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Enhancement in Magnetorheological Effect of Magnetorheological Elastomers by Surface Modification of Iron Particles

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In order to obtain magnetorheological (MR) elastomers with high magnetorheological effect, a family of anisotropic rubber-based MR elastomers was developed using a new form of chemical modification. Three different kinds of surfactants, i.e. anionic, nonionic and compound surfactants, were employed separately to modify iron particles. The MR effect was evaluated by measuring the dynamic shear modulus of MR elastomer with a magneto-combined dynamic mechanical analyzer. Results show that the relative MR effect can be up to 188% when the iron particles are modified with 15% Span 80. Besides the surface activity of Span 80, however, such high modifying effect is partly due to the plasticizing effect of Span 80. Compared with the single surfactant, the superior surface activity of compound surfactant makes the relative MR effect reach 77% at a low content of 0.4%. Scanning electron microscope observation shows that the modification of compound surfactant results in perfect compatibility between particles and rubber matrix and special self-assembled structure of particles. Such special structure has been proved beneficial to the improvement of the relative MR effect.

Key words: Magnetorheological elastomers, Shear modulus, Surfactant, Microstructure

I. INTRODUCTION

Magnetorheological (MR) materials represent a kind of intelligent material whose rheological properties can be controlled rapidly by the application of an external magnetic field. Since the MR effect was discovered by Rabinow in 1948 [1], MR materials have become a large family with MR fluids, MR foams, and MR elastomers etc. [2]. The most common MR material is MR fluids [3,4], comprising micron-sized or sub-micron-sized magnetizable particles dispersed in liquid-state materials. MR elastomers are the solid analog of MR fluids, where the oil has been replaced by a rubber material or a gel [5-8]. The obvious advantages from using elastomer materials are that the particles are not able to settle with time and that there is no need to use containers to keep the MR materials in place [9]. Generally, elastomers are cured under a strong uniaxial magnetic field to fix chain-like or columnar structures of magnetic particles in the matrix [10-12]. Under an external magnetic field, the modulus of a MR elastomer can be controlled rapidly and reversibly by an applied magnetic field. Such field-dependant characteristic makes MR elastomers have promising industrial applications, such as tuned vibration absorbers [13,14], stiffness tunable mounts and suspensions [15,16], and variable impedance surfaces [17].

The MR property of MR elastomer is evaluated by the relative MR effect, i.e., the ratio of ΔG to G_0 . Here, G_0 is the shear modulus of MR elastomers when the external magnetic flux density $B=0$ and ΔG is the magnetically induced change of the shear modulus at saturation magnetization of particles. Currently developed MR elastomers have not large enough relative MR effects, which has limited their broad industrial applications. One possible way to improve the MR effect is to increase ΔG by using large content of iron particles. However, too large an amount of particles would result in a high G_0 and a low relative MR effect. Also, the mechanical properties, stability and inoxidizability of MR elastomers would deteriorate rapidly with increasing amount of iron [18,19].

On the other hand, the matrix material also has influence on the MR effect of the MR elastomers. Lokander and Stenberg have showed that the relative MR effect is higher in the softer elastomers [18]. However, MR elastomers based on those soft elastomer matrices, like silicone rubbers [20], gels [21,22], or poly (vinyl alcohol) [11] are usually ill-suited for most load-bearing applications due to their low strength and reduced fatigue life [3]. Further, the addition of plasticizer to MR elastomers has also been proved effective in decreasing the zero-field shear modulus and enhancement of the relative MR effect of materials [14]. However, if there is too much plasticizer, the rubber will become too soft to sustain the load [23]. Recently, Wang *et al.* prepared isotropic MR elastomers and used silane coupling agent to modify iron particles. The results have showed that the modification leads to the uniform dispersion of iron

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particles, which decreases the relative MR effect [24].

