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Investigation of the durability of anisotropic magnetorheological elastomers based on mixed rubber

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Abstract
Magnetorheological elastomer (MREs)-based devices often operate at cyclic loading and high temperature conditions, which may cause fatigue and aging problems of MRE materials. This paper investigates the durability properties of MRE materials based on a mixed matrix: cis-polybutadiene rubber (BR) and natural rubber (NR). Six MREs samples were fabricated and their mechanical properties under cyclic loading with a constant strain amplitude of 50% and different aging temperatures were measured. The absolute MR effect, storage modulus ($G'$) and loss modulus ($G''$) of MRE samples after cyclic loading and aging were evaluated by a modified dynamic mechanical analyzer (DMA). The results revealed that the MR effect, $G'$ and $G''$ of all samples depended on the number of loading cycles, but samples which contained different ratios of two rubbers showed distinct properties. $G'$ and $G''$ of all samples which contained only BR change little, but $G'$ and $G''$ of samples which contained NR was large and decreased with the increment of the cycle number. Meanwhile, all their MR effects increased after cyclic loading. The results also revealed that the MR effect, $G'$ and $G''$ of all samples were dependent on the time of aging at different aging temperatures. $G'$ and $G''$ of all samples increased with the increment of aging time, but the properties of samples which contained more NR had better durability properties because their MR effect was higher and decreased more slowly than that of samples which contained more BR. The relationship between the durability properties, and cyclic loading and aging conditions were also analyzed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Magnetorheological (MR) materials are a kind of smart material whose rheological properties can be controlled by an applied magnetic field. The most common MR materials are MR fluids (MRF) whose yield stress and apparent viscosity can be changed from a Newtonian liquid to a non-Newtonian liquid when a magnetic field is applied [1, 2]. MR elastomers (MREs) are a new branch of MR materials. Their mechanical properties, including modulus and damping capability, can be controlled by an external magnetic field. MREs are composed of magnetizable particles (iron particles) and a soft rubber-like matrix [3–7]. MREs are divided into isotropic MREs and anisotropic (chain-like structure) MREs based on different curing conditions. The MR effect of chain-like-structure MREs is larger than that of isotropic MREs under the same strength of magnetic field [8–10].

MREs are promising for many applications, including adaptive tuned vibration absorbers [11], stiffness tunable mounts and suspensions [12], and variable impedance surfaces [13–15]. MRE devices often work in dynamic modes, where the MRE materials undergo repetitive loadings during...
working at wide temperature ranges. Thus, the stability or lifespan of MRE materials plays an important role in practical MRE applications. In other words, it is crucial to investigate the properties of MREs under cyclic loading. However, there is little work to address this important issue of MREs [16–27]. The fatigue and aging mechanisms need an in-depth study. This work aims to study fatigue and aging properties of chain-like-structure MREs, including the storage modulus, loss modulus and absolute MR effect, which have different mass ratios of cis-polybutadiene rubber (BR) and natural rubber (NR) with the evolution of the microstructure of MREs.

2. Experimental details

2.1. Sample preparation

The MRE components include two kinds of different rubbers (cis-polybutadiene rubber (BR) and natural rubber (NR)), carbonyl iron particles (the average radius is 7 μm) and other additives containing carbon black, ZnO, stearin, MDA (4,4'-methyleneedianiline), sulfur, cz (N-cyclohexyl-2-benzothiazole sulphenamide) and plasticizer. Six samples were fabricated and their mass ratios of BR and NR were 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100, respectively. In all samples the mass fraction of the carbonyl iron particles was 60%. The fabrication procedure of MREs was as follows: the iron particles and other additives were firstly mixed into the rubber in a double-roll mill. The resulting material was then compression-molded into a mold in the self-developed magnet–heat coupled device, which is composed of a magnetic field, a mold and a controllable heating system. The mixture is then exposed to the magnetic field and tightly fixed with the heating plate. The magnetic field is capable of applying an external magnetic flux density of 0–1 T over the samples to form chain-like structures. The heating plate is co-terminal with a temperature controller whose temperature can be set in the range from 50 to 200°C. In our experiments, the mixture was exposed to a magnetic field of 800 mT at 160°C for 30 min, after which the sample was cured at 160°C for 20 min under a pressure of 1.5 atm. Then the samples were prepared.

