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The effect of pre-structure process on magnetorheological elastomer performance

On fabricating magnetorheolgoical elastomer, the mixture of iron particles and un-vulcanized rubber is placed under a curing magnetic field for some time so that iron particles are driven by the magnetic force to form a columnar structure; this process is called the pre-structure process. The microstructure of a magnetorheological elastomer sample is influenced by the pre-structure process, however, few reports address this problem in detail. This paper aims to study the effect of the pre-structure process on the magnetorheological elastomer performance. The pre-structure process is dominated by three influencing factors: magnetic field, curing time and temperature. A variety of magnetorheological elastomer samples were fabricated under different pre-structure conditions and their shear moduli were measured by using a dynamic mechanics analyzer machine. Scanning electron microscope images of these samples were also taken. The results demonstrated the magnetic field-induced modulus shows an increasing trend with magnetic strength before the magnetorheological elastomer samples reach magnetic saturation. The relative magnetorheological effect has an optimal value when the pre-structure field is 110 mT. The effects of the pre-structure time and temperature on the magnetorheological effect were also addressed by using the optimal pre-structure field. These three pre-structure conditions also affect each other. Thus, to fabricate higher-performance magnetorheological elastomer, these pre-structure conditions should be optimized. These results were also explained by study of the particle motion within the matrix.

Keywords: Mangetorheological elastomer; Pre-structure process; Dynamic shear modulus

1. Introduction

Magnetorheological (MR) materials, including MR fluids, MR elastomer and MR foams [1], are an important branch of smart materials. Research on MR fluids has generated intensive studies for the past two decades [1–4], however, a particle settling problem in MR fluids prevents their wider application. To solve this problem, MR elastomers (MREs) were fabricated with rubber as the matrix instead of liquid and iron. MREs have both the MR effect and good mechanical performance from using rubber as the matrix. Recently, MREs have attracted considerable interest and many applications of MRE have been reported [5–10].

Compared with MR fluids, the conventional MREs have a distinct shortcoming in that their MR effects are not strong enough, which limits their wider application. For example, the highest MR effect given in literature is about 133 % [11]. Many groups have being making efforts to improve MRE's performance. Perhaps the easy method is to increase the iron particle volume fraction. Davis used the finite element analysis method to analyze and compute the effect of iron particle content on the MR effect [12]. His theoretical analysis indicated that the optimum volume fraction of iron particles was about 27 %. This result was also experimentally verified by other groups [11, 13–18]. Our group has been doing intensive work to improve MRE performance [11, 19, 20]. The inclusion of the addition of plasticizer in MRE was found to increase the MR effect [11, 19]. Surface modification of the iron particles was found to improve the rubber–particle interaction [20], which consequently improves the MR effect by strengthening the interaction between rubber and particles to decrease the gaps between iron particles and rubber matrix. The effects of curing conditions, including the curing magnetic field and the curing temperature, on MRE performance were also studied [11]. It was found that the MR effect shows an increasing trend with the curing magnetic field strength and the curing temperature.

On fabricating magnetorheolgoical elastomer, the mixture of iron particles and un-vulcanized rubber is cured under a magnetic field for some time. In this process, the iron particles are driven by the magnetic force, and chain-like or columnar structures are formed in the mixture. This process is called the pre-structure (PS) process. There are three main factors that affect the PS process: magnetic field, curing time and temperature. Our previous study [11] indicated that the curing condition plays an important role in MRE performance. However, the comprehensive and intensive studies of the PS condition influences are not ready yet. In this article, the effect of the three factors on the MRE performance will be thoroughly studied. The microstructure of MRE samples under these PS conditions will be observed and the relation between the PS process and the microstructure will be discussed.

2. Experimental

2.1. Materials fabrication

The materials for fabrication of MRE samples consist of iron particles, silicone rubber, silicone oil and vulcanizing agent. The iron powder used was carbonyl iron powder CN bought from the BASF Company. The mean particle size of the iron powder was 6 μm, the density was 3.5 g cm^{-3}, the parameter of BET surface was about 0.14 m^2 g^{-1}, and the saturation intensity of magnetization was 2.1T. 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 620 000. Double methyl double benzoyl hexane (DMDBH), the formulation of which is $C_{16}H_{34}O_{42}$, 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.

