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Behavior of magnetorheological elastomers with coated particles

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Abstract
Iron particle coating can improve the behavior of magnetorheological elastomers (MREs) by inhibiting iron particle rusting; however, such a process can change physical properties of MREs such as oxidation resistance, shear modulus, and stiffness change due to an applied magnetic field. In this study, MRE samples are fabricated with regular and polymerized iron particles. To investigate the possibility and extent of these changes, polymerized particle MRE samples are made using a combination of reversible addition fragmentation chain transfer and click chemistry. Shear test sample MREs with pure elastomer and 50 wt% MRE with and without polymerization are fabricated. To observe the effect of oxidation on shear properties of MREs, pure elastomer and 50 wt% coated and non-coated samples are oxidized using accelerated oxidation procedure. Experimental results show that oxidation significantly reduces the shear modulus of the elastomer matrix. The coating process of iron particles does not significantly change the shear modulus of resulting MREs but reduces the loss of shear modulus due to oxidation.

Keywords: magnetorheological elastomers, coated particles, shear behavior

1. Introduction

Magnetorheological elastomer (MRE) is a type of material which is composed of magnetic permeable particles dispersed in an elastomeric medium and show variable mechanical properties within a magnetic field. To fabricate MRE, magnetic particles are added to liquid-state mixture of polymer parts and the resulting mixture is cured either inside or outside of an external magnetic field resulting in isotropic or directional (orthotropic) MRE, respectively [1, 2]. When particles are aligned within the magnetic field, chain-like structures of magnetic particles are formed and locked in place. Gong et al [3] showed that isotropic MRE does not have a chain-like structure because it is cured without a magnetic field. The advantage of directional MREs is higher stiffness change, if the load is applied in the direction of the alignment or perpendicular to it. Magnetization of directional MRE is higher, when the magnetic field is applied parallel to the direction of the iron particle chains [4]. Also, higher compressive modulus, thermal conductivity and MR effect are observed for aligned polyurethane MREs [5] compared to homogenous MREs. Researchers have found that MR effect is more pronounced for softer elastomer matrix and the storage modulus can be increased from 400 times [6] to 800% [7], if the off-state shear modulus is low, i.e. in order of kilo Pascal. Davis has theoretically found the optimum particle concentration for increasing the shear modulus to be 27% by volume [8]. Using shear tests, it has been shown that MR effect increases at higher frequencies [9] and a normal applied compressive load causes a reduction in MR effect during shear deformation [10].

MRE can show stiffness, damping, and hysteresis change within a magnetic field; however, damping change is minimal compared to stiffness change [11]. Such controllable properties can be utilized in vibration isolation applications such as variable stiffness elements, since MREs have a response...
time in order of milliseconds [12]. The controllable properties can be utilized in variable stiffness and damping devices such as vehicles’ engine mounts [12], vibration isolator for vehicle transmission system [13], adaptive vehicle seat suspension [14], adaptive tuned vibration absorbers [15, 16], and base isolator for building structures [17, 18]. Other researches proposed soft MRE for air flow controllable valve [19] and adjustable springs in springs in prosthetic devices [20]. There is also limited work for modeling MRE behavior and it poses its own challenges since MRE shows non-linear viscoelastic behavior which is affected by magnetic field and loading frequency. A model is presented by Shen et al [21] for predicting the stress strain behavior of MREs within magnetic field as well as phenomenological models based on Ramberg-Osgood [22] and Bouc-Wen model [11].