With the hope of improving the relative MR effect, we firstly applied surfactants to modify the iron particles. Three different kinds of surfactants, i.e. anionic, nonionic or compound surfactants were applied and their modifying effect on the relative MR effect were compared. Under the modification of surfactants, the influences of both particle-matrix interaction and self-assembled structure of particles on the MR effect are discussed in detail.

II. EXPERIMENTS

A. MR elastomers preparation

The iron particles used are carbonyl iron particles from BASF, Germany. The particles are well spherical with an average diameter of 3.5 μm . The matrix material is natural rubber. The recipe of vulcanization system is: 100 phr natural rubber, 5 phr zinc oxide (ZnO), 1 phr stearic acid, 3 phr sulphur, and 2 phr 2-mercaptobenzothiazole (MBT). The vulcanization system is provided by Hefei Wangyou Rubber Company, China. According to the optimum particle volume reported by Davis [25], the volume fraction of carbonyl iron particles in all of the samples is roughly kept at 30%. Ethanol is purchased from Shanghai Suyi Chemical Reagent Company (AR).

As main branches of surfactant, anionic and nonionic surfactants have different surface activity. Lauryl sodium sulfate (SDS) and sorbitan monooleate (Span 80) are the typical anionic and nonionic surfactants. With enhanced surface activity, the compounds of nonionic and anionic surfactants have a distinct ability to reduce the interfacial tension as compared to the use of single surfactants for practical application. In order to better examine the influence of surface activity, we studied the modifying effect of SDS, Span 80 and compound of SDS-Span 80. Surfactants SDS and Span 80 are provided by Shanghai Chemical Company, China.

The process of modification of iron particles is to disperse surfactant in ethanol at room temperature. Carbonyl iron particles are added and stirred for 10 min. Then, the mixture is stirred at 80 $^{\circ}\text{C}$ for half an hour. According to the conventional rubber-mixing technique, the modified iron particles together with vulcanization system are mixed in a Double-Roll Mill (Taihu Rubber Machinery. Inc. China, Model XK-160) at 40 $^{\circ}\text{C}$ for 15 min. The resulting material is then compressed in a mold. The mold is specially designed for delivery of heat and uniform magnetic field. The temperature is kept at 145 $^{\circ}\text{C}$ for 15 min until the rubber is cured completely. During the cross linking reaction of the natural rubber, the magnetic field is turned on so that the iron particles can be magnetized and then form chains aligned along the field direction. The magnetic field is generated by a magnetic coil, which is capable of applying the external

magnetic flux density of 1 T over the sample. In the experiment, a Tesla gauge (Shanghai Hengtong Magnetoelectricity Co. Ltd, China) was used to test the magnetic flux density. Beside the different content and type of surfactant, all the samples were prepared and tested under the same conditions.

B. MR measurements of MR elastomers

A dynamic mechanical analyzer (DMA) is common equipment for dynamic testing of viscoelastic material. In this work, the DMA (Triton Technology Ltd. UK, Model Tritec 2000B) system was modified to characterize MRE performances by introducing a self-made electromagnet which can generate a variable magnetic flux density up to 1 T. The MR effect is evaluated by measuring the dynamic shear modulus of MR elastomer using a magneto-combined DMA. The specimen, with a dimension of 10 mm \times 10 mm \times 3 mm, is sandwiched between two poles of magnetic field. The direction of iron chains embedded in the specimen is parallel to that of the magnetic field. The testing system applies a fixed oscillatory strain to the specimen and measures the amplitude and phase of the output force, from which stress and dynamic shear modulus can be calculated. The modulus is measured at constant 10 Hz frequency and 3% strain amplitude. The experiment is started at the room temperature, and the increment of temperature of the electromagnet is less than 3 $^{\circ}\text{C}$ throughout the measurement.

