

Study on the properties of liquid silicone rubber with different foaming agents during the foaming and addition molding process

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Abstract: The addition-type liquid silicone rubber was foamed using physical foaming agents, sodium bicarbonate as a foaming aid, and hollow glass microspheres, respectively, to obtain foamed silicone rubber. This paper deeply investigated the effects of three foaming aids and their different dosages on the foaming effect, and conducted characterization and testing of the structure and properties of the successfully prepared foamed silicone rubber. The research results showed that the foaming effect of the foamed silicone rubber prepared using physical foaming agents was more ideal, and medium-foaming foam materials could be prepared; the tensile strength and elongation increased with the increase in the density of the foamed silicone rubber; the pressure during molding has a significant impact on the foaming effect, and the foaming ratio increased as the pressure decreased.

Key words: addition-type liquid silicone rubber; foaming agent; foamed silicone rubber; foaming ratio; tensile strength

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Foam silicone is a porous material with a silicone base that contains numerous air bubbles. It possesses lightweight, sound insulation, heat insulation, impact load absorption, sealing, shock absorption, and other properties, and is widely used in national defense, aerospace, transportation, electronics, agriculture, and daily necessities.

Currently, the molding technologies for silicone foam materials primarily include precipitation pore-forming molding, chemical foaming molding, hybrid foaming molding, and physical foaming molding. The matrix of silicone foam materials can be made from high molar mass solid silicone or liquid silicone. Currently, the preparation of silicone foam materials via the liquid method mainly involves room temperature vulcanized silicone foam materials, with the gas source primarily coming from internal blowing agents, such as the reaction between Si—OH or R—OH and Si—H, which produces H₂ to promote internal foaming in the system. Tan Yu et al. reviewed the research progress of room temperature vulcanized silicone foam materials in recent years, noting that

these materials typically utilize condensation dehydrogenation reactions. Su Junjie et al. used deionized water and hydrogen-containing silicone oil to generate gas under platinum catalysis, and prepared foamed silicone using vinyl silicone oil. There are relatively few research reports on the foaming of liquid silicone with foaming aids.

This article uses addition-type liquid silicone rubber as the matrix, selects different foaming agents, and employs the molding process to obtain foamed silicone rubber. The appropriate foaming agent is determined by measuring the foaming effect, mechanical properties, and morphology.

1 Experimental part

1.1 Experimental materials

The addition-type liquid silicone is in a two-component form, with the main agent and crosslinking agent equally

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divided into components A and B. Components A and B are mixed and supplied in a 1:1 ratio, and both components have essentially the same viscosity and density. The catalyst is a platinum-based catalyst. The performance indicators of the selected addition-type liquid silicone are shown in Table 1.

Table 1 Properties of addition-type liquid silicone rubber

Viscosity / (Pa·S)	Relative Density (25 °C) / (g·cm ⁻³)	Hardness / (ShoreA)	Tensile Strength / MPa
3 500	1.09	50	10.0

Organic compounds containing N, P, and S can poison platinum catalysts, leading to poor sulfiding and inhibiting the reaction. Therefore, the foaming agent should be selected without the aforementioned elements. Currently, three foaming agents are being used, as follows:

(1) A kind of physical foaming agent: It has a core-shell structure, with the outer shell being a thermoplastic acrylic resin polymer and the inner core being spherical plastic particles composed of alkane gases. The diameter is

approximately 25~45 um, and after heating, the volume rapidly expands to several dozen times its original size, thus achieving the foaming effect. The microsphere foaming can withstand temperatures up to 180°. The typical filling amount is 1%~5%.

(2) Sodium bicarbonate: Selecting sodium bicarbonate that has undergone surface treatment can improve the foaming effect.

(3) Hollow glass microspheres: Hollow glass microspheres are a kind of micron-sized hollow glass microspheres with a smooth surface. Their main chemical composition is soda-lime borosilicate glass, and they appear as hollow transparent spheres under a microscope. Hollow glass microspheres possess various properties such as low density, high strength, low thermal conductivity, electrical insulation, high temperature resistance, acid and alkali resistance, good fluidity, and chemical stability. The performance indicators of this type of hollow glass microspheres are shown in Table 2, and the typical addition amount is 5% to 8%.

