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Material Properties

Influence of particle coating on dynamic mechanical behaviors of magnetorheological elastomers

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ABSTRACT

In this paper, core-shell structured poly methyl methacrylate (PMMA) coated carbonyl iron (CI) particles were prepared to study the influence of particle coating on the dynamic properties of magnetorheological elastomers (MREs). The CI-PMMA composite particles were encapsulated via an emulsion polymerization method. Two MRE samples were prepared with CI-PMMA composite particles and CI particles, respectively. Their microstructure was observed by using a scanning electron microscope (SEM). Dynamic properties of these two samples under various strain and magnetic fields were measured with a dynamic mechanical analyzer (DMA). The experimental results indicate that the MRE sample with CI-PMMA composite particles has larger storage modulus, smaller loss factor and smaller Payne effect than that of the sample with only CI particles. The analysis indicates that the use of CI-PMMA particles would increase the bond strength between particles and matrix. These experimental results were also verified by the SEM images.

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1. Introduction

Magnetorheological (MR) materials, including MR fluids, MR elastomers and MR foams, are an important branch of smart materials [1–4]. MR elastomers (MREs) are generally fabricated with rubber as the matrix. MREs have both MR effect and good mechanical performance from using rubber as the matrix. Recently, MREs have attracted considerable interest and some applications of MREs on vibration control have been reported [5–9]. In these studies, MREs were used as variable stiffness springs, whose stiffness or modulus can be controlled by an external magnetic field. As the stiffness is directly related to storage modulus of MREs, the study of the effects of influencing factors on MR effect would be very important. Two key factors have been extensively studied from both

experimental and modeling approaches: one is the magnetic field, and the other is the strain effect. The effect due to the magnetic field is called MR effect while the effect due to the strain is the Payne effect. The phenomenon of strain dependence of dynamic properties is called Payne effect named after the British rubber scientist A.R. Payne, who made extensive studies of the effect [10]. The effect is observed under cyclic loading conditions with small strain amplitudes, and is manifested as a dependence of the viscoelastic storage modulus on the amplitude of the applied strain. For MR fluids, above approximately 0.1% strain amplitude, the storage modulus decreases rapidly with increasing amplitude [11]. Similar cases also happen to MREs. Jolly et al. studied the Payne effect of MREs theoretically and found that there was a pronounced drop off of MR effect and an increase in field dependent energy dissipation [12]. A few other groups also studied the Payne effect of anisotropic and isotropic MREs and found that MREs have much larger storage modulus at low strains than that at high strains [13–17]. All the above reports had

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found the Payne effect did play an important role in MREs dynamic properties. However, very few reports can be found to investigate how to control or reduce this effect. That is the motivation of this study.

This study aims to find an effective fabrication method to control the Payne effect. This idea was borrowed from Choi's group on development of composite particles for MR fluid preparation [18–21]. They fabricated a kind of poly methyl methacrylate (PMMA) coated CI composite particles, which were used to replace pure iron particles. The composite based MR fluid solved the settling problem. However, there is not any report on study of the Payne effect in composite particle based MREs. We would like to extend their application of such composite particles for MRE fabrication. The Payne effect of such particle based MREs will be investigated.

In this article, CI-PMMA particles will be fabricated. Both CI-PMMA composite particles based and CI particles based MRE samples will be prepared. Both the MR effect and the Payne effect of these two samples will be tested and compared. The microstructures of composite particles based MRE samples and their possible relation with the Payne effect will be investigated.

2. Materials and method

2.1. CI-PMMA composite particles preparation

All the reagents except carbonyl iron (CI), i.e. methyl methacrylate (MMA, CP), acetic acid (AR), sodium laurylsulfonate (SDS, CP), ammonium persulfate (APS, AR), sodium hydroxide (NaOH, AR), ethanol (AR) and silicon oil (H201-500), were purchased from Sinopharm Chemical Reagent Co. Ltd. CI particles were bought from BASF (model CN) with size distribution of $d_{10} = 3.5 \mu\text{m}$, $d_{50} = 6 \mu\text{m}$ and $d_{90} = 21 \mu\text{m}$.

