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Preparation and Properties of Conductive Foamed Silicone Rubber

□ XIONG Man¹, BIE Xuan², WANG Ben²,
DONG Yawei², ZHANG Qunchao^{1†},
HUANG Ronghua^{2‡}

1. School of Materials Science and Engineering, Hubei University, Wuhan 430062, Hubei, China;

2. School of Power & Mechanical Engineering, Wuhan University, Wuhan 430072, Hubei, China

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Abstract: The conductive foamed silicone rubber was prepared by Polymethylvinylsiloxane (PMVS) mixed with acetylene black, fumed silica, and AC foaming agent (azodicarbonamide). Influences of fillers on the microstructure, electrical conductivity and mechanical property were discussed. The results showed that the pore structure was affected by acetylene black. Acetylene black delayed the vulcanization speed of silicone rubbers, leading to bigger pores. Higher content of acetylene black decreased the mechanical properties and the electrical resistivity of rubbers. Fumed silica increased the mechanical properties and limited the aggregation of gas. Higher content of fumed silica led to small and obturator pores generated. Higher content of fumed silica increase the mechanical properties and the electrical resistivity of rubbers. AC foaming agents generated more gas, leading to bigger and irregular pores which affected the mechanical properties negatively, meanwhile AC foaming agents increased the conductivity of rubbers.

Key words: conductive foamed silicone rubber; resistivity; mechanical strength

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Biography: XIONG Man, male, Master candidate, research direction: silicone material. E-mail: bearxm1023@163.com

† To whom correspondence should be addressed. E-mail: zhangqc1976@hubei.edu.cn; huangronghua@whu.edu.cn

0 Introduction

Foam silicone rubber is distinguished for its light weight, as well as high electrical resistivity and thermal stability. It is widely used in military, transportation and other equipment. The common methods of preparing foamed silicone rubber include supercritical foaming, hydrogen silicon condensation reaction foaming, agent foaming and so on^[1-5]. Supercritical foaming injects supercritical stated inert gas into half-vulcanized silicone rubber and generates holes by heating. Supercritical foaming is a green technology, and the pore size is small and uniformed^[6], but it needs high pressure and special equipment. Liao *et al*^[7] successfully prepared foamed silicone rubber by supercritical foaming with supercritical CO₂, and Hong *et al*^[8] successfully prepared foamed silicone rubber with an average pore size of 12 μm via this method. Hydrogen-silane condensation foaming generates pores via hydrogen H₂ from hydrogen-silane condensation reaction at room temperature, but the pore structure is difficult to control because the generating velocity of H₂ is hardly fitted to the rubber vulcanization. Tan *et al*^[9] prepared foamed silicone rubber at room temperature by hydrogen-silane condensation. Chemical foaming is made by adding foaming agent that are easy to decompose and generate gas to release gas when heated. This method is simple and easy to control, thus it is the most commonly used method. Liu *et al*^[10] successfully prepared foamed silicone rubber by AC foaming agent. It was found that when AC foaming agent was 10 phr (parts per hundreds of rubber), the rubber density was reduced to the minimum.

Conductive silicon rubber is widely used in antista-

tic, electromagnetic shielding, pressure sensitive conductive and other fields. For example, as excellent shock absorbing material, the electromagnetic shielding of conductive foamed silicone rubber can reduce the damage caused by static electricity in the process of transporting electronic products. Adding electrical conductive fillers is the effective method for preparation electrical conductive silicon rubber. Endowing foaming to conductive silicone rubber will provide low temperature resistance and light weight, which expands its applications. Bai *et al*^[11] and Jia *et al*^[12] prepared conductive foamed silicone rubber with carbon black and carbon nanotubes as conductive materials by means of supercritical CO₂ foaming. But generally, research on this field is relatively few.

In this paper, polymethylvinylsiloxane was used to prepare conductive foamed silicone rubber, using acetylene black, fumed silica and AC foaming agent as fillers. The effect of different contents of fillers on the tensile strength, the elongation at break, the resistivity and the microstructure of conductive foamed silicone rubber were studied.

1 Experimental

1.1 Materials and Methods

Polymethylvinylsiloxane (PMVS, 5 000 mPa·s) was supplied by Wuda Silicone Co., Ltd; fumed silica, commercially available; Acetylene black, industrial pure from Tianjin Zhengning Co., Ltd; azodicarbonamide (AC foaming agent), industrial pure, from Zhejiang Shuntai Co., Ltd; 2, 5-dimethyl-2, 5-bis(tert-butylperoxy)hexane (DBBH) was used as catalyst, industrial pure, and commercially available.

