Research Article

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Dough moulding compound reinforced silicone rubber insulating composites using polymerized styrene butadiene rubber as a compatibilizer

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Abstract: Dough moulding compound (DMC) reinforced polymerized styrene butadiene rubber (SBR) / methyl vinyl silicone rubber (MVQ) composites were prepared, in which MVQ was matrix, DMC was a reinforcement phase and SBR was a compatibilizer. Dynamic thermomechanical analysis (DMA), infrared spectrum analysis (IR) and the effect of SBR and DMC content on mechanical properties, electrical insulating property and compatibility of the composites were investigated. The results showed that the morphology and thermal properties of the composites were improved when dough moulding compound was used as a reinforcement, and styrene butadiene rubber was compatibilizer, and had excellent insulating property with volume resistivity above $4.8 \times 10^{12} \, \Omega \cdot m$.

Keywords: DMC; SBR; MVQ; insulating composites

1 Introduction

The various abilities and power in human production and life are provided by the energy sources. From this view, the energy is the important material foundation of national economy, and depends on its control in the future world [1]. However, the existing energy shortage is becoming more and more serious, and the energy waste is also very serious, thus it has become the focus topic problem [2]. Based on this background, the use of nuclear power to generate energy has become one of the important ways to solve this problem [3, 4]. The development of nuclear power brings a broad development space for the cable materials of distributing the electricity produced by the nuclear power; actively researching and developing cable materials for nuclear power plants are of great significance for the use of nuclear energy [5]. As a material of nuclear power cables, silicone rubber is a kind of cable insulating material with high quality [6]. The thermal degradation resistance of silicone rubber is the best in all kinds of rubbers [7, 8]; silicone rubber also has excellent weather resistance, aging resistance and good electrical insulating properties, which make it irreplaceable by other materials [9]. However, the mechanical properties of silicone rubber are poor [10, 11]; the addition of inorganic filler, such as silica, to reinforce rubber composite systems has been researched for several decades [12–15], thus the need for further research. On the other hand, in recent years scholars at home and abroad have been focusing attention on the research of fiber reinforced rubber composites [16–19]. Therefore, a dough moulding compound (DMC), of which is a uniform mixture mainly made of glass fibers and unsaturated polyester with the excellent mechanical properties and electrical insulation properties [20], was adopted to reinforce methyl vinyl silicone rubber (MVQ) in this work. In addition, polymerized styrene butadiene rubber (SBR) has many branched chains, as a result, the space between the molecular backbones was large, which makes the compatibility between MVQ and DMC is good; and SBR with MVQ and unsaturated polyester in the DMC are all organic compounds, according to the similar chemical materials dissolve mutually theory, thus the SBR was added to improve the compatibility of DMC and MVQ, and the influencing factors on the properties of the DMC / SBR / MVQ composites were investigated.
2 Materials and methods

2.1 Materials

Polymerized styrene butadiene rubber (SBR 1500, styrene and butadiene copolymer in the emulsion polymerization, styrene content is 23%, ML1001+4 viscosity is 51), as a result of our research is the insulation material, so we choose a non-oil-extended rubber SBR 1500 of excellent mechanical properties. The methyl vinyl silicone rubber (MVQ, the number average molecular weight is $5.8 \times 10^6$ and the vinyl content is 0.09 wt%) was supplied by DC Chejue Organic Silicon Aggregation Group (China). Dough moulding compound (DMC), as an industry product, was obtained from Harbin Insulated Material Factory (China); it was a uniform mixture made up of 21% (mass percentage) unsaturated polyester (UP), 8% ethyl methyl ketone peroxide, 1% styrene, 50% calcium carbonate, and 20% short glass fibres. Butadiene rubber (BR 9000, 1,4-cis-content 96%, ML1001+4 viscosity is 45, number-average molecular weight $6.0 \times 10^5$) was purchased from Shanghai Yuda Petroleum Chemical Industry Co., Ltd. (China). Ethylene propylene diene monomer (EPDM Z3080P, ethylene/propylene is 80/20, a ethylene propylene diene tripolymer) was supplied by Jilin Chemical Industrial Ltd (China). Butadiene acrylonitrile rubber (NBR 230, a acrylonitrile butadiene copolymer, ML1001+4 viscosity is 56, acrylonitrile content is 35%, prepared by emulsion polymerization) were supplied by China National Petroleum Corporation (China). Silica (383) was obtained from Qingdao Sweet Silica Co., Ltd (China). Acrylate rubber (ACM 200, ML1001+4 viscosity is 40, an ethyl acrylate copolymer) was supplied by Suining Qinglong Pory-acrylate Rubber Manufactory (China). The other agents are all common commercially available materials and were obtained in the market (China).