The particles were coated with poly methyl methacrylate (PMMA) by the means of emulsion polymerization. Initially, the CI particles were activated with acetic acid for a few minutes to etch off a layer of surface of the CI particle and form a new one. The modified CI particles were then dispersed in distilled water and additional SDS stabilizer was introduced to ensure that CI particles dispersed randomly in this mixture. Then, the MMA and APS were added into the mixture. When the temperature rose to 80°C the polymerization reaction started and was maintained for at least 10 h under nitrogen purging. After the polymerization, the cross linked CI-PMMA was separated by a magnet and washed with distilled water and methanol to remove SDS, untreated monomer and PMMA oligomers. Finally, the CI-PMMA composite particles were dried at 60°C in an oven for 7 days.

2.2. MRE sample preparation

There were two kinds of iron particles used as fillers. One was CI particles which were the CN particles from BASF and the other was the fabricated CI-PMMA composite particles. The rubber matrix used was ethyl vinyl silicone gum (MVQ) 110-2 (Dong Jue Fine Chemicals, Nanjing Co, Ltd), a kind of high temperature vulcanized (HTV) silicone

rubber. The vinyl content of the silicone rubber is 0.17% and the mean molecular weight is 620,000. The vulcanizing agent was double methyl double benzoyl hexane (DMDBH) from the Shenzhen Gujia Company. Plasticizer used here was methyl silicone oil, viscosity 50cP (from Shanghai resin factory Co. Ltd).

Firstly, the HTV silicone rubber was heat treated at 100°C for an hour. Then, the rubber was mixed on a two-roll mill (Taihu Rubber Machinery Inc. China, Model XK-160) for an hour. During this mixing process the iron powder, silicone oil and vulcanized agent were added. Then, the mixture was sent for a pre-structure process, during which the mixture was heated and kept under a magnetic field for some time. The pre-structure process was operated by using a special Magnet-Heat coupled device, the sketch of which is shown in Fig. 1. It consists of two parts: an electromagnetic and a hot plate. Prior to the pre-structure process, the mixture was put into a mold and the mold was closed tightly with the hot plate. Then the mold and hot plate were placed under a magnetic field of 1000 mT for 10 min. After the pre-structure process the mold was sent to be vulcanized on a flat vulcanizer (Bolon Precision Testing Machines Co. China, Model BL-6170-B). The vulcanizing was conducted under 160°C for 4 min which completed the production.

Two different samples were prepared. Sample 1 was prepared using CI-PMMA composite particles and sample 2 with CI particles. Two samples were prepared with the same CI particle content of 30% Wt. The recipe of sample 1 was: HTV silicone rubber 100 phr, CI-PMMA composite particles 51 phr, silicone oil 11 phr, and vulcanized agent 2 phr. The recipe of sample 2 was: HTV silicone rubber 100 phr, CI particles 47 phr, silicone oil 11 phr, and vulcanized agent 2 phr.

2.3. SEM

The micrographs of CI-PMMA, CI particles and MRE samples were taken by using a FE SEM 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 prior to observation.

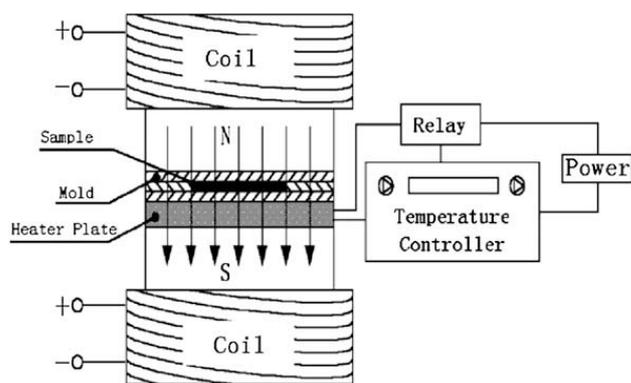


Fig. 1. Sketch of the Magnet-Heat coupled device.

2.4. Dynamic property measurement

Dynamic mechanical properties of MRE samples were measured by using a modified dynamic mechanical analyzer (DMA). As shown in Fig. 2, this system consists of two parts. Part A is the Trite 2000 DMA (Triton technology Co. Ltd, UK, model Tritec 2000B). There is a shaft, a motor and a sensor in the DMA. The shaft connects the sample and the motor. During the test the motor drive the shaft and the sample moves at given amplitude and frequency. The stress in the sample is measured with the sensor and the strain is taken as the displacement amplitude. The shear modulus and loss factor are computed from the data of strain and stress. Part B is an electromagnet used to generate a magnetic field. The testing magnetic field, controlled by coil currents, can vary from 0 mT to 1000 mT. The MRE test samples have dimensions of 10 mm × 10 mm × 3 mm.

