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Investigation on magnetorheological elastomers based on natural rubber

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Abstract Magnetorheological Elastomers (MR Elastomers or MREs) are a kind of novel smart material, whose mechanical, electrical, magnetic properties are controllable under applied magnetic fields. They have attracted increasing attentions and broad application prospects. But conventional MREs are limited to wide applications because their MR effects and mechanical performances are not high enough. This paper aims to optimize the fabrication method and to fabricate good natural rubber based MREs with high modulus by investigating the influences of a variety of fabrication conditions on the MREs performances, such as matrix type, external magnetic flux density, and temperature, plasticizer and iron particles. Among these factors, the content of iron particles plays a most important contribution in shear modulus. When the iron particle weight fraction is 80% and the external magnetic flux density is 1 T, the field-induced increment of shear modulus reaches 3.6 MPa, and the relative MR effect is 133%. If the iron weight fraction increases to 90%, the field-induced increment of shear modulus is 4.5 MPa. This result has exceeded the best report in the literatures researching the MREs on the same kind of matrix. The dynamic performances of MREs were also experimentally characterized by using a modified Dynamic Mechanical Analyzer (DMA) system. The effects of strain amplitude and driving frequency on viscoelastic properties of MREs were analyzed.

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Introduction

Magnetorheological (MR) materials belong to a class of function materials and smart materials, due to their rheological properties can be changed continuously, rapidly and reversibly by applied magnetic fields. Recently, MR materials play important roles in the domain of the automotive vehicles, architecture, and vibration controls, etc. [1].

The most common MR materials are MR fluid (MRF) [2], comprising micro-sized or sub-micro-sized magnetizable particles dispersed in liquid-state materials. Two or three orders of magnitude may happen on the yield stress and apparent viscosity as well as the suspension system changes from Newtonian liquid to non-Newtonian liquid when a magnetic field applied on MRF [3–5].

MRE is the solid-state analogue of MRF, and a new branch of MR materials. The problems existing in MRF such as particle sediment are well overcome via replacing the fluid matrix by solid matrix, such as rubber. MRE is the resulting composites made up by soft magnetic particles embedded in a polymer. The interactions between magnetic particles under a magnetic field result in field-dependent mechanical performances [6, 7]. Having both excellences of MRF and elastomers, MRE has attracted considerable interest recently [8–10]. Some MRE based devices have been reported. For example, a proof-of-concept variable-rate automotive suspension bushing consisting of concentric outer and inner sleeves based on MRE was designed by Ford Research Laboratory [10].

A few research groups used silicone rubber, gels and resin as soft matrix [6, 8, 11, 12], which can be easily processed from liquid precursors; several kinds of MREs are prepared on polymers which are in possession of excellent mechanical properties such as natural rubber and nitrile rubber [10, 13]. However, MREs fabricated with such methods are limited for wide applications because they are difficult to own good bearing capacity and good MR effects at the same time.

This work aims to fabricate high-efficiency natural rubber based MREs. The effects of fabrication conditions (matrix type, external magnetic flux density, and temperature), and materials (plasticizers and iron particles) on MRE performances were experimentally investigated. Dynamics properties of the fabricated MREs were also characterized and analyzed (Fig. 1).