Table 2 Performance indicators of hollow glass microspheres

Serial Number	Detection Content	Unit	Control Indicator	Test Results
1	Exterior color	—	white	white
2	Humidity	%	≤ 0.50	0.2
3	Floatation rate	%	≥ 95	98
4	bulk density	g/cm ³	0.19~0.22	0.2
5	particle size	μm	D90 ≤ 65	63.86
6	true density	g/cm ³	0.37~0.39	0.386 5
7	Compressive strength (crushing rate)	%	5500psi	qualified

1.2 Sample preparation

Add the physical foaming agent to the addition-type liquid silicone rubber according to the filling ratio in Table 3 and mix them evenly. Use a flat curing press to press the mixture into sheets to obtain foaming materials, with the process parameters shown in Table 3. After molding, cut the test pieces into standard samples with a cutting knife.

Table 3 Experimental formula and process parameters using physical foaming agent

Serial number	Fill and Add proportion	Process temperature/ °C	Curing Time (in minutes)	Molding Pressure / MPa
W1	1%	120	10	15
W2	1%	120	10	none
W3	2%	120	10	15
W4	2%	120	10	none
W5	4%	120	10	15
W6	4%	120	10	none

Add the surface-treated foaming aid, sodium bicarbonate, to the addition-type liquid silicone rubber according to the

filling ratio specified in Table 4 and mix them evenly. Use a flat curing press to press the mixture into sheets to obtain foaming materials. The process parameters are shown in Table 4, and no pressure is applied during curing. After molding, use a cutter to cut the test pieces into standard samples.

Table 4 Experimental formula and process parameters using sodium bicarbonate as a foaming aid

Serial Number	Fill and Add Proportion	Process Temperature / °C	Curing Time (in minutes)
T1	0.5%	130	10
T2	2%	130	10
T3	3%	130	10

Add hollow glass microspheres into the addition-type liquid silicone rubber according to the filling ratio specified in Table 5 and mix them evenly. Use a flat curing press to press the mixture into sheets to obtain foamed materials. The process parameters are shown in Table 5, and no pressure is applied during curing. After molding, use a cutting knife to cut the test

pieces into standard specimens.

Table 5 Experimental formula and process parameters using hollow glass microspheres

Serial number	Fill and add proportion	Process temperature / °C	Curing time (in minutes)
B1	5%	130	10
B2	6%	130	10
B3	8%	130	10

1.3 Testing and characterization

(1) Testing of foam material density and expansion ratio:

Cut the foamed silicone into cuboids, weigh its mass, measure the side length, calculate the volume, and obtain the density. Then compare it with the parameters of unfoamed silicone to obtain the expansion ratio, which is calculated according to formula 1 or formula 2.

Foaming ratio=volume after foaming / original volume (1)

$$N=\rho_1/\rho_2 \quad (2)$$

In the formula, N represents the foaming ratio, ρ_1 denotes the initial apparent density of silica gel, and ρ_2 signifies the apparent density of foamed silica gel.

(2) Mechanical property testing: Cut the foamed silicone rubber into standard dumbbell-shaped tensile specimens. The tensile strength is tested using dumbbell-shaped specimens with a testing speed of 100 mm/min, a gauge length of 25 mm, and a testing environment temperature of 23 ± 2 °C and humidity of $50\pm 5\%$. The tensile properties of the specimens are tested using a tensile machine that complies with ISO5893 and has a force measurement accuracy of Level 2. The accuracy of the extensometer used in the testing machine is Level D for Type I, Type II, and Type IA dumbbell-shaped specimens, and Type A ring specimens; Level E for Type III and Type IV dumbbell-shaped specimens, and Type B specimens. The testing machine should be capable of operating at a minimum of 100 mm/min \pm 10 mm/min, 200 mm/min \pm 20 mm/min, and 500 mm/min \pm 50 mm/min.

(3) Observing the morphology of foamed silicone rubber using an electron microscope: Take a cross-section of the foamed solid silicone rubber and observe it under a microscope.

2 Results and discussion

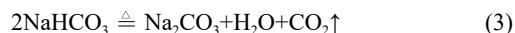
2.1 Density and expansion ratio of foamed materials

2.1.1 Density and expansion ratio of foamed silicone rubber with physical foaming agent added

Through calculation, the density and expansion ratio of foamed silicone rubber prepared with different proportions of physical foaming aids under pressurized and unpressurized conditions were obtained. As shown in Figure 1, with the increase of the content of physical foaming aids, the density of foamed silicone rubber gradually decreases, and the expansion ratio gradually increases. When the mass fraction of physical foaming aids reaches 2% under unpressurized conditions, the density of foamed silicone rubber is 0.4 g/cm³, and the expansion ratio is 2.73 times; when the mass fraction reaches 4%, the density of foamed silicone rubber is 0.27 g/cm³, and the expansion ratio is 4.04 times, making it a medium-expansion foam material. Pressure has a significant impact on the foaming density and expansion ratio during the foaming process. The density of foamed silicone rubber obtained under unpressurized conditions is lower than that obtained under pressurized conditions, and the expansion ratio of foamed silicone rubber obtained under unpressurized conditions is higher than that obtained under pressurized conditions, indicating that reducing pressure can yield better foaming materials.