2.2. Cyclic loading

A cyclic loading tester (JC-1008, Jiangdu Jingcheng Test Instruments Factory) was applied in measuring the fatigue properties of MREs after cyclic loading. The samples were tested respectively by cycle-tensile loading with three different kinds of strain amplitudes (50% of the length of the samples) at a frequency of 300 r min\(^{-1}\), which was carried out according to Chinese National Standard (GB 1688-86). All the samples were prepared as dumbbell test pieces according to Chinese National Standard (GB 528-82) to carry out cyclic loading. We used two different shapes and dimensions of MRE samples, including dumbbell and beam-like, for fatigue tests and property testing. The dumbbell samples (6 mm wide and 3 mm thick in the central section) were used for cyclic loading as the first step. Then the beam-like samples (6 mm (L) × 6 mm (W) × 3 mm (T)), which were cut from the dumbbell samples, were used to test properties after cyclic loading. The MR effect of each beam-like sample was evaluated by using our modified dynamic mechanical analyzer (DMA) [5, 6]. The principle diagram of the modified DMA is shown in figure 1. This system is composed of two parts: part A and part B. Part A is a common DMA (Triton Technology Ltd UK, Model Tritec 2000B), while part B is a self-developed electromagnet which can generate a variable magnetic flux density up to 1 T. The specimen was set between the driving shaft of part A and the magnetic core of part B. When the shaft moves, the specimen was deformed in a shear mode. This system applies a fixed oscillatory strain to the specimen and measures the amplitude and phase of the output force, from which the shear storage modulus \(G'\) and loss modulus \(G''\) can be calculated. The morphology of the samples after fatigue testing was observed using SEM.

2.3. Aging

An aging box (401A, Jiangdu Jingcheng Test Instruments Factory) was used to measure the properties of MREs after aging. The MRE samples were put into the aging box for testing at five different temperatures: 70°C, 100°C and 150°C, respectively, for 1, 2, 4, 8, 24 and 32 h, respectively, which were set according to Chinese National Standard (GB 3512-2001). Each sample size was 10 mm length, 10 mm width and 3 mm thickness. Each sample had the fatigue testing conducted three times under the same conditions. The results were then averaged. The MR effect of each sample was evaluated by our modified DMA.

3. Results and discussions

3.1. Durability after cyclic loading

The properties of the samples after cyclic loading depend on the number of cycles. The storage and loss modulus for the six MRE samples with different BR/NR ratios are shown in figure 2. As can be seen from these experimental data, both the storage modulus \(G'\) and the loss modulus \(G''\) for all samples show a decreasing trend with the number of cycles. However, at low cyclic numbers, the initial modulus for the sample is connected to the ratio of NR: the more NR, the larger the
Figure 2. Modulus after cyclic loading of samples with different ratios of BR/NR. (a) (100:0), (b) (80:20), (c) (60:40), (d) (40:60), (e) (20:80) and (f) (0:100).

As shown in figure 1, it could be seen that the relationship between the modulus and the number of cycles is linear from the experimental data. Additionally, it is noted that the samples were fractured when the number of cycles was above $10^5$.

The surface morphology of the MRE sample with the BR/NR ratio of 100:0 after more than $10^5$ cycles at a constant applied strain amplitude (50%) is shown in figure 3. As shown in figure 3, it could be seen that there is a crack on the sample and the chain-like structure around the crack has been destroyed after cyclic loading. An interphase is shown in the middle of figure 3(b) (with suitable magnifications). The result is the same as conventional polymer materials whose propagation path is vertical to the direction of stretching (the same direction of cyclic loading) [17, 28].