Experimental

Preparation of MRE materials

The fabrication of MREs consists of three major steps: mixing, forming pre-configuration and sulfuration. The mixture is processed with conventional rubber-mixing techniques. A Double-Roll Mill (Taihu Rubber Machinery Inc. China, Model XK-160), is used to fabricate rubber. When the machine is running, two rolls are rotating on opposite directions with different speeds whilst the roll gap can be set in a very small scale. The massive natural rubber on the rolls is subjected to strong extrusion pressure and shear force. Through the rolls uninterrupted rotating, the molecular chains in natural rubber are breakdown, and the natural rubber losses its elastic and becomes viscous body gradually. So crosslinkers and processing aids, the carbonyl iron particle and plasticizers can be easily added into the natural rubber. The resulting material is then compression-molded into a mold in the self-developed Magnet-Heat Coupled Device, as shown in Fig. 2. It is composed of a magnetic field, a mold, and a controllable heating system. The MRE sample is in the mold which is exposure to the magnetic field and tightly fixed with heat plate. The magnetic field is generated by a magnetic coil, which is capable of applying the external magnetic flux density of 0 to 1 T over the samples. The heat plate is conterminal with a temperature controller whose temperature can set in the range from 50 °C to 200 °C. During the pre-configuration stage, the heating system and the magnetic field are both turned on so that both the temperature and the external magnetic flux density can be set properly. The particles are magnetized and then form chains aligned along the field direction. 30 min later, the procedures of forming pre-configuration is finished. After shutting down the magnetic field, the temperature is raised to 153 °C. At this condition, the sample is on sulfuration for 15 min. Then the MRE based on natural rubber is prepared. The used carbonyl iron particles are supplied by BASF, Germany, model CD , the particle size distribution: d10 = 3 μm, d50 = 6 μm, d90 = 11 μm. The natural rubber, plasticizers and other additives are provided by Hefei Wangyou Rubber Company, China. The main ingredients in plasticizers are vaseline and paraffine.

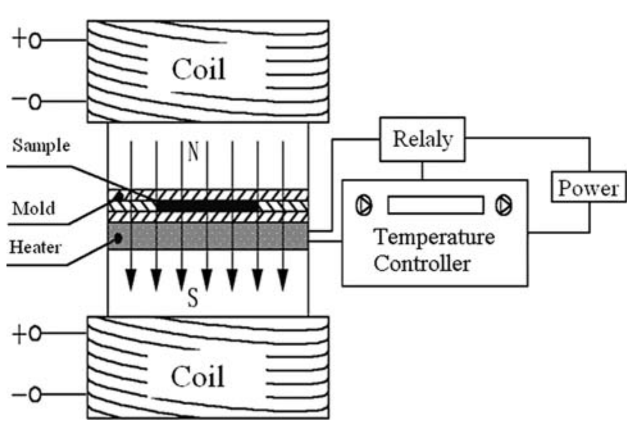

Fig. 1 The sketch map of self-assembled magnet-heat coupled device. The dimensions of sample in the mold are 80 mm × 80 mm × 3 mm (length, width and thickness)

For the purpose of comparison, other MRE samples based on silicone rubber matrix are also prepared. The iron particle, Dimethyl-silicon oil (Shanghai Resin Factory, China, with the viscosity of 300cp) and RTV silicone rubber (Xida Adhesives Factory, China, Model 704) are mixed together, then the hybrid is put into the mold under the magnetic flux density of 1 T, for curing up to 24 h at room temperature.

In the experiment, a Tesla gauge (Shanghai Hengtong Magnetoelectricity Co. Ltd, China) is used to test the magnetic flux density outside the MRE.

Dynamic testing system of MRE performance

A Dynamic Mechanical Analyzer (DMA) is the common equipment for dynamic testing on viscoelastic material. In this work, the DMA (Triton Technology Ltd. UK, Model Tritec 2000B) system, is modified to characterize MRE performances by introducing a self-made electromagnet which can generate a variable magnetic flux density up to 1 T (sketch map shown in Fig. 2). This system applies a fixed oscillatory strain to the specimen and measures the amplitude and phase of the output force, from which stress, modulus (shear storage modulus G′ and loss modulus G″

