

Mechanical Properties and Antibacterial Activity of Peroxide-Cured Silicone Rubber Foams

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ABSTRACT: Silicone rubber (SR) foams were prepared by the peroxide curing of a silicone compound with 2,4-dichlorobenzoyl peroxide (DCBP), di-*t*-butyl peroxide (DTBP), or 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane (DBPH) in the presence of 2,2'-azobisisobutyronitrile (AIBN) as a blowing agent. The cells were formed in the foam as a result of nitrogen produced by the decomposition of AIBN during the foaming process. The cell size, hardness, and tensile properties of the SR foams were examined as a function of the peroxide concentration. When the peroxide concentration increased, the hardness and tensile strength of the SR foams increased, whereas the cell size and elongation at break decreased. The anti-

bacterial activity of the prepared foams was also evaluated via their effects on *Staphylococcus aureus* and *Escherichia coli*. The peroxide-cured SR foams had antibacterial activity because a toxic residue was generated by the peroxide decomposition. The foam prepared by the AIBN/DCBP system showed more antibacterial activity than the AIBN/DBPH and AIBN/DTBP ones. However, after postcuring at 250°C for 2 h, the antibacterial activity of the SR foams significantly decreased. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1723–1729, 2008

Key words: blowing agents; compounding; crosslinking; silicones

INTRODUCTION

Silicone rubbers (SRs) are synthetic polymers with a giant backbone of alternating silicon and oxygen atoms.¹ The silicon–oxygen backbones and organic side groups of SR give the elastomer its unique performance properties, including biocompatibility,² superior temperature and chemical resistance,³ and good electrical insulation properties.^{4,5} Its characteristics are such that it provides the perfect balance of mechanical and chemical properties required by many of today's most demanding applications.⁶ They are used as protection between finished parts direct from the cure oven, sound deafening in automotive floorboards, gaskets, large reusable masks, die cuts for masking, large irregularly shaped holes, and various foams.

SR foams have the combined properties of a light weight, resilience, high temperature stability, and low compression set. They are usually made with an excess of a blowing agent and peroxide crosslinking agents. Blowing agents are divided into physical blowing agents and chemical blowing agents. Physical blowing agents undergo only physical changes. The most common are low-boiling organic liquids,

such as hydrocarbons and halogenated hydrocarbons, which develop cells within the plastic material by changing from liquids to gases during foaming under heating conditions. Chemical blowing agents are materials that are stable at normal storage temperatures and under specific processing conditions but undergo decomposition with controllable gas evolution under reaction conditions. The blowing agents of this class are organic nitrogen compounds, such as azodicarbonamide and 2,2'-azobisisobutyronitrile (AIBN). They produce mainly nitrogen gas, along with smaller proportions of other gases.

In this study, various SR foams were prepared by the peroxide curing of a silicone compound in the presence of an AIBN blowing agent. The physical and mechanical properties and thermal properties of the prepared foams were investigated. Traditional curing agents for SR compounds are organic peroxides, which, when heated, decompose to form free radicals that react with the pendant organic groups on the SR.^{7,8} However, the peroxide curing reaction leaves a toxic acid residue in the rubber that can deposit a powder or bloom on the part surface that gives rise to a poison. The toxicity of the prepared foams was also tested against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) cells with the shake flask method and was compared with that of postcured foams.

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TABLE I
Physical and Mechanical Properties of the Peroxide-Cured SR Foams