C. Mechanical measurements of MR elastomers and microstructure observation

The basic mechanical properties of MR elastomer, such as tensile strength, resilience factor and hardness, are also measured. Tensile strength of the material is tested on JPL mechanical test machine. The sample is "dog bone" with a cross-section of approximately 2 mm \times 10 mm. The tensile speed is 300 mm/min. Resilience factor and hardness of the material are tested on JC-1007 elasticity test machine, LX-A hardness gauge, respectively. All of these apparatus are manufactured by Jiangdu Jingcheng Test Instruments Factory, China. Meantime, the morphologies of MR elastomers and modified particles are observed by a Philips XL30 ESEM, at an accelerating voltage of 5 kV. The morphology of MR elastomers were observed by using a scanning electron microscope (SEM) (model: XL30 ESEM, Philips, Japan) at an accelerating voltage of 5 kV.

III. RESULTS AND DISCUSSION

A. MR effect of MR elastomers

The dynamic shear modulus of MR elastomers is determined by the magneto-combined DMA. Also, the MR effects of MR elastomers without and with different contents of anionic, nonionic or compound surfactants

TABLE I Comparison of mechanical performance of MR elastomers with and without surfactant

Samples	Tensile strength/MPa	Resilience factor/%	Hardness
Without surfactant	7.3	55	46
With 10% Span 80	4.8	48	44
With 10% SDS	6.8	50	48
With 10% compound surfactants	6.5	53	45

are compared. It is noted that all percentages used in the context refer to weight percentages.

1. MR effect of MR elastomers with the modification of SDS

Lauryl sodium sulfate (SDS) is a common hydrophilic anionic surfactant. It has strong ability to reduce interfacial tension. In this part, four samples were fabricated and the iron particles were modified with different content of SDS, i.e., 0, 3%, 6%, 10%, and 15% respectively. It can be seen from Fig.1 that there is a continuous increase (in MPa) in shear modulus G caused by an applied magnetic field. At the magnetic flux density B of 800 mT, the iron particles reaches saturation magnetization and the magneto-induced modulus ΔG reaches the maximum. When the particles have not been modified with SDS, the maximum relative increase in shear modulus ($\Delta G/G_0$), i.e. the relative MR effect, is 45%. Further, experimental results show that the modification of SDS reduces the zero-field shear modulus and enhances the relative MR effect of MR elastomers (Table I). For example, when the content of SDS is 3%, G_0 is 1.7 MPa and $\Delta G/G_0$ is 67%. A possible explanation for the improvement in $\Delta G/G_0$ is due to the better structured iron particles. With strong surface activity, surfactant molecules arrange at the interface of iron and rubber. Diminished boundary tension enables better alignment of iron particles. The reassembled structure of particles is beneficial to the improvement of the relative MR effect.

However, the decreasing tendency of zero-field modulus is not very obvious with the growing content of SDS. For example, the relative MR effect is 64% and the zero-field shear modulus is 1.5 MPa when the content of SDS is 15%. This may be because of the solid nature of SDS.

Meantime, the experimental data demonstrate that the growing content of SDS does not affect the absolute MR effect ΔG . Ginder *et al.* have proved that the magnetically induced change in modulus of MR elastomers is proportional to the product of the saturation magnetization of bulk iron and the volume fraction of the particles [3,10]. In this experiment, the magnetic flux density through the samples is 1.0 T, which enables the iron particles to get fully saturated. Besides this, the iron volume fraction of all the samples remains the same. Therefore, it is understandable that ΔG does not change with the content of surfactant.

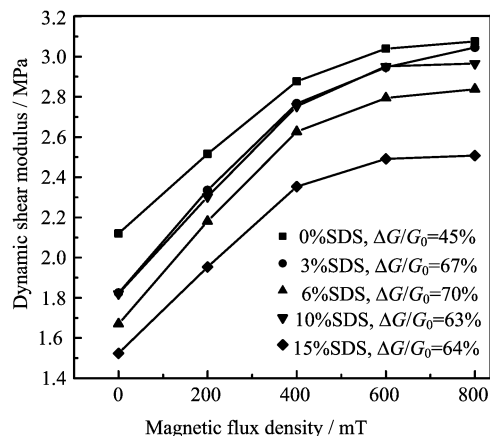


FIG. 1 Dynamic shear modulus of MR elastomers with SDS.