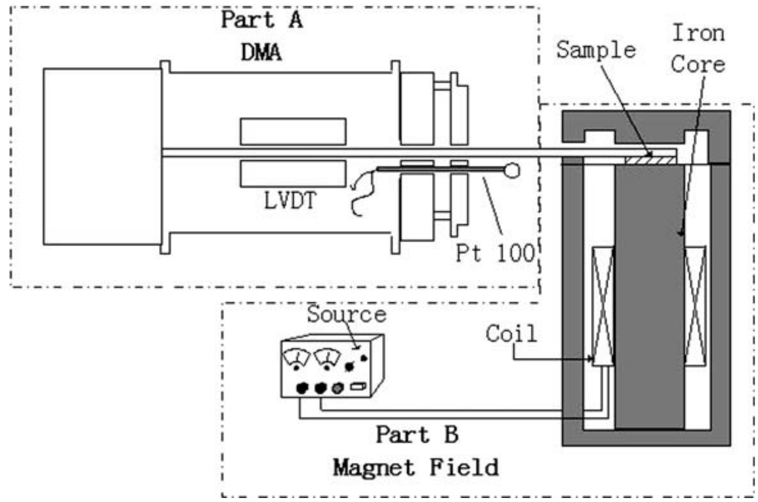

Fig. 2 A sketch map of magnet-mechanics coupled DMA. The dimensions of testing sample are 10 mm × 10 mm × 3 mm (length, width and thickness). The direction of the external magnetic flux density is perpendicular to surface of the testing sample

included) and the loss tangent (tan $\delta = G''/G'$) can be calculated. Testing involved recording the modulus and the loss tangent of various specimens at various frequencies, strains and applied magnetic fields. In the context, the shear storage modulus is studied and the phrase ''modulus'' refers to the shear storage modulus.

The experiment is started in the room temperature, and the increment of temperature of the electromagnet is less than 3 °C during the stage of the whole experiment.

Mechanical measurements

In order to supply reference for properties of materials and applications, the basic mechanical properties of MRE are also measured. Tensile strength, angle tear strength, resilience factor and hardness are the most basic and important factors of mechanical performances in rubber industry [14], and are tested on JPL mechanical test machine, JC-1007 elasticity test machine, LX-A hardness gauge, respectively. These apparatus are all manufactured by Jiangdu Jingcheng Test Instruments Factory, China.

Results and discussion

Influence of fabrication conditions on the MRE performances

The influences of matrix type, external magnetic flux density (B), and temperature in the stage of forming pre-configuration, content of plasticizers and iron particles on the MRE performances are experimentally investigated, and discussed below. It is noted that all percentages used in the context refer to weight percentages.

When the dynamic testing done in paragraph 3.1, the exciting frequency is fixed as 5 Hz and the dynamic stain amplitude is set at 0.3%.

Matrix type

Two kinds of MREs based on silicone rubber and natural rubber are prepared. The two kinds of MREs have the same ingredient proportions (60% of iron particle, 10% of plasticizers, and 30% of matrix). The only difference between them is the matrix used: one is natural rubber and the other is silicone rubber. Mechanical performances in terms of tensile/tear strength, resilience factor and harness of the two kinds of MREs were measured and compared. As can be seen from Table 1, MRE based on natural rubber generally have better performances than that based on silicon rubber. For example, both the tensile strength and the tear strength of nature rubber based MREs are almost 10 times as that of silicone rubber based MREs Therefore, MREs whose matrix is well mechanical performance polymers such as natural rubber instead of soft materials, would gain wide applications (Fig. 3).

External Magnetic flux density in forming pre-configuration

In this group, four natural rubber based MRE samples with the same compositions (60% of iron particles, 20% of natural rubber, and 20% of plasticizers) were pre-configu-

Table 1 Comparison of mechanical performance of MRE based on natural rubber and silicon rubber

Test samples	Tensile strength/MPa	Angle tear strength N/mm	Resilience factor	Hardness
Silicone rubber MRE	0.7	1.7	28%	33
Natural rubber MRE	6.5	16.3	52%	45

