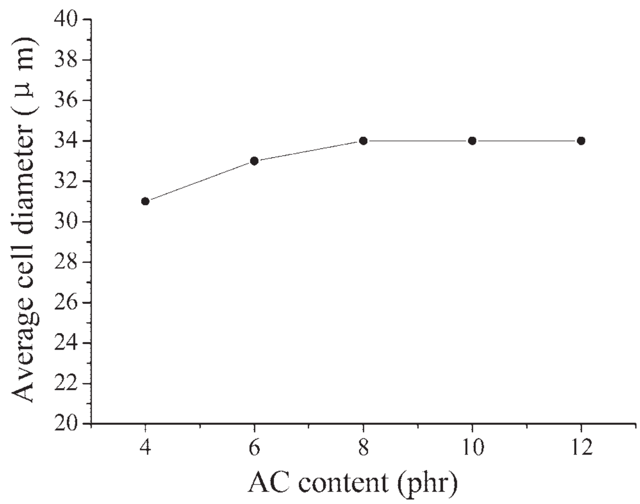

Figure 3 Average cell diameter of silicone rubber foam vs. AC content (MVQ/fumed silica/hydroxyl silicone oil = 100/30/6, irradiation dose before foaming = 10 kGy).

electron beam crosslinking of rubbers has a number of technical advantages. As shown in Figure 1, silicone rubber is crosslinked effectively by electron beam irradiation without any chemical agent. At low-irradiation dose, the crosslink density of silicone rubber increases very obviously. When the irradiation dose is higher than 40 kGy, the increase of crosslink density of silicone rubber slows down.

The variation of tensile strength of silicone rubber with irradiation dose is shown in Figure 2. With the increase of irradiation dose, the tensile strength of silicone rubber reaches a maximum value when irradiation dose is 40 kGy. This is because that with the increase of irradiation dose, the crosslink density of silicone rubber is increased rapidly. When the irradiation dose exceeding 40 kGy, the crosslinked

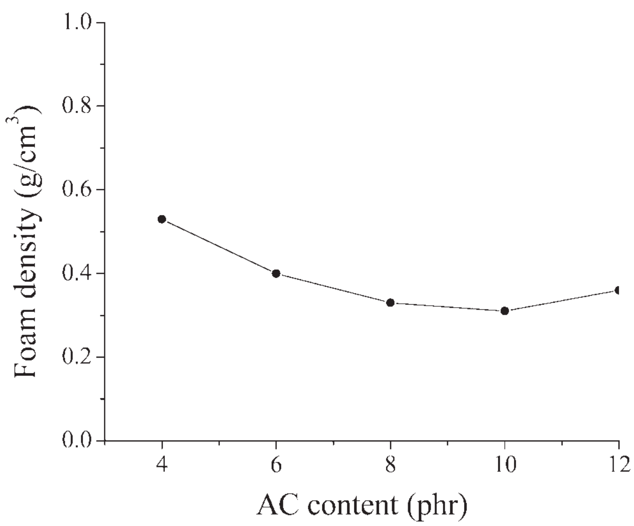

Figure 4 Density of silicone rubber foam vs. AC content (MVQ/fumed silica/hydroxyl silicone oil = 100/30/6, irradiation dose before foaming = 10 kGy).