The tensile strength and the elongation at break was measured according to GB/T528-2008 and the tensile rate was 500 mm/min (MTS, CMT4104). The hardness of Shore A was measured according to GB/T531-2008 with rubber hardness tester (Shanghai Chemical Machinery Factory, XY-1). The density was measured by formula $\rho=m/V$, cutting a simple with 2 cm×2 cm×0.25 cm to calculate its volume. The resistivity was measured by four-probe method and calculated according to the formula $\rho=RS/L$ (KEITHLEY, 2000MULTIMETER). The fractured surface morphologies were observed using a scanning electron microscope (TESCAN Brno, MIRA 3, LMH). The samples were cryo-fractured and sputter-coated with gold before photographed under the microscope.

1.2 Preparation of Electrical Conductive Foamed Silicone Rubber

The PMVS, acetylene black, fumed silica, and AC foaming agent were mixed in a kneader for 3 h according to the proportion in Table 1, and then 2, 5-dimethyl-2, 5-bis(tert-butylperoxy)hexane were added and grounded several times on the three-roller machine (Wujin Dongfang Machine, S65). After fully grinding, the rubbers were poured into a mold (130 mm×100 mm×2 mm) and vulcanized on a plate vulcanizing machine for 20 min at 170 °C, 10 MPa, followed by a second-stage vulcanization in oven for 2 h, at 200 °C.

Table 1 Composition of electrical conductive foaming silicon rubbers g

Number	PMVS	Acetylene black	Fumed silica	AC agent	DBBH
1	100	20	20	4	3
2	100	20	20	6	3
3	100	20	20	8	3
4	100	20	20	10	3
5	100	30	20	4	3
6	100	40	20	4	3
7	100	40	30	4	3
8	100	40	40	4	3
9	100	40	0	4	3

2 Results and Discussion

2.1 Microtopography of Porous Structure

2.1.1 Influence of acetylene black

Figure 1 shows the cellular morphology of foams silicone rubber with different acetylene black content. From Fig. 1, different from other two, 20 phr content of acetylene black, provides uniformed and spherical pores with the average size at about 25 μm. When the content of acetylene black is 30 phr, the average size of the holes becomes a little bigger. But when the content of acetylene black reaches 40 phr, pore shape changes to be flat, and the size increases. Jia *et al*^[12] discussed the relationship between different carbon black contents on the size and density of the pore. They found that the increase of carbon black content delayed the crosslinking speed of rubber and the cell became larger. In our research, when at 40 phr of acetylene black content, the vulcanization speed is greatly delayed, and the thermal generated gas from AC foaming agents cannot be encapsulated in time.

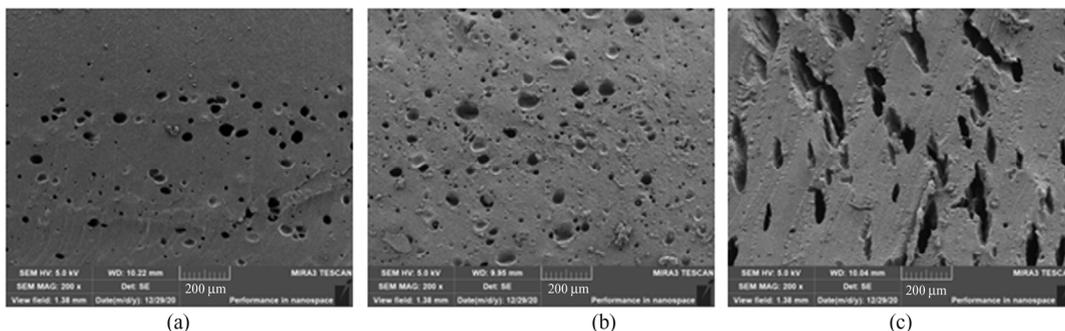


Fig. 1 Microtopography of cellular morphology of foams silicone rubber with (a) 20 phr, (b) 30 phr, (c) 40 phr acetylene black content

Thus, the gas diffuses, aggregates, and forms bigger and irregular pores.