2.2 Sample preparation

The fundamental formulation of the blends was 100 phr (parts per hundred rubber) relative to total rubber components (MVQ + other rubber), 45 phr silica, 50 phr DMC, 1.5 phr sulfur accelerator M, 4 phr dicumyl peroxide (DCP), 2 phr zinc oxide (ZnO), 2 phr ferric oxide (Fe$_2$O$_3$), and 1 phr antioxidant D.

The MVQ and SBR were masticated on a XK-160 two-roll mill (Tianjin Electrical Machinery Plant, China) with the nip gap about 0.5 mm, at 45°C for 5 min. After that, adjusting roll temperature to 55°C and nip gap to 1.0 – 2.0 mm, various other ingredients (silica, Fe$_2$O$_3$, DCP, sulphur accelerator M, antioxidant D and ZnO) were added and mixed for 20 min. Then the mixture was mixed with the masticated-DMC about 5 min. Finally the mixture was cured in an electrically heated hydraulic press (XLB-D350 × 350, Shanghai First Rubber Machinery Co., Ltd, China) at 175°C under pressure of 1.2 MPa for 10 min. Heat aging test samples were obtained by putting samples in an aging box (401B, Jiangdu True Power Machinery Co., Ltd, China) at 200°C under normal pressure for 2 hours.

2.3 Physical and mechanical analysis

The mechanical properties of the blends, such as tensile strength and elongation at break, were determined by a universal testing instrument (model CSS-2200, Zhongji Application Technical Institute, China) with a strain rate of 100 mm/min according to the ASTM D638 method. Heat aging of the samples was measured according to ISO 188-1998. For each of the measurements, with the average reported at least five readings were taken, errors in the measurement of mechanical properties were within 10%.

The oxygen index refers to the minimum oxygen concentration required for flame burning in an oxygen-nitrogen mixed gas stream under specified conditions, expressed as a percentage of the volume of oxygen. The oxygen index is high indicates that the material is not easy to burn, on the contrary, the low oxygen index means that the material is easy to burn. The oxygen index of the samples was measured with an oxygen index apparatus (model HC-2, Jiaxing County Analysis Instrument Factory, China) according to ISO 4589:1996.

The electrical volume resistivity, the current impedance of the material per unit volume, was used to characterize the electrical properties of the material. Generally, the higher the volume resistivity is, the better the electrical insulation properties of the material are. In this test, the electrical volume resistivity of the samples was conducted according to IEC 93:1980.

2.4 Dynamic thermomechanical analysis

The dynamic thermomechanical analysis was performed using a dynamic mechanical analyzer (model Q800, TA Instrument Co., USA). The temperatures of the tests ranged from $-150$ to $100°C$, with a $3°C$/min heating rate. The frequency was 1 Hz and the oscillation amplitude was 15 μm. The measurement was carried out using the sin-
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2.5 Morphological analysis

The infrared spectra of the samples were recorded by using Fourier transform infrared spectrometer (FTIR; model Spectrum One, PEKINEIMER Co. Ltd., USA), FTIR spectra were collected after 256 scans at 2 cm$^{-1}$ resolution among the region of 4000-500 cm$^{-1}$ at room temperature.

The samples were fractured in liquid nitrogen, then the fracture surface was sputtered with gold and the fracture morphology of the samples was observed by scanning electron microscopy (SEM, model S-4300, Hitachi Limited, Japan).

3 Results and discussion

3.1 Effect of various rubbers on the mechanical and oxygen index of the composites

The methyl group on silicone rubber can revolve around the -Si-O- bond axis; the spacing of Si and O on neighboring molecules is large and the inter-molecular forces are small, which leads to the poor mechanical properties of silicone rubber. The performance of silicone rubber can be significantly improved by adding silica and DMC, but it is not sufficient. Silicone rubber possesses chemical inertness, according to the chemical materials similar dissolve mutually theory, various rubbers with good mechanical properties were used as a compatibilizer between the DMC and MVQ to improve the mechanical properties of MVQ and the comprehensive performance of the composites, and the blends of MVQ and the various rubbers were the matrices. The effect of the various rubbers on the mechanical properties and the oxygen index of the composites are shown in Figure 1 (DMC / rubber / MVQ = 50 / 20 / 80, the heat aging was done at 200$^\circ$C for 24 hours in air).