Firstly, the HTV silicone rubber was subjected to heat treatment at 100 °C for an hour. Then the rubber was placed in a double-roll mill (Taihu Rubber Machinery Inc. China, Model XK-160) to be throughly mixed with iron powder, silicone, vulcanizing agent and oil for one hour. Then, the mixture was used to fabricate MRE sample based on different PS conditions.

A special Magnet-Heat coupled device was used for the PS process of MRE. As shown in Fig. 1, the device consists of two parts: an electromagnetic device and a hot plate. The electromagnetic device is used to generate a magnetic field, which is controlled by an electrical current and the hot plate is used to control the temperature. During the PS process, the mixture was put into a mold, which was fixed tightly to the hot plate to make sure the mold and the hot plate had the same temperature. Then the mold and hot plate were placed under the electromagnetic field, making sure that the magnetic lines went through the mixture vertically. With this configuration, both the PS magnetic field and the PS temperature can be applied to fabricate MRE samples.

After the PS processing, the mold with mixture was placed on a flat vulcanizer (Bolon Precision Testing Machines Co. China, Model BL-6170-B) for vulcanizing. The vulcanizing was conducted at a temperature of 160 °C for 4 min. After vulcanizing the MRE sample fabrication was completed.

Using the same fabrication processes but different PS conditions, five groups of MRE samples were prepared using the following identical compositions: HTV silicone rubber 100 phr, iron powders 167 phr, silicone oil 11 phr, and vulcanized agent 2 phr. The first group was prepared under different PS magnetic field. The second group was

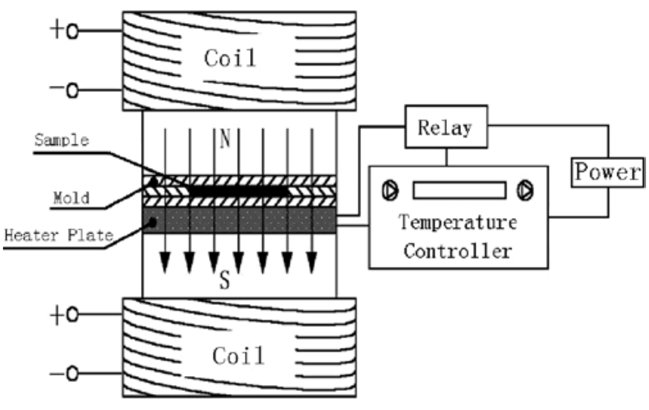

Fig. 1. Sketch of the PS device.

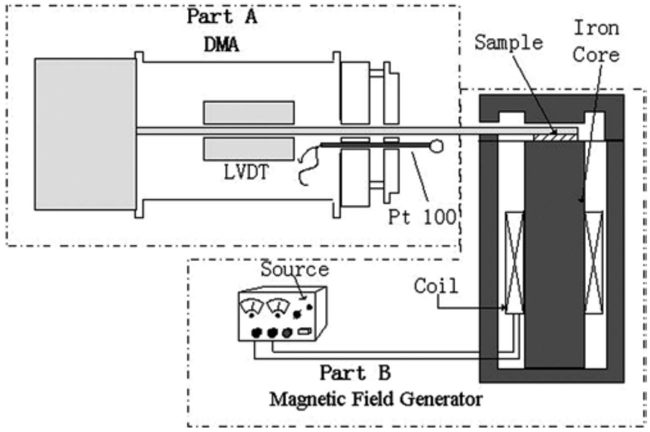

Fig. 2. Sketch of the modified DMA.

prepared with different PS time and the third, fourth and fifth groups were prepared with different PS temperature.