Two testing modes, strain dependence testing and magnetic field dependence testing, were employed to measure dynamic properties of MRE samples. The conditions for both these modes are listed below:

(a) Strain dependence testing

Frequency: 10 Hz; temperature: 20 °C; field: 0 mT; strain: 0.17–3%

(b) Magnetic field dependence testing

Frequency: 10 Hz; temperature: 20 °C; strain: 0.67%; field: 0–1000 mT;

3. Results

3.1. Morphologies of CI-PMMA particles

The SEM images of CI particles and CI-PMMA composite particles are shown in Fig. 3. It can be seen clearly that the surface of CI-PMMA composite particles is much coarser than CI particles. The size of composite particles is larger

than that of CI particles, simply because the surface of composite particles is covered with a layer of PMMA.

3.2. Strain dependence of MREs

The strain dependence of storage modulus and loss factor of two MRE samples is shown in Fig. 4(a) and (b). It can be seen from Fig. 4(a) that these two samples show the Payne effect as their storage modulus decreases steadily with the increase of strain. However, these two samples show some distinct differences. Firstly, the storage modulus of sample 1 is much larger than that of sample 2, while the situation for the loss factor is the opposite. Secondly, the Payne effect in sample 1 is weaker than that of sample 2. To quantitatively evaluate the Payne effect of the samples, a “Payne effect factor” is introduced. This factor is defined as the ratio of the modulus change and its initial value, i.e. $PE = \Delta G/G_0$, where G_0 is the initial modulus and ΔG is $G - G_0$. The Payne effect factors of the two samples are list in Table 1. It can be seen that when the strain amplitude is 0.17% the storage modulus of sample 1 is 0.24 MPa, and when the strain amplitude is 3% the storage modulus of sample 1 decreases to 0.21 MPa. The change following strain amplitude of storage modulus of sample 1 is 0.03 MPa and the Payne effect factor of storage modulus of sample 1 is 13%. Similarly, the Payne effect factor of storage modulus of sample 2 is 36%.

3.3. Magnetic field dependence of MREs

The magnetic field dependence of storage modulus and loss factor is shown in Fig. 5(a) and (b), with the magnetic field being swept from 0 mT up to 1000 mT. Obviously, both these samples exhibit MR effects as their storage moduli show increasing trends with magnetic field. The loss factors of these two samples decrease steadily with the increase of magnetic field. It is also noted that when the magnetic field is higher than 800 mT the increase of storage modulus tends to saturation. However, there are some differences between two samples. Compared to sample 2, sample 1 has the larger initial modulus and the smaller loss factor, which has been found in the strain dependence test. The MR effect of the two samples is also different; the MR effect of sample 1 is about 22% while the effect of sample 2 is 44%. Hence, samples with CI-PMMA composite particles have smaller MR effect.

4. Discussion

4.1. Use of CI-PMMA particles increases the storage modulus of MREs

The storage modulus of composite materials can be simply estimated from the mix law:

$$G_c = \frac{G_f \cdot G_m}{G_f V_f + G_m V_m} \quad (1)$$

where G_c is the storage modulus of the composite, G_f and G_m are the storage moduli of filler and matrix, V_f and V_m are the volume fractions of filler and matrix. The storage

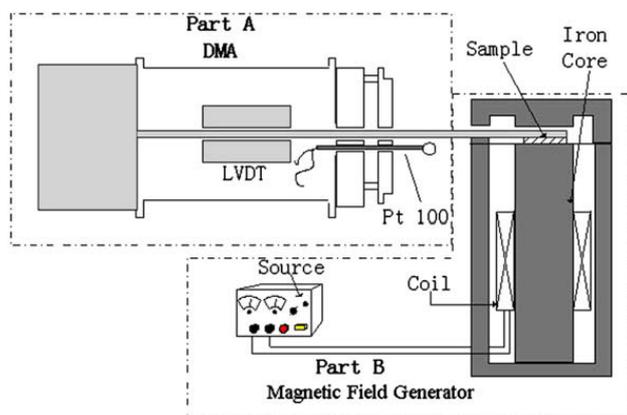


Fig. 2. Sketch of the modified DMA.