2.1.2 Influence of fumed silica

From Fig. 2, as silica content increases, the pore size becomes smaller. Silicon rubber without fumed silica presents a typical porous structure (Fig. 2(a)). But that with 20 phr just presents rubbers dotted with some pores (Fig. 2(b)). When the content increases to above 30 phr, no open pores, but obturator ones could be observed even at 5 000-fold magnifying (Fig. 2(c) and 2(d)). We suggest this might be assigned to that silica increases the tensile strength of silicone rubber, the gas cannot diffuse

and aggregate to form pores^[13].

2.1.3 Influence of AC foaming agent

As shown in Fig. 3, when the foaming agent content is below 6 phr, the pores are round and of similar size. When the foaming agent content increases to above 8 phr, they become flat strip. More AC foaming agents will produce more gas, and lead to higher pressure. Higher pressure reasonably leads to thinner porous wall, or broken pores, finally leads to the aggregation of gas. So, in the condition of lower AC foaming agent content, the pores grow evenly and form like a round hole. As the content increases, bigger and irregular pores (flat strips) generate.

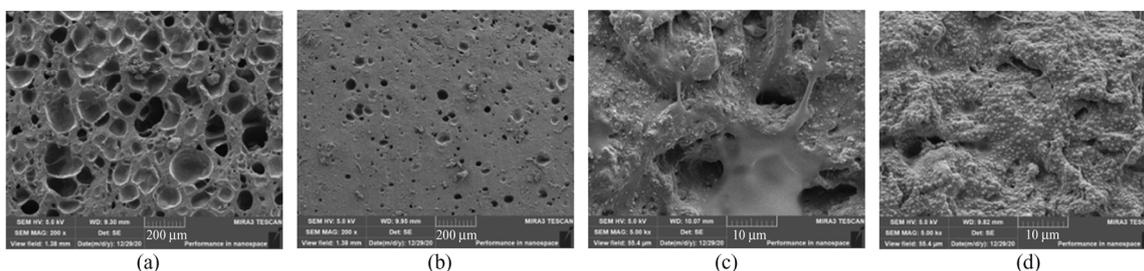


Fig. 2 Microtopography of cellular morphology of foams silicone rubber with (a) 0 phr, (b) 20 phr, (c) 30 phr, (d) 40 phr fumed silica

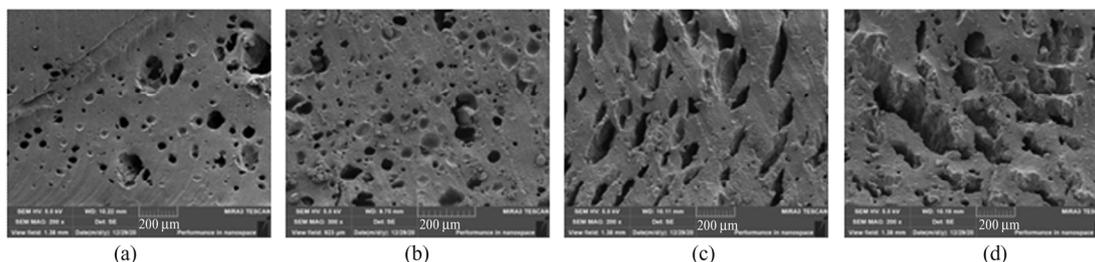


Fig. 3 Microtopography of cellular morphology of foams silicone rubber with (a) 4 phr, (b) 6 phr, (c) 8 phr, (d) 10 phr AC foaming agent

2.2 Mechanical Property of Rubbers

Table 2 shows the data of density and foaming ratio with different filler contents. The increase of acetylene black has no obvious effect on the density, and when the acetylene black exceeds a certain amount, the density

decrease. The reason is that the large pores formed makes the density reduced. The influence of silica on density is obvious. Increasing the amount of filler also makes the pores unable to occupy the volume due to the increased mechanical properties of silica. The influence of the

Table 2 Density and foaming ratio with different filler content

Filler	Content/g	Density/g·cm ⁻³	Foaming ratio
Acetylene black	20	0.980 9	1.138
	30	0.980 4	1.139
	40	0.954 8	1.175
Fumed silica	0	0.713 3	1.56
	20	0.954 8	1.17
	30	1.209 9	0.923
	40	1.215 8	0.919
AC foaming agent	4	0.980 9	1.139
	6	0.924 9	1.208
	8	0.913 4	1.223
	10	0.889 7	1.255

foaming agent on the density is also obvious. The more gas is generated by the foaming agent, the smaller density is and the larger the foaming ratio is.