The decrease in storage and loss modulus upon increasing the number of cycles is attributed to the filler network breaking down. The trapped or caged rubber in the filler network is released through the large number of cycles [29, 30]. The performances of the samples are obvious because a large number of particles exist in the matrix and the formation of agglomerates or chain-like structures is much easier. As shown in figure 3(b), the crack propagation begins with the interface between the particles and the matrix. The agglomerate is easy to disaggregate when a tensile stress is applied to the sample. Meantime, the bonding force between particles and BR chains is stronger than the force between particles and NR, so the filler network in the sample, whose mass ratio of BR and NR is 100:0, is hardly broken down. Because the force between particles and BR chains is stronger than the force between particles and NR, so the formation of the chain-like structure is more easily broken and the storage modulus $G'$ and loss modulus $G''$ for samples which contain NR always decrease with the increment of fatigue time. When polymer chains
fracture under the high number of cycles, the corresponding storage modulus will decrease. The loss modulus is determined mainly by the hydrodynamic effect of the filler so the strain amplitude dependence will be eliminated. This result also agrees well with [30].

The absolute MR effect is a key parameter for evaluating MRE performance. The MR effect is commonly used to characterize the material. The MR effect is defined as $\text{MRE} (%) = \Delta G_{\text{max}} / G_0$, in which $G_0$ is the initial modulus and $\Delta G_{\text{max}} = G_{\text{max}} - G_0$. $G_{\text{max}}$ is the storage modulus when the particles are at magnetic saturation (800 mT). In this study, the applied magnetic field is from 0 to 900 mT. The relation between the MR effect and magnetic field for different cyclic loadings was shown in figure 4. Obviously, the MR effects of all samples showed a remarkable change with the strain amplitudes and number of cycles. They also increased slightly with the increment of the number of cycles. In addition, the samples which contain more NR have a higher MR effect than samples which contain more BR.

Particle aggregates exist in the chain-like structures, which were seen as the larger carbonyl iron particles, as shown in figure 5. More and more iron particles disperse because of the
increase in cycle numbers which break the interaction between particle aggregates, particles and matrix. The MR effects increased with the increment of the cycle numbers, as the interaction between particles with the same size is larger than that with different particle sizes. The perfect linear relationship between the MR effect and the number of cycles was found based on experimental data.

Figure 6 shows the relationship between MR effect and cycle numbers. The points are experimental results. The line is calculated from a model (which is given at the end of this section) by using the method of least squares. They agree very well.

Figure 7 shows the interface of MRE samples after cyclic loading with the different mass ratios of NR/BR. It can be observed from this figure that the particles and the matrix are well combined, and fewer cavities exist in the sample whose mass ratio of BR/NR is 100:0 than in other samples. So, the sample whose mass ratio of BR/NR is 100:0 has better fatigue properties than other kinds of samples. This finding was proved by experiment.

Based on the above experimental results, an evolution mechanism is proposed to explain the fatigue process. The particle chain structure of the sample is shown in figure 8. Chains are formed with all aggregates and separate particles and wrapped in rubber. As can be seen from this process, a few particles form the aggregates while each particle is enveloped by the inner and outer rubber. The schematic of aggregates is analogous to the carbon-black-filled rubber [30].

The properties of samples are influenced by the interaction forces between particle aggregates, particles and the matrix. It is known that the adhesion between a single particle and the matrix is better than between the aggregates of particles in which cavities are present, so the MR effect of samples after cyclic loading is better because there are more dispersed particles. But the material modulus shows a decreasing trend with the number of cycles because there are more cracks and other defects coming out which can reduce the modulus of the samples.