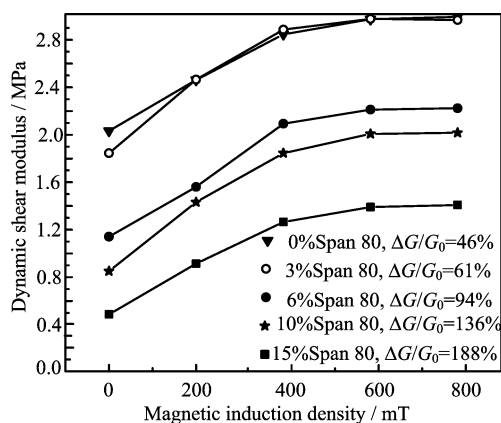


FIG. 2 Dynamic shear modulus of MR elastomers with Span 80.

2. MR effect of MR elastomers with the modification of Span 80

Span 80 is an oil-soluble nonionic surfactant with relative low surface activity compared to SDS. In this group, four MR elastomer samples were fabricated and the iron particles were modified with different content of Span 80. The measurement results show that when the content of Span 80 is 3%, 6%, 10%, and 15%, the zero-field shear modulus G_0 is 1.8, 1.1, 0.8, and 0.5 MPa respectively. The corresponding relative MR effect $\Delta G/G_0$ is 61%, 94%, 136%, and 188% respectively (Fig.2).

Such improvement in the relative MR effect may be partly because of the plasticity of Span 80. The strong oil solubility of Span 80 makes its molecules intermingle with rubber molecules, which softens MR elastomers and reduces the zero-field modulus. However, the weak surface activity of Span 80 is disadvantageous to the uniform arrangement of surfactant molecules at the interface of iron particles and rubber. As a result, the modifying effect of Span 80 is inferior to that of SDS. For example, when the content of Span 80 is 3%, the relative MR effect of MR elastomers is 61%, while at the same content of SDS, the relative MR effect is 67%.

3. MR effect of MR elastomers with the modification of compound surfactants

In order to further examine the influences of surfactants on the MR behavior of MR elastomers, we studied the modifying effect of compound of SDS and Span 80. It is noted that SDS and Span 80 are added with the same content. In this part of experiment, two groups of samples were fabricated. In the first group, the dynamic shear modulus of natural rubber was tested without and with compound surfactants. When there is no surfactant, the shear modulus of cured rubber is 0.92 MPa. When the compound surfactants are mixed into nature rubber at the content of 10%, the shear modulus is 0.93 MPa. Clearly, the influence of physical property of compound surfactants on the shear modulus of materials can be neglected.

In the second group, three MR elastomers samples were prepared with different content of compound surfactants, i.e., 0.4%, 6%, and 12%. Figure 3 shows that when the content of compound surfactants is merely 0.4%, the relative MR effect is 77% and the zero-field modulus is reduced to 1.4 MPa. Therefore, compound surfactants have better modifying effect compared to single surfactants. The reason will be discussed in detail below.

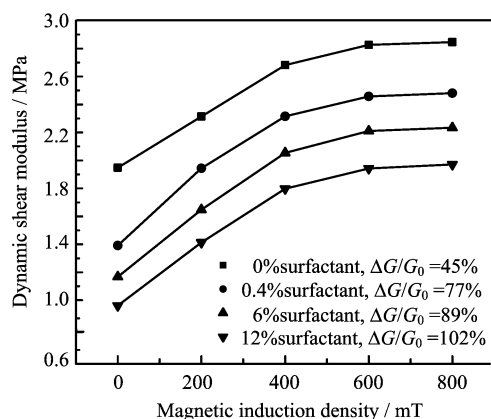


FIG. 3 Dynamic shear modulus of MR elastomers with compound surfactants.