2.2. Dynamic property measurement

The dynamic shear modulus of the MRE samples under various magnetic fields was measured using a modified dynamic mechanics analyzer (DMA), as shown in Fig. 2. In this system, an electromagnetic field generator was added on a DMA (Triton technology Co. Ltd, UK, model Tritec 2000B) to provide the necessary magnetic fields. The Tritec 2000 DMA is equipped with a shaft, a motor and a sensor. One end of the shaft is connected to the sample while the other side is connected to the motor. When the shaft and the sample are driven by the motor with a certain amplitude and frequency, the stress in the sample is measured by the sensor and the strain is derived from the amplitude. Both the shear modulus and the loss factor are calculated from the data of strain and stress. The electromagnetic device, driven by electric current, can generate magnetic fields ranging from 0 mT to 1000 mT. The samples have standard sizes of 10 mm × 10 mm × 3 mm.

The dynamic shear modulus of MREs is time and strain dependent. In this work, the applied strain amplitude and frequency are fixed at 2 % and 10 Hz respectively. The applied magnetic fields vary from 0 mT $\sim$ 1000 mT.

2.3. Scanning electron microscopy

Micrographs of MRE samples fabricated with different PS conditions were taken using a field emission scanning electron microscope machine from FEI Co. (model Sirion200). The accelerating voltage was set at 5 kV. All the samples were coated with a thin layer of gold before examination.

3. Results

The effect of the PS process conditions, including magnetic field, time and temperature, on the MRE performances was experimentally studied and is discussed below.

3.1. Effect of the PS magnetic field

With the same PS time 10 min and temperature 120 °C, 6 MRE samples with various PS magnetic fields, 0, 14, 25, 54, 110, and 350 mT, were fabricated to study the effect of

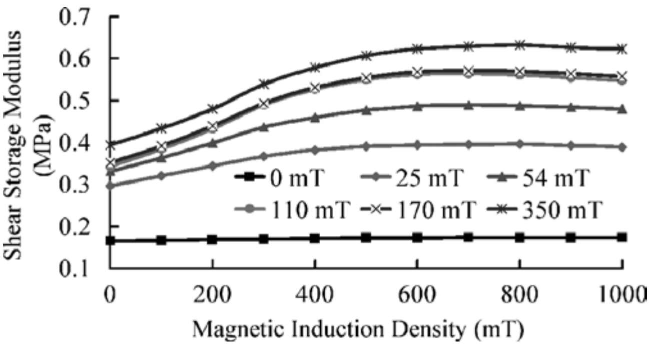

Fig. 3. Shear storage modulus of MRE samples prepared with different PS magnetic field (PS temperature is 120 °C, PS time is 10 min).

Table 1. Samples prepared with different PS magnetic fields.

Samples	1_1	1_2	1_3	1_4	1_5	1_6
PS magnetic field (mT)	0	25	54	110	170	350
Initial Modulus (MPa)	0.17	0.3	0.33	0.34	0.35	0.39
Magneto-induced Modulus (MPa)	0.006	0.1	0.16	0.22	0.22	0.24
MR effect (%)	3.5	33.3	48.5	64.7	62.9	61.5

PS magnetic field. Their field-dependent shear modulus was measured and is shown in Fig. 3. As can be seen, all these MRE samples exhibit similar performance. The modulus of the samples increases steadily with the testing magnetic field until reaching a saturation value. This property is very common and has been successfully explained by the particle interaction theory [1]. The saturation of shear modulus is due to the magnetization saturation of the iron particles. The initial modulus, magneto-induced modulus, and MR effect of these 6 samples are summarized in Table 1.

As listed in Table 1, the initial modulus, or zero-field modulus, increases dramatically with the PS magnetic field. The increase can be explained using Medialia's theory [21, 22], which takes into account the formation of restrained rubber formed during the PS process. The initial modulus can be described in Eq. (1):

$$G_0' = G_{\text{pure}}'(1 + 2.5\varphi_{\text{eff}} + 14.1\varphi_{\text{eff}}^2) \tag{1}$$

where G_0 and G_{pure}' are the moduli of filled materials and pure rubber, respectively, φ_{eff} is the effective volume fraction of filler, which is lager than the volume fraction of filler due to the presence of the restrained rubber. A schematic and picture of the restrained rubber are shown in Fig. 4, the restrained rubber is the rubber trapped in the aggregates of iron powders. The increase in modulus is due to the fact that restrained rubber is protected by the particles around it and shielded from the stress/strain. More restrained rubber means a higher modulus. Restrained rubber is generated because of the particle motion driven by the magnetic force during the PS process. Figure 5 shows the microstructure of the fabricated MRE samples under different PS magnetic fields. Clearly, the samples prepared under stronger PS magnetic fields have more restrained rubber trapped between particles. So samples prepared with stronger magnetic field have a greater initial modulus.