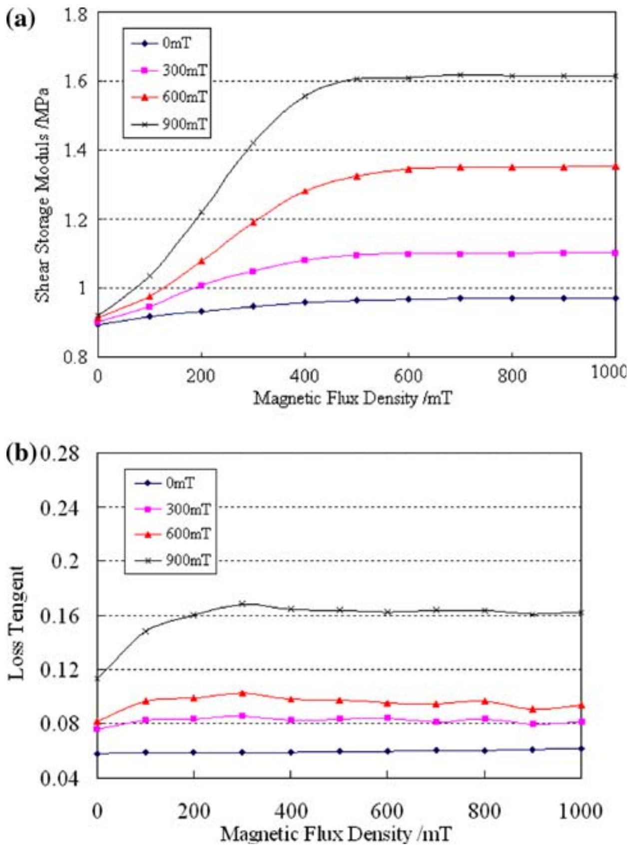

Fig. 3 Increment of the magneto-induced modulus (**a**) and loss tangent (**b**) with applied magnetic strength for MREs pre-configurated under B = 0, 300, 600 and 900 mT, respectively

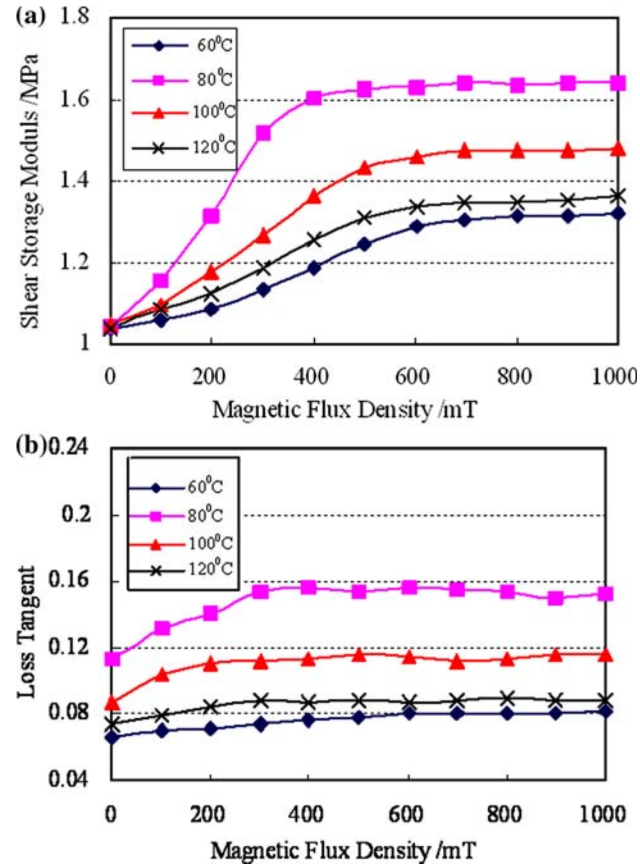

Fig. 4 Increment of the magneto-induced modulus (**a**) and loss tangent (**b**) with applied magnetic strength for MR elastomers pre-configurated at the temperature of 60 °C, 80 °C, 100 °C and 120 °C, respectively

rated at the temperature of 80 °C, but fabricated at four external magnetic fields with B = 0,300, 600, 900 mT, respectively. The field dependence of shear modulus for these four samples is shown in Fig. 4(a). As can be seen from this figure, shear modulus of each sample shows an increasing trend with the external magnetic flux density prior to the iron particle saturation. This is because the shear modulus comes from the actions of magnetizable particles. When iron particles reach saturation magnetization, the actions between magnetizable particles can't vary with the external magnetic flux density, thus, the magneto-induced modulus reach the maximum. By comparing these four samples, it is found that strong external magnetic flux density applied in forming pre-configuration leads to the high magneto-induced modulus. For example, the maximum modulus of MRE pre-configurated in the magnetic flux density of 900 mT is above 1.6 MPa while the one pre-configurated without field is 0.9 MPa. This is obvious because stronger external magnetic flux density helps to form more stable chain or column structures and consequently induce higher magneto-induced modulus. It is also indicated in Fig. 4(a) that external magnetic flux density in forming pre-configuration has no influence on the MRE zero-field modulus. It is because there is no magnetic interaction between the iron particles in MRE when no magnetic field is applied. On the other hand, the field dependence of loss tangent for these four samples is shown in Fig. 4(b). It can be seen from this figure that the loss tangent follows the same rule to the external magnetic flux density during the stage of forming pre-configuration.