2.1.2 Density and expansion ratio of foamed silicone rubber with sodium bicarbonate as foaming agent

Sodium bicarbonate is an endothermic foaming agent that decomposes endothermically at a temperature ranging from 60 to 150 °C, producing gases CO₂ and H₂O. The chemical equation for its thermal decomposition is shown in Equation 3.



The influence of the mass fraction of sodium bicarbonate, a foaming aid, on the density and foaming ratio of foamed silicone rubber is shown in Figure 2. As can be seen from Figure 2, with the increase in the proportion of sodium bicarbonate added as a foaming aid, the density of foamed silicone rubber decreases, and the foaming ratio increases. When 2% sodium bicarbonate is added, the density of foamed silicone rubber is 0.67 g/cm³, and when 3% sodium bicarbonate is added, the density is 0.66 g/cm³. The foaming effects of adding 3% and 2% sodium bicarbonate are not significantly

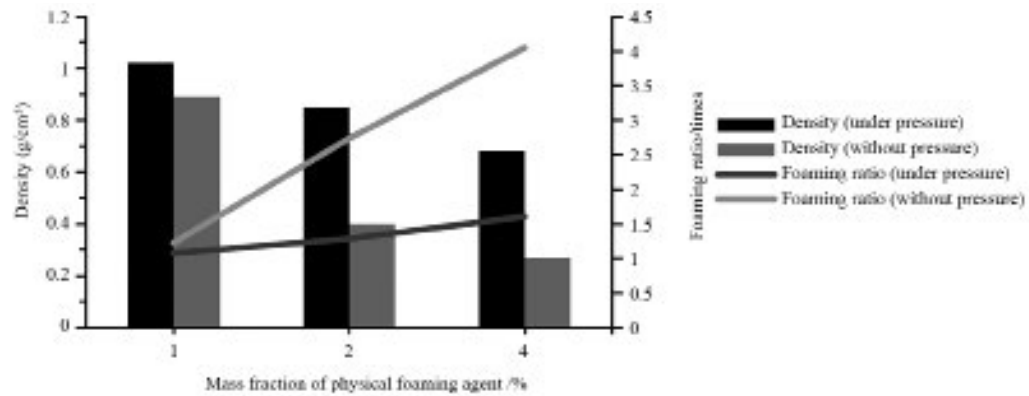


Figure 1 The influence of physical blowing agent mass fraction on the density and expansion ratio of foamed silicone rubber under different molding pressures

different, and the foaming effect is limited.

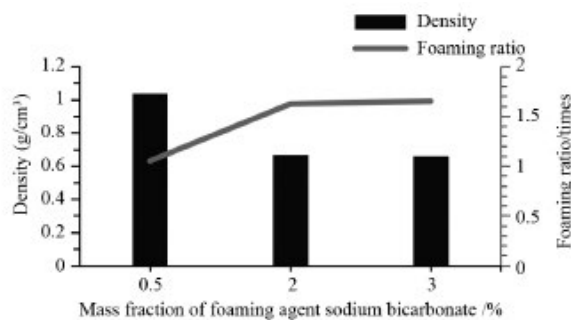


Figure 2 Effect of mass fraction of sodium bicarbonate as foaming agent on the density and expansion ratio of foamed silicone rubber

2.1.3 Density and expansion ratio of foamed silicone rubber filled with hollow glass microspheres

The influence of the mass fraction of hollow glass microspheres on the density and expansion ratio of foamed silicone rubber is illustrated in Figure 3. As evident from Figure 3, the density of foamed silicone rubber decreases as the proportion of hollow glass microspheres increases. When the mass fraction of hollow glass microspheres is 8%, the density of foamed silicone rubber is 0.83 g/cm³, and the expansion ratio is 1.31 times. Hollow glass microspheres are hollow, transparent, and spherical in shape, primarily serving as a filler in foamed silicone rubber.