Alternatively, the fiber-like structure, formed by the iron particles and rubber between particles, may strengthen the materials. This fiber like structure has been discussed by Bellan [23], and is formed when particles form a columnar structure. If particles disperse randomly the distance between particles is great. Most of the rubber between particles can be considered as free rubber under stress. But when the particles form a columnar structure, the distance between particles is smaller than the distance before column forming. The rubber between particles is not able to be considered as free. The particles and rubber form a fiber-like structure together. The strength effect of the "fiber" is greater than the strength of the particle, the MREs with particles forming a columnar structure have a larger initial shear modulus. It can be seen from Fig. 5 that samples prepared with higher PS magnetic field have more columnar structure, so samples with higher PS magnetic field have larger initial modulus.

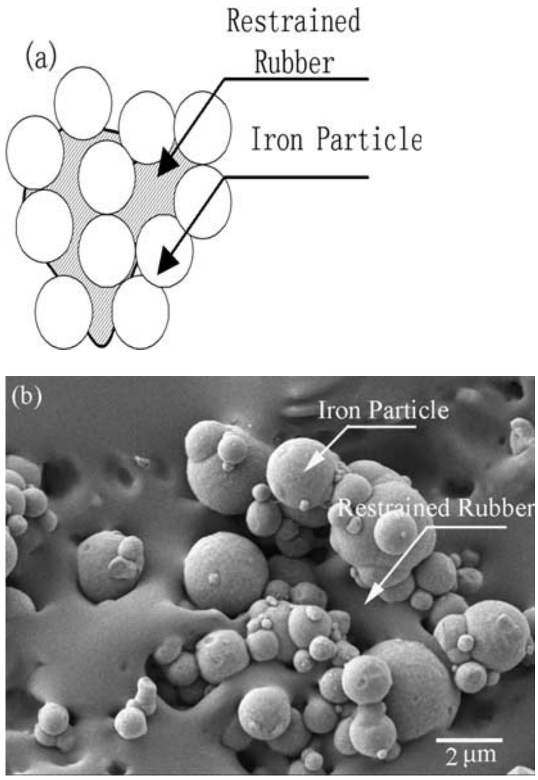

Fig. 4. Restrained rubber, (a) schematic diagram (b) SEM image.

The maximum magneto-induced modulus, defined as the difference between the saturation value of shear modulus and the initial modulus, for all samples was calculated and is shown in Table 1. Similarly, this also shows an increasing trend with magnetic field. This is due to the different dispersion of iron particles of samples prepared with different PS magnetic fields. It can be seen from Fig. 5 that samples fabricated without a PS magnetic field have particles dispersing randomly, while those samples fabricated with PS magnetic field have particles forming regular column structures. The magneto-induced modulus is due to the interaction between iron particles. The more regular the columnar structure, the larger the maximum shear modulus [12]. Therefore samples prepared with high PS magnetic field have greater magneto-induced modulus.

The relative MR effect is the ratio of magneto-induced modulus and initial modulus. As shown in Table 1, the relative MR effect firstly shows a gradually increasing trend until reaching a magnetic field of 110 mT. Above which the relative MR effect decreases steadily. This could be due to a saturation stage for the PS dependence of the MR effect. At this saturation stage, the microstructure of MRE shows little difference with magnetic fields. This was justified in Fig. 5c and d. For our fabricated MRE samples, the maximum relative MR effect is about 60% when the PS magnetic field is 110 mT.