In MREs iron particles are embedded in an elastomeric medium and are not exposed to air; however, the moisture and oxygen can penetrate with time and alter the properties of elastomeric matrix or the bonding between the matrix and the particles. Also, the hygrothermal effects may reduce the strength of the bonds among iron particles and the elastomeric matrix or may affect the elastomeric matrix itself. It is shown that oxidation can significantly reduce the stability of natural rubber based MREs and higher oxidation rates are observed for MREs containing larger percentage of iron particles [23]. To prevent the oxidation of iron particles and hence increase the durability of the MREs, iron particles can be coated with different techniques including reversible addition fragmentation chain transfer (RAFT) and click chemistry. However coating may change mechanical, electrical, and magnetic properties of MREs that need to be investigated further. Coating carbonyl iron particles with Polypyrrole ribbons has other advantages such as improving sedimentation properties of MR fluid [24]. Also, coating particles of MR fluid with a layer of polysiloxanes can increase the oxidation and chemical stability [25]. It is shown that coating with poly methyl methacrylate can increase the shear modulus over 200%, and thus, reduce the relative MR effect [26]; but Lauryl Sodium Sulfate (SDS) and Sorbitan Monoleate (Span 80) as a coating layer have reduced the base shear modulus and increased the relative MR effect [27]. Compression test results have shown that polymerized iron particle MREs have higher oxidation stability [28]. The combination of RAFT and click chemistry reactions for surface polymerization of iron particles has been studied by Yuan et al [29]. Moreover, it is shown that coating particles reduces the magnetization saturation point [30]. Although previous studies have investigated the effect of particle coating on magnetization of particles and changes in properties of MRF, only a few studies have been performed on the effect of coating on mechanical properties on MRE.

In this research, particles of 50 wt% MRE samples are coated utilizing a combination of RAFT and click chemistry methods. To investigate the effect of coating on the performance of MREs, ASTM standard double lap shear samples are fabricated for pure elastomer, 50 wt% coated, and 50 wt% non-coated iron particles. MRE samples are oxidized using an accelerated heat chamber. Shear experiments are performed to investigate the effect of coating and oxidation on MRE samples. Results show that oxidation reduces the off-state shear stiffness of the MREs and hence increases the relative stiffness changes due to magnetic field. Finally coating of iron particles does not significantly change the shear modulus, but protects the MREs by reducing the loss of stiffness due to oxidation.

### 2. Coated and non-coated particle MRE samples

#### 2.1. Surface coating mechanism of iron particle via click chemistry

Polymer coating on iron particle surface can enhance both chemical and physical performances of MRE. A RAFT technique is employed to graft the polymers. Since the surface coating materials are non-magnetizable, they do not affect the magnetic field while they improve the endurance of MRE. It is shown that 20 wt% polymer coating on the iron particles surface decreases the magnetic saturation about 5% in compared with pristine iron particles [31]. The effect of coating on the magnetic saturation of iron particles may be negligible because the thickness of coating is in nanometer scale and mass percentage of polymer coating is lower than previously reported [31]. RAFT method offers a narrow polydispersity index which means polymer has uniform molecular weight [32–38] polymer can be covalently bonded to the substrate.

To coat the iron particles, the substrate should be functionalized using azide, and the tandem molecule is functionalized using alkyn group in order to react through click chemistry. Copper (II) sulfate is reduced in the presence of sodium ascorbate, which becomes Cu (I), denoted as [LnCu]+. In click chemistry, the ligand (Ln) can be the solvent, such as acetonitrile, and water [35]. The reduced copper/Ln reacts with alkyn group and this is followed by interaction with nitrogen from azide group. Finally, the reaction between the alkyn and azide functional groups yields a ring closed triazole group.

In this process, 0.5 g of azide modified iron particles was added into a glass vial and followed by adding poly(tetrafluropropyl methacrylate, MW 200.13 g mol⁻¹ [39]) (0.5 g) CuSO₄ (6.65 mg), sodium ascorbate (241 mg) and dimethylformamide (DMF) (2 mL). The mixture was sonicated for 5 min and continuously stirred in oil bath at 70 °C for 18 h. The conjugated poly(tetrafluropropyl methacrylate)/iron particles were filtered, and washed using DMF several times with toluene consecutively. Then, the poly(tetrafluropropyl methacrylate) coated iron particles were dried in a vacuum oven at 50 °C for 24 h.

Initially, iron particles were functionalized with 2-4(-chlorosulfonylphenyl)-ethytrichlorosilane in toluene. The particles were washed using distilled water and ethanol, consecutively, and dried in vacuum oven [28]. Surface initiated iron particles were then reacted with sodium azide in DMF to provide azide terminated particles which would be reacted with alkyn through click chemistry reaction [40]. 3-benzylsulfanylthiocarbonylsulfanyl-propionic acid as chain
transfer agent (CTA) was synthesized according to the reported literature [41]. The synthesized CTA was modified with propargyl alcohol to provide alkyne group [40]. The alkyne terminated CTA was used to polymerize tetrafluoropropyl methacrylate monomer. This reaction resulted in alkyne functionalized poly(tetrafluoropropyl methacrylate).

The mechanism of surface coating of iron particles poly(tetrafluoropropyl methacrylate) through a combination of reversible addition fragmentation chain transfer (RAFT) and click chemistry is shown in Figure 1.

Figure 1. The mechanism of surface coating of iron particles poly(tetrafluoropropyl methacrylate) through a combination of reversible addition fragmentation chain transfer (RAFT) and click chemistry.

The chemical analysis and surface morphologies of grafted poly(tetrafluoropropyl methacrylate)–iron particles was characterized using Hitachi S-4700 equipped with an Oxford EDS System. The samples were magnified from 800X to 35 000X at an accelerating potential of 20 kV. The SEM images of non- and surface coated iron particles are shown in figures 2(a) and (b), respectively. Thin and uniform grafted polymers on a single iron particle can be seen in these pictures.

2.2. MRE Fabrication

For this research pure rubber samples, 50 wt% coated and non-coated Silicone MREs were prepared. Silicone QM113A
and B (Quantum Silicones) with the hardness of seven durometer were used for elastomer matrix and carbonyl iron powder CN (3–7 microns, BASF) with a density of 3.5 (g cm$^{-3}$) was used as iron particles. The two components were mixed with a mixer for 7 min at a weight ratio 10:1. Then, iron particles were added at the desired weight percentage, mixed, and the resulting mixture is poured into the mold. Then, the polymer was degassed at 25 in Hg vacuum for 30 min to remove the bubbles, and cured under 1.0 T of magnetic flux density for 5 h at 70 °C to align the iron particles. The curing process was continued in the oven at 70 °C for 12 h. The shear samples were fabricated based on the ASTM standard [42]. The electromagnet with the shear sample mold is shown in figure 3(a) and the shear MRE mold is shown in figure 3(b). The MRE mold is capable of curing 12 samples at a time. The picture of silicone MRE samples is shown in figure 4(a) and a silicone MRE double lap shear test is shown in figure 4(b). Sil-Poxy silicon adhesive was used and cured for 12 h to bond MREs and steel bars. The surface of steel bars were roughened using 220 grit sandpaper.

2.3. Oxidation of MREs

Elastomer matrix and MRE samples were exposed to air at room temperature for one week after they were removed from the mold prior to oxidation. Rectangular shape elastomer matrix and MRE samples were placed on three aluminum racks and the position of each sample was marked. The racks were placed into the chamber and the chamber was sealed. Compressed air was added to the chamber until the pressure reached 100 psi. The thermo-controller was set to 100 °C. When the temperature stabilized at 100 °C, the pressure was adjusted back to 0.68 MPa. The samples were taken out after one weeks. The oxidative test procedure for the MRE samples
with polymer coated iron particles was treated, similarly. The accelerated aging chamber is shown in figure 5.

3. Shear experiments

Shear properties of MREs can be examined using a quasi-static shear experiment. To correlate the input electric current with the magnetic field inside MRE samples, the magnetic field is measured using a magnetometer. As shown in figure 6(a) the probe of the magnetometer is inserted in a small slit inside the sample and the electric current is changed to measure the magnetic field of different samples. The actual magnetic field inside MREs is expected to be a little higher since the slit is expected to reduce the flux density.

Figure 6(b) demonstrates the magnetic field which is strongly related to the iron particle concentration and does not change considerably with the oxidation of the samples. For coated particles the magnetic field is 9.35% lower on average since the coating layer occupies space and reduces the amount of iron particles per unit volume. In the case of the pure elastomer samples, there is 150 mT magnetic flux density at 5 amp; but as it is shown in figure 8, the effect of magnetic field, when iron particles are not present, is minimal.

To investigate the effect of coating and oxidation on MRE samples, double lap shear tests are performed on an Instron electromechanical testing system (model 4210), as shown in figure 7. Shear test setup is consisted of two thick steel plates, and an electromagnet that can generate a closed-loop magnetic field, when the sample is installed. Shear test specimens are bolted to the Instron actuator and the shear test setup. All parts are parallel to ensure pure shear test condition. A 500lbf Lebow load cell (model number 3132-500) and a RDP Electronics LVDT (model number DCTH100AG) dc to dc displacement transducer with ±2.5 mm range and 1494 mV mm⁻¹ is used to measure force and displacement, respectively.

Figure 5. High pressure reactor for MRE ageing.

Figure 6. (a) Magnetic flux density measurement test set up and (b) magnetic flux density for different samples at different amps.

Figure 7. Double lap shear test setup and INSTRON dynamic testing system.
Shear experiments are performed on pure elastomer and 50 wt% coated and non-coated samples with the input frequency of 0.1 Hz and 17.5% strain amplitude. The input electric current is increased from zero to 4 amp to observe the effect of induced magnetic field within MREs. The applied magnetic field within MREs is parallel with the iron particle chains to achieve highest possible MR effect. Each test has been performed four times to ensure the consistency of the results and to obtain the standard deviation. Figure 8(a) demonstrates shear test results of the pure elastomer samples. As can be seen, the magnetic field does not affect the shear test results. As shown in figure 8(b), oxidation for a period of one week significantly reduces the shear modulus of the elastomer.

Figure 9 shows the stress–strain loop of the shear MRE samples with 50 wt% non-coated particle concentration. As can be seen, by increasing the input electric current the maximum stress in the loop increases, which corresponds to increase in the stiffness. However, area of the loop stays almost unchanged; thus, the change in the damping is minimal. On the other hand, since the base stiffness decreases after oxidation, then the relative change of the stiffness increases. This occurs since the stiffness change remains constant, but the off-state stiffness is reduced.

Figure 10 shows similar results for MREs with 50 wt% coated particles. Comparing the two Figures shows that the off-state stiffness does not change with coating of the iron particles, but after oxidation the off-state stiffness is less reduced as compared to the non-coated particles. This suggests that the coating preserves the stiffness better under oxidation.

The effective shear modulus helps to understand the MR effect under polymerization. The effective shear modulus is obtained based on maximum strain and maximum stress [43]. The MR effect is calculated using equation (1). MR effect for pure elastomer and 50 wt% coated and non-coated MRE is presented in table 1 along with the standard deviation of the effective shear modulus. As can be seen from table 1, oxidized coated samples tend to preserve the MRE properties compared to non-coated samples.

\[
\text{MR effect} = 100 \times \frac{G_{\text{on}} - G_{\text{off}}}{G_{\text{off}}} \quad (1)
\]

4. Summary and conclusions

In this study iron particles are polymerized using a combination of RAFT and click chemistry techniques. Shear MRE samples are prepared based on the ASTM standard using...
coated and non-coated particles. Some MRE samples are oxidized and their shear properties are examined utilizing double-lap shear tests to observe the effect of coating on performance of MREs.

Results show that oxidation significantly reduces the shear modulus of the pure elastomer as well as the MREs. The shear modulus of the pure elastomer is reduced three times while shear modulus of non-coated MREs is reduced nearly four times. This demonstrates that oxidation mainly affects the elastomer matrix, and also affects the bonding among particles and the matrix. It is shown that the effective modulus of coated MREs reduces 2.3 times, and that coating particles preserves the stiffness of MREs in oxidative environments.

Acknowledgments

This work was supported by the US National Science Foundation. The authors are grateful for the support.

Table 1. Effective shear modulus and percentage of MR effect.

<table>
<thead>
<tr>
<th>Input current (A)</th>
<th>Effective shear's modulus (kPa)</th>
<th>Standard deviation</th>
<th>MR effect (%)</th>
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<tbody>
<tr>
<td>0 wt%</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Non-oxidized</td>
<td>0</td>
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<td>1.21</td>
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<td>Oxidized</td>
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<td></td>
<td>4</td>
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<tr>
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<tr>
<td></td>
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<tr>
<td>Non-oxidized</td>
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<td>7.37</td>
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<td></td>
<td>4</td>
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<td>2.11</td>
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<td>4</td>
<td>168.6</td>
<td>2.17</td>
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