Surface Polymerization of Iron Particles for Magnetorheological Elastomers

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ABSTRACT: Magnetorheological Elastomers (MREs) are synthesized from silicone RTV (room temperature vulcanizing) elastomer with magnetically soft iron particles. The iron particle concentration of the MREs is 70 wt %. To reduce the effect of oxidation on the MREs, the ATRP technique is used for surface polymerization of iron particles with fluorinated styrene as monomer. The mechanical properties of MREs are characterized using a mechanical testing instrument, and the surface coated polymer is characterized using Fourier transform infrared spectroscopy (FTIR), X-ray energy dispersive spectrometry (XEDS), differential scanning calorimetry (DSC), and the alignment of iron particles within MRE was characterized using scanning electron microscopy (SEM). The MRE samples are characterized using the mechanical testing instrument at 0 Tesla (off–state) and applied magnetic field from 0.46 Tesla to 0.62 Tesla (on–state). The required force at 0.62 Tesla increased approx. 3% to achieve 20% strain after 72 h of oxidation for surface coated MRE. On the other hand, the required force for non-surface coated MREs at 0.62 Tesla increased up to 17% to achieve 20% strain after 72 h of oxidation. MREs with surface coated iron particles have higher oxidation stability based on the force–displacement test results, and MREs have excellent potential to be used as intelligent materials with high durability for a vibration isolator. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 934–942, 2010

Key words: ATRP; MREs; poly(fluorostyrene); surface polymerization; composites; elastomers; fluoropolymers; FTIR

INTRODUCTION

Magnetorheological Elastomers (MREs) are intelligent materials which are fabricated from magnetic particles and a crosslinked polymer matrix. MREs have viscoelastic and magnetorestrictive properties which can be used for vibration isolation. These distinguishable properties are because of the alignment of the magnetic particles in the polymer matrix that create a chain-like structure. These chains are locked in place by placing the material in a magnetic field during chemical crosslinking of the elastomer. The changes of viscoelastic and magnetostrictive properties can be controlled by varying the applied external magnetic field, which will cause a change of displacement between magnetic particles in the elastomer matrix. As a result, the stiffness and dimensions of MREs are controllable. In addition, chain-like magnetic particles provide a rapid time response of milliseconds.[1] This phenomenon is suitable for the vibration isolation. The response of MREs when an external magnetic field is applied is shown in Figure 1.

The excellent durability of MREs can be achieved because the magnetic particles are held in place by the polymer matrix. The MRE provides controllable stiffness by design of the elastomer magnetic particles, (e.g.) concentration and size. Potential problems with MRE for vibration isolation include: oxidation, stiffness, elastomeric hysteresis, and durability. The optimum concentration of magnetic particles in MREs needs to be determined. There are two issues which need to be considered. As a vibration isolator, the stiffness of the MRE should not be too high and oxidation of the iron particles needs to be prevented.

Oxidation takes place when the MRE is in contact with air. This effect can be reduced by surface treatment of the carbonyl iron particle surface. "Bridging" between iron particles because of surface coating is an additional concern. Two approaches to deal with this "bridging" issue include: (1) using a hard polymer coating in which the particles do not agglomerate, or (2) using a soft polymer coating with diluents in which the coated particles are maintained in liquid until they are added to the elastomer. Silicone and polyurethane based elastomers are good candidates as polymer matrices which have good
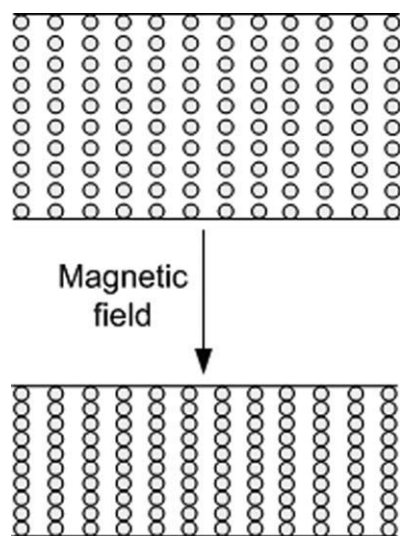
Figure 1 Sample deformation in magnetized MRE caused by external magnetic field.

thermo-oxidative, chemical resistance, and mechanical properties.[2,3]

Many living polymerizations have been studied including: ionic polymerization, emulsion polymerization, nitroxide radical polymerization (NMP), ring opening polymerization (ROMP), atom transfer radical polymerization (ATRP), and reversible addition fragmentation chain transfer (RAFT). ROMP has been used for surface polymerization of gold particles.[4–6] The small molecule, for example: a thio functional group (—SH), and chloro silane, has been used for covalently bonding the surface initiator. The monomers used include imide cyclic monomer and norbornene. Grubbs catalyst, 1st generation $((PCy_3)_2Cl_2Ru = CHPh)$, was used as a catalyst. A new method to prepare chitosan grafting copolymers with polystyrene using NMP technique has been investigated.[7]