Sample	Compound composition (phr) ^b				Specific gravity (25°C)	Foaming ratio (%)	Cell size (μm)	Hardness (Shore A)	Tensile properties	
	AIBN	DBPH	DCBP	DTBP					Tensile strength (N/mm ²)	Elongation at break (%)
SR ^a	—	—	—	—	1.345	—	—	60	6.37 \pm 0.55	282 \pm 30
SRF1	9.0	1.0	—	—	0.380	360	315	3.0	0.86 \pm 0.02	261 \pm 29
SRF2	9.0	2.0	—	—	0.406	340	272	3.7	0.88 \pm 0.01	257 \pm 28
SRF3	9.0	4.0	—	—	0.444	300	251	4.0	0.92 \pm 0.01	214 \pm 60
SRF4	9.0	—	1.0	—	0.265	280	257	1.2	0.29 \pm 0.01	358 \pm 51
SRF5	9.0	—	2.0	—	0.326	240	242	4.2	0.43 \pm 0.01	225 \pm 24
SRF6	9.0	—	4.0	—	0.419	220	232	6.5	0.69 \pm 0.02	160 \pm 28
SRF7	9.0	—	—	1.0	0.370	320	510	2.0	0.20 \pm 0.01	304 \pm 26
SRF8	9.0	—	—	2.0	0.381	300	469	4.5	0.46 \pm 0.05	199 \pm 10
SRF9	9.0	—	—	4.0	0.397	290	465	7.0	1.00 \pm 0.09	140 \pm 33

^a The composition of SR was 99 g of GP60 and 1 g of DCP.

^b 100 g of SR [GP60 (99 g) and DCP (1 g)]/g of AIBN and peroxide.

EXPERIMENTAL

Materials

SR (GP60, Hae Ryong Silicone Co., Ltd., Kyonggido, Korea), di-*t*-butyl peroxide [DTBP (50% paste in silicone oil); Hae Ryong Silicone Co.], AIBN (40% paste in silicone oil, Hae Ryong Silicone Co.), dicumyl peroxide [DCP; Perkadox BC-40S-ps (40% paste in silicone oil), Akzo Nobel Polymer Chemicals BV, Rotterdam, The Netherlands], and 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane [DBPH; Trigonox 101-45S-ps (45% paste in silicone oil), Akzo Nobel Polymer Chemicals BV] were used as received. 2,4-Dichlorobenzoyl peroxide [DCBP; DCLBP-50-PSI (50% paste in silicone oil)] was purchased from Akrochem Co. (Akron, OH). Other chemicals were used as received without further purification.

Instrumentation

The thermal stability of the SR foams was determined by thermogravimetry (TG; TGA Q50, TA Instruments, New Castle, DE). The TG curves were obtained under an N₂ atmosphere at a flow rate of 4 mL/min and with scanning from 20 to 800°C with a heating rate of 20°C/min.

The hardness of the specimens was measured with a Shore A hardness tester (GS-706, Teclock Co., Nagano, Japan), and the readings were averaged. Five locations were measured for each specimen and surface.

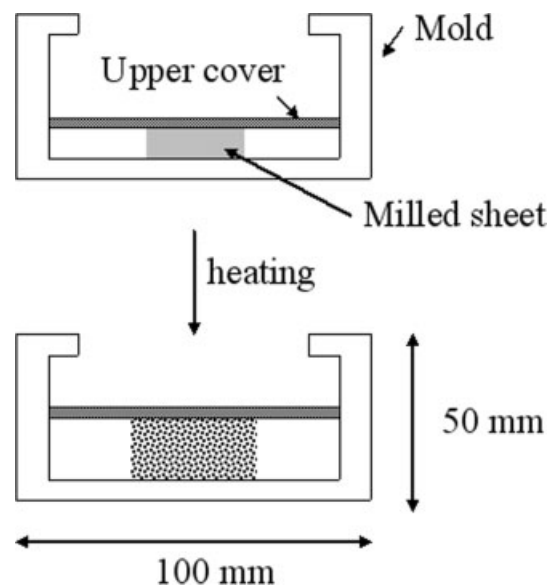
The Fourier transform infrared (FTIR) absorption spectra of the sample films were measured with a PerkinElmer infrared spectrometer (Spectrum 2000, Shelton, CT) over the range 350–4000 cm⁻¹.