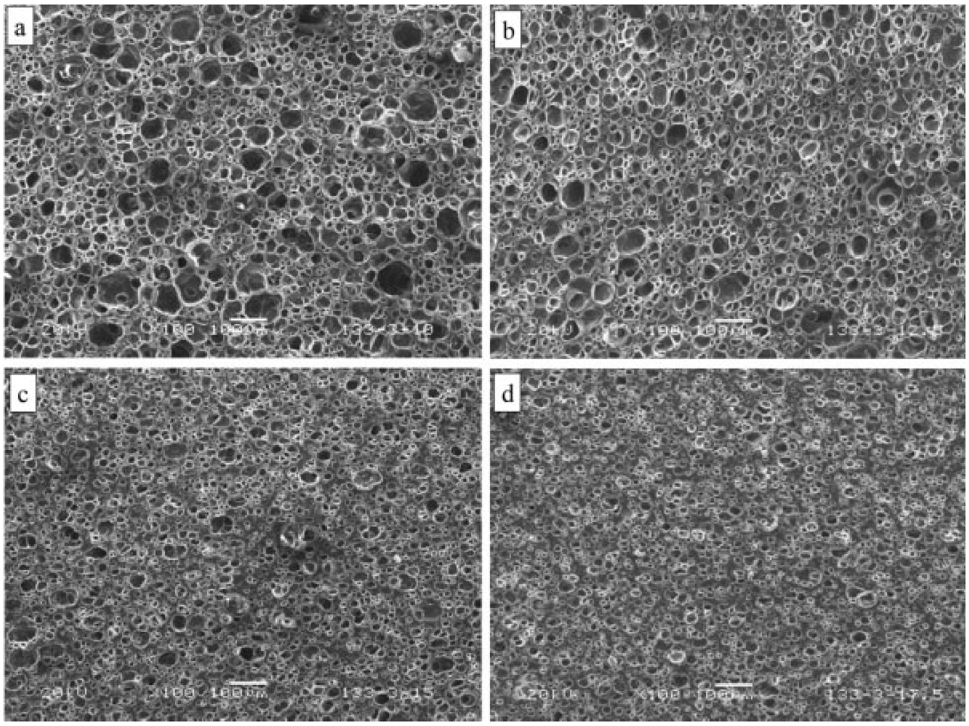

Figure 5 SEM photographs of silicone rubber foam irradiation crosslinked at different dose before foaming (×100): (a) 10 kGy, (b) 12.5 kGy, (c) 15 kGy, and (d) 17.5 kGy (MVQ/fumed silica/hydroxyl silicone oil/AC = 100/25/4.3/10).

network of the rubber becomes excessively tighter and flexibility of the rubber is diminished, leading to less ductile behavior and thus lower tensile strength.[10] With the increase of irradiation dose, the elongation at break of silicone rubber decreases steadily (Fig. 2), also indicating that the network

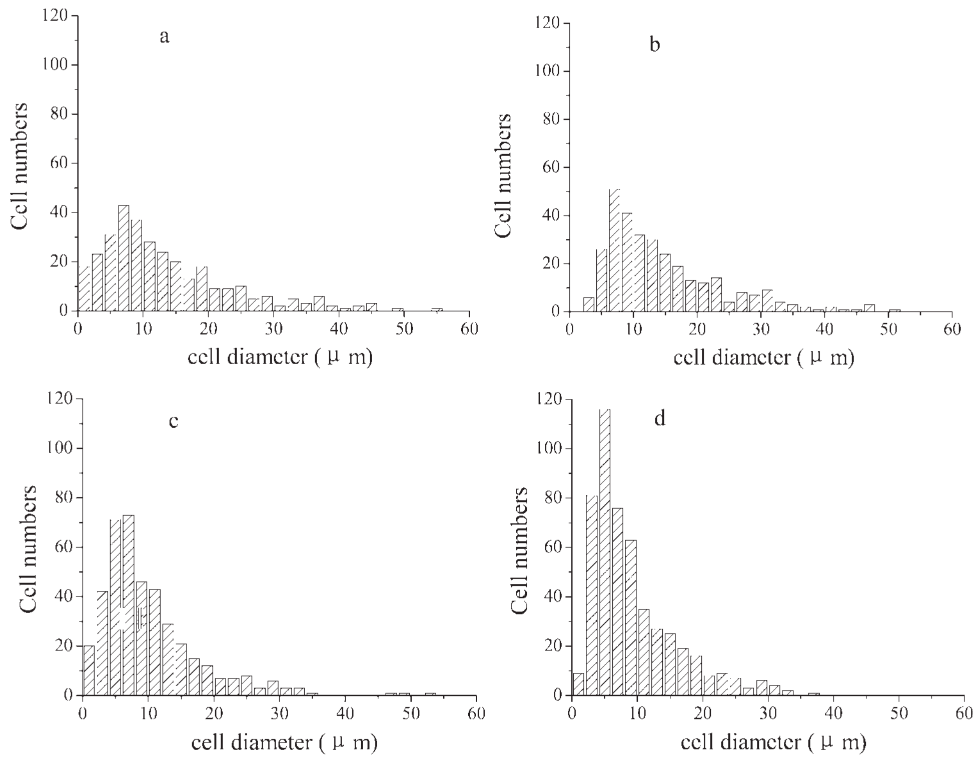

Figure 6 Statistical cell size distribution of silicone rubber foam irradiation crosslinked at different dose before foaming: (a) 10 kGy, (b) 12.5 kGy, (c) 15 kGy, and (d) 17.5 kGy (MVQ/fumed silica/hydroxyl silicone oil/AC = 100/25/4.3/10).

