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Material Behaviour

Effects of rubber/magnetic particle interactions on the performance of magnetorheological elastomers

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Abstract

In this paper, we prepared MR elastomers containing carbonyl iron particles based on silicon rubber without using a magnetic field during curing by γ-ray radiation. The effects of interactions between iron particles and the matrix on the performance of MR elastomers based on silicon rubber, including MR effect and mechanical properties, were investigated. The rubber/magnetic particle interactions were controlled by the modification of the iron surface using different kinds of silane coupling agents and characterized by SEM and DSC. The results showed that tensile strength increased with the increased interaction. However, the MR effect had a certain relationship with the structure of silane coupling agents and this is discussed in detail in relation to the mechanism of the MR effect.

Keywords: MR elastomer; Silicon rubber; Interaction; Microstructure; Mechanical properties

1. Introduction

Magnetorheological (MR) materials are a group of smart materials whose rheological properties can be controlled rapidly by the application of an external magnetic field. MR fluids are well-known smart materials which exhibit Newtonian-like behavior in the absence of a magnetic field and become a weak viscoelastic solid with a certain yield stress when a magnetic field is applied [1].

MR elastomers can be thought of as a new generation of MR materials following on from MR fluids where the matrix is a solid elastic polymer rather than carrier oil. They have controllable magnetic field-dependent modulus rather than field-dependent yield stress and stable performance without the problem of sedimentation of magnetic particles that exists in MR fluids. MR elastomers also have sensitive response to magnetic fields and the time of response of MR elastomers is less than 10 ms [2]. MR elastomers hold promise in adaptive tuned vibration absorbers, stiffness tunable mounts, automobile suspensions [2] and artificial muscles [3].

MR elastomers are mainly composed of magnetic particles and an elastic polymer matrix. The magnetic particles are usually carbonyl iron particles and the reported polymer matrix includes soft silicone elastomers [4–6], poly (vinyl alcohol) [7], gelatin [8], hard

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natural rubber [9] and RTV polyurethane sealant [10]. Typically, magnetic particles are first embedded in the uncured polymer and then the mixture is cured under a strong magnetic field. Hence, the magnetic particles form a special chainlike structure in the direction of the magnetic field. This kind of MR elastomer can be called anisotropic MR elastomer. However, the typical magnetic field needed is very strong, about 8×10^6 A/m [5], which makes the manufacture complicated and difficult to be widely applied.

Recently, M. Lokander etc. [11,12] studied isotropic magnetorheological rubbers that are prepared without applying magnetic fields. They found that isotropic magnetorheological elastomers using large irregularly shaped iron particles have a large absolute MR effect of about 0.4 MPa at 0.24 T.

We prepared MR elastomers containing carbonyl iron particles based on silicone rubber without using magnetic fields during curing by γ-ray radiation. However, the mechanical properties of MR elastomers based on silicone rubber are poor with a high concentration of iron particles. If the iron particles are considered as reinforcement agents, such reinforcement is related to the rubber/filler interactions [13]. Hence, to improve the rubber/filler interaction is an effective method to improve the mechanical properties. However, this will result in a change of microstructure and perhaps it will have some influence on the MR effect. It has been proved that the size of magnetic particles and the fraction of magnetic particles can affect the MR effect whether in a single matrix [11,12] or blend matrix [14]. However, the influence of interaction on the MR effect has not been reported.

In this paper, the rubber/magnetic particle interactions were controlled by the modification of the iron surface using different kinds of silane coupling agent and the effects of interactions on the performance of MR elastomers based on silicone rubber, including the MR effect and mechanical properties, were investigated.

2. Experimental

2.1. Materials

The spherical carbonyl iron particles used were commercial FTF-4 type with size range of 3–5 μm bought from Hebao Nanomaterial Co., Ltd. The silicone rubber used in this study was methyl vinyl gum (MVQ), 110-2, the vinyl content = 0.7% (Dong Jue Fine Chemicals, Nanjing Co., Ltd). Toluene was purchased from Shanghai Suyi chemical reagent company (A.R. grade). Silane coupling agents KH-550 and AH-151were provided by Nanjing Crompton Shuguang Organosilicon Specialties Co., Ltd). Their molecular formula can be seen in Table 1.

