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Effect of curing temperature on the properties of conductive silicone rubber filled with carbonyl permalloy powder

Xiaoya Wang *, Zhidong Xia, Bo Yuan, Hu Zhou, Zhe Li, Nannan Chen

College of Material Science and Engineering, Beijing University of Technology, No. 100 Pingleyuan, Chaoyang District, Beijing 100124, China

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ABSTRACT

In this paper, conductive silicone rubbers filled with carbonyl permalloy powder (CPP) have been prepared at different curing temperatures. The volume resistivity, crosslink density, tensile strength, elongation at break, Shore A hardness and morphology structure have been investigated. The results indicated that the correlation between electrical conductivity and curing temperature was significant. Volume resistivity of the composite decreased about four orders of magnitude in the range of curing temperature from 125 °C to 225 °C, which was related to the changes of crosslink density, but the change on mechanical properties was relatively small.

1. Introduction

Conductive rubbers as a novel electromagnetic interference shielding material have drawn considerable interest for a long time. In order to achieve good electrical conductivity, numerous researches have been done on fillers, rubber matrix and processing parameters to identify the factors responsible for improved electrical property of conductive rubber.

It is well known that the insulating host material can be made conducting or semi-conducting, depending on the amount of filler particles dispersed in the matrix [1]. Variety rubbers have been used for preparation of such conductive rubbers, including natural rubber (NR) [2], nitrile rubber (NBR) [3], styrene–butadiene rubber (SBR) [4], silicone rubber [5], etc. Among all rubbers, silicone rubber exhibits a list of excellent characteristics including oxidation resistance, thermal stability, climate resistance, low surface tension and unique high permeability because of the unique structure of polysiloxane [6,7].

Fillers also play an important role in the application of conductive rubbers. Common fillers included conductive carbon black [8], graphite [9], carbon fiber [10], metal powder [11], metal-coated inorganic particle [12], etc. However, high conductivity and good magnetic property are the main requirements in the electromagnetic interference shielding application. Hence, pure metal powder or metal-coated material may be a better choice, because of their higher conductivity at lower loading. Metallic magnetic filler materials incorporated in the rubber matrix can impart magnetic property and electromagnetic characteristics to the host in electromagnetic field [13]. This phenomenon has attracted the attention of many researchers. At present, ferromagnetic iron, nickel, and permalloy may be good choices as metallic magnetic filler materials. However, composites filled magnetic filler exhibit good electromagnetic characteristics with their electrical property is not satisfactory.

In order to improve their electrical conductivity, adjustment of the preparation process should also be paid attention. Das et al. reported that the processing parameters, such as mixing time, rotating speed, curing time and pressure, had strongly influence on the electrical conductivity of rubber composite [14].

Curing temperature is one of the most basic parameters in the preparing process. Due to the specific characteristics of silicone rubber, it can be cured in a wide range of temperature. To our knowledge, however, there are few papers concerning the effect of curing temperature on the properties of conductive silicone rubbers (CSRs). In this paper, different curing temperatures were applied with the other process parameters fixed. Electrical and mechanical properties of CSR filled with carbonyl permalloy powder (CPP) were investigated. Moreover, the network structure of CSR was also proposed to identify the relationship between curing temperature, network structure, electrical conductivity and other properties.

* Corresponding author. Tel.: +86 15811255420.
E-mail address: wangxiaoya813@emails.bjut.edu.cn (X. Wang).

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2. Experimental details

2.1. Materials

Methyl vinyl silicone rubber (MVQ) was obtained from Bluestar Silicone Co. Ltd. Shanghai, China. Its average density was 1.08 g/cm^3. Vulcanizing agent, polymethyl hydrogen siloxane (PHMS), was supplied by Li Xiang Organ Silicone Material Co. Ltd. Guangzhou, China. Carbonyl permalloy powder (CPP) with a weight composition of 20–30% Fe and 4% C, was purchased from Jiangyou Hebao Nanomaterial Co. Ltd. Sichuan, China. The particle size range was 1–6 μm with an average particle size of 2 μm. The true particle density and the apparent density of CPP powder were 5.26 g/cm^3 and 1.44 g/cm^3, respectively.

2.2. Preparation of conductive silicone rubber

The compound formulations of pure silicone rubber (PSR) and methyl vinyl silicone rubber filled with carbonyl permalloy powder (MVQ/CPP) were given in Table 1.

According to our earlier literature [15], the preparation process was as follow. Firstly, vulcanizing agent was mixed with MVQ at 15 °C for 2 h in the double planetary mixing equipment. The viscous mixture was poured into a 20×20 cm^2 stainless picture-frame mold with a thickness of 2 mm. The mold was placed in a QLB-25T plate vulcanizing instrument at different curing temperatures (125 °C, 145 °C, 165 °C, 185 °C, 205 °C and 225 °C, respectively). Pressure of 10 MPa was applied and held for 5 min to get a group of PSR sheets.