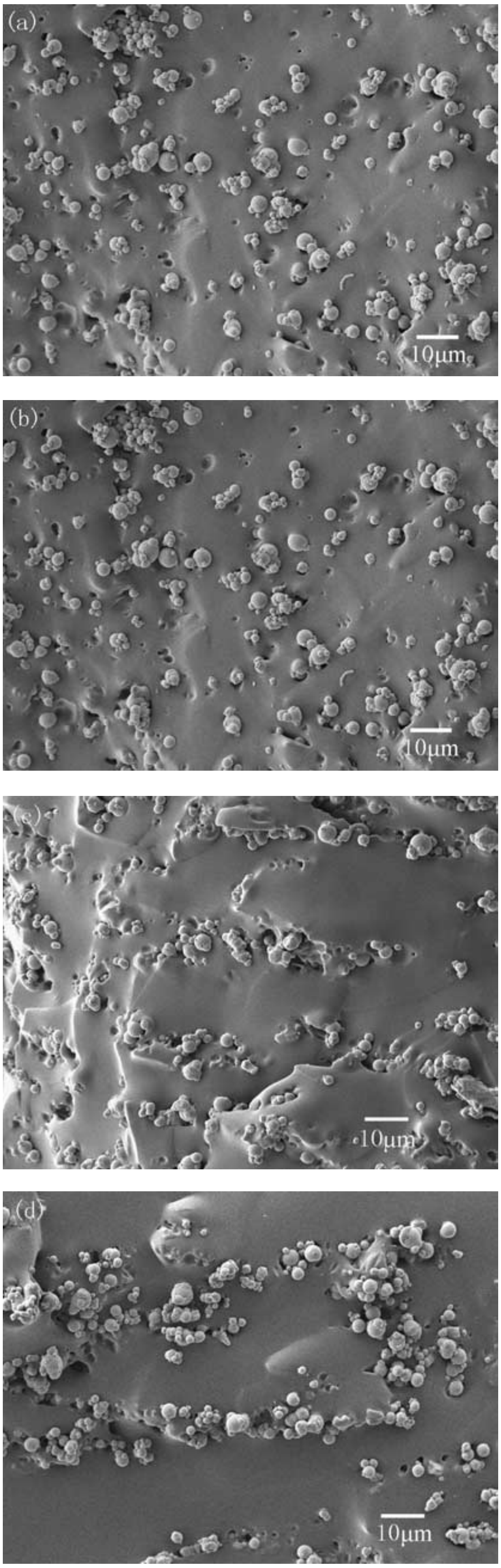

Fig. 5. SEM images of samples with different PS magnetic fields, (a) 0 mT, (b) 54 mT, (c) 110 mT, and (d) 350 mT.

3.2. Effect of the PS time

For the same magnetic field of 110 mT and the same PS temperature of 120 °C, the magnetic field dependent shear modulus at 6 different PS times, 0, 1, 2, 3, 10, and 30 min, is shown in Fig. 6. Similarly, the initial modulus, magneto-induced modulus and MR effect are given in Table 2.

As shown in this table, both initial and magnetic moduli increase steadily with the increase in PS time. That is because of the increase in restrained rubber and columnar structure during the PS process. When the PS magnetic field and the temperature are fixed, PS time is the only factor affecting the particle motion. Longer PS time means particle motion, more restrained rubber generated and more columnar structure formed.

A saturation stage of the PS time dependence of MR effect was also found. When PS time is longer than 10 min, the MR effect will not increase further. Similarly, the appearance of the saturation stage is because there is no further micro-structural change when the PS time is long enough as all particles move to steady positions.

3.3. Effect of the PS temperature

The rubber used as the matrix of MRE is a plastic material before vulcanization. Its plasticity property is a function of temperature. When a higher PS temperature is applied, the flow resistance of the rubber matrix decreases, and so particles are easy to move and form columnar structures, which would result in more restrained rubber and columnar structure. Thus MRE samples fabricated at the higher PS temperature exhibit a higher initial modulus, magneto-induced modulus and MR effect, which can be seen from Fig. 7.

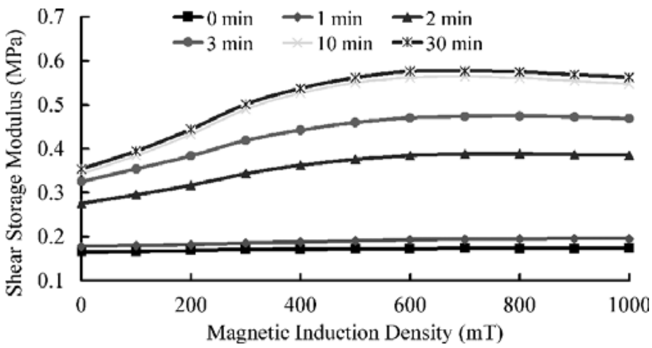

Fig. 6. Shear storage modulus of MRE samples prepared with different PS times (PS magnetic field 110 mT, PS temperature is 120 °C).