ATRP for surface polymerization of iron particles has been investigated by Fuchs and coworkers.[8] The iron particles were coated using poly(butyl acrylate). Organic halide initiator, 2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane (CTCS), was covalently bonded onto the surface of iron via the silanol functional group. Copper based metal and sparteine were used as metal catalyst and ligand, respectively. Surface modified iron particles were used in magnetorheological fluids (MRFs). As a result, MRFs with surface coated particles showed improved performance as compared with traditional MRF. The grafting technique of thermo-responsive poly(N-isopropylacrylamide) poly(NIPAAm) onto silica nanoparticles using ATRP has been investigated.[9,10] Hollow sphere fabrication using ATRP was used.[11] The application of RAFT for surface polymerization of flat silicon substrate has been studied.[12,13]

Conductive polymers for interconnection (CPI) are prepared from a thin sheet with aligned magnetic particles. CPI has potential applications in device interconnection and circuit testing.[14] Sheets of transparent polymer with dispersed and vertically aligned ferromagnetic spheres have been used for touch-sensitive screens and other visual communication devices.[15] Ginder et al. used MRE with carbonyl iron and natural rubber for automotive mounts.[1] Isotropic MRE using polyurethane/Si-rubber hybrid gave higher MR effect than pure polyurethane or Si-rubber matrix.[16] Tunable automotive bushings have been developed using MRE.[17] MRE has been used for displacement and force sensors, tunable automotive bushings to increase vehicle handling, and to reduce vibration and noise.[18,19]

In this work, MREs are synthesized from silicone RTV (room temperature vulcanizing) elastomer with soft magnetic iron particles. The iron particles concentration was 70 wt %. The ATRP technique was used for surface polymerization of iron particles with fluorinated styrene as a monomer. The mechanical properties of MREs, properties of surface coating polymer, and the alignment of iron particles within MRE are characterized. To the best our knowledge, this is the first time that surface coated iron particles using poly(fluorostyrene) are used for MREs.

EXPERIMENTAL

Materials

Silicone RTV was synthesized using: silicones RTV615A which is vinylmethylpolysiloxane and RTV615B which is methylhydrogenpolysiloxane (GE) (molecular weight is about 10,400), carbonyl iron powder CN (3–7 microns, BASF), 4-fluorostyrene (Aldrich), methanol (Aldrich), ethanol (AAPER), 1-octyl-2-pyrrolidone (Aldrich), CuBr (Aldrich), $CuBr_2$ (Aldrich), sparteine (Aldrich), toluene (Aldrich), 2-4(-chlorosulfonylphenyl)-ethytrichlorosilane (CTCS) (Gelest), azobisisobutyronitrile (AIBN) (Aldrich), polydimethylsiloxane (Silicone oil) (GE).

Synthesis

MRE synthesis

The two components (10 : 1 vinylmethylpolysiloxane (a) methylhydrogenpolysiloxane (b) ratio by weight) were mixed and then 30 wt % silicone oil was added as a plasticizer and mixed with a high speed mixer for 5 min. Iron particles, 8 μm, were added at 70 wt % and mixed completely. After mold injection, the pre-cured polymer was degassed at 25 in Hg vacuum for 30 min to remove the bubbles, and then cured under 0.6T magnetic flux density for 24 h and demolded.[2,20] The MRE has round shape with 6 cm diameter and
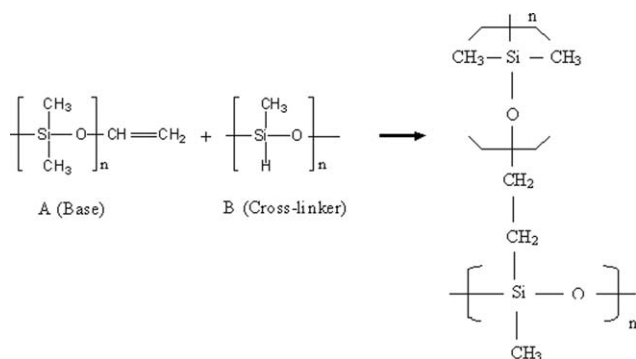
Figure 2 The reaction of silicone elastomer.[2,20]

3 mm thickness. The scheme of silicone RTV reaction from vinylmethylpolysiloxane and methylhydrogenpolysiloxane is shown in Figure 2.

ATRP for surface polymerization iron particles

ATRP was used for controlled radical polymerization as a surface polymerization technique. The procedures were as follows: 400 g of iron particles were washed with distilled water and ethanol. Then, they were dried in a vacuum oven at 50°C and under nitrogen purge for 24 h and cooled down. Dried iron particles were added and reacted at 85°C with 6 g CTCS for 24 h under nitrogen with 110 g of toluene as a solvent. The mixture was filtered and washed with methanol in order to remove excess CTCS. The residue (Fe-CTCS) was dried in a vacuum oven at 40°C for 24 h. 4-fluorostyrene (monomer) 1.5 g, 120 g of functionalized Fe-CTCS were reacted with 0.1 g CuBr, 0.05 g $CuBr_2$, 0.1 g spartein in 65 g octyl pyrrolidone at 85°C in a four port reactor flask for 24 h under nitrogen. Finally, the mixture was filtered, washed several times with methanol and dried in a vacuum oven at 40°C before use.