The mechanical properties of the DMC reinforced MVQ composites were best when SBR was selected as the compatibilizer in the Figure 1, followed by EPDM, and no test data were obtained due to poor compatibility between NBR and MVQ, resulting in no prepared rubber sheet. The mechanical properties of the composites were poor when the BR or ACM was used as a compatibilizer. It is interpreted as MVQ and SBR are both non-polar rubber, they can combine together well according to the chemical materials similar dissolve mutually theory; in addition, the relative molecular weight of MVQ was smaller than that of SBR, and the SBR has many branched chains, as a result, the space between the molecular backbones was large, which makes the compatibility between MVQ and SBR good; thus the addition of SBR improved the mechanical properties of the composites. And the oxygen index of the sample with the SBR as the compatibilizer was the largest, so the comprehensive properties of the proposed electrical insulating materials were best when the compatibilizer of DMC / MVQ was SBR.

Figure 1: Mechanical properties and the oxygen index of various rubber filled DMC/MVQ composites (DMC/rubber/MVQ = 50/20/80).

Figure 2: FTIR spectra of DMC/SBR/MVQ composites.
Figure 3: Mechanical properties and the oxygen index of DMC/SBR/MVQ composites. (a: 50/0/100, b: 50/20/80, c: 50/25/75, d: 50/30/70, e: 50/40/60, f: 50/50/50, g: 50/60/40).

Figure 4: SEM images of (A) DMC/SBR/MVQ (0/0/100), (B) DMC/SBR/MVQ (60/0/100) and (C) DMC/SBR/MVQ (60/25/75).

Figure 5: Volume resistivity of DMC/SBR/MVQ composites.

Furthermore, it could be seen from Figure 2 that the curve of DMC / SBR / MVQ retained the absorption peaks of C-H of CH₂ (2920 cm⁻¹) or CH₃ (1430 cm⁻¹), C=C (1630 cm⁻¹), and Si-O (1131 cm⁻¹) characteristic peak formed by MVQ and silica. Compared with the MVQ curve, new absorption peak of C=O bond at 1730 cm⁻¹ appeared in the DMC/SBR/MVQ curve, it was caused by C=O bond of the unsaturated polyester in the DMC, and the absorption peak of Si(CH₃)₂ at 802 cm⁻¹ decreased with the addition of SBR and/or DMC, and the absorption peak of C-Si bond appeared in the curve of DMC / SBR / MVQ; it was due to the MVQ reacted with the C=C bond of SBR and generated C-Si bond, it further explained that MVQ and SBR had cross-linked reaction, and thus proved the inevitability of the results in Figure 1.

3.2 Effect of SBR content on the mechanical and oxygen index of the composites

It could be seen from Figure 3 that with the addition of the SBR, the tensile strength, elongation at break and the oxygen index of all samples increased first and then decreased. Compared with the mechanical properties of all samples before and after heat aging, it is obviously observed that the tensile strength, elongation at break and oxygen index of the DMC / SBR / MVQ composites were best when the SBR/MVQ mass ratio was 25/75. It can be interpreted that a small quantity of SBR can not affect the properties of the composites, whereas too much SBR will increase the rigidity of the blends, the SBR is major component when SBR content is 50, 60 phr, the bending and tearing of the SBR is poor, so the properties of the DMC/SBR/MVQ composites get worse.
In addition, compared with Figure 4A, Figure 4B existed obvious separation phenomenon between DMC and MVQ; the fracture surface was rough on a local scale, it showed that the compatibility between DMC and MVQ was poor. However, the DMC dispersed in the rubber evenly in Figure 4C, the fracture surface of the sample was flat and smooth, it indicated that the rubber and DMC combined tightly. It suggested that the addition of SBR improved the compatibility between DMC and MVQ, and the mechanical properties of the composites were improved, too. Therefore, we concluded that the best mass ratio of SBR / MVQ was 25 / 75 when DMC content was 50.