The cell size of the SR foams was measured a video microscope (Inf-500TM charge-coupled device (CCD) video microscope, Moritex Corp., Tokyo) with a PC that contained video capture software (i-Solution Lite,

Image & Microscope Technology, Daejeon, Korea). Most images of individual particles were captured at either 200 or 400 \times . After a simple calibration, I acquired both the area and the dimensions of an individual particle by simply clicking on the particle. Ten locations of five specimens were measured, and the readings were averaged.

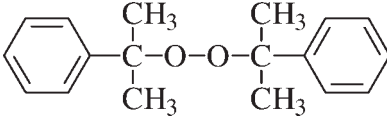
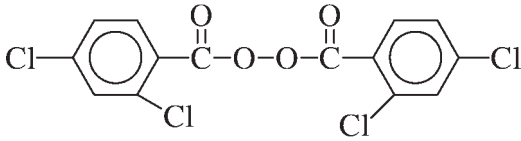
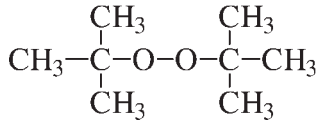
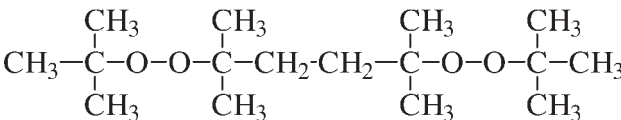
Mixture of the SR/AIBN/peroxide compounds

The silicone compound [GP60 (99 g) and DCP (1 g)] was premixed with a two-roll mill (20 cm diameter \times 50 cm wide iron cored rolls) operating at 25 rpm with a friction ratio of 1 : 1 : 1 at room temperature for 5 min; AIBN (9 g) and peroxide [4 g (DCBP, DTBP or DBPH)]



Scheme 1 Foaming process of the SR/AIBN/peroxide compound.

TABLE II
Structure of the Organic Peroxides and Heat Decomposition Products

Peroxide	Abbreviation	Structure
Dicumyl peroxide	DCP	
Di-(2,4-dichlorobenzoyl) peroxide	DCBP	
Di- <i>t</i> -butyl peroxide	DTBP	
2,5-Dimethyl-2,5-di(<i>t</i> -butylperoxy) hexane	DBPH	
Peroxide	Major decomposition products	
DCP	Methane, acetophenone, 2-phenylpropanol-2, and α -methylstyrene	
DCBP	2,4-Dichlorobezoic acid, 2,4-dichlorobezene, CO ₂ , and CO	
DTBP	Acetone, methane, and <i>tert</i> -butanol	
DBPH	Acetone, methane, <i>tert</i> -amyl alcohol, and <i>tert</i> -butanol	

were then slowly added to the flux roll according to the formulations given in Table I. The compound band was then sheeted, folded, and rebanded for mixing. This process was repeated 30 times to ensure thorough mixing, and the flexible sheet was finally brought to a thickness of 10.0 mm for the foaming test.

Foaming process of the SR/AIBN/peroxide compounds

The milled rubber sheet (20 × 20 × 10 mm³) was fed into a mold cavity (100 × 200 × 50 mm³) with a freely moving upper cover. The mold was placed in a heating oven at 200°C for 20 min. When the foaming process was finished, the mold was cooled to room temperature. The foaming process of the milled sheet is summarized in Scheme 1.

Tensile testing procedure

Dumbbell specimens for mechanical tests were prepared in accordance with ASTM D 412 specifica-

tions. The test specimens were preconditioned to 20% relative humidity and 23 ± 1°C to standardize the test conditions. The tensile properties of the samples were determined with a universal test machine (model DECMC00, Dawha Testing Machine, Kyong-gido, Korea) at a crosshead speed of 50 mm/min at 20 ± 1°C. The mean value of at least five specimens of each sample was taken, although specimens that broke in an unusual manner were disregarded.