Characterization

The performance of MR elastomers was characterized in terms of thermo-oxidative stability and mechanical properties. The properties of MR elastomers were characterized using several approaches such as oxidative testing, Scanning Electron Microscopy-X-ray Energy Dispersive Spectrum (SEM-XEDS), Mechanical Testing Instrument (Instron), Fourier Transform Infrared (FTIR), and Differential Scanning Calorimetry (DSC). The characterization methods are discussed in the following section and the samples have been tested in triplicate.

Oxidation test

The oxidation of the MRE surface is an important issue. The oxidation process can change the proper-

ties of the MRE due to the formation of a chemical layer on the surface of the MRE. An ageing study was conducted to accelerate the oxidation and degradation of the polymer at high temperature and pressure. The MRE was aged using a high pressure and high temperature reactor. The reactor was equipped with inlet and outlet gas ports, thermometer port, and pressure gauge. The ageing study conditions were set at 100–110°C and 100 psi of pressurized air for 48 h.[2,3,20]

Scanning electron microscopy–x-ray energy dispersive spectrum (SEM-XEDS)

The alignment of iron particles within the polymer matrix and chemical analysis of surface coated iron particles were characterized using scanning electon micrcrosope–X-ray energy dispersive spectrum (SEM-XEDS) by Hitachi S-4700 equipped with an Oxford EDS System.

MRE force–displacement test

The force-displacement of MR elastomers was investigated with respect to applied force with different supplied currents (0A supplied current corresponds to 0 Tesla; 1A supplied current corresponds to 0.46 Tesla; 2A supplied current corresponds to 0.54 Tesla; 3A supplied current corresponds to 0.62 Tesla). The MR elastomer was placed in a fixture that has 6 cm inside diameter, equipped with coiled wires to generate magnetic fields, which perpendicular to sample. Then, compressive force was exerted on the MR elastomer using the material testing instrument. The displacement was set up to 20% strain and recorded using the data acquisition system (30 data points per second) through linear variable differential transformer that was connected to the computer system and test fixture. The relationship between magnetic field and supplied current in the test fixture was simulated using Ansoft. The force–displacement instrumentation, the test fixture scheme, and the simulation result of magnetic field within the fixture are shown in Figure 3, 4, and 5, respectively. Error analysis of experiment, 95% confidence interval (CI) was used, was performed based on three experimental measurements for data taken (each required force to achieve 20% strain).

Differential scanning calorimetry

The thermal properties of the MRE for surface coated iron particles were characterized using Perkin-Elmer Pyris-1 DSC. Two pans placed in the DSC were used for holding the sample and reference. The samples were dried in vacuum oven at 60°C for 24 h and stored in desiccator before characterization. The
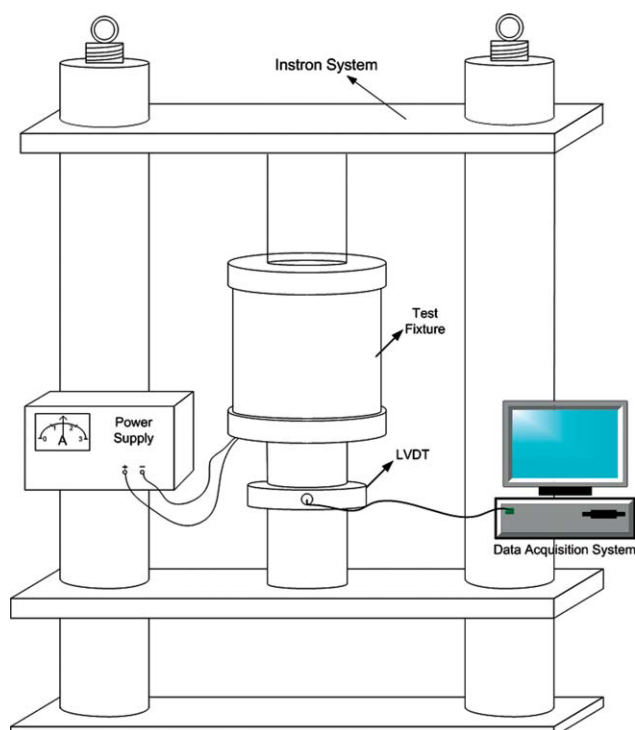
Figure 3 The force-displacement test set up.[21] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface coated iron particles (17.3 mg) were placed in the sample pan and scanned from 50°C to 600°C with heating rate 10°C/min. The temperature scanning has been done under high purity nitrogen purge with volumetric flow rate of 20 mL/min.
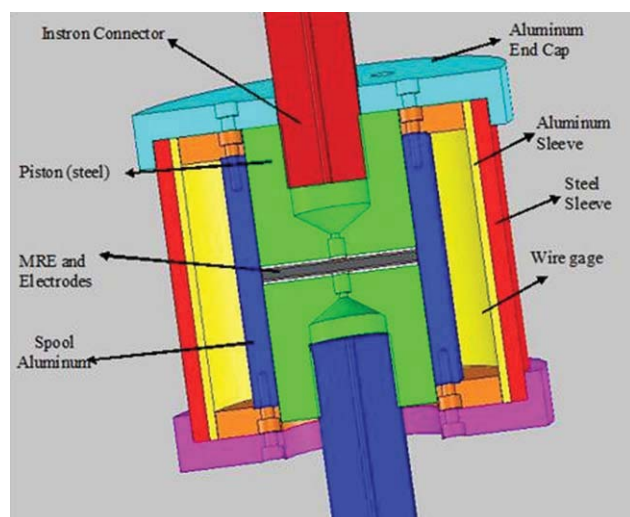

