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Radiation Vulcanization of Magnetorheological Elastomers Based on Silicone Rubber

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The fabrication of magnetorheological (MR) elastomers was studied by two vulcanization methods, including heat vulcanization (HV) and radiation vulcanization (RV), were employed to fabricate MRE samples. The dynamical mechanical properties were characterized by using a dynamic mechanic analyzer. In particular, both the MR effect and its durability were investigated. The experimental results showed that RV samples have large magneto-induced modulus, large zero-field modulus, and good durability property of MR effect. To explain these results, cubic deformation and plasticizer migration were analyzed. Large magneto-induced modulus of RV sample results from cubic deformation during vulcanization process. And the plasticizer migration results in better durability of MR effect.

Key words: Magnetorheological elastomer, Radiation vulcanization, Heat vulcanization

I. INTRODUCTION

Magnetorheological (MR) materials, including MR fluids [1], MR elastomers (MREs) [2], MR foams [3], and MR gels [4], are an important branch of smart materials. Among these materials, MREs are generally fabricated by dispersing iron powders into rubber matrix. MREs have both MR effect and good mechanical performance for using rubber as the matrix. Recently, MREs have attracted considerable interest and some applications of MREs on vibration control have been reported [5–10]. In these studies, MREs were used as variable stiffness springs, whose stiffness or modulus can be controlled by an external magnetic field. However, compared with MR fluids, the MREs applications are limited, which are probably due to the shortcomings of MREs performances, such as relatively low MR effect and weak mechanical performance.

MREs are prepared with rubber as their matrix, thus, their properties were strongly dependent on the rubber matrix. Generally, there are two major vulcanization methods: heat vulcanization (HV) and radiation vulcanization (RV). The HV method has been used for hundred years, while the RV method was developed in recent years. For the HV method, vulcanizing agent is needed to be mixed into rubber, and high temperature is also needed to initiate the crosslink action between the molecule of rubber and vulcanizing agent.

For the RV method, vulcanizing agent and high temperature are not needed. High-energy radiation is used to initiate the crosslink between the adjacent molecules of rubber. The RV method is developing rapidly in rubber industry. Compared with the HV method, the RV method has several merits, including low cost and less pollution, in fabricating high-performance MREs. Furthermore, MRE samples prepared with this method have little cubic deformation. It is noted that the study of the RV method on MREs fabrication is very limited. In our group, Wang *et al.* reported the MRE samples fabricated with this method, however, the study is not still in-depth and systematic [11]. In this work, we aim to extend and advance the research by investigating the influence of different vulcanization methods. Two different MRE samples were prepared with different vulcanization methods. Their dynamic properties under different magnetic field were tested by using a dynamic mechanic analyzer (DMA). The MR effect and MR effect durability of two samples were characterized and the experimental results were explained by analyzing the plasticizer migration of two samples. Also, a mechanic model was established to predict the shear modulus of two samples.

II. MATERIALS AND TESTING METHOD

A. MRE sample preparation

The components for MREs fabrication consist of iron particles, silicone rubber, silicone oil, and vulcanizing agent. The iron powders, supplied from BASF (model CN) have the size distributions of $d_{10}=3.5\ \mu\text{m}$,

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$d_{50}=6\ \mu\text{m}$, and $d_{90}=21\ \mu\text{m}$. Methyl vinyl silicone gum (MVQ) 110-2 (Dong Jue Fine Chemicals, Nanjing Co., Ltd.), a kind of high temperature vulcanized (HTV) silicone rubber, was used as the rubber matrix. The vinyl content of the silicone rubber is 0.17% and the mean molecular weight is 620 kg/mol. Double methyl double benzoyl hexane (DMDBH), (formulation: $\text{C}_{16}\text{H}_{34}\text{O}_{42}$), ordered from the Shenzhen Gujia Company, was used as the vulcanizing agent. Methyl silicone oil, viscosity 50 cP (from Shanghai resin factory Co. Ltd), was used as a plasticizer.