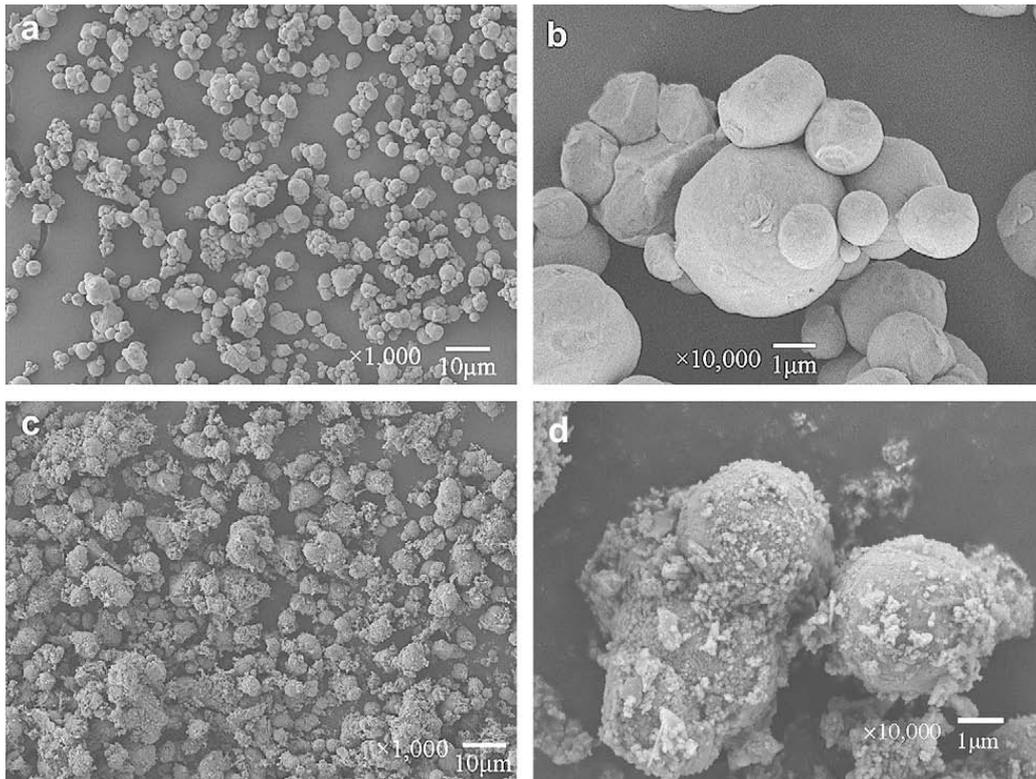


Fig. 3. SEM images of different iron particles: bare CI: (a). 1000 \times and (b). 10,000 \times , CI-PMMA particles: (c). 1000 \times and (d). 10,000 \times .

modulus of MREs can also be calculated with equation (1). As the contents of CI particles and matrix of the two samples are same, the storage moduli of the two MRE samples are only influenced by their different matrix storage modulus. The two samples were prepared with different iron particles as filler. As the content of CI particles of the two samples is the same, the PMMA used in sample 1 can be recognized as matrix. Thus, the matrix of sample 1 is a kind of “mixed matrix” consisting of silicone rubber and PMMA, the mixture modulus of which is calculated by using equation (1). The matrix of sample 2 is purely silicone rubber. As the storage modulus of PMMA is larger than that of silicone rubber, the modulus of the mixed matrix is larger than that of silicone rubber. Hence, the storage modulus sample 1 is larger than that of sample 2.

4.2. Use of CI-PMMA particles enhances the bond between particles and matrix

MREs are a kind of particle reinforced rubber matrix composite material. Their mechanical behavior is strongly influenced by the bond strength between particles and rubber matrix. The bond strength is determined by the compatibility of particles and matrix. As the particles used in MREs are iron, which is metal, and the matrix of MREs is silicone rubber, which is polymer, they have poor compatibility. This can be seen from the SEM micrograph of sample 2 showed in Fig. 6(c) and (d). In Fig. 6(c) and (d), iron particles can be seen clearly on the surface of the rubber matrix and small pits can also be found. The observed sections of Fig. 6 were obtained by tearing

the MRE samples. If the bond between particles and matrix is weak, failure will be at the surface and most particles would be on the top of the observed section, with some particles being removed during the tear process. When using CI-PMMA particles, there will be a layer of PMMA covered on the particle surface. As PMMA and silicone rubber both are polymers, the compatibility of CI-PMMA composite particles and rubber matrix is likely to be better. This can also be observed from the SEM micrograph of sample 1 in Fig. 6(a) and (b). It can be seen that it is hard to find particles on the surface of the matrix and there are no small pits.