TABLE I
Effect of Irradiation Dose Before Foaming on N_0, N_f, Average Cell Diameter and Foam Density

Irradiation dose before foaming (kGy)	N_0 (cells/cm^3)	N_f (cells/cm^3)	Average cell diameter (μm)	Foam density (g/cm^3)
10.0	1.68×10^8	4.86×10^7	30	0.33
12.5	1.71×10^8	7.88×10^7	25	0.45
15.0	1.76×10^8	9.56×10^7	21	0.59
17.5	2.23×10^8	1.29×10^8	18	0.60

MVQ/fumed silica/hydroxyl silicone oil/AC = 100/25/4.3/10, irradiation dose after foaming = 30 kGy.

structure of the crosslinked rubbers becomes tighter and less flexible, the molecular movements are thus restricted.

Effect of foaming agent content on the structure of silicone rubber foam

AC is one of the most commonly used chemical blowing agent for applications of plastic and rubber foam because of its low toxicity and high efficiency. Its decomposition temperature is beyond 200°C. The addition of metal salts (activators) could reduce its decomposition temperature. In actual application, certain amounts of ZnO are often used to decrease the decomposition temperature of AC and accelerate its decomposition.

With the increase of AC amount, the average cell diameter of silicone rubber foam increases little. Although the AC amount is beyond 8 phr, the cell diameter remains unchanged (Fig. 3). The cell size of foam is affected by the melt viscosity of the rubber matrix. A higher melt viscosity generally implies a higher resistance to bubbles expanding and a smaller cell size. The increase of AC amount has a little effect on the melt viscosity of silicone rubber, and the bubbles expand in the same environment, so the cell size changes little.

With the increase of AC content, the foam density decreases till the AC amount is 10 phr, then it increases (Fig. 4). This is because that the amount of gas available for foaming is directly related to the amount of the blowing agent. With the increase of AC amount, the gas yield increases, and the number of the bubbles increases, so the foam density decreases. When AC is beyond 10 phr, the surplus amount of gas from the decomposing of AC make some bubbles break down, so the foam density increases little.

TABLE II
Effect of Irradiation Dose Before Foaming on Mechanical Properties of Silicone Rubber Foam

Irradiation dose before foaming (kGy)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
10.0	1.20	0.72	255
12.5	1.40	0.88	280
15.0	2.04	1.21	295
17.5	2.22	1.29	300

MVQ/fumed silica/hydroxyl silicone oil/AC = 100/25/4.3/10; irradiation dose after foaming = 30 kGy.

The effect of irradiation dose before foaming on the structure and properties of silicone rubber foam

From a modeling point of view, the foaming process can be divided into three stages: bubble initiation (nucleation), bubble growth, and stabilization. For preparing uniform and low-density foams, it is essential to control bubble nucleation and growth. During foaming process, the gas from the decomposition of blowing agent gets together at the particle surface of blowing agent. When sufficient gas clustering in a given area, a microvoid is created and eventually becomes part of a bubble. The diffusion of the gas into the bubble makes it grow rapidly. Once a bubble grows to a critical size, it continues to grow as gas rapidly diffuses into it and then continues growing until the bubble stabilizes or breaks down.[26]

The cell structure of silicone rubber foam was observed with SEM and the cell size and its distribution were statistically analyzed (Fig. 5 and Fig. 6). The average cell diameter was also calculated and listed in Table I. These results indicate that while irradiation dose before foaming increases from 10 to 17.5 kGy, the cell size of silicone rubber foam decreases and its distribution becomes narrower.