Shake flask test

The antibacterial activity of the samples was tested against *S. aureus* (ATCC 25923) and *E. coli* (ATCC 25922) with the shake flask method. The bacteria were subcultured on nutrient broth and incubated overnight at 37°C. The cells were suspended in 50 mL of phosphate-buffered saline to yield a suspension of 1.05 × 10⁶ cfu/mL. The sample powder (200 mg) was weighed and shaken in 10 mL of a bacterial

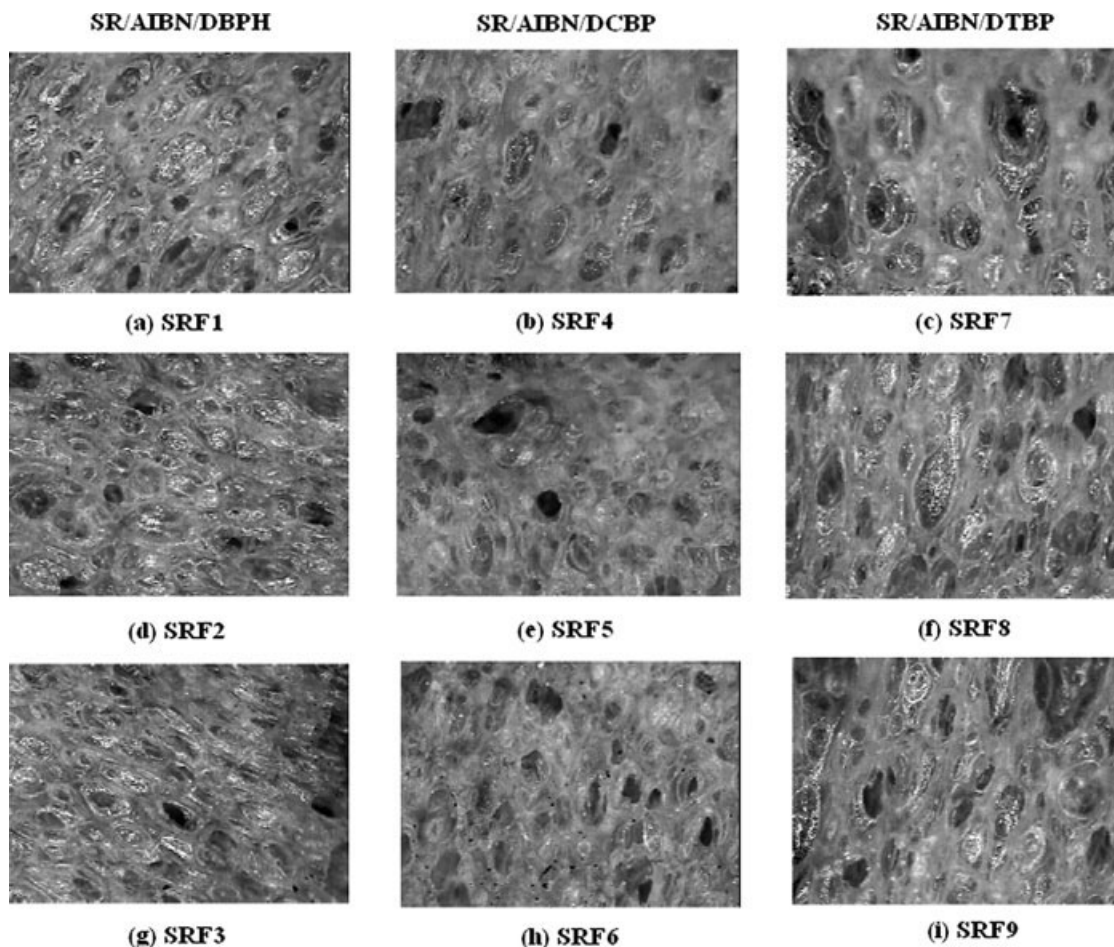


Figure 1 Microphotographs (200 \times) of the peroxide-cured SR foams.

suspension for 24 h. The suspension (20 w/v %) was serially diluted in phosphate-buffered saline and cultured on nutrient broth at 37°C for 24 h. The number of viable organisms in the suspension was determined by multiplication of the number of colonies with the dilution factor, and the percentage reduction was calculated on the basis of the initial count.