B. Microstructures of MR elastomers

It has been expected that the addition of compound surfactants could improve the compatibility of iron particles and the matrix. Scanning electron microscope (SEM) analysis provides direct evidence for evaluating the compatibility of these two phases. Figure 4 shows the microstructure of the surface of MREs at 10^4 magnitude of enlargement. Figure 4(a) presents the rough surface condition of sample without any modification. Figure 4(b) is the SEM image of samples modified with compound surfactants. It can be seen clearly that the surface of sample with compound surfactants is uniform and smooth and almost no particles or gaps are observed. The process of rubber-iron mixing can be thought of as being that the iron particles soak into rubber media. Chemical modification on the surface of iron particles makes them more hydrophobic and compatible with the matrix.

Further, the modification of compound surfactants leads to a partial microstructure of iron particles. Figure 5 exhibits the microstructure of cross-section condition of samples without (Fig.5(a)) and with compound surfactant (Fig.5(b)) both at 500 enlargement magnitude. Larger particles and bulkier chains in the MR elastomers with surfactant can be clearly observed compared with the MR elastomers without surfactant. This can be explained by the self-assembled structure of iron particles caused by the modification, which can be understood from the sketch in Fig.6. The hydrophilic group of compound surfactant contains oxygen and sulfur atoms bearing lone pair electrons which can form

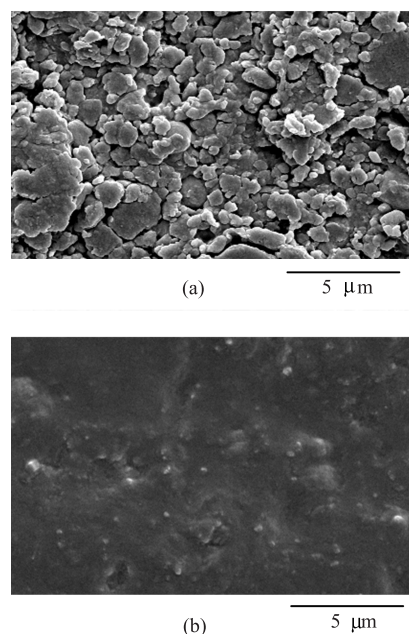


FIG. 4 Surface microstructures of MR elastomers (a) without surfactant and (b) with compound surfactants.

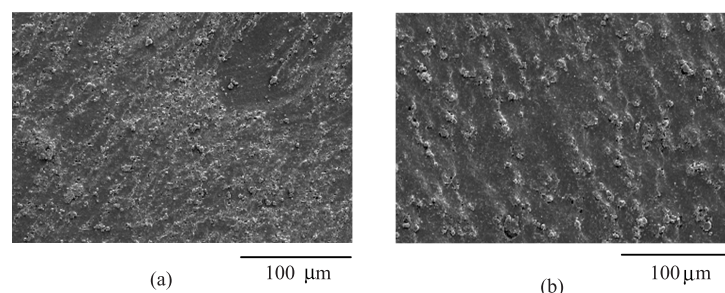


FIG. 5 Cross-section microstructure of MR elastomers (a) without surfactant and (b) with compound surfactant.