With the irradiation dose before foaming increasing from 10 to 17.5 kGy, the cell nucleation density

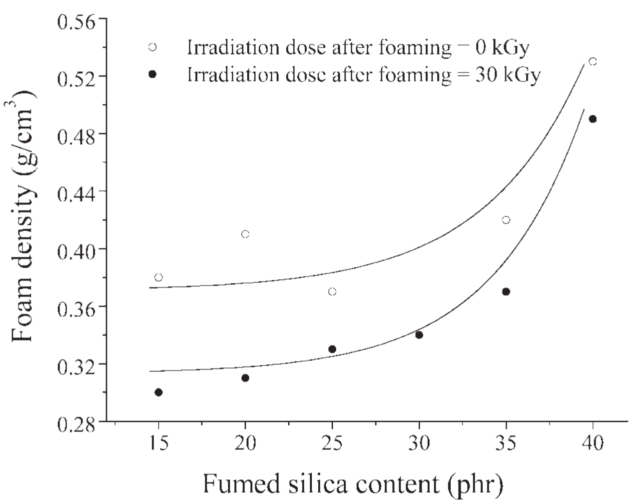

Figure 7 Density of silicone rubber foam vs. fumed silica content (MVQ/fumed silica/AC = 100/fumed silica/10, fumed silica/hydroxyl silicone oil = 25/4.3, irradiation dose before foaming = 10 kGy).

TABLE III
Effect of Irradiation After Foaming on the Mechanical Properties of Silicone Rubber Foam

Irradiation dose after foaming (kGy)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Compression set (%)
0	1.20	0.74	300	51
30	1.40	0.88	280	4

MVQ/fumed silica/hydroxyl silicon oil/AC =100/25/4.3/10, irradiation dose before foaming = 12.5 kGy.

(N_0) and cell density (N_f) increase (Table I). This is because that with the increase of irradiation dose, the crosslink density of silicone rubber increases. Compared with inflating an existing bubble by diffusion and mass transfer, creating a new one by nucleation requires less energy and is easier,[24] so the nucleation density increases. Although the nucleation density increases, the bubble growth is suppressed and the expanding ratio decreased, which make the cell size and foam density decrease and foam density increase (Table I).

With the increase of irradiation dose, the tensile strength of silicone rubber increase, and the elongation at break would decrease (Fig. 2). On the other hand, the expanding ratio of silicone rubber foam decreases with the increase of irradiation dose, which brings up increase of both the tensile strength and the elongation at break. For the silicone foam, the mechanical properties are determined by the mechanical properties of both the silicone rubber matrix and the foam. So the tensile strength, tensile modulus, and the elongation at break of silicone rubber foam increase, whereas the irradiation dose before foaming increases from 10 to 17.5 kGy (Table II).

The effect of irradiation after foaming on the properties of silicone rubber foam

For preparing silicone rubber foam in this research, the total irradiation dose was delivered in two stages. The irradiation before foaming is to provide suitable crosslinking for foaming process and the irradiation after foaming is to stabilize the foam structure and further improve the mechanical properties of silicone foam. Through irradiation crosslinking again after foaming, the foam density of silicone rubber foam decreases (Fig. 7). The tensile strength and tensile modulus increase, and the elongation at break and compression set decrease (Table III).

CONCLUSIONS

The MVQ is crosslinked effectively by electron beam irradiation. With the increase of irradiation dose, the crosslink density of silicone rubber increases, the tensile strength reaches a maximum value when the irradiation dose is 40 kGy. The elongation at break of silicone rubber decreases with the increase of irradiation dose. After irradiation crosslinking, the closed-cell foam is prepared through the decomposition of blowing agent AC. With the increase of AC content, the average cell diameter increases a little, the foam density decreases to a minimum value when AC content is 10 phr. With the irradiation dose before foaming increasing from 10 to 17.5 kGy, the cell nucleation density of silicone rubber foam increases, average cell diameter decreases, and the foam density increases. With the increase of irradiation before foaming, the tensile strength, tensile modulus, and the elongation at break of the silicone rubber foam increase. Through irradiation crosslinking again after foaming, the foam density is decreased and the mechanical properties of silicone foam are further improved.

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