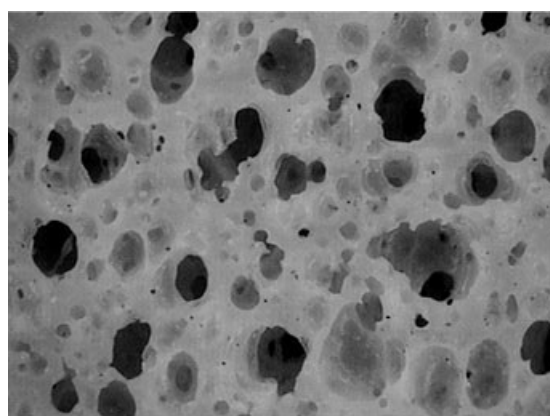
RESULTS AND DISCUSSION

Foaming process of the SR/AIBN/peroxide compounds

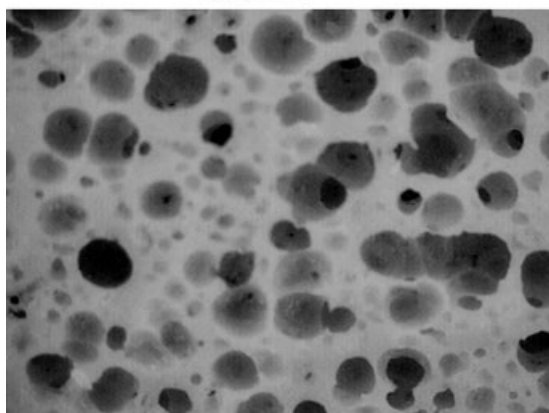
Table II shows the structure and heat decomposition products of the peroxide curing agents. Free-radical cure systems use peroxides that are either vinyl-specific or vinyl-nonspecific in nature. Vinyl-nonspecific peroxides such as DCBP do not require the presence of vinyl or other unsaturated alkyl species in the polymers making up the rubber formulations. They are commonly used in the extrusion process for tubing rods, large gaskets, and wire insulation. These rubber compounds are cured via hot-air vulcanization immediately following extrusion. DCP, DTBP,

and DBPH are vinyl-specific peroxides and require the presence of vinyl species and external pressure during vulcanization. Therefore, vinyl-specific peroxides do not perform well in extrusion applications and are thus limited to use in molding.

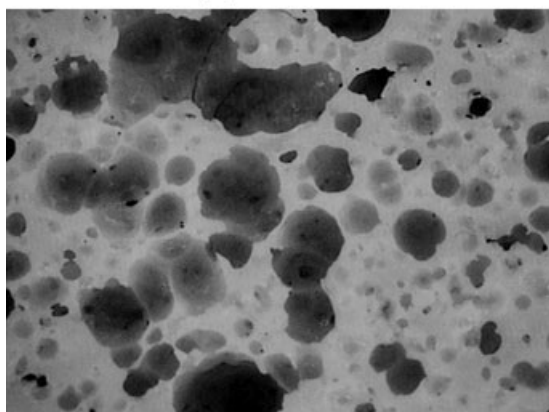
The SR compound, AIBN, and peroxide were mixed with a two-roll mill and were foamed at 200°C for 20 min (Scheme 1). AIBN is often used as nitrogen-generating chemical blowing agent within peroxide-cured, high-consistency rubber foams. AIBN decomposes under heated conditions. The resulting liberation of nitrogen provides the cells or bubbles that result, whereas the curing of the rubber occurs in a parallel process. Figure 1 compares the cross section of foamed SR with different peroxides. All foams have a predominantly closed-cell structure. The polymeric foams are classified as open cell or closed cell. In closed-cell foams, each cell is completely enclosed by a thin wall or membrane of rubber, whereas, for open-cell foams, the individual cells are interconnected. When DTBP was used as a curing agent, the cell sizes were much larger than those of the foams in which DCBP or DBPH was used. The half-life of DCBP was longer than that of



(a) SRF3



(b) SRF6



(c) SRF9

Figure 2 Cross-section images (200 \times) of the 1 wt % TiO₂-containing SRF3, SRF6, and SRF9.