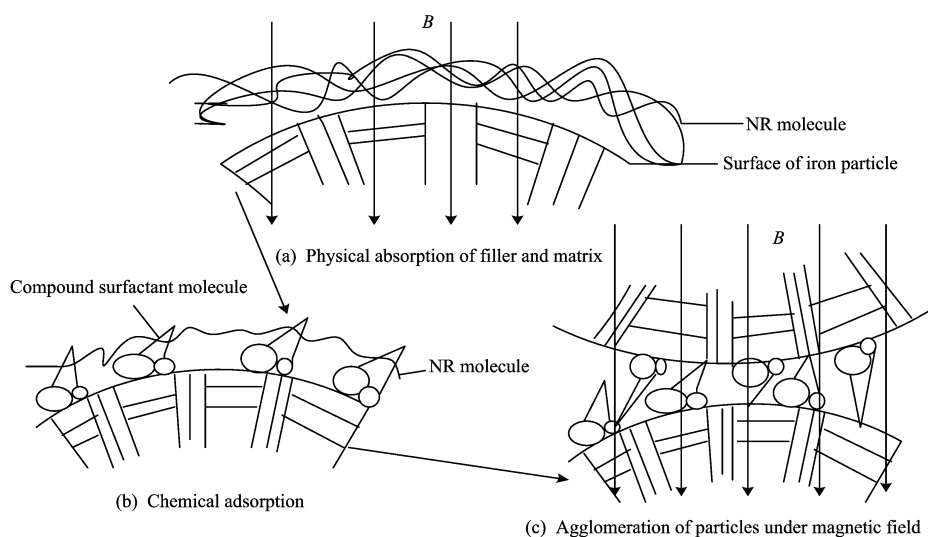


FIG. 6 The mechanism of self-assembled structure of modified particles.

chemical absorption at the surface of iron particles. Besides this, the hydrophobic group of surfactant combines with the rubber molecule by non-polar action before complete vulcanization of rubber. The resultant forces make surfactant molecules arrange at the interface of iron particles and rubber matrix. Such arrangement reduces the boundary tension and allays the resistance against free motion of iron particles through the rubber host. As a result, better structured iron particles are obtained.

Actually, particle size plays a vital role in the material's magneto-rheological behavior. Large or agglomerate particles can decrease the zero-field shear modulus [11,12,23]. Surface modification is conducive to the self-assembly structure of iron particles, which results in the decrease of the zero-field shear modulus of MR elastomers, and therefore, enhances the relative MR effect.

C. Mechanical properties of MR elastomers

Table I shows the mechanical performances of MR elastomers with and without the modification of different kinds of surfactants. When there is 10% Span 80, an obvious decrement in tensile strength and resilience fac-

tor can be observed. This is because of the plasticizing effect of Span 80. When the content of compound surfactants is 10%, there is so little decrease in mechanical properties that it can be neglected.

In addition, the high iron concentrations required in order to get a substantial MR effect may influence the long-term stability of the materials. The inoxidizability of MR materials with high volume of iron dropped rapidly for the reason that the corrosion of iron particles at the surface of material accelerated the oxidation of rubber [18]. Surfactants usually served as mordant to isolate the metal from corrosion substances. Further, SDS and Span 80 are effective corrosion-proofs owing to their linear chains which facilitate the closer arrangement of adsorbed layer than those surfactants with branched chains. Therefore, they are helpful to maintain the chemical and physical stability of materials.

IV. CONCLUSION

In order to prepare MR elastomers with high relative MR effect, this paper considers the influence of surface activity on the MR effect. Anionic, nonionic and

compound surfactants were applied to modify the iron particles and their modifying effect was compared. The results show that: (i) The relative MR effect can be up to 188% when the iron particles are modified with Span 80. Besides the surface activity, the plasticizing effect of Span 80 plays an important role in the enhancement of the relative MR effect. However, such plasticizing effect deteriorates the mechanical properties of MR elastomers. (ii) With stronger surface activity, the modifying effect of SDS is better than Span 80 with the content of 3%. However, the solid nature of SDS is disadvantageous to the improvement of the relative MR effect. Therefore, the relative MR effect does not lead to an increase of SDS. (iii) As for the compounds SDS and Span 80, the effect of their physical nature on the elastomers can be counteracted. The superior surface activity of compound surfactant makes the relative MR effect reach 77% when the surfactant content is only 0.4%. Compound surfactant wraps the iron particles with hydrophobic coating which improves the compatibility of iron and matrix remarkably. Furthermore, the distribution of surfactant molecules at the interface of two phases contributes to the self-assembled structure of iron particles. Such special structure of particles has been proved beneficial to the improvement of the relative MR effect.

V. ACKNOWLEDGMENTS

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