The fabrication procedures are discussed below. Firstly, the HTV silicone rubber was heated at 100 °C for an hour. Then the rubber was placed in a Double-roll mill (Taihu Rubber Machinery Inc. China, Model XK-160) and mixed with the iron powders for an hour. Meanwhile, silicone oil and vulcanizing agent were added for mixing together. After the mixing step, the mixture was sent for the pre-structure process, during which the mixture was heated and kept under a magnetic field for some time. Following the pre-structure process, the mold was sent to be vulcanized. In this study, both the HV and RV vulcanization methods were used. In the HV process, a flat vulcanizer (Bolon Precision Testing Machines Co., China, Model BL-6170-B) was used. The vulcanizer can supply heating from 0 °C to 300 °C and pressure from 0 to 50 MPa. The HV of MRE samples was conducted under 160 °C and 10 MPa for 4 min. The RV of MRE samples was conducted by using a Co60 radiation source. The RV reaction was completing by laying MRE sample in the radiating source with radiation dose rate 120 Gky/min for 5 h.

The MRE samples have the same compositions: HTV silicone rubber 100 phr, iron powders 348 phr, silicone oil 16 phr. But HV samples have vulcanizing agent 2 phr and RV samples don't have vulcanizing agent).

B. Measurement of dynamic mechanical properties

In this study, dynamic performances of MREs were measured by using a modified DMA system, where an electromagnetic field was added on a DMA (Triton technology Co. Ltd, UK, model Triton 2000B). The electromagnetic field can generate magnetic fields ranging from 0 to 1 T. The samples for testing are cube, with the size of 10 mm×10 mm×3 mm. During test, the strain amplitude and frequency were set as constant values of 0.67 and 10 Hz, respectively. The testing was conducted at the room temperature of 20 °C.

III. RESULTS

A. MR effect

The magnetic field dependence of dynamic shear modulus of two samples was shown in Fig.1.

It can be seen that the shear modulus increases steadily with the magnetic field until a saturation mag-

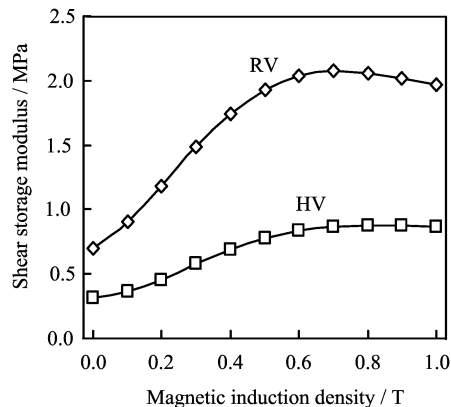


FIG. 1 Magnetic field dependence of dynamic shear modulus of two samples.

netic field, above which the modulus reaches a saturation range. Assume that the modulus without applied test magnetic field is called G_0 , while the value at the saturation magnetic field is G_s . To quantitatively evaluate the MR effect of samples, the magneto-induced modulus ΔG , and the relative MR effect, MR, are used, which are defined as $\Delta G=G_s-G_0$, and $\text{MR}=\Delta G/G_0$. The zero-field and magneto-induced modulus, and relative MR effect of two samples were list in Table I.

TABLE I Zero-field modulus, magneto-induced modulus, and relative MR effect of MRE samples.

Sample	G_0/MPa	$\Delta G/\text{MPa}$	MR/%
HV	0.31	0.56	181
RV	0.70	1.38	197

It can be found a great difference between HV and RV samples. Not only the zero-field modulus but also MR effect of RV sample is obviously larger than those of HV samples.

B. MR effect durability

When used as a stiffness changeable spring, the MR effect is needed to be kept constant with time change. If the MR effect keeps changing with time, the control of mechanical property of MREs will become very complex. To evaluate the MR effect durability of MREs, the MR effect of two samples were tested every week for total three weeks. Figure 2 shows the testing results, where the solid curves are for HV samples and the dashed lines are for RV samples.