Temperature in forming pre-configuration

In this group, four natural rubber based MRE samples with the same compositions (60% of iron particles, 20% of natural rubber, and 20% of plasticizers) were pre-configurated in the applied external magnetic field with B = 1 T, but at four different temperatures of 60 °C, 80 °C, 100 °C, 120 °C, respectively. The field dependence of modulus for these four samples is shown in Fig. 5. It can be seen from this figure that the MRE pre-configurated in 80 °C has the best MR effects in this group. This result is probably due to temperature effect on the natural rubber matrix. It is known that the natural rubber is a sort of temperature dependence

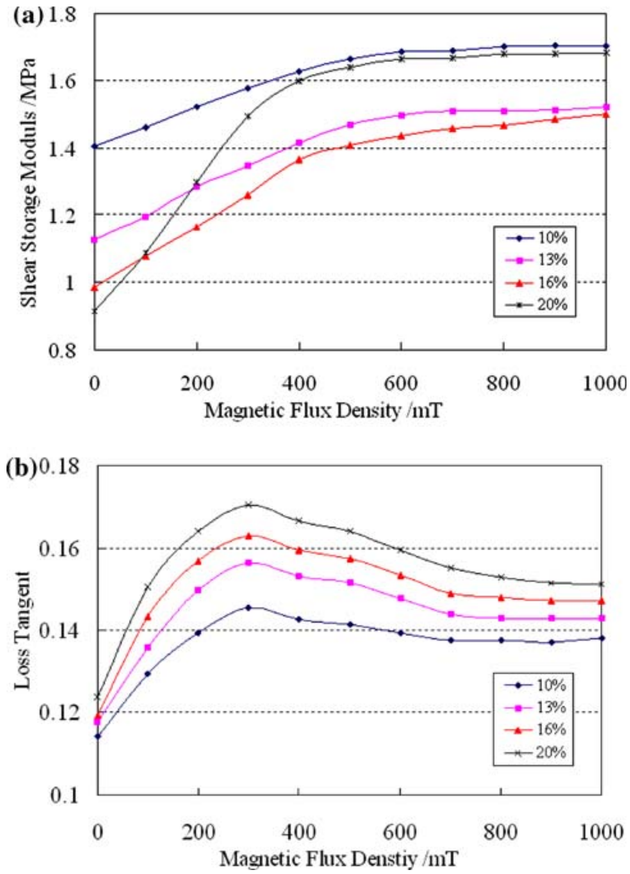

Fig. 5 Influence of content of plasticizers on the MR effects of variation of magneto-induced modulus and loss tangent

of viscoelastic material. Such material behaves as elastomer at room temperature but turns into a soft viscoplastic or fluid substance when it is heated. Further increasing temperature, the matrix will become hard again because chemical crosslinking plays an increasing role with increasing temperature. As shown in Fig. 5, 80 °C is the ideal temperature for the particles to move and form ordered pre-configuration. Same as the sample group in 3.1.3, the zero-field moduli are not changed by the results of pre-configuration.