Table 2. Samples prepared with different PS magnetic time.

Samples	2_1	2_2	2_3	2_4	2_5	2_6
PS Time (min)	0	1	2	3	10	30
Initial Modulus (MPa)	0.16	0.18	0.28	0.33	0.34	0.35
Magneto-induced Modulus (MPa)	0.008	0.017	0.112	0.15	0.22	0.223
MR effect (%)	5.0	9.4	40.0	45.5	64.7	63.7

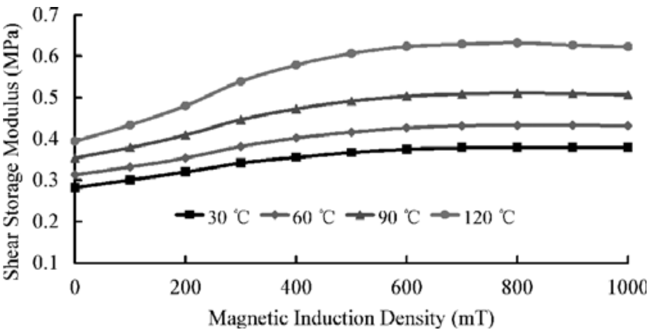

Fig. 7. Shear storage modulus of MRE samples prepared with different PS temperatures (PS magnetic field is 350 mT, PS time is 10 min).

To study the effect of the PS temperature on the MRE effect, four groups of MRE samples were fabricated. The PS temperatures for these four groups were 30 °C, 60 °C, 90 °C and 120 °C. In each group, 6 MRE samples were fabricated with the same PS time (10 min) and, of course, the same PS temperature, but with different PS magnetic fields. The variation of their shear moduli versus magnetic field was measured and is shown in Fig. 8. Obviously, these four samples all exhibit saturation, which is summarized in Table 3. It can be seen from this table that the saturation MR effect shows an increasing trend with the PS temperature. For example, the saturation value of the MRE sample fabricated at a PS temperature of 30 °C is about 35 %, while the MRE sample fabricated at a PS temperature of 120 °C is 64 %.

The increase in saturation value with PS temperature is due to the increase in the average distance between particles. As discussed in Section 3.1 and also as shown in Fig. 5, iron particles of MRE form a regular columnar structure at the saturation stage. In this stage, the magneto-induced modulus is strongly affected by the average distance between particles [12]. Samples with smaller average distances exhibit greater magneto-induced modulus and MR effect. There are two kinds of rubber trapped between particles: the restrained rubber and bound rubber, as shown in Fig. 9a. The restrained rubber described before is trapped between chains of columnar structure. The bound rubber is a layer of rubber molecules covering the iron particles. This bound rubber was first found by Zhang et al. [24] in fabricating MRE by dispersing carbon black in natural rubber. The average distance is decided by the thickness of the bound rubber. It was found that the thickness of bound rubber is influenced strongly by the temperature [25]. When the PS temperature is high, the mobility of the rubber molecules is good, there are few rubber molecules covering the particles, the thickness of the covering is small and the average distance between particles is short, this can be seen in Fig. 9b. Samples with high PS temperature have short average separation of particles and great saturation MR effect.

Table 3. Saturation MR effect of each sample group prepared with different PS temperature.