It can be seen that the shear modulus of the same sample varies with time. The variation trends of zero-field modulus and MR effect are different. The zero-field modulus increases with time. For example, the zero-field modulus of HV sample at the first week was 0.31 MPa. One week later, its value is increased to

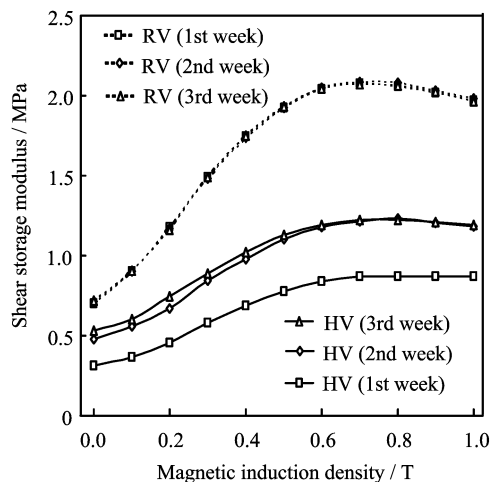


FIG. 2 Shear modulus of two MRE samples tested in different weeks.

0.49 MPa, and then followed by 0.53 MPa at the third week. The same data of RV samples are: first week 0.70 MPa, second week 0.71 MPa, and third week 0.72 MPa. Contrary to the zero-field modulus, the MR effect of HV sample decreases from 181% at 1st week, to 157% at 2nd week and 130% at 3rd week. Similarly, the results for RV samples are: 196% (first week), 192% (second week), and 187% (third week).

To evaluate the MR effect durability, the decrease ratio, DR, was used here. The decrease ratio is the ratio between MR effect decrement with time and the initial value at first week. Generally, lower DR value means better MR effect durability. The DR values of two samples are listed in Table II. Obviously, RV samples have better MR effect durability.

IV. DISCUSSION

A. MR effect

MRE samples prepared with the RV method have less cubic deformation during the vulcanization process than those with the HV method. The HV method needs high temperature; materials are heated and have some expanding. And the air bubbles in materials will also come out from the roll materials when heated. So there is some cubic deformation after HV process. The RV method doesn't need high temperature and consequently the cubic deformation do not happen. This difference between these two methods can be seen from the cross section of different MRE samples in Fig.3. There is a clearly arched shape in the cross section of HV sample while there is just a regular cubic shape in RV sample.

The particles distance of MREs is influenced by the cubic deformation. During the pre-structure process,

TABLE II Initial MR effect and decrease ratio of two samples.

Samples	Initial MR effect/%	DR/%	
		After a week	After two weeks
HV	181	13.30	28.20
RV	197	2.00	4.60

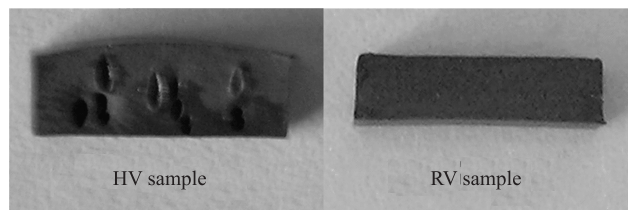


FIG. 3 Cross sections of different MRE samples.

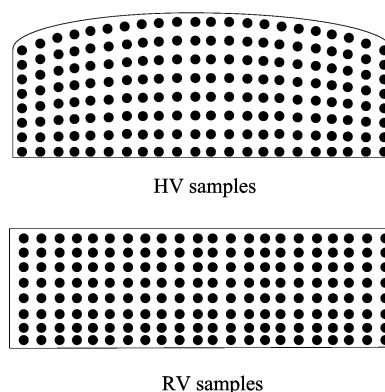


FIG. 4 Sketch of microstructure of different MRE samples.

un-vulcanized MREs are laid under an applied magnetic field. Iron particles are forced by the applied magnetic field to move in the un-solidified matrix and form a regular columnar structure. After this, the MREs are sent to be vulcanized and the rubber matrix is solidified and the positions of iron particles are fixed. If there is a cubic deformation during vulcanization process, the particles will move following the expansion of the rubber matrix and the distance between particles will be increased. The sketch of microstructure of different MRE samples can be seen from Fig.4. Obviously, the particles distance of HV samples is larger than that of RV samples.