Figure 4 The cross sectional of test fixture.[21] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
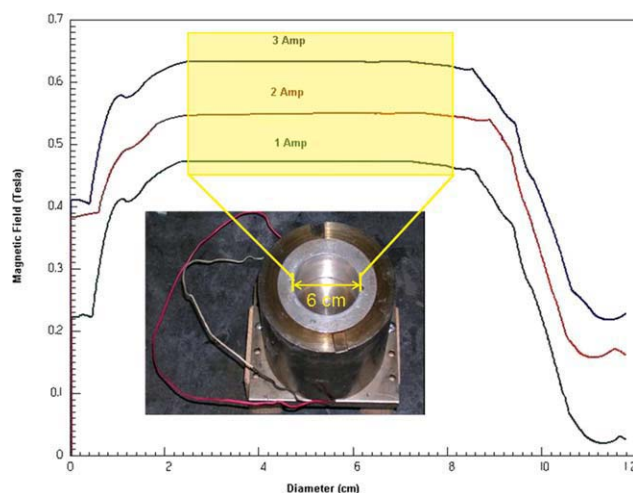

Figure 5 Simulation result of magnetic field within the fixture.[21] [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Fourier transform infrared

The surface modified iron particles were characterized using Perkin-Elmer Spectrum 2000 FTIR spectroscopy. The sample of uncoated iron (Fe), immobilized surface initiator iron particles (Fe–CTCS), and polymer grafted iron particles (Fe–CTCS–poly(fluorostyrene) were scanned from 4000 cm^{-1}–400 cm^{-1} at room temperature. The samples were dried in vacuum oven at 60°C for 24 h and stored in desiccator before characterization.

RESULTS AND DISCUSSION

Optical microscopy and scanning electron microscopy–energy dispersive x-ray spectrophotometer

The distribution of iron particles within MRE was imaged using SEM. The applied magnetic field during curing of MREs yields ordered iron particles in the shape of a chain–like structure (anisotropic MRE). On the other hand, the unoriented curing process, without applying magnetic field, of MRE yields a nonoriented (isotropic MRE) iron particle (>10 wt %) within MRE and has been imaged.[2,20] The iron particles are randomly distributed within the MRE. The cross sectional image of isotropic and anisotropic MREs are shown using SEM in Figure 6.

Controlled living polymerization, such as atomic ATRP, has significant advantages as compared with the regular radical polymerization process because the polymer is covalently bonded on the iron surface, and uniform molecular weight of the polymer results.[8–11] The synthesized polymer using ATRP commonly has polydispersity index close to 1.[8–11] This results in production of uniform coating thickness. The presence of atomic fluorine on the polymer
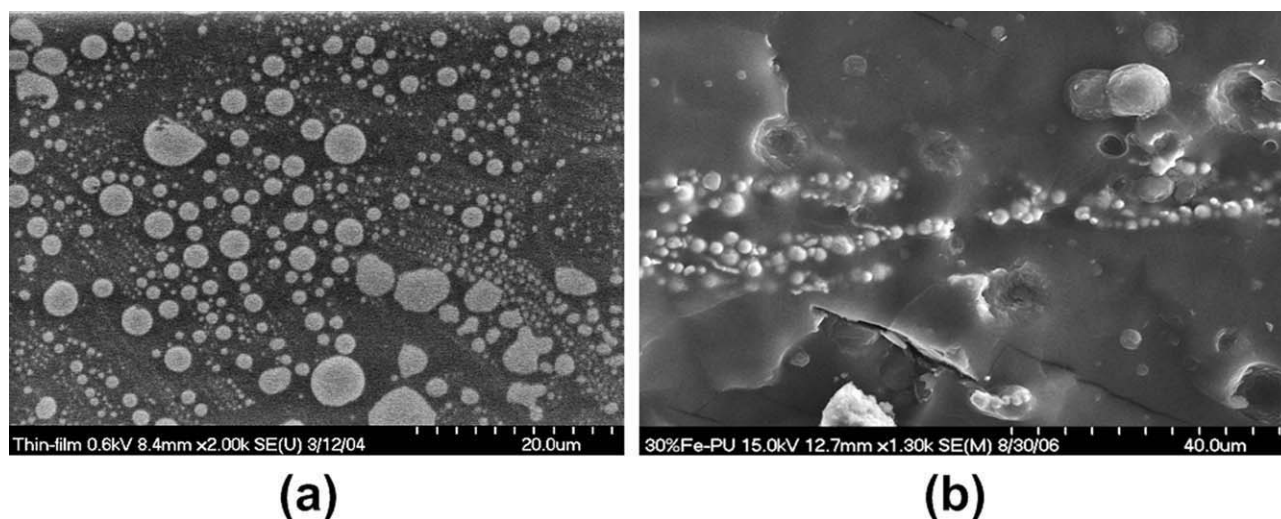
Figure 6   SEM images of cross sectional MRE: (a) isotropic[2] and (b) anisotropic.