Figure 9 illustrates the schematic of microstructure evolution for samples during the processing of cyclic loading. Firstly, a large number of particle chains and aggregates exist in the matrix and the trapped or caged rubber is restrained in the filler network. The filler network will be disrupted and restrained rubber is released when the sample is loaded with an external force. The interaction force between the particle aggregates and the matrix will dramatically decrease and the magneto-induced shear modulus of MREs will also fall off. Meanwhile, the MR effect increases because particles separate from the aggregates. When the number of cycles is further increased, the upper rubber chains or the shorter chains between particles will be torn from the particles. The crack propagation will be present along the section of the particles. The circled inner rubber of particles cannot be detached from the particles due to the strong chemisorption and physisorption [17]. So the magneto-induced modulus will decrease further. More and more particles separate from aggregates to enhance the interaction force between particles under the external magnetic field, so the MR effect increases with the increment of cycle number. All samples will fracture when the number of cycles is above $10^5$. Samples which contain more BR have more cycles to reach fracture, so they have better durability properties than samples which contain more NR after cyclic loading. As shown in figure 10, where particle aggregates are in the MREs before the cyclic test, particle aggregates disappear and many particles separate from the particle aggregates after the cyclic loading test. This can
Figure 7. SEM images of the samples with different mass ratios of BR/NR. ((a) 100:0, (b) 60:40 and (c) 0:100).

prove the schematics of microstructure evolution for samples during the process of cyclic loading. This result is also proved by figure 5.

Figure 2 shows that the material modulus and the number of cyclic loadings are consistent with a linear relationship. A fatigue formula of rubber composites is given by [31, 32]

\[ S_{\text{max}} = a + b \log N_f. \]  \hfill (1)

In this study, a modified fatigue formula was developed to explain fatigue properties of MREs:

\[ G = a + b \log N_f + a' N_f + b' \log N_f \]  \hfill (2)

where \( G \) is material modulus, and \( a \) and \( b \) are constants which correlate with material properties and loading frequency. \( a' \) and \( b' \) are correction factors for ferromagnetic particles. \( N_f \) is the number of cyclic loadings. All the constants and correction factors can be calculated from experimental data by using the method of least squares.

3.2. Durability after aging

The storage and loss modulus for the six MRE samples were shown in figure 11. The storage modulus \( G' \) and loss modulus \( G'' \) for all samples increase with the time of aging at a constant aging temperature of 70 °C. However, the increasing trend for the first 8 h is higher than that longer time. Also, the material modulus shows a linear relationship with the aging time when it is longer than 8 h.

On the other hand, the MR effect of the samples shows a decreasing trend with the aging time. The change of MR effects with more NR is less than for the samples containing more BR, as shown in figure 12. This is because NR has better aging properties than BR.

MR effects for all samples decrease with the increment of aging time at 100 °C. However, the samples which contain more BR are more dependent on the aging time than the samples containing more NR, as shown in figure 13. At the aging temperature of 150 °C, which is close to the vulcanization temperature [6], the \( G' \) and \( G'' \) for all samples increase with the aging time, but their MR effects are all
Figure 9. The schematics of microstructure evolution for samples during the process of cyclic loading.

Figure 10. SEM images of the samples before (a) and after (b) the cyclic loading test (the arrow represents the direction of chain-like structure).

Figure 11. Modulus after aging of samples with different ratios of BR/NR. (a) (100:0), (b) (80:20), (c) (60:40), (d) (40:60), (e) (20:80) and (f) (0:100).

strongly dependent on the aging time, as shown in figure 14. This is because rubber becomes harder quickly when it is at the vulcanization temperature, and particle chains and aggregates in rubber are restrained harder after aging, so the MR effects of all samples dramatically decrease with the increment of aging time but the $G'$ and $G''$ for samples increase. After 48 h, the
matrix rubber is totally hardened when all parts of the samples are over-vulcanized, and then the $G'$ and $G''$ for all samples no longer increase and the MR effect become constant (10%), as shown in figure 14.