In summary, as the amount of foaming agent increases, the density of foamed silicone decreases, and the foaming ratio increases. Silicone with physical foaming agent added exhibits better foaming effect. When the addition ratio of physical foaming agent is 2% without pressure, the density of foamed

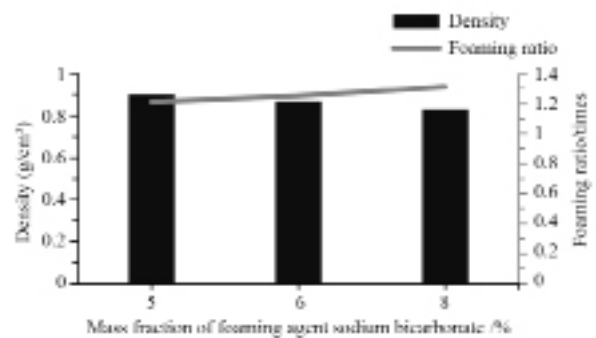


Figure 3 The influence of hollow glass microsphere mass fraction on the density and expansion ratio of foamed silicone rubber

silicone is 0.4 g/cm³, and when the addition ratio reaches 4%, the density of foamed silicone is 0.27 g/cm³. When the addition ratio of foaming agent sodium bicarbonate is 2% and 3%, the density of foamed silicone changes little. When using hollow glass microspheres, the density and foaming ratio change slowly when the addition ratio increases from 5% to 8%.

2.2 Mechanical properties

2.2.1 Tensile strength

Under non-pressurized conditions, the tensile strength of foamed silicone rubber obtained using physical foaming agents, sodium bicarbonate as a foaming agent, and hollow glass microspheres is shown in Figure 4. As the amount of foaming agent added increases, the tensile strength decreases; as the density of the foamed silicone rubber increases, the tensile strength increases. When using physical foaming agents without pressurized curing and molding, the tensile strength of the foamed silicone rubber is 0.7 MPa when the addition level is 2%, and the density is 0.4 g/cm³. Shao Shuiyuan et al. used methyl vinyl silicone rubber as the matrix, added

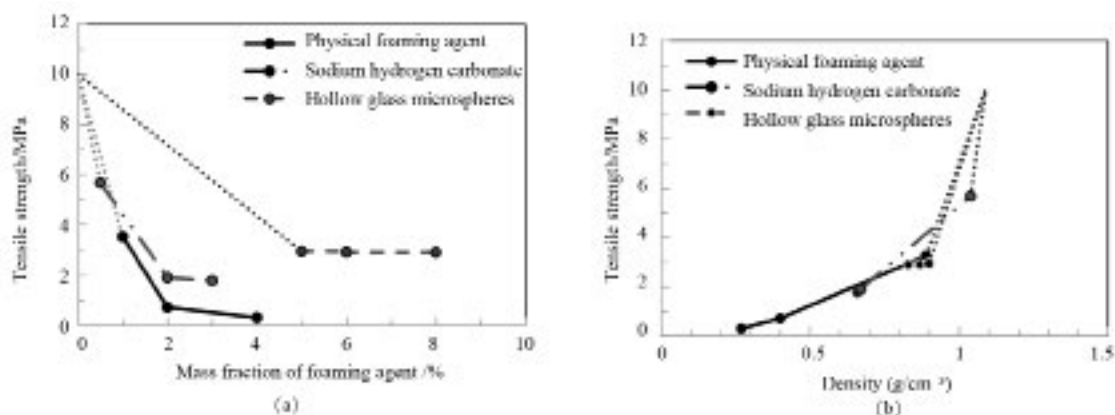


Figure 4 Relationship between the tensile strength of foamed silicone rubber filled with different foaming agents and the mass fraction (a) and density (b) of the foaming agent