The strengthening of the bond between particles and matrix leads to a small loss factor and weak Payne effect. Loss factor of composite materials has three components: loss factors of matrix, filler and from the interface between filler and matrix. Usually, the last component is the main source of loss factor of composite because of the weak bond between fillers and matrix. When the bond is weak, there will be relative motion between fillers and matrix and the resulting friction causes energy dissipation. Sample 1 with CI-PMMA composite particles has stronger bond between particles and matrix, and it also has a small loss factor.

In the past, the Payne effect of composite had been studied by some scholars. Payne believed that the effect can be attributed to deformation-induced changes in the material's microstructure, i.e. to breakage and recovery of weak physical bonds linking adjacent filler clusters. Medalia developed this theory and thought that fillers and matrix would form small structures in the composite [22,23]. In this small structure, particles nearby are

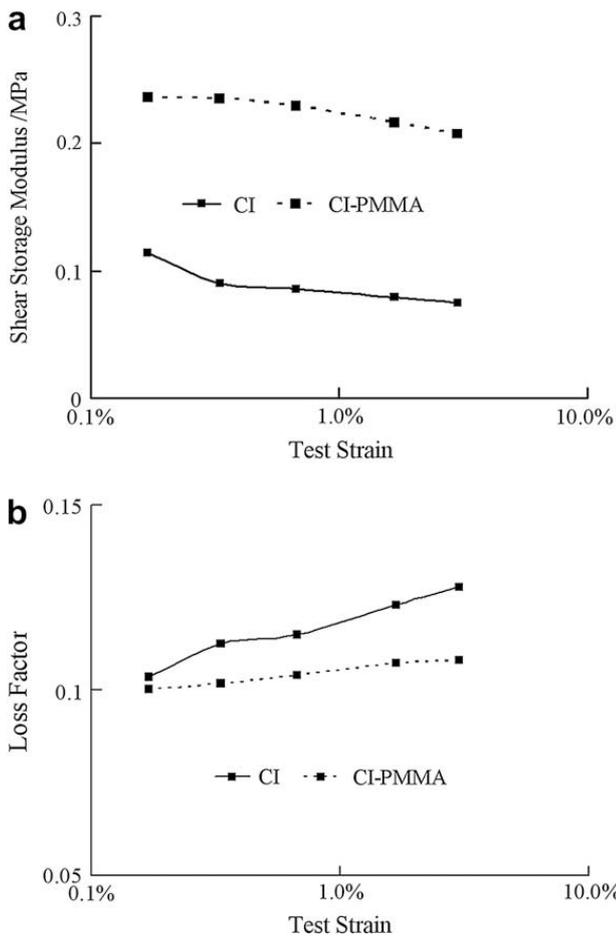


Fig. 4. Test curves of the strain dependence of two samples: (a). Dynamic storage modulus, (b). Loss factor.

connected by the matrix. When the strain amplitude is large, the distance between particles will increase, the bond between particles and matrix may be broken, hence breaking the structure, and storage modulus will decrease. At the same time, with increasing strain amplitude and breaking of the connection between particles and matrix, the relative motion and friction between particles and matrix will increase resulting in increase of the loss factor. The Payne effect is strongly influenced by the bond strength. If the bond strength is strong, the number of broken small structures is small and there is little decrease of storage modulus. There will also be little relative motion between particles and matrix and the increase of loss factor will be small. As the bond strength of sample 1 is larger than that of sample 2, the Payne effect of sample 1 is weaker which means that particle encapsulation is useful for decreasing the Payne effect in MREs.

Table 1
Payne effect factors of two samples.