Figure 15 shows the interface of MRE samples after aging with the different mass ratios of BR/NR at aging temperature 70 °C. It can be observed that there are less cavities existing in the sample when the mass ratio of BR/NR is 0:100 than in other samples after the aging test. The interface between particles and the matrix is not good when there are so many cavities. The other samples have a differential concentration of plasticizer and cavities in them, so they are loose. Particles are not easy to move or to change their positions because the modulus of the matrix becomes large after aging. MR effects also decrease with the increment of time of aging. Also, it shows that the sample which contains more NR has better durability properties than other samples after the aging test.
Figure 15. SEM images of the samples with different mass ratios of BR/NR (the arrow represents the direction of chain-like structure). ((a) 100:0, (b) 60:40 and (c) 0:100.)

Table 1. Aging test data of pure BR MREs.

<table>
<thead>
<tr>
<th>Aging time (log t)</th>
<th>70 (°C)</th>
<th>100 (°C)</th>
<th>150 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MR effect/effect_{max}</td>
<td>MR effect/effect_{max}</td>
<td>MR effect/effect_{max}</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3.556</td>
<td>0.96</td>
<td>0.91</td>
<td>0.54</td>
</tr>
<tr>
<td>3.857</td>
<td>0.93</td>
<td>0.87</td>
<td>0.44</td>
</tr>
<tr>
<td>4.158</td>
<td>0.90</td>
<td>0.77</td>
<td>0.12</td>
</tr>
<tr>
<td>4.459</td>
<td>0.86</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>4.937</td>
<td>0.75</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>5.061</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.238</td>
<td>0.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.414</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Arrhenius correction formula can be used to explain aging properties of MREs:

$$k(T) = BT^{b/R}e^{-(E'_a + bT)/RT}. \quad (3)$$

The relationship between performance and aging time is

$$F_X(t) = k(T)gt. \quad (4)$$

Substituting equation (3) into (4):

$$F_a(t_i) = BT^{b/R}e^{-(E'_a + bT)/RT}gt_i. \quad (5)$$

Using the log function on both sides:

$$\log t_i = a_m - b_{m1} \log T_i + b_{m2}/T_i \quad (6)$$

where $a_m$, $b_{m1}$, $b_{m2}$ are constants, $t_i$ is the time used to get to the critical performance at aging temperature $T_i$. In this study we say that the MR effect reduced to half its maximum is the critical performance.

A random variable $\log t_i$ and independent variables $\log T_i$ and $1/T_i$ are consistent with a binary linear regression model. Then we calculated aging properties of MREs using material constants $a_m$, $b_{m1}$ and $b_{m2}$ which are obtained through experiments. Temperature is kelvin in the formula.

Using pure BR MREs as an example, we did an aging test of samples at three different aging temperatures (70, 100 and 150 °C). Experimental data are listed in table 1 which we used to draw a curve, as shown in figure 16.

So we can fit the data with a Boltzmann correction formula to get values of $t_1$, $t_2$ and $t_3$ and three different aging temperatures (343, 373 and 423 K) to calculate the material constants $a_m$, $b_{m1}$, $b_{m2}$. The Boltzmann correction formula can be rewritten as

$$y = \frac{A_1 - A_2}{1 + e^{(x-x_0)/\delta}} + A_2. \quad (7)$$
Then we can use the same method to get aging data of the other five samples, and they all fit the experimental data very well.

4. Conclusion

In this paper, the durability properties of MREs were investigated through both theoretical and experimental approaches. The results reveal that the MR effect, $G'$ and $G''$ of all samples depend on the number of cycles, but samples which contained a different ratio of BR to NR show distinct properties. $G'$ and $G''$ of all samples which contained only BR change little, but $G'$ and $G''$ of samples which contained NR were large and decreased with the increment of cycle number. Meanwhile, all their MR effects increased after cyclic loading. The material modulus and cyclic number of loading have a linear relationship. The aging properties strongly depend on aging conditions such as time and temperature. The results also reveal that $G'$ and $G''$ of all samples increased with the increment of aging time, but the properties of samples which contained more NR had better durability properties because their MR effect was higher and decreased more slowly than that of samples which contained more BR. The relationship between the durability properties, and cyclic loading and aging conditions were also analyzed.

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