Table 1
Molecular formula of silane coupling agents KH-550 and AH-151

Sample	Molecular formula
Vingyltriethoxysilane (AH-151)	$CH_2{=}{=}CHSi(OC_2H_5)_3$
Aminopropyltriethoxylsilane (KH-550)	$H_2N–CH_2–CH_2–CH_2–Si–(OC_2H_5)_3$

2.2. Sample preparation

Firstly, MVQ was dissolved in toluene at 80 °C and then carbonyl iron particles were added and stirred strongly for an hour. The viscous mixture was poured into a mold and dried in an oven at 80 °C. Finally, the mixture was radiated with a Co-60 source at room temperature for 6 h with a dose rate of 167.2 Gy/min to produce unmodified MR elastomers.

Silane coupling agents AH-151 or KH-550 were dispersed in toluene at room temperature. Carbonyl iron particles were then added and stirred for half an hour. Then, the mixture was stirred at 80 °C for an hour. Next, MVQ was directly dissolved into this mixture. The other procedures and conditions were the same as for unmodified MR elastomers.

The main composition of all samples can be seen in Table 2.

Table 2
Composition of MR elastomers with and without silane coupling agents

Composition (g)	MVQ/Fe without modifications	MVQ/Fe/ KH-550	MVQ/Fe/ AH-151
MVQ	50	50	50
Carbonyl iron	150	150	150
KH-550	–	3	–
AH-151	–	–	3

2.3. Differential scanning calorimetry (DSC)

DSC analysis was carried out over the temperature range from −160 to 20 °C at 10 °C/min by means of a Perkin–Elmer Diamond instrument.

2.4. Mechanical measurements

Tensile tests were performed on a Universal Testing Machine (WD-5D, Changchun, China) with a crosshead speed of 50 mm/min at 25 °C. The average of five tests is reported here.

2.5. MR measurements

The magnetorheological effect was evaluated by measuring the dynamic shear modulus with and without an applied magnetic field. The schematic equipment set-up and the principle of the tests can be seen in Ref. [15].

The magnetic field was made by electromagnet and the magnetic induction through samples could be adjusted from 0 to 1 T. The samples tested were $30\times 8\times 3$ mm and sandwiched between a brass and an aluminium plate.

2.6. Morphological characterization of MR elastomers

The morphologies of MR elastomers with different volume content of carbonyl iron particles were observed using a XL30 ESEM at an accelerating voltage of 10 kV. All the samples were coated with a thin layer of gold before SEM observations.

3. Results and discussion

3.1. Microstructure—interaction

It was expected that the addition of silane coupling agents could improve the dispersion of iron particles in the matrix. Scanning electron microscopy provides direct evidence for evaluating the dispersion of iron particles. Fig. 1 shows the SEM microstructure of MR elastomers with and without silane coupling agents. For MR elastomers without silane coupling agents, iron particles seem to be packed into agglomerates of large size and there are obvious gaps between iron particles and silicon rubber (Fig. 1a). However, in Fig. 1b and c with different silane coupling agents, iron particles distribute uniformly in the matrix almost without large agglomerates. The gaps between iron particles and silicon rubber cannot be seen and instead bound rubber exists around each iron particle. The bound rubber can be seen very clearly in Fig. 1d, the SEM microstructure of MVQ/Fe/AH-151 at larger magnification. It can be seen that the addition of silane coupling agents did improve the dispersion of iron particles and the adhesion between iron particles and matrix.