DCBP and DBPH at the same temperature. Organic peroxides break apart in a very predictable manner. At any given temperature, peroxides have a half-life. This is the time it takes for one-half of the currently present peroxide to homolytically cleave. At 110 $^{\circ}$ C, the half-life for AIBN is less than 7 min; for DCBP, it is about 1 min; and for DCP, it is almost 12 h.⁹ At 115 $^{\circ}$ C, the half-life for DTBP¹⁰ is 34 h and for DBPH¹¹ is almost about 10 h. As the SR/AIBN/per-

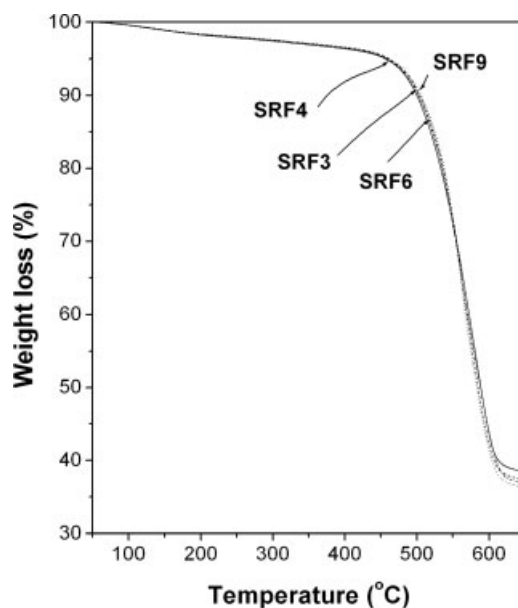


Figure 3 TG curves of the peroxide-cured SR foams.

oxide compound heated up, volatiles that formed under the surface of the central mass moved laterally outward and escaped at the edges of the bonding area. The progression of the curing reaction was faster than the escape of the volatiles, and bubbles formed and became entrapped at the time of vulcanization. The longer half-life delayed the curing reaction and raised the foaming time. Accordingly, the individual cells came together and became an interconnected cell structure (Fig. 2).

Physical, tensile, and thermal properties of the prepared SR foams

Table I demonstrates the effect of peroxide concentration on the foaming ratio, cell size, specific

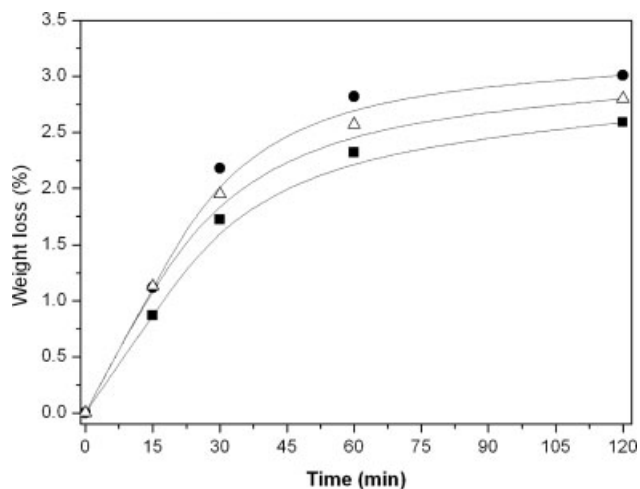


Figure 4 Weight loss of SR foams as a function of post-curing time [(■) SRF3, (●) SRF6, and (△) SRF9].