Sample Group	a	b	c	d
PS Temperature (°C)	30	60	90	120
Saturation MR effect (%)	35	38	43	64

4. Discussion

The above research showed that the magnetic field dependence of shear of MRE is strongly influenced by the particle motion in the rubber matrix during the PS process. In the PS process, particles are driven by the magnetic force to overcome the resistance from the matrix and to move. A columnar structure is formed and restrained rubber is generated. The initial modulus and magneto-induced modulus are affected by the content of restrained rubber and the column

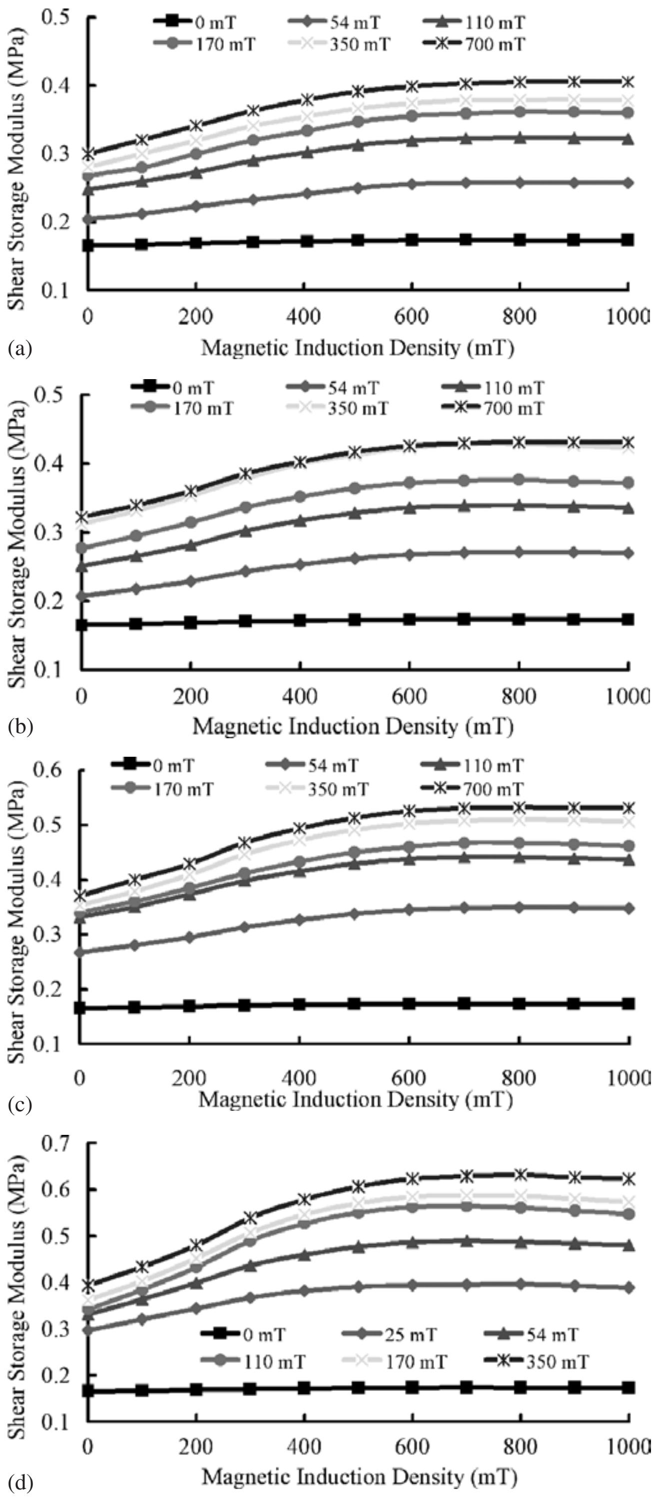

Fig. 8. Shear storage modulus of four groups of MRE samples whose PS temperature was (a) 30 °C, (b) 60 °C, (c) 90 °C and (d) 120 °C.