Figure 4(a) shows the mechanical property of silicone rubber at different acetylene black content. As can be seen, with the increase of acetylene black, the elongation at break and the tensile strength decrease, while the hardness (unit: HA) increases. For acetylene black is hard fillers for polysiloxanes, the increased hardness is understandable. Moreover, there is no chemical reaction between acetylene black and silicone rubber, and it has no reinforcing effect on silicone rubber. More acetylene black will destroy the arrangement of polysiloxane chains, and result in the decrease of the elongation at break and the tensile strength. Zhang *et al.*^[7] also reported the similar results in their paper. The pore structure differences at different acetylene black would also affect the mechanical properties because the irregular flat strips in foaming silicon rubber (Fig.1) should decrease the mechanical property.

Figure 4(b) shows the mechanical property of silicone rubber influenced by fumed silica content. It can be seen that the increase of fumed silica content results in the decrease of the elongation at break and the increase of the tensile strength and the hardness. Because of the chemical bonds between fumed silica and rubber, the obvious reinforcing effect reflected by hardness, the tensile strength and the elongation at break is observed. When the content of silica is 40 phr, the tensile strength is 2.25 MPa, the elongation at break is 18.16%, and the hardness is Shore A 79. This is in accordance with that

reported by Jiao *et al.*^[8]. Higher mechanical properties would affect the pore structure as Fig. 2 presents.

Figure 4(c) shows the variation of mechanical property on AC foaming agent content. As can be seen, with the increase of the content of foaming agent, the elongation at break and the tensile strength decreases, but the hardness varies little. For the increase of AC foaming agent content makes the pore volume increase, the pore wall becomes thinner and the foaming agent has a neglective effect on the silicone rubber.

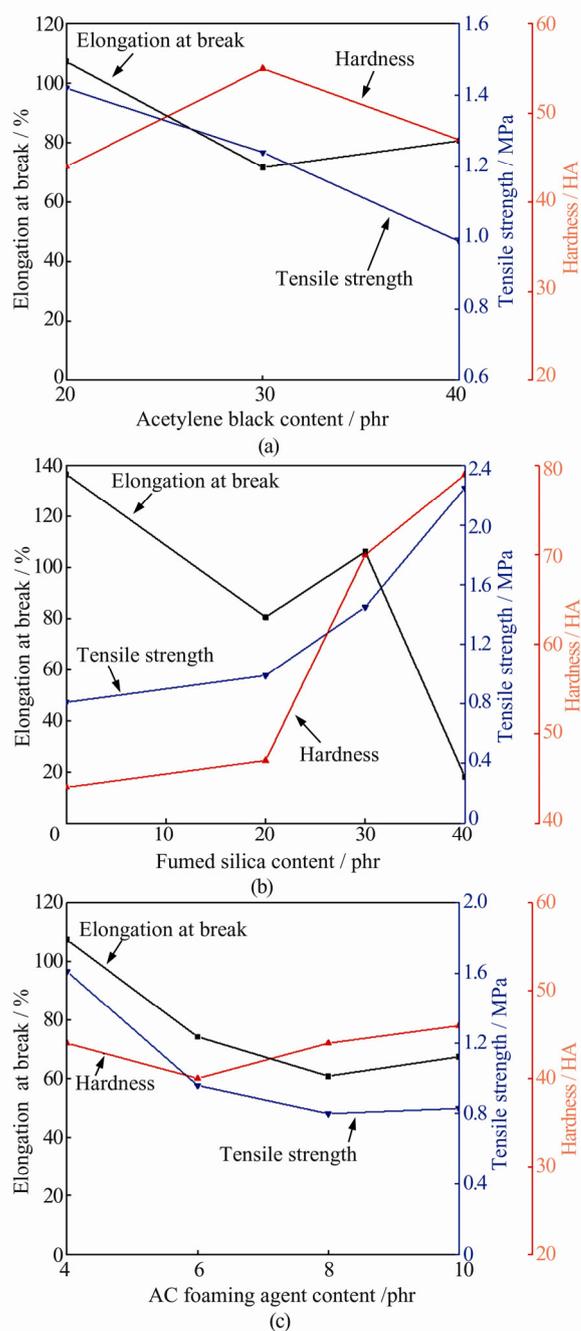


Fig. 4 Mechanical property curves of foamed silicone rubber with (a) acetylene black, (b) fumed silica and (c) AC foaming agent