Samples	Initial value	Change following strain amplitude	Payne effect factors
1	0.24 MPa	0.03 MPa	13%
2	0.11 MPa	0.04 MPa	36%

4.3. Use of CI-PMMA particles decreases the MR effect of MREs

MR effect had been studied and found to be strongly influenced by the particle dispersion [13,24,25]. The position of iron particles of MREs is fixed during the pre-structure process. As the pre-structure process involves heating, the rubber matrix is in a plastic state and the iron particles driven by the magnetic force can move and form chain or column structure. Past studies have shown that MREs with regular chain structure have greater MR effect. When particles move during the pre-structure process, the driving force is the applied magnetic field and the resistance to flow comes from the rubber matrix. As the two samples were prepared using the same magnetic field, the driving force is the same. Whether it is hard or easy for particles to move depends on the resistance of the matrix. If the particles are larger the resistant force will be greater. The CI-PMMA composite particles are larger than the pure CI particles because of the layer of PMMA. Hence, the resisting force for CI-PMMA particles is larger so it is more difficult for sample 1 to have regular particle structure. This can also be seen in Fig. 6(a) and (c) where sample 2 has more regular particle structure than sample 1. As sample 1 has less regular particle structure, the MR effect of sample 1 is smaller than sample 2.

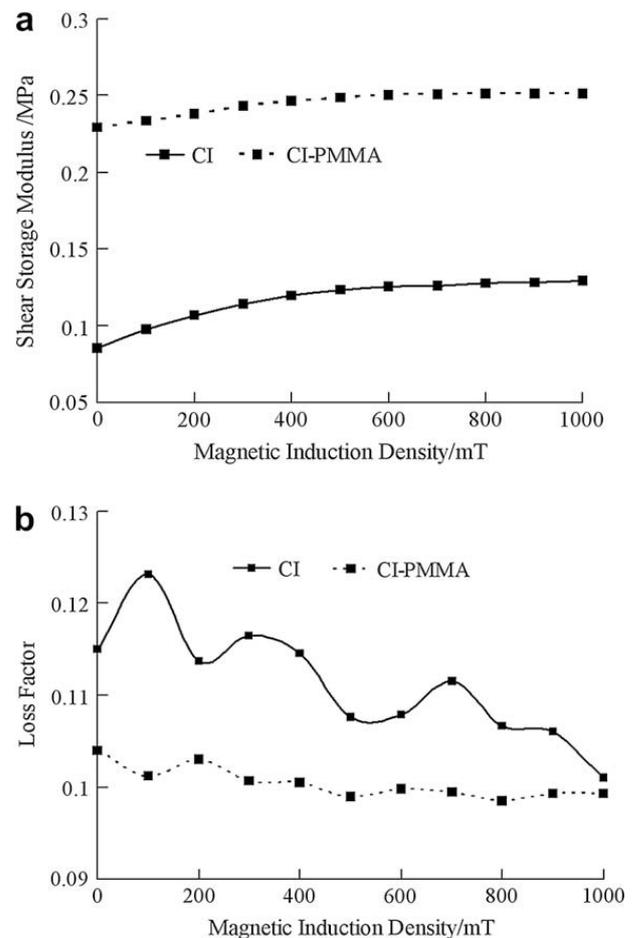


Fig. 5. Test curves of the magnetic field dependence of two samples: (a). Dynamic storage modulus, (b). Loss factor.