Content of plasticizers

In this group, four MRE samples based on natural rubber are fabricated with 60% of iron particles, pre-configurated in the applied external magnetic field with $B = 1$ T and at the temperature of 80 °C. But the contents of plasticizers are 10%, 13%, 16% and 20%, respectively. Plasticizer is a kind of additions in the rubber technology; it can be dissolved in rubber after mixing them together. Plasticizers act as the lubricant and let the molecular chains of rubber glide easily, and then the rubber matrix shows a low adhesiveness. So adding the plasticizers in the MREs is expected to improve MRE performances, because plasticizers can not only change the rubber mechanisms but also modify particle properties. Figure 6 shows the influence of plasticizers on MRE performances. From this figure, the zero-field moduli (G_0, the shear storage modulus of MRE when the external magnetic flux density $B = 0$) of the samples with 10% and 20% weight fraction of plasticizer are 1.4 MPa and 0.9 MPa, respectively. Also, their corresponding saturation magneto-induced moduli(ΔG, the change of the shear storage modulus when saturation magnetization) are 0.2 MPa and 0.7 MPa. So the relative MR effects $\Delta G/G_0$ are 14% and 78%, respectively. Therefore, the amount of plasticizers in the matrix plays an important role in improving MR effects, especially the relative MR effects. The field dependence of loss tangent is shown in Fig. 6(b), where the loss tangent firstly increases steadily with the increment of external magnetic flux density up to a maximum value at 300 mT. Above $B = 300$ mT, the loss tangent shows a decreasing trend with flux density. This may be due to the temperature effect in the testing system. The testing sample is attached to the

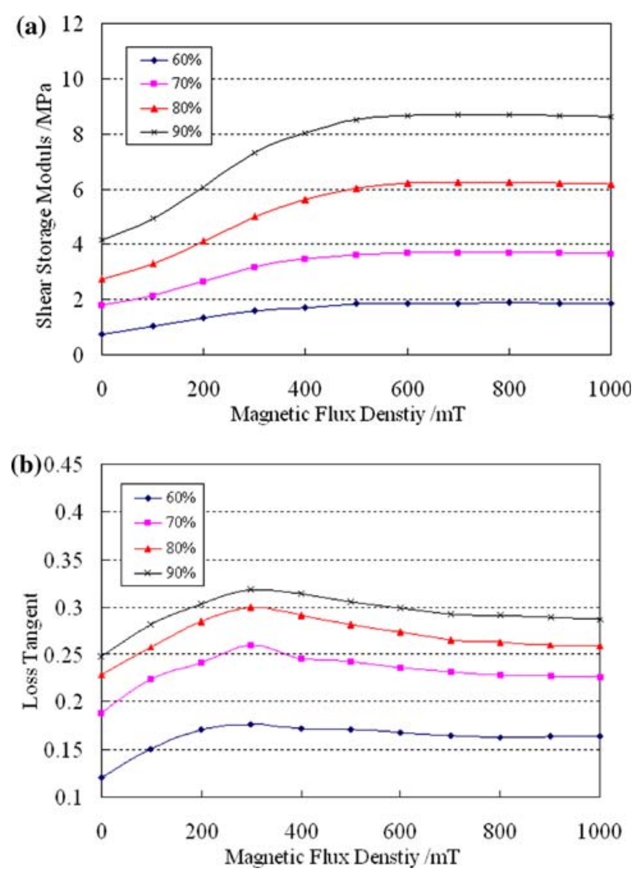

Fig. 6 Dependence of MR effects of variation of magneto-induced modulus and loss tangent on content of iron particles embodied in MREs

electromagnet whose temperature rises steadily when the magnetic flux density increases.

Content of iron particles

In this group, four MRE samples based on natural rubber are pre-configurated in the applied external magnetic field with $B = 1$ T and at the temperature of 80 °C. According to the results in 3.1.5 and in order to get the best MR effect, the ratio of plasticizers to natural rubber is set at 1. But their iron particles contents are 60%, 70%, 80% and 90%, respectively. The influence of content of iron particles on MR effects are shown in Fig. 7 and summarized in Table 2. The results show that the magneto-induced modulus increases dramatically with the particle content increases. For example, the magneto-induced modulus is as high as 4.5 MPa when the content is 90%. This is because the modulus is induced by interactional force between the iron particles. So, more the particles are, higher the magneto-induced modulus is. However, the increment of iron particles also enhances the zero-field modulus, which may decrease the relative MR effect. For example, the relative MR effect is reduced from 133% to 107% when particles content changed from 80% to 90%. It is also shown in Table 3 that the mechanical performances of MRE filled with different content of iron particles are quite different. Increment of content of iron leads to the decrement of tensile strength and angle tear strength of MRE. Thus, it is not applicable to fabrication practical MRE by solely increasing particle contents.

Dynamic properties of MREs

MRE based device often operates in dynamic mode. So the study of dynamic properties of MREs will provide an important reference to their practical applications.