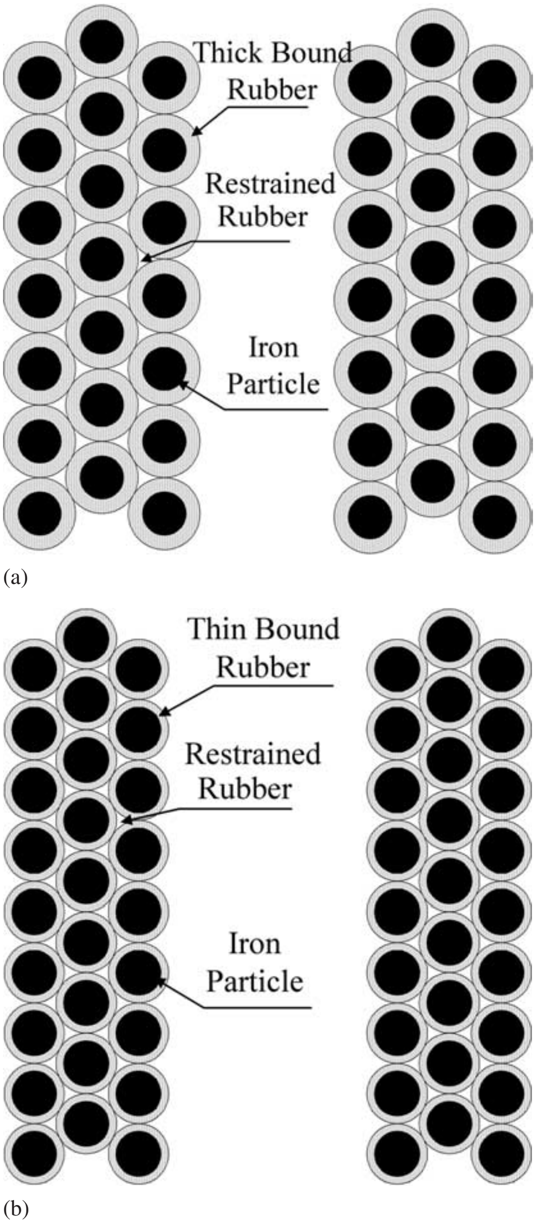

Fig. 9. Sketch of MRE's microstructure (a) MRE is prepared under low PS temperature: having thick bound rubber; (b) MRE is prepared under high PS temperature: having thin bound rubber.

structure in the materials, so particle motion affects the shear performance of MRE.

The particle motion during the PS process is dominated by the PS conditions. The tendency of particle motion is to find a steady position under the PS magnetic field. The column structure was found to be a steady structure of particles [26]. Therefore, the ideal dispersion state for particles is that they all form a regular columnar structure. Then the situation of particle motion during PS is like your drive home from the office after work. The office is the starting point like the initial randomly dispersing state of particles. Home is the end point like the regular column structure of particles. The magnetic force is like the power of your car's engine, the flow resistance of rubber influenced by the PS temperature is like the condition of the road, and the PS time is the length of your drive. The two conditions, PS magnetic field and temperature, decide how quickly the particles move, in the same way that the drive speed is decided by your power of your car's engine and the condition of the road. The PS time, like drive time, determines how long the particles can move for. So larger PS magnetic field, longer PS time and higher PS temperature lead to more particle motion. And there is also a critical value for these PS conditions. When the PS temperature and time are fixed, there is a critical magnetic field larger than which the particle dispersion and MR effect will not change. This can be understood when you drive home with the road condition and driving time fixed. If your car's engine has greater power then you can drive further. If your car's engine is powerful enough you can drive home in time and this power can be considered as critical power. Unless your car's engine is larger than the critical power, you can drive home in time. Similarly there is also a critical temperature and time.

The three PS conditions also affect each other. To get the saturation MR effect, different PS conditions can be used. Strong PS magnetic field and short PS time can be used; weak PS magnetic field and long PS time can also be used. To get greater MR effect, PS conditions should be optimized.

5. Conclusions

The PS process strongly affects the magnetic field dependence of the shear modulus of MRE and this was studied thoroughly in this paper. The influence of three PS conditions was discussed by measuring the shear modulus of samples with different PS conditions. When PS temperature and time are fixed, the initial modulus and magneto-induced modulus increase steadily with the PS magnetic field because the increasing magnetic field results in an increase in restrained rubber and columnar structure content. The relative MR effect increases with PS magnetic field until a saturation value. When the PS temperature is fixed at 120 °C and PS time is 10 min, the saturation MR effect is about 60 % and the critical PS magnetic field is 110 mT. Similar results were also found when studying the effects of the PS time and temperature. These three PS conditions affect each other. Thus, to fabricate higher-performance MRE, these PS conditions should be optimized.

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