2.3 Influencing Factors on Electrical Conductive Property

Figure 5(a) shows the electrical conductivity at different acetylene black content. With the increase of acetylene black content, the electrical resistivity decreases. The influence of acetylene black on electrical conductivity becomes not so obvious over 30 phr. The electrical resistivity of silicone rubber greatly decreases from 3 456 k Ω ·mm to 321 k Ω ·mm when acetylene content increase from 20 phr to 30 phr, but rubber with 40 phr acetylene black is 81.5 k Ω ·mm. Enough acetylene black in the silicon rubber usually forms a “ball chain” conductive path and makes the silicon rubber contain conductivity. The acetylene black content at point is named as threshold content. Above this content, the conductivity increase with content would be not so distinguished^[14-16]. Further, the pores structure seems to affect the conductivity little. Even the pores structure of three samples is greatly different, the relationship between the conductivity and pore structure can hardly be summarized.

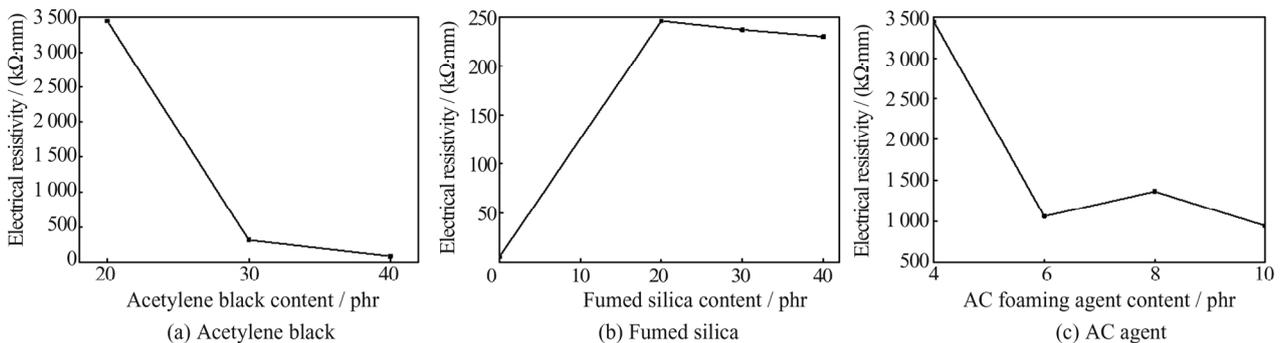


Fig. 5 Electrical conductivity of foamed silicone rubber with different fillers

3 Conclusion

Electrical conductive foamed silicon rubbers were successfully prepared and the influences of conductive fillers, reinforcement fillers, and AC foaming agents were discussed. Firstly, the pore structure was affected by conductive fillers, acetylene black. Acetylene black delays the vulcanization speed of silicone rubbers, thus leads to the aggregation of thermal generated gas, and results in irregular and bigger pores. Reinforcement fillers, more AC foaming agents generate more gas, thus lead to bigger and irregular pores. Secondly, acetylene plays a negative role in mechanical properties, while fumed silica does as positive one. Bigger and irregular pores resulted from higher AC foaming agent content

Figure 5(b) shows the electrical conductivity of silicone rubbers at different fumed silica content. The resistivity increases with fumed silica content, and the resistivity changes little after reaching a certain amount. Due to the high resistivity of silica, when it is added to silicon rubber, the conductive path formed by acetylene black is destroyed, so that the resistivity increased^[14]. When fumed silica content continues to increase, the resistivity reaches the maximum value and changes little.

Figure 5(c) shows the electrical conductivity at different AC foaming agent content. The resistivity of foamed silicone rubber greatly decreases from 4 phr of AC foaming agents to 6 phr, and then varies little as more AC foaming agents added. The reason may be that more pores generated under higher pressure resulted from higher content of AC foaming agent content, and acetylene black in the silicone rubber was extruded with higher forces, thus easy to form conductive path and give lower electrical resistivity. With the continuously increasing of gas, the influence of pressure reaches a maximum point, and the resistivity changes little.

destroy the regular arrangement of polysiloxanes, which affect the mechanical properties negatively. Thirdly, as conductive fillers, higher content of acetylene decreases the electrical resistivity of rubbers reasonably. For its higher resistivity, fumed silica greatly decreases the conductivity of rubbers. Interestingly, AC foaming agents also increase the conductivity of rubbers. We suggest that acetylene black is easily to form conductive path under higher pressure resulted from higher content of AC foaming agents.

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