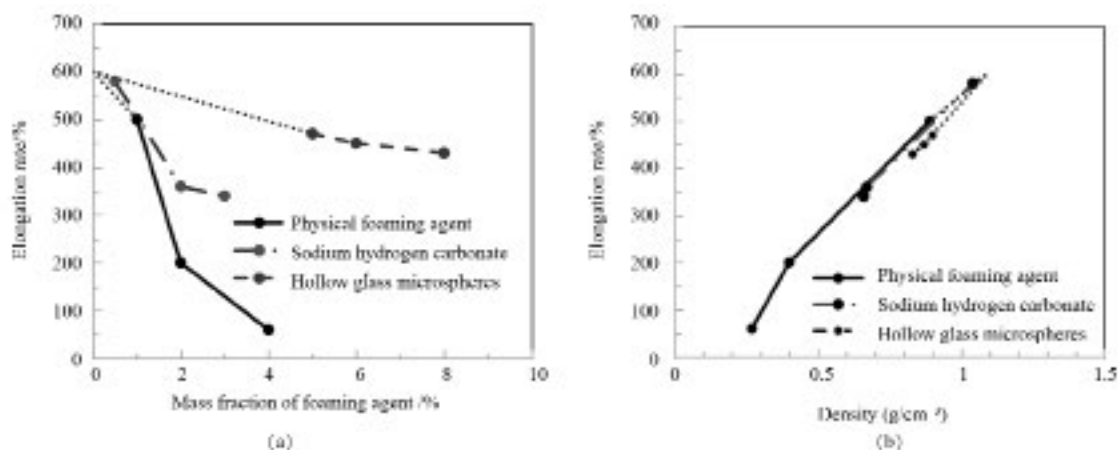


Figure 5 Relationship between elongation rate and mass fraction (a) and density (b) of foaming agent in foamed silicone rubber with different foaming agents added

surface-modified fumed silica and other additives to prepare foamed silicone rubber with a tensile strength of 0.697 MPa and an apparent density of 0.553 g/cm³. Compared to this, the foamed silicone rubber with 2% physical foaming agent has a higher tensile strength and lower density. When using sodium bicarbonate for foaming, the tensile strength and elongation of foamed silicone rubber with 3% and 2% sodium bicarbonate added show little change. When using hollow glass microspheres, the tensile strength and elongation of foamed silicone rubber decrease slowly with increasing addition level. Among these three foaming agents, to obtain foamed silicone rubber with the same tensile strength, the amount of physical foaming agent required is smaller.

2.2.2 Elongation

The elongation rate of foamed silicone obtained using physical foaming aids, sodium bicarbonate as a foaming aid,

and hollow glass microspheres is shown in Figure 5. As the filling amount increases, the elongation rate decreases; as the density of the foamed silicone increases, the elongation rate increases. When adding physical foaming aids, the elongation rate changes more significantly with changes in the filling ratio, and the trend of elongation rate change is the same as the trend of density change.

2.3 Morphology of foamed silicone rubber

Based on the relationship between the dosage of three foaming aids and their foaming effects, silicone rubber samples were prepared with the following proportions of foaming aids: 4% physical foaming agent (labeled as W6), 3% sodium bicarbonate (labeled as T3), and 8% hollow glass microspheres (labeled as B3). The cell structure of these samples was observed using an electron microscope, as shown in Figure 6. The silicone rubber with the physical foaming agent exhibited

relatively uniform cell size, with an average diameter of around 100 μm . The silicone rubber with sodium bicarbonate showed poorer uniformity in cell size, with some cells reaching up to 1.6 mm in diameter and large inter-cell spacing, indicating poor dispersion of the foaming aid in the polymer. The silicone rubber with hollow glass microspheres had the smallest cells, with diameters ranging from 40 to 65 μm .



Figure 6 Electron microscope photographs of W_6 , T_3 , and B_3 samples

3 Conclusion

(1) When using addition-type liquid silicone rubber as the matrix for foaming, the foaming effect of using physical foaming aids is superior to that of using sodium bicarbonate and hollow glass microspheres as foaming aids. Using sodium bicarbonate and hollow glass microspheres as foaming aids can only produce low-foaming foam materials, while using

physical foaming aids can produce medium-foaming foam materials.

(2) During the foaming molding process, pressure affects the foaming effect. The lower the pressure, the better the foaming effect, and the greater the foaming ratio.

(3) When using the aforementioned three foaming aids to foam liquid silicone rubber, the change trends of the tensile strength and elongation of the foamed silicone rubber are the same, and their change trends are also the same as the change trend of density, that is, the lower the density of the foamed silicone rubber, the lower the tensile strength and elongation.

(4) When using the aforementioned three foaming aids to foam liquid silicone rubber, the amount of physical foaming agent added is smaller, and the pore size of the foamed silicone rubber is more uniform. By adding 2% physical foaming aid and curing under non-pressurized conditions, a foamed silicone rubber with a density of 0.4 g/cm^3 , a tensile strength of 0.7 MPa, and an average pore size of approximately 100 μm can be obtained.



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