The MR effect of MREs is greatly influenced by the particles distance, which has been found by a number of groups. Jolly *et al.* developed an idealized dipole model to study MRE performances based on the assumption that MREs have regular columnar structures [12]. They found that the magneto-induced modulus decreases with particles distance. In other words, samples with larger particles distance have smaller MR effect. As the HV sample has larger particles distance, so

HV sample have smaller MR effect than RV sample.

B. Zero-field modulus

The plasticizer was used to soften the rubber matrix. The more plasticizer is used in materials, the softer the materials are. The plasticizer was mixed into the rubber matrix when prepared. The plasticizer cannot keep constant in the rubber matrix as it diffuses from the place where the plasticizer concentration is high to the place where that is low. As there is a differential concentration of plasticizer between the inside and outside of MREs, plasticizer goes out from the rubber matrix, which is the plasticizer migratory aptitude.

The two samples were prepared under the same conditions except for the vulcanization method. The HV sample was prepared with heating while the RV sample was prepared without heating. It is known that high temperature is good for plasticizer migration. The plasticizer molecule motion is active at high temperature. There is more plasticizer coming out of the HV sample. And there are more plasticizer found on the surface of HV sample. This can be verified from Fig.5, where the two samples were just prepared. It can be seen clearly that there is more plasticizer on the surface of HV sample. When the plasticizer migrates, plasticizer in the central part comes to the surface part firstly. So the plasticizer concentration at the surface of sample is larger than that of central part. As there is more plasticizer migrating from the central part of HV sample, the plasticizer concentration at the surface of HV sample is much larger than that of RV sample. It is simply considered that there is no differential concentration inside the RV sample.

To analyze the problem simply, the HV sample was divided to three parts, the central part and two surface parts, as shown in Fig.6. The total height of whole sample is L_0 , the height of central part $L_2=L_0/2$ and the height of two surface parts $L_1=L_0/4$. With the plasticizer migration, the plasticizer concentrations of

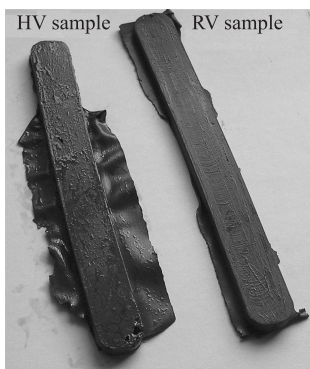


FIG. 5 Photo of two different MRE samples.

three parts are different. The plasticizer concentration of central part is ϕ_2 , that of surface part is ϕ_1 , and that of RV sample is ϕ_0 . As the plasticizer content in the two samples was the same, so

$$\phi_0 V_0 = 2\phi_1 V_1 + \phi_2 V_2 \quad (1)$$

where V_0 is the volume of sample and can be computed as $V_0=SL_0$, V_1 and V_2 are volume of surface and central parts and can be expressed $V_1=SL_1$, and $V_2=SL_2$ separately. So $V_1=V_0/4$ and $V_2=V_0/2$. Then Eq.(1) can be simplified as:

$$\phi_1 + \phi_2 = 2\phi_0 \quad (2)$$

As the modulus of sample directly decreases with plasticizer concentration ϕ , the modulus can be expressed as:

$$G = G_1 - k\phi \quad (3)$$

where G is the modulus of sample, G_1 is the modulus of sample without plasticizer, and k is a constant parameter. Thus the modulus of surface and central parts in the RV sample is:

$$\begin{cases} G_1 = G_1 - k\phi_1 \\ G_2 = G_1 - k\phi_2 \\ G_0 = G_1 - k\phi_0 \end{cases} \quad (4)$$

By simplifying Eq.(4), it is obtained:

$$\begin{cases} k(\phi_1 + \phi_2) = 2G_1 - G_1 - G_2 \\ k2\phi_0 = 2(G_1 - G_0) \end{cases} \quad (5)$$