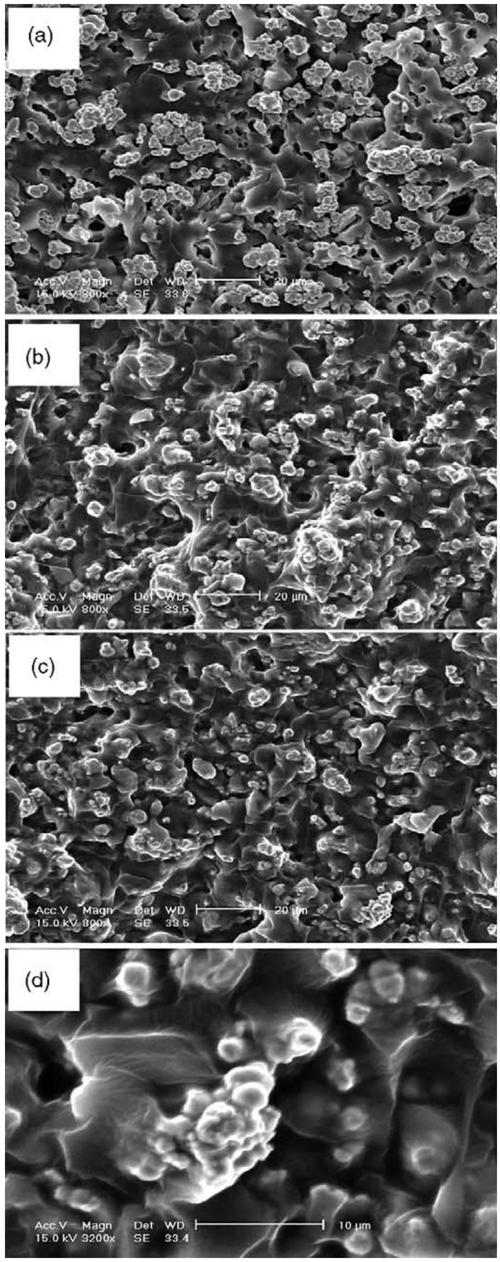

Fig. 1. SEM microstructure of MR elastomers (a) without silane coupling agents (b) with KH-550 (c) with AH-151 (d) magnification of (c).

3.2. DSC results

To further characterize the interactions between iron particles and matrix with different silane coupling agents, DSC measurements were conducted on the samples. Fig. 2 shows the DSC curves of MR elastomers without and with different silane coupling agents. It could be seen that an endothermic peak exists in each curve from −60 to −40 °C. According to the literature [16], the glass temperature (T_g) of pure silicone rubber is under −100 °C and MVQ is a semicrystalline

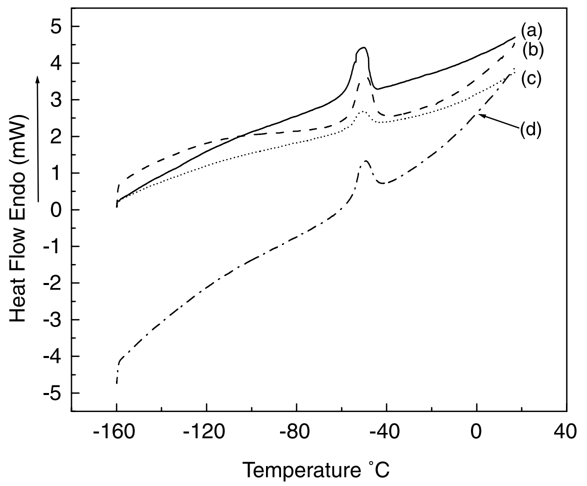

Fig. 2. DSC curves of MR elastomers without and with different silane coupling agents: (a) pure MVQ; (b) MVQ/Fe without modification; (c) MVQ/Fe/KH-550; (d) MVQ/Fe/AH-151.

rubber so this peak is attributed to the melting of crystals. The melt temperatures (T_m) of all samples are listed in Table 3.

It can be seen from Table 3 that the addition of iron particles improves the melting temperature. The gel contents of the samples above were tested by soxhlet extraction using toluene as solvent for 24 h and there is almost no difference between them. It can be concluded that the increase in melting temperature has no relationship with the crosslink density. We think that the interaction between iron particles and the matrix limits the molecular mobility of MVQ chains and, hence, improves the melting temperature. The addition of KH-550 and AH-151 further improve the melting temperature, which proves that they can improve the dispersion of iron particles and interaction between iron particles and the matrix.

It is also observed that the T_m of MVQ/Fe/AH-151 is lower than that of MVQ/Fe/KH-550, which gives evidence that AH-151 may have a plasticizing effect on the silicone rubber matrix. However, KH-550 has no, or at least much less, plasticizing effect on the silicone rubber matrix. This will be mentioned again below.