Then, filler material CPP was stirred with the above-mentioned viscous mixture at 15 °C for 1 h to achieve a uniform dispersion. According to the above vulcanizing procedures and conditions, a group of MVQ/CPP sheets were obtained.

Finally, two group sheets were kept at room temperature (20 ± 5 °C) for 24 h before testing.

2.3. Characterization

2.3.1. Electrical test

The volume resistivity (ohm-cm) of composition samples was measured by YD2511 resistance test equipment with a four-point probe following the CEPS-0002 standard test method. Before tested, the aforementioned MVQ/CPP sheets were cut into 2 mm × 6 mm × 30 mm strips. Volume resistivity data used were the average value of seven samples.

2.3.2. Crosslink density test

In order to study the effect of filler on network structures of silicone vulcanizate at different curing temperatures, the crosslink density was measured by the equilibrium swelling method [16]. Furthermore, the weight of PSR samples should be equal to the weight of the rubbery phase in MVQ/CPP to eliminate the disturbance caused by the different rubbery phase weight of PSR and MVQ/CPP on crosslink density.

Table 1
Formulation of MVQ/CPP and PSR phr.[a]

Sample	Filler	Base gum		Weight fraction of CPP (wt.%)
	CPP filler	MVQ	PHMS	
MVQ/CPP	210	100	5	67.7
PSR	0	100	5	0

[a] phr is the abbreviation of parts per hundred of polymer matrix, which is the weight parts per 100 weight parts of rubber in this study.

A specific procedure is as follows on the basis of literature [17]. Firstly, PSR and MVQ/CPP sheets were cut into small cubes in a certain amount (0.4 ± 0.01 g and 0.13 ± 0.01 g, respectively). These samples were put into excess anhydrous toluene in a sealed vessel at 25 °C for 3 days. After that, the samples were taken out and weighted, then immersed into toluene again. Repeated previous step until their weight kept constant, and then these samples are dried out at 80 °C to constant weight.

According to Flory's equation, the crosslink density (V_e) could be calculated by the following equation,

$$V_e = -2[\ln(1 - V) + V + \chi V^2]/(2V_0 V^{1/3} - V_0 V) \quad (1)$$

where χ is the interaction parameter of polymer and solvent (0.454), V_0 is the molar volume of the solvent (106.7×10^{-3} L/mol, toluene); V, which is calculated by Eq. (2), is the volume fraction of rubbery phase in the swollen molded–cured vulcanizate,

$$V = (M_2/\rho)/[M_2/\rho + (M_1 - M_0)/\rho_s] \quad (2)$$

where M_0 and M_1 are weight of the original sample and swollen weight (g), respectively; M_2 is weight of the rubbery phase in samples; ρ and ρ_s are the density of the vulcanizate and the toluene (0.85 g/cm^3 and 0.866 g/cm^3), respectively.

2.3.3. Mechanical test

Tensile properties were measured according to the standard of ASTM: D412-06ae2 using a tensile testing machine (LLYOD, Lloyd Instruments Ltd., UK) at a crosshead speed of 500 mm/min. Shore A hardness was measured based on ASTM: D2240-05(2010) standard by a Shore A durometer (LX-A, Wenzhou SUNDOO Instrument Co. Ltd., China). The data of mechanical properties were the average value of five samples.

2.3.4. Morphology observation

Scanning electron microscopy (SEM) (S3400, HITACHI Ltd., Japan) was used to observe the distribution of fillers of the composites and the tensile fracture morphology.

3. Results and discussion

3.1. Morphology observation of CPP filler

Morphology of the CPP observed by the SEM was showed in Fig. 1. In addition to spherical CPP particles, there were also some fiber-like CPP particles consisting of many small particles, which resulted from the carbonyl powder process.

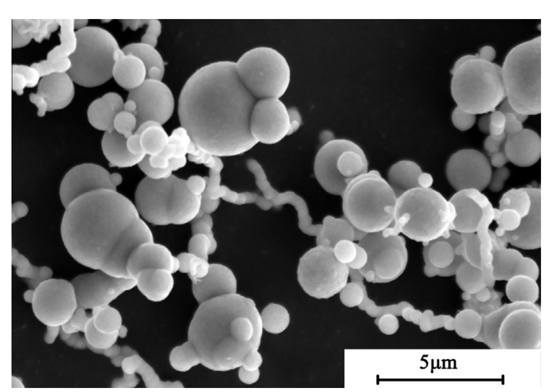

Fig. 1. The morphology of carbonyl permalloy powder (CPP) filler materials.