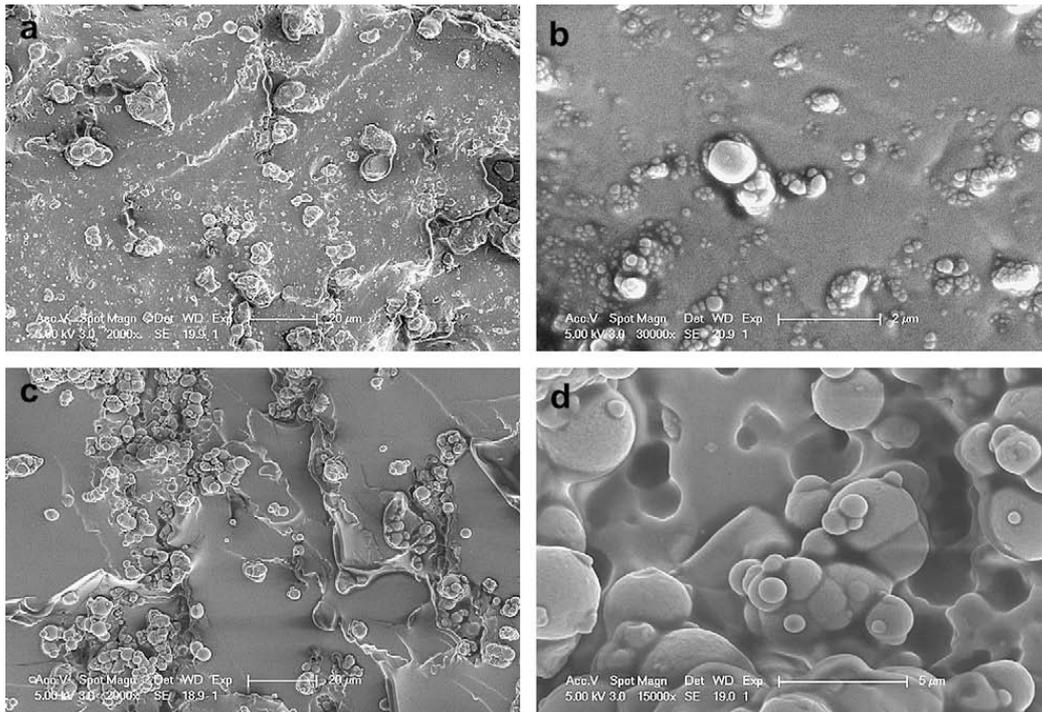


Fig. 6. SEM graph of two samples: Sample 1: (a). 2000 \times and (b). 30,000 \times , Sample 2: (c). 2000 \times and (d). 15,000 \times .

There are mainly three differences between samples with CI-PMMA particles and CI particles. Firstly, MREs with CI-PMMA have a mixed matrix made up of PMMA and silicone rubber, while MREs with CI particles have a single silicone rubber matrix. As the PMMA is harder than silicone rubber, the storage modulus of MREs with CI-PMMA particles is larger than MREs with CI particles. Secondly, MREs with CI-PMMA particles have stronger bond between particles and matrix. When the bond between particles and matrix is strong, there will be less breaking of small structure and less relative motion between particles and matrix which leads to smaller Payne effect and loss factor. Thirdly, the CI-PMMA particles have larger resistance to movement during the pre-structure process so it is harder for regular particle structure to be formed. Hence, MREs with CI-PMMA particles will have smaller MR effect.

5. Conclusions

In this paper, two different kinds of MRE samples were prepared with different iron particles as filler. One used CI-PMMA composite particles and the other CI particles. The magnetic field and strain dependence of the two samples were characterized by using DMA giving the following results:

- Sample with CI-PMMA composite particles has larger storage modulus because PMMA is harder than silicone rubber matrix.
- Sample with CI-PMMA composite particles has less Payne effect because using PMMA coated particles will increase the bond strength between particles and matrix. Hence, using particle encapsulation is useful

for decreasing this nonlinear dynamic mechanical behavior.

- Sample with CI-PMMA composite particles has smaller and more stable loss factor because using PMMA coated particles will decrease the relative motion between particles and matrix.
- Sample with CI-PMMA composite particles has lower MR effect because it is harder for CI-PMMA to move during pre-structure process.

Although the MREs prepared with CI-PMMA particles have low MR effect, they have weak Payne effect and small steady loss factor. Hence, MREs with CI-PMMA particles are more practicable.

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References

- [1] J.D. Carlson, M.R. Jolly, MR fluid, foam and elastomer devices, *Mechatronics* 10 (2000) 555.
- [2] G.H. Hitchcock, X.J. Wang, F. Gordaninejad, A new bypass magnetorheological fluid damper, *Journal of Vibration and Acoustics* 129 (2007) 641.
- [3] X.J. Wang, F. Gordaninejad, Flow analysis and modeling of field-controllable, electro- and magnetorheological fluid dampers, *Journal of Applied Mechanics* 74 (1) (2007) 13.
- [4] W.H. Li, H. Du, Development of an ankle physiotherapy device using an MR damper, *International Journal of Advanced Manufacturing Technology* 25 (3–4) (2005) 205.