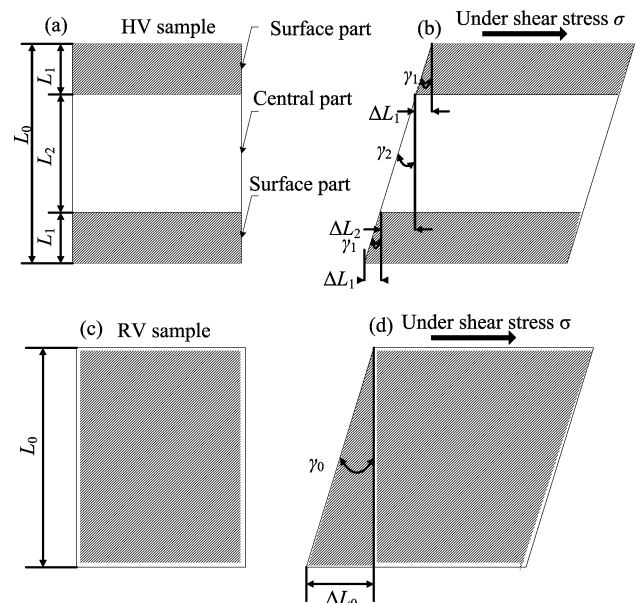


FIG. 6 Sketch of two different MRE samples.

Substitute Eq.(2) into Eq.(5) and simplify:

$$G_1 + G_2 = 2G_0 \quad (6)$$

When samples are under a shear stress σ , the strains of these three parts are: $\gamma_0 = \sigma/G_0$, $\gamma_1 = \sigma/G_1$, and $\gamma_2 = \sigma/G_2$.

The modulus of HV sample G_{HV} is given by:

$$\begin{aligned} G_{HV} &= \frac{\sigma}{\gamma_{HV}} = \frac{\sigma}{\Delta L_{HV}/L_0} \\ \Delta L_{HV} &= 2\Delta L_1 + \Delta L_2 \\ &= 2\gamma_1 L_1 + \gamma_2 L_2 \\ &= \frac{1}{2}(\gamma_1 + \gamma_2)L_0 \\ &= \frac{1}{2} \left(\frac{\sigma}{G_1} + \frac{\sigma}{G_2} \right) L_0 \end{aligned} \quad (7)$$

Thus

$$G_{HV} = \frac{2G_1 G_2}{G_1 + G_2} \quad (9)$$

when

$$G_2 = 2G_0 - G_1 \quad (10)$$

Then

$$\frac{G_{HV}}{G_0} = 2\frac{G_1}{G_0} - \left(\frac{G_1}{G_0} \right)^2 \quad (11)$$

G_{HV} is a function of G_1/G_0 , and the curves of G_{HV}/G_0 versus G_1/G_0 are shown in Fig.7. It can be seen that the value of G_{HV}/G_0 is smaller than 1. thus, $G_{HV} < G_0$. It means the shear modulus of HV sample is smaller than that of RV sample. It has already been known from the test results that the zero-field modulus of HV sample is smaller than that of RV sample.

The fact that HV samples have smaller zero-field modulus is because of the differential concentration of plasticizer. The differential concentration is formed for

the plasticizer migration. High temperature is good for plasticizer migration. And that is the reason why HV samples have more obvious differential concentration of plasticizer inside. So high temperature used during HV process is a key factor to contribute to the difference of zero-field modulus between HV and RV sample.

C. Anti-migratory aptitude of plasticizer

The MR effect and zero-field modulus of MRE samples prepared both with HV and RV method vary with time. The zero-field modulus is found to increase with time while the MR effect shows a decreasing trend with time, as the MR effect is the ratio between magneto-induced and zero-field modulus. The magneto-induced modulus has a litter change with time. So the decrease of MR effect can be understood as the result of the increase of zero-field modulus. The reason why the zero-field modulus increases with time is also because of the migratory aptitude of plasticizer. As there is a differential concentration of plasticizer between the inside of MRE samples and outside, plasticizer goes out of the rubber matrix. So the content of plasticizer in MREs decreases with time and the zero-field modulus increases and the MR effect decreases.