backbone in the surface coating of the iron particles has been confirmed by X–EDS. The ATRP mechanism is shown in Figure 7. The SEM and X-EDS images of surface coated iron particles are shown in Figure 8.

Differential scanning calorimetry

The thermal properties of polymer coated on the surface of iron particles were characterized using DSC. Fluorinated styrene coating shows the thermal transition temperature at 221.8°C. The poly(fluoro styrene) synthesized in our laboratory has higher thermal transition temperature than grafted polystyrene on silica surface, which has a thermal transition temperature of 133°C.[22] In addition, the bulk polystyrene has thermal transition temperature of 102°C.[22] Higher thermal transition temperature for grafted polymer is because of the covalently bonded polymer onto the surface that restricts the mobility of molecules.[22] As a result, additional energy is required to achieve the rubbery state of the grafted
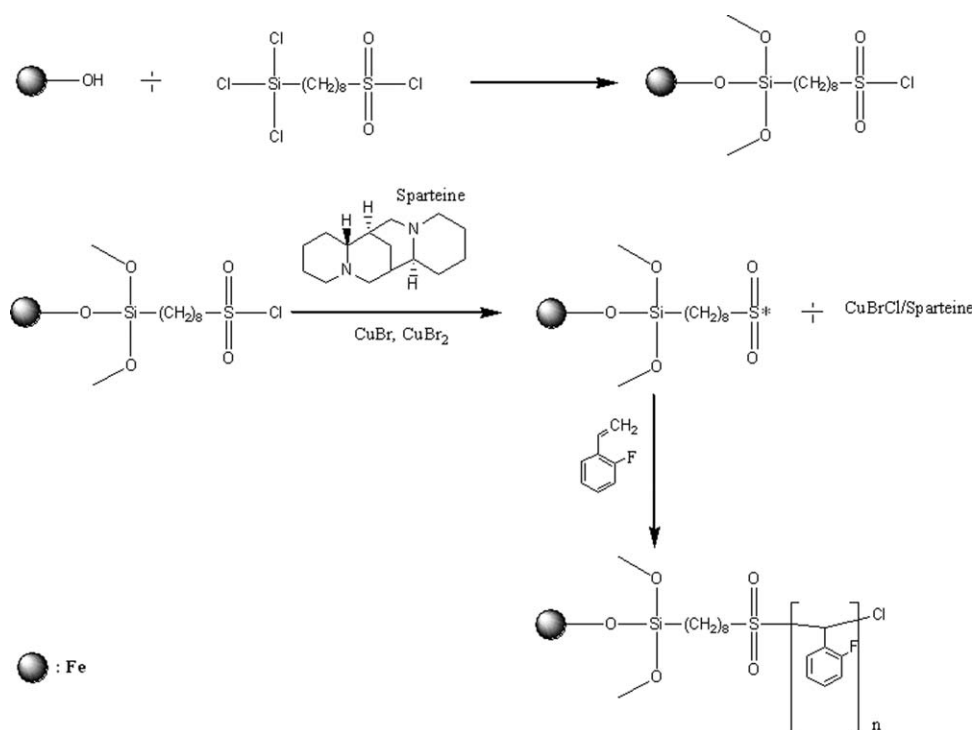

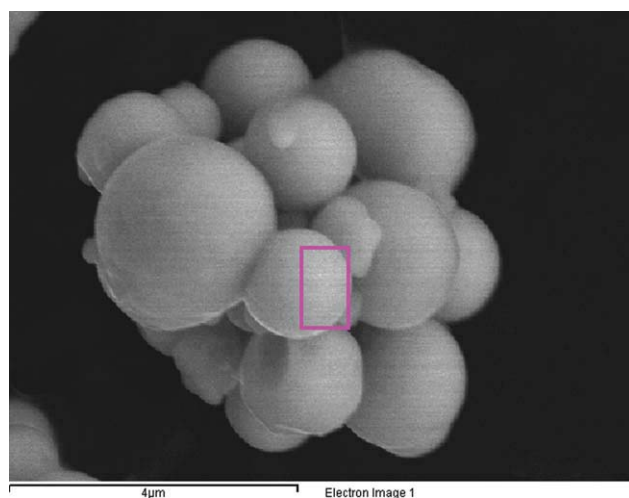**Figure 7**   ATRP mechanism of iron particle surface coating.