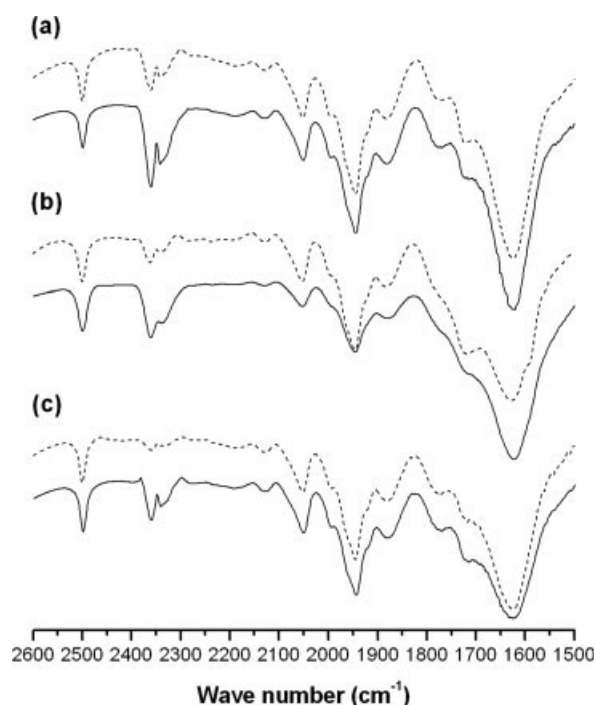


Figure 5 FTIR spectra of the (a) SRF3, (b) SRF6, and (c) SRF9 SR foams [(---) after-foamed and (—) postcured].

gravity, hardness, and tensile properties of the SR foams. As the proportion of peroxide increased from 1 to 4 phr, the cell size, foaming ratio, and elongation at break decreased. A rubber with a high crosslinking density will have less movement, relaxation, and rearrangement when stressed. Therefore, the elongation at break of a cured rubber has almost a linear decrease with increasing crosslinking density.¹² Organic peroxides undergo homolytic cleavage at elevated temperatures. The resulting free radicals induce hydrogen abstraction of hydrogen atoms from the polymer backbone. These, in turn, create free radicals on the polymer backbone, which allow the chains to form carbon-carbon crosslinks with one another. That means that total crosslinking density increased with increasing peroxide levels up to 4 phr. In contrast, significant improvements in the

tensile strength, specific gravity, and hardness of the foams were observed. The tensile strength of SRF09 was 0.2 MPa at the 1-phr DTBP concentration level. The tensile strength reached a maximum value of 1.0 MPa at the 4-phr level. This improvement was likely associated with the crosslinking density increase of SR.

Figure 3 represents the thermograms of SRF3, SRF4, SRF6, and SRF9 obtained by TG at the heating rates of 20°C/min. All of the foams showed an initial degradation temperature at about 320°C because of the lower bond energy of Si-C bonds (Si-C bond dissociation energy = 306 kJ/mol).¹³ These data also indicated that a significant initial weight loss occurred in all of the samples, which had about a 2.5% weight loss up to 250°C. The weight loss was associated with the evolution of small molecules, initially beginning with water, then low-molecular-weight volatiles, and finally CO₂. The TG traces showed no significant change or shift in the weight loss toward higher temperatures depending on peroxide content (SRF4 and SRF6) and peroxide shape (SRF3, SRF6, and SRF9).

Weight loss and FTIR analysis

Figure 4 reveals the test results for the weight loss of the SR foams after the postcuring process at 250°C for 2 h. I measured the weight loss of each sample after postcuring by weighing the specimens. When the weight loss was plotted as a function of postcuring time for SRF3, SRF6, and SRF9, it increased up to 1 h and then was almost maintained. During the foaming process, peroxide decomposition byproducts, such as 2,4-dichlorobenzoic acid, acetone, *tert*-butanol, and *tert*-amyl alcohol, should be produced depending on the curing agents.¹⁴ Therefore, the closed-cell foams contained these materials in the individual cells in addition to nitrogen gas. When the foam was heated, these materials vaporized and increased the inner cell pressure. Finally, the expansion force applied to individual cells caused the volatiles to be gradually squeezed through the thin cell membranes. When the foam was cooled, the cells