Table 3
T_m of MR elastomers from DSC

DSC characteristics	Pure MVQ	MVQ/Fe without modifications	MVQ/Fe/KH-550	MVQ/Fe/AH-151
T_m (°C)	−53.95	−50.82	−48.84	−49.97

Table 4
Tensile strength and elongation at break of MR elastomers

	MVQ/Fe without modifications	MVQ/Fe/KH-550	MVQ/Fe/AH-151
Tensile strength (MPa)	0.75	1.10	1.33
Elongation at break (%)	244	283	265

3.3. Mechanical properties

It was assumed that the uniform dispersion of iron particles and stronger interfacial interaction between modified iron particles and silicone rubber matrix should have a significant effect on the mechanical properties. Tensile testing was performed on MR elastomers with and without silane coupling agents and the results are listed in Table 4.

From Table 4, it can be seen that for MR elastomers with silane coupling agents the tensile strength and elongation at break significantly increased. The tensile strength of MVQ/Fe/AH-151 increased by 77%and that of MVQ/Fe/KH-550 increased by 62%, which indicates that AH-151 is better at improving the interaction between iron particles and the matrix and, hence, improving the mechanical properties.

3.4. MR effect

The effects of interaction between iron particles and silicone rubber on the MR effect were also investigated. Fig. 3a and b shows the relative and absolute MR effect, respectively, of MR elastomers with and without silane coupling agents as a function of strength of magnetic field. It can be seen that AH-151 improves the relative MR effect, especially at higher magnetic fields, but has no significant influence on the absolute MR effect. However, both relative and absolute MR effect of MR elastomers with KH-550 decreased in the magnetic field range 200–600 mT.

Both kinds of silane coupling agents improve the dispersion of iron particles and the interface interaction of iron particles and the matrix. Why do they have different influence on the MR effect?

The mechanism of MR elastomers can be understood from the sketch in Fig. 4. Iron particles uniformly disperse in the matrix without application of a magnetic field. Under a magnetic field, iron particles tends to align in the direction of the field and the elastic matrix is deformed, which results in the change of shear modulus, namely so-called MR effect. It can be deduced from the mechanism that the following factors will improve the MR effect. First, the dipole–dipole

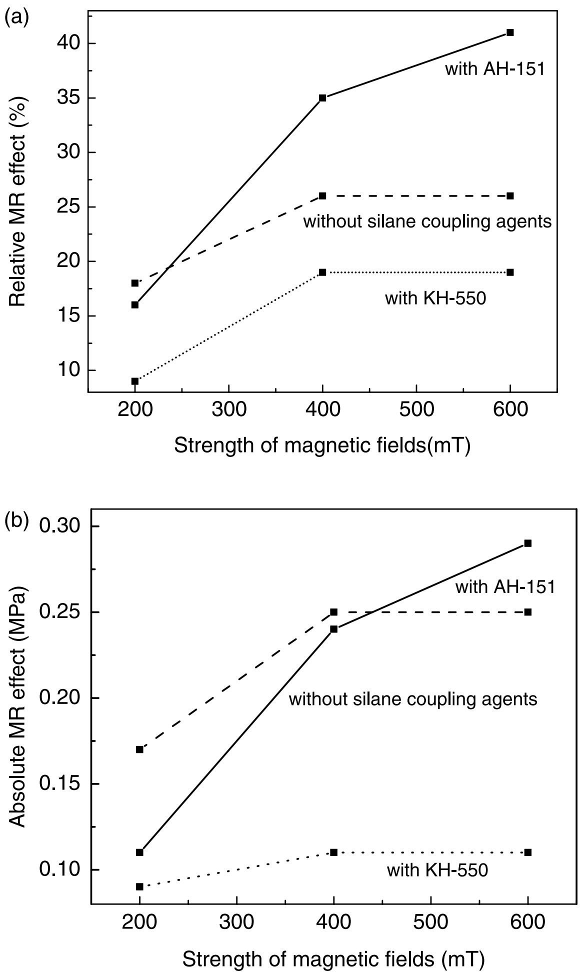

Fig. 3. Relative (a) and absolute (b) MR effect of MR elastomers with and without silane coupling agents as a function of strength of magnetic fields.