The MR effect of both HV and RV samples decreases with time, the MR effect durability of two MRE samples is different. The RV sample has better MR effect durability property. That means RV samples have better anti-migratory aptitude of plasticizer. To explain this, two processes are needed to be analyzed. One is the vulcanization process and the other is the lay-side process. It has been known that there was a differential concentration of plasticizer inside of HV sample because of plasticizer migration during vulcanization process. And the plasticizer concentration at the surface of HV sample is larger than that of RV sample. After the vulcanization process, samples are lay-aside. During this process, the plasticizer continue to come out. The migration speed is decided by the differential concentration between surface part of sample and outside of sample. As the plasticizer concentration at surface of HV sample is lager, the migration speed of HV sample is lager. So after the same time, there is more plasticizer coming out of the HV sample. It is the reason why the zero-field modulus of HV sample increases more quickly.

The main difference of two vulcanization method is that HV method using high temperature during vulcanization process, which results in the three differences of two MRE samples. Using high temperature, there generate cubic deformation and differential concentration of plasticizer. The cubic deformation results in lager particle distance in HV sample. Larger particle distance leads to smaller MR effect. The differential concentration makes HV sample have lamination inside, two surface parts with lager plasticizer concentration, and one central part with smaller plasticizer concentra-

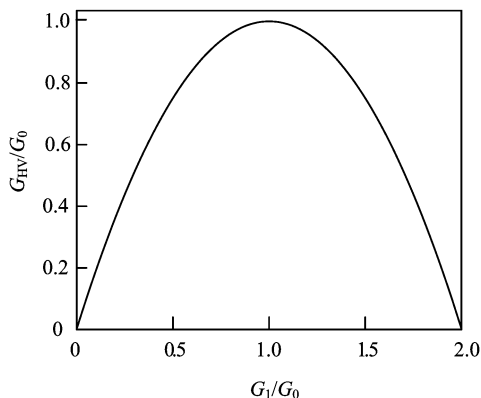


FIG. 7 Curves of G_{HV}/G_0 versus G_1/G_0 .

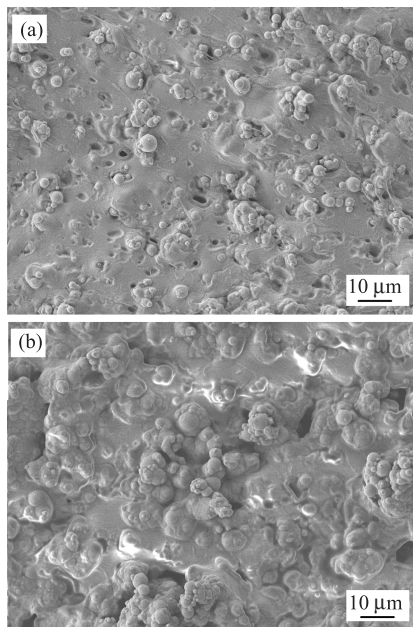


FIG. 8 Interface of the HV sample (a) and RV sample (b) by SEM.

tion. The lamination results in smaller zero-field modulus. The lamination is also the cause of quick plasticizer migration of HV sample during lay-side process, which induces the quick increase of zero-field modulus.

D. The interface of particles and the matrix

Figure 8 shows the interface of MRE samples prepared by HV and RV methods. From Fig.8(a), it can be observed that some cavities exist in the matrix, such as air bubbles. The interface between particles and the matrix is not good. From Fig.8(b), it can be observed that the particles and the matrix are well combined. So, the RV samples have better MR effect durability than the HV samples.

V. CONCLUSION

In this study, two different kinds of MREs samples were prepared with two different vulcanization methods: the HV method and the RV method. The MR

effect, MR effect durability of two samples was experimentally studied. The main results are summarized as below: (i) The RV sample has large magneto-induced modulus. The reason is that RV samples have small particles distance. (ii) The RV sample has large zero-field modulus. HV sample has the differential concentration of plasticizer and air gaps in, so it is loose. (iii) The RV sample has good MR effect durability. HV sample has air gaps for the plasticizer moving. The speed of plasticizer migratory of HV sample is large. So the zero-field modulus increases quickly with storage period.

VI. ACKNOWLEDGMENT

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