3.3 Effect of DMC content on electrical volume resistivity of the composites

In order to prevent the insulating materials occurring current leakage or breakdown in the process of use, the insulating materials must possess and retain excellent electrical insulating properties. The volume resistivity was used in this experiment to characterize the electrical insulating properties of the blends. DMC has better electrical insulation than rubber matrix, so the addition of DMC can enhance the electrical insulating property of the composites. The effect of DMC content on the volume resistivity of the composites was characterized. It can be seen from Figure 5 that with the increase of voltage, the volume resistivity of all samples increased first and then decreased. The volume resistivity of DMC / SBR / MVQ composites with various mass ratio were all above $4.8 \times 10^{12} \ \Omega \cdot \text{m}$; for 500 V applied voltage, the volume resistivity was largest when the mass ratio of DMC / SBR / MVQ was 60 / 25 / 75, it illustrates that the composites have excellent electrical insulating property. But the electrical insulating property decreased when the DMC content was less than or more than 60. It might be due to too small an amount of DMC were not enough to improve the insulating effect, whereas too much DMC could not disperse homogeneously and even aggregate together, which led to some flaws appearing in the matrix, as a result, the electrical insulating property of the composites decreased.

3.4 DMA analysis of DMC/SBR/MVQ composites

It can be seen from Figure 6A that at the same temperature, the storage modulus ($E'$) of the DMC / SBR / MVQ composites were in the order $60 / 25 / 75$ (mass ratio) $> 60 / 0 / 100 > 0 / 25 / 75$; the $E'$ of the sample with DMC was obviously higher than those without DMC. It can be assumed that the $E'$ represents the elasticity of the materials; the DMC was more rigid than rubber no matter whether in the glass state or high elastic state; the DMC in the matrix could generate chemical cross-linking or physical tangles with the molecular chains of rubbers, on one hand, it could load part of the mechanical stress when the samples were stretched or compressed in the test, on the other hand, it could limit the movement of the molecular chains of rubbers. Therefore, the $E'$ of DMC reinforced composites were significantly higher than those without DMC below $T_g$. In addition, the $E'$ of the DMC / SBR / MVQ ($60 / 0 / 100$) was lower than that of the DMC / SBR / MVQ ($60 / 25 / 75$), it was probably due to the poor compatibility between DMC and MVQ. Moreover, The glass fiber in the DMC, playing a stiff-
ening role, can be well-distributed in rubber blends of SBR / MVQ, the unsaturated polyester in the DMC can cross-link with SBR / MVQ and form a large number of across-link; thus the addition of DMC blocked the motion of molecular chain segments of SBR / MVQ blend rubbers, and therefore the thermal stability of the composites was improved as well. Figure 6A also showed that the turning points in the curves, with the addition of the DMC, gradually moved in the direction of high temperature; it suggests that the addition of the DMC can increase the Tg of the composites.

It can be seen from Figure 6B that there was only a glass transition temperature (Tg) for the DMC / SBR / MVQ composites with various mass ratio; the area of the tan δ peak was widest when the mass ratio of DMC / SBR / MVQ was 60 / 25 / 75; it suggests this was due to limited miscibility of the various components; the SBR and MVQ were only partially miscible. On the other hand, the DMC can fully disperse in rubbers, improving the interface action between components, limiting the movement of the chain segments of rubbers. So, the Tg of DMC / SBR / MVQ (60 / 25 / 75) was higher than that of DMC / SBR / MVQ (0 / 25 / 75).

4 Conclusions

The compatibility and mechanical properties of the DMC / MVQ composites were improved by the SBR as a compatibilizer, and the best mass ratio of DMC / SBR / MVQ was 60 / 25 / 75. The electrical volume resistivities of the composites were all above $4.8 \times 10^{12}$ Ω·m, when the mass ratio of DMC / SBR / MVQ was determined as 60 / 25 / 75, the composites had the largest volume resistivity value and excellent electrical insulating property. Compared with the DMC / MVQ or SBR / MVQ composites, the $E'$ of DMC / SBR / MVQ was the largest and the area of the tan δ peak was the widest. MVQ reacted with SBR and generated C-Si bond, the glass fiber in the DMC, playing a stiffening role, can be well-distributed in the DMA / SBR / MVQ and improve the thermal property of the composites.

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