TABLE III
Shake Flask Test Results for the SR Foams

Sample	After foaming				After postcuring			
	<i>S. aureus</i> (+)		<i>E. coli</i> (-)		<i>S. aureus</i> (+)		<i>E. coli</i> (-)	
	cfu/mL ^a	Reduction (%)	cfu/mL	Reduction (%)	cfu/mL	Reduction (%)	cfu/mL	Reduction (%)
Blank	1.05 × 10 ⁶	—	3.01 × 10 ⁵	—	1.05 × 10 ⁶	—	3.01 × 10 ⁵	—
SRF3	0.82 × 10 ⁶	21.9	1.11 × 10 ⁵	63.1	0.88 × 10 ⁶	16.2	2.20 × 10 ⁵	26.9
SRF6	0	100	2.32 × 10 ¹	99.9	0.73 × 10 ⁶	30.5	1.83 × 10 ⁵	39.2
SRF9	0.75 × 10 ⁶	28.5	1.85 × 10 ⁵	38.5	0.85 × 10 ⁶	19.1	2.36 × 10 ⁵	21.6

^a For 24 h of contact.

returned to their original shape, and air was drawn back into the individual cells.

Figure 5 exhibits the FTIR spectra of the after-foamed and postcured SR foams. The stretching vibration peak of CO₂ appeared at 2340 cm⁻¹. The peak at 1720 cm⁻¹ corresponded to the stretching vibration peak of carbonyl groups in the carboxylic acids. Si—H exhibited its peak at 2125 cm⁻¹. After postcuring, the CO₂ stretching peak increased considerably because SR had a higher permeability to CO₂ than to O₂ and N₂. During the postcuring and cooling process, the thermally expanded cells fully recovered to their original shape, drawing air back into themselves, and CO₂ was more easily accumulated in the foam. Also, the intensity of the carbonyl group peak at 1720 cm⁻¹ for SRF6 significantly decreased after the postcuring because of the volatile acidic residues.

Antibacterial activity changes after the postcuring process

The antibacterial activity of after-foamed and postcured SR foams was measured by the shake flask test against *S. aureus* and *E. coli* as test organisms because they represent Gram-positive and Gram-negative bacteria, respectively. The number of viable bacteria and the percentage reduction of the number of bacteria are shown in Table III. At 10 w/v % in the bacterial suspension, SRF3, SRF6, and SRF9 powders possessed antibacterial activity against these organisms. Also, SRF6 had more antibacterial activity than SRF3 and SRF9. As shown Table II, 2,4-dichlorobenzoic acid was generated by the DCBP thermal decomposition. Benzoic acid and its derivative possess antimicrobial activity and are used as food preservatives, antiseptics, and edible coatings.¹⁵ The minimum inhibitory concentrations of benzoic acid on the growth of several species of yeasts range from 100 to 1250 mg/L.^{16,17} In addition, the decomposition byproducts of DTBP and DBPH were more easily vaporized than those of DCBP. In contrast, the antibacterial activity of the postcured foams was reduced significantly. The percentage reductions of *S. aureus* and *E. coli* were 69.5 and 60.7%, respectively, compared with those of the foamed SR.

CONCLUSIONS

Various SR foams were prepared by the peroxide curing of a silicone compound in the presence of an

AIBN blowing agent. During the foaming process, heating caused AIBN to decompose and created bubbles of gas entrapped in the rubber, which formed the cells of the silicone foam. All of the prepared foams had a predominantly closed-cell structure. When DTBP was used as a curing agent, the cell sizes were much larger than those of the foams that used DCBP or DBPH. As the proportion of the peroxide increased from 1 to 4 phr, the cell size, foaming ratio, and elongation at break decreased, whereas the tensile strength, specific gravity, and hardness of the foams increased.

The prepared SR foams had antibacterial activity because a toxic residue was generated by the peroxide decomposition. SRF06 was highly active against both the Gram-positive and Gram-negative bacteria. Many of the low-molecular-weight byproducts steadily permeated out from the polymer matrices, which gave rise to the toxicity of final products. In contrast, the antibacterial activity of postcured foams was reduced significantly. This indicated that the postcuring process reduced the peroxide toxic byproducts from the final SR foam products.

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