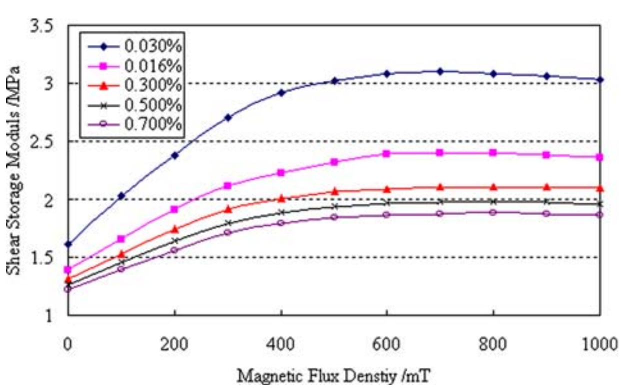

Fig. 7 Shear storage modulus as a function of magnetic strength measured at different strain amplitudes

Table 2 MR effect of four MRE samples filled with different percentage of the iron particles

Content of Fe	G_0	ΔG	$\Delta G/G_0$	Tanδ_0	Tanδ_{max}
60%	0.9	0.7	78%	0.12	0.17
70%	1.8	1.9	110%	0.18	0.24
80%	2.7	3.6	133%	0.20	0.27
90%	4.2	4.5	107%	0.25	0.31

Zero-field moduli G_0, is the shear storage moduls of MRE when the external magnetic flux density $B = 0$ and saturation magneto-induced moduli ΔG is the change of the shear storage moduls when saturation magnetization, $\Delta G/G_0$ is the relative MR effect, while Tanδ_0 is the zero-field of the loss tangent and Tanδ_{max} is the maximum of the loss tangent in the range of applied field from 0 to 1 T

Table 3 Mechanical performances of four MRE samples filled with different percentage of the iron particles

Content of Fe	Tensile strength /MPa	Angle tear strength N/mm	Resilience factor	Hardness
60%	3.25	11.4	28%	35
70%	2.27	10.7	21%	46
80%	1.29	7.6	14%	67
90%	0.32	3.7	5%	85

The dynamic testing is carried out using the modified DMA system. The sample measured is fabricated with the contents of iron particles of 60%, and plasticizers of 16%, at the applied external magnetic field with $B = 1$ T, and at the temperature of 80 °C in the stage of forming pre-configuration. Figure 8 shows the field dependence of modulus at various strain amplitudes, where the driving frequency is fixed as 5 Hz. The experimental results demonstrate the MREs behave as classical viscoelastic materials. In other words, the modulus of MREs shows a decreasing trend with applied strain amplitude. When the applied strain amplitude increases, the distance between particles within MRE will increase. This will induce the decrease of interactive forces between particles which result in the decrease of the magneto-induced modules.

Under the same dynamic stain amplitude of 0.7%, the frequency dependence of MRE shear modulus is measured and the result shows that the exciting frequency has little influence on the magneto-induced modulus.

Conclusions

The effects of both fabrication and working conditions on MRE performances were experimentally explored in this paper. Main finding are summarized below.

- Replacing the silicone rubber with natural rubber as the matrix can get good MREs with improved mechanical performances. This could be the first step for MREs to walk out from laboratory and walk into practical applications.
- The optimal pre-configuration conditions are: augmenting the magnetic fields, setting the temperature at 80 °C, and adding more plasticizers to matrix.
- The content of iron particles plays a significant role in improving MRE performances. When the iron particle weight fraction is 80%, the MRE shear modulus at the applied external magnetic field with $B = 1$ T reaches 3.6 MPa, and the relative effects is 133%. When 90% iron particles are embedded in MRE, the magneto-induced modulus reaches as high as 4.5 MPa. This result has exceeded the best report in the literatures regarding MREs based on the same kind of matrix. But increment of content of iron leads to the decrement of tensile strength and angle tear strength of MRE. Thus, it is not applicable to fabrication practical MRE by solely increasing particle contents.
- MREs behave as viscoelastic materials and their dynamic properties were measured using the modified DMA. The shear modulus decreases with the increment of strain but is almost independent of driving frequency.

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