- [5] J.M. Ginder, M.E. Nichols, L.D. Elie, I.L. Tardiff (Eds.), *Smart Structures and Materials 1999*, Smart Materials Technologies, Newport Beach, 1999, pp. 131–138.
- [6] J.M. Ginder, M.E. Nichols, L.D. Elie, S.M. Clark (Eds.), *Smart Structures and Materials 2000*, Smart Structures and Integrated Systems, Newport Beach, 2000, pp. 418–425.
- [7] J.M. Ginder, W.F. Schlotter, M.E. Nichols (Eds.), *Smart Structures and Materials 2001*, Damping and Isolation, Newport Beach, 2001, pp. 103–110.
- [8] H.X. Deng, X.L. Gong, L.H. Wang, Development of an adaptive tuned vibration absorber with magnetorheological elastomer, *Smart Materials and Structures* 15 (2006) N111.
- [9] M.H. Holdhusen, K.A. Cunefare, A state-switched absorber used for vibration control of continuous systems, *Journal of Vibration and Acoustics* 129 (2007) 577.
- [10] A.R. Payne, The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I, *Journal of Applied Polymer Science* 6 (19) (1962) 57.
- [11] W.H. Li, H.J. Du, G. Chen, S.H. Yeo, N.Q. Guo, Nonlinear viscoelastic properties of MR fluids under large-amplitude oscillatory shear, *Rheologica Acta* 42 (3) (2003) 280.
- [12] M.R. Jolly, J.D. Carlson, B.C. Munoz, A model of the behaviour of magnetorheological materials, *Smart Materials and Structures* 5 (1996) 607.
- [13] C. Bellan, G. Bossis, Field dependence of viscoelastic properties of MR elastomers, *Journal of Modern Physics B* 16 (17–18) (2002) 2447.
- [14] M. Lokander, B. Stenberg, Improving the magnetorheological effect in isotropic magnetorheological rubber materials, *Polymer Testing* 22 (2003) 677.
- [15] M. Kallio, T. Lindroos, S. Aalto, E. Järvinen, T. Kärnä, T. Meinander, Dynamic compression testing of a tunable spring element consisting of a magnetorheological elastomer, *Smart Materials and Structures* 16 (2007) 506.
- [16] P. Blom, L. Kari, Amplitude and frequency dependence of magneto-sensitive rubber in a wide frequency range, *Polymer Testing* 24 (2005) 656.
- [17] G.V. Stepanov, S.S. Abramchuk, D.A. Grishin, L.V. Nikitin, E.Y. Kramarenko, A.R. Khokhlov, Effect of a homogeneous magnetic field on the viscoelastic behavior of magnetic elastomers, *Polymer* 48 (2007) 488.
- [18] M.S. Cho, S.T. Lim, I.B. Jang, H.J. Choi, M.S. Jhon, Encapsulation of spherical iron-particle with PMMA and its magnetorheological particles, *IEEE Transactions on Magnetics* 40 (4) (2004) 3036.
- [19] H.J. Choi, B.J. Park, M.S. Cho, J.L. You, Core-shell structured poly (methyl methacrylate) coated carbonyl iron particles and their magnetorheological characteristics, *Journal of Magnetism and Magnetic Materials* 310 (2007) 2835.
- [20] M.S. Kim, M.S. Cho, H.J. Choi, PMMA coated carbonyl iron microbeads and their magnetic characteristics, *Physica Status Solidi (a)* 204 (12) (2007) 4198.
- [21] F.F. Fang, H.J. Choi, Noncovalent self-assembly of carbon nanotube wrapped carbonyl iron particles and their magnetorheology, *Journal of Applied Physics* 103 (2008) 07A301.
- [22] A.I. Medalia, Morphology of aggregates I. Calculation of shape and bulkiness factors; application to computer-simulated random flocs, *Journal of Colloid Interface Science* 24 (1967) 393.
- [23] A.I. Medalia, Effective degree of rubber occluded within carbon black aggregates, *Rubber Chemistry and Technology* 45 (1972) 1171.
- [24] L.C. Davis, Model of magnetorheological elastomers, *Journal of Applied Physics* 85 (6) (1999) 3348.
- [25] L. Chen, X.L. Gong, W.Q. Jiang, J.J. Yao, H.X. Deng, W.H. Li, Investigation on magnetorheological elastomers based on natural rubber, *Journal of Materials Science* 42 (2007) 5483.