Figure 8 SEM image of iron particles. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 10 The FTIR curve for grafted poly(fluorostyrene).

polymer. The DSC curve for grafted poly(fluorostyrene) on the iron particles is shown in Figure 9.

Fourier transform infrared

Transmission data for uncoated iron particles, iron particles–CTCS, and iron particles–CTCS–poly(fluorostyrene) are shown in Figure 10. Comparing the curves of Fe and Fe–CTCS, the peak is shifted at 600 cm-1 represents the alkyl halide (C—F) stretch from the poly(fluorostyrene). Shifted peak at 1600 cm^{-1} (C=C) and 3600 cm^{-1} (Si—OH stretch) can be associated with the presence of surface initiator (CTCS) on the iron particles. In addition, another peak appears in the range of 1000–1250 cm^{-1} (SO$_2$ stretch) on the Fe–CTCS and Fe–CTCS–poly(fluorostyrene) if compared with Fe, which means the surface initiator has been covalently attached to the Fe.

The effect of surface coating and oxidation on the force–displacement curve

The mechanical properties of MRE were characterized before and after oxidation for 24 h to 72 h using mechanical testing instrumentation. The effect of magnetic field, from 0 Tesla to 0.62 Tesla, was also investigated. For MRE with noncoated and coated iron particles, required force was obtained to be increased by increasing magnetic field to achieve 20% strain. The similar phenomena were occurred for MRE before and after the oxidation process. As a result of mechanical test, MRE exhibited the properties which can be used as vibration isolator, which the MRE stiffness can be adjusted by magnetic field to store the desired amount of energy.

The MR effect was generated by applying magnetic field (0 Tesla; 0.46 Tesla; 0.54 Tesla; 0.62 Tesla), varied by supplied current in the range of 0A to 3A, and measured as force/displacement between surface coated and nonsurface coated iron particles. Before the oxidation test, the required force increased approximately 14% to achieve 20% strain for surface coated iron particles from 0 Tesla to 0.62 Tesla and nonsurface coated iron particles was increased around 23%. This difference was presumably caused by decreasing the magnetic permeability of surface coated iron particles as the polymer coating is not magnetizable. The force displacement curve of nonsurface coated and surface coated iron particles with varying magnetic fields before oxidation are shown in Figures 11 and 12, respectively. The data at 0.54 Tesla for noncoated and coated MRE lie between 0.46 Tesla and 0.62 Tesla, so they are superimposed in Figure 11.

To investigate the affect of oxidation, the MREs with and without surface coated iron particles were exposed to air at high pressure and temperature (100 psi and 100–110°C). Then, the MR effect change was evaluated at a variety of applied magnetic
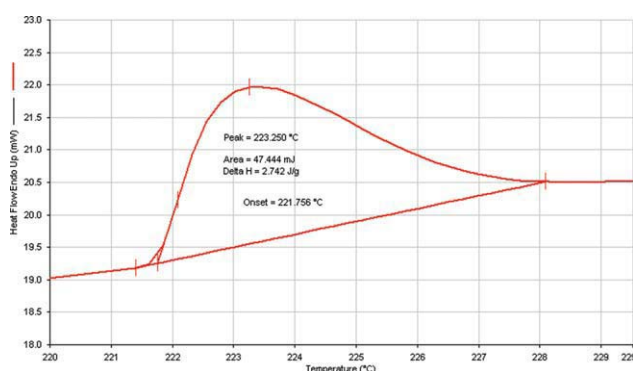