action of larger size of iron particles will make it easier to be aligned in the direction of the magnetic field, and thus have higher MR effect. This has been shown in the literature [11]. Secondly, the softer the matrix, the smaller the resistance to iron particles getting aligned in

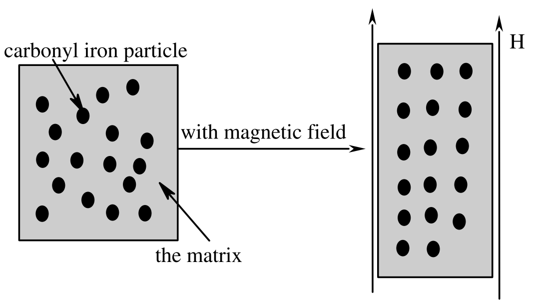

Fig. 4. The sketch of mechanism of MR elastomers under magnetic fields.

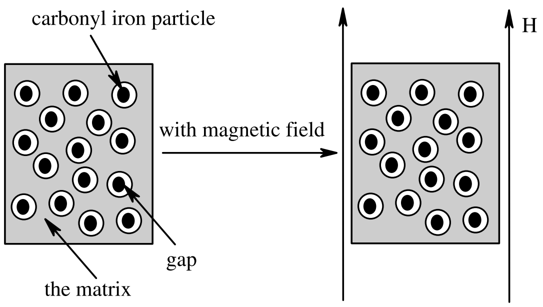

Fig. 5. The sketch of mechanism of MR elastomers with poor interaction between magnetic particles and matrix under magnetic fields.

the direction of the magnetic field. Hence, the addition of plasticizer will improve the relative MR effect [12]. Thirdly, it was considered that the interaction between iron particles and matrix should be helpful to improve the MR effect. If gaps exist between iron particles and matrix, see Fig. 5, magnetic energy would be lost and the microstructure would not change much under the magnetic field so that the shear modulus would have little change.

Both kinds of silane coupling agents improve the dispersion of iron particles and the interface interaction of iron particles and the matrix. However, the uniform dispersion of iron particles decreases the size of iron particles, which will decrease the MR effect. So, KH-151 decreases the MR effect. It can be seen that the strong interaction contributes little to the MR effect compared with the size of magnetic particles. But why does AH-151 improve the relative MR effect of MR elastomers? We think that it has a plasticizing effect on the MR elastomers which makes the matrix softer and helps to improve the MR effect. The plasticizing effect can be seen from the DSC results, which have been discussed above and the zero-modulus of MR elastomers provides further evidence for it. The zero-modulus of all samples can be calculated according to the literature [15] and the results are listed in Table 5. It can be seen that zero-modulus of MVQ/Fe/AH-151 is far lower than that of MVQ/Fe without modification, however, the zero-modulus of MVQ/Fe/KH-550 is little different compared with that of MVQ/Fe without modification.

4. Conclusions

In this paper, we prepared MR elastomers containing carbonyl iron particles based on silicone rubber without using magnetic fields during curing by γ-ray radiation. The effects of interactions between iron particles

Table 5
Zero-modulus of MR elastomers

	MVQ/Fe without modifications	MVQ/Fe/ KH-550	MVQ/Fe/ AH-151
Zero-modulus (MPa)	1.02	0.70	1.01

and the matrix on the performance of MR elastomers, including MR effect and mechanical properties, were investigated.

(1) Two kinds of silane coupling agents KH-550 and AH-151 were used to modify the surface of carbonyl iron particles. The dispersion of iron particles and the interaction between iron particles and the matrix were all improved which can be proved by SEM image and DSC results. The mechanical properties were significantly improved. Tensile testing results showed that the tensile strength of MVQ/Fe/AH-151 increased by 77% and that of MVQ/Fe/KH-550 increased by 62% (Table 5).
(2) Different kinds of silane coupling agent have different influence on the MR effect. AH-151 improved the relative MR effect by 37% under a magnetic field of 0.6 mT. However, KH-550 decreased both relative and absolute MR effect. It can be concluded that good dispersion is disadvantageous to the MR effect while a plasticizing effect is helpful to improve the relative effect. The stronger interaction between iron particles and matrix should be advantageous to improve the MR effect, however, the contribution is not obvious from the experiment results.

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