Figure 9 The DSC curve for grafted poly(fluorostyrene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
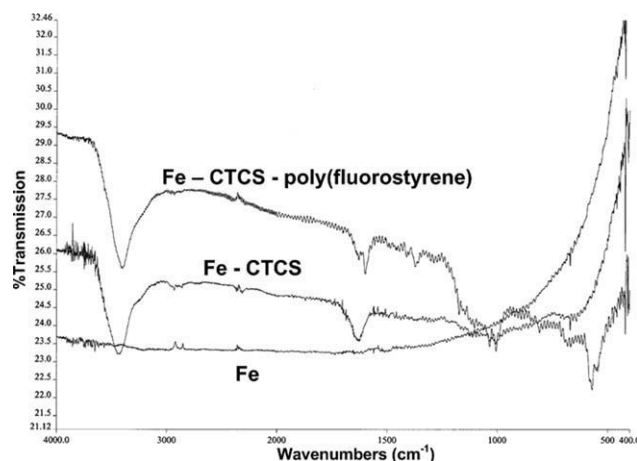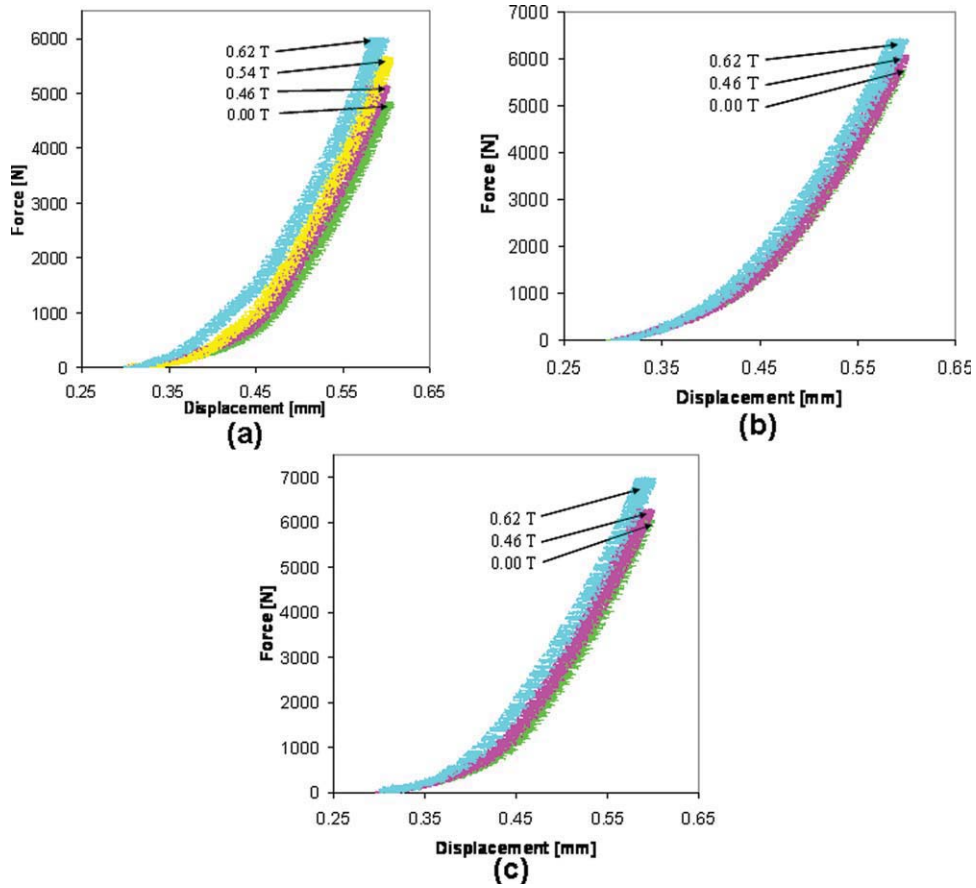
Figure 11 Force–displacement curve for MRE non surface coated iron particles with different applied magnetic fields; (a) before oxidation test, (b) after 24 hrs oxidation test, and (c) after 72 hrs oxidation test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 12 Force–displacement curve for MRE surface coated iron particles with different applied magnetic fields; (a) before oxidation test, (b) after 24 hrs oxidation test, and (c) after 72 hrs oxidation test. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
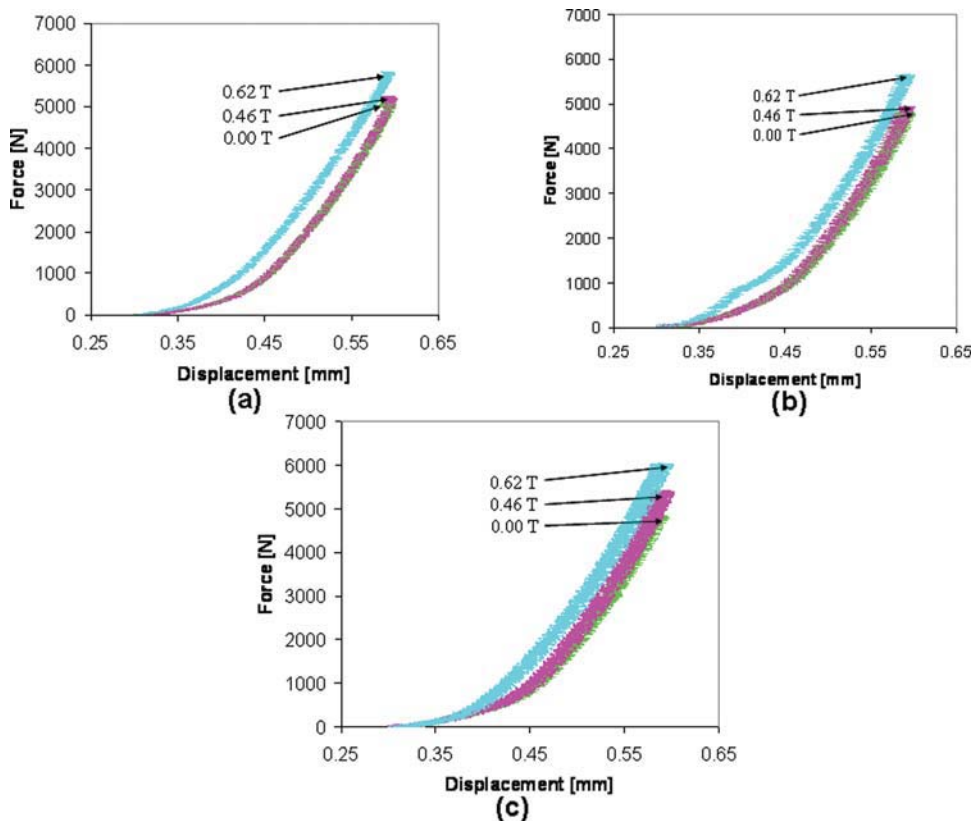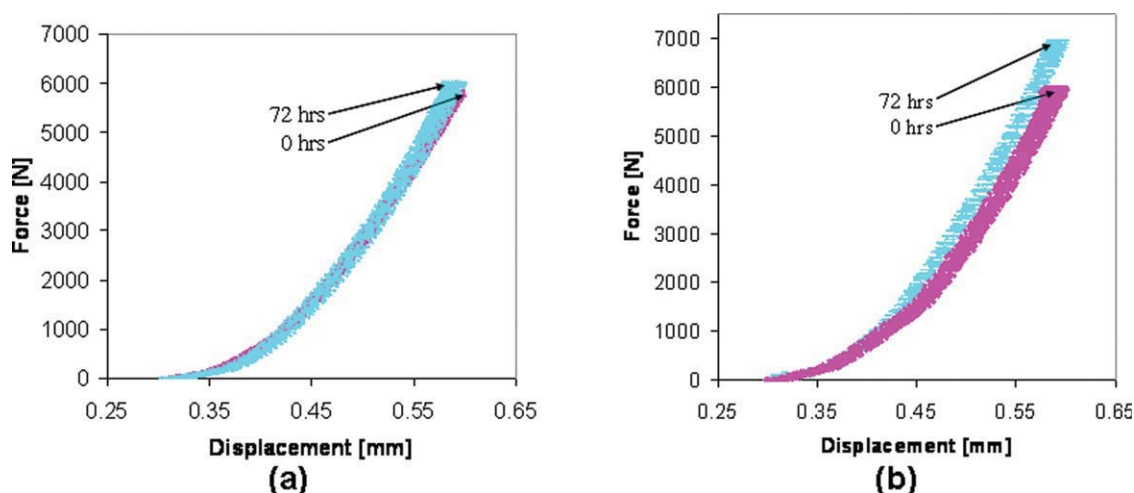
Figure 13 Force–displacement curve for MRE before and after 72 h oxidation test with applied magnetic fields 0.62 Tesla; (a) Surface coated, and (b) non surface coated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fields, which varied from 0 Tesla to 0.62 Tesla, and measured in terms of force–displacement between surface coated and nonsurface coated iron particles. After the oxidation test for 72 h, the required force increased approx. 18% to achieve 20% strain for surface coated iron particles from 0 Tesla to 0.62 Tesla and nonsurface coated iron particles was increased around 16%.

$$\text{MR Effect} = \left| \frac{F_f - F_i}{F_i} \times 100\% \right|$$

where F_f is final required force to achieve specified strain, F_i is initial required force to achieve specified strain.

The maximum force required at 20% strain and 0 Tesla (off–state) is 4% higher for surface coated iron particles before and after oxidation for 72 h. This phenomenon indicates that surface coating can be used for maintaining the performance of MREs (iron particles, polymer matrix, and polymer matrix–iron particles interface) exposed to an oxidative environment. On the other hand, MREs with nonsurface

coated iron particles requires a higher force (24% increases) to achieve 20% strain.

Higher required force (17% difference) required at 20% strain for applied magnetic field (0.46 Tesla and 0.62 Tesla) is exhibited by MRE with nonsurface coated iron particles after oxidation. On the other hand, MRE with surface coated iron particles before and after oxidation for 72 h exhibits 3% higher required force to achieve 20% strain. Again, this phenomenon indicates that surface coating can be used for maintaining the performance of MRE. The force displacement curve of nonsurface coated and surface coated iron particles with 0.62 Tesla magnetic fields before and after oxidation test for nonsurface coated and surface coated is shown in Figure 13. The summary of oxidation effects on MRE in terms of required force to achieve 20% strain for each supplied current before and after 72 hrs oxidation processes are listed in Table I.

CONCLUSIONS

A surface grafting technique of fluorinated polymer on the inorganic substrate via atom transfer radical polymerization (ATRP) has been developed for iron particles. The coated iron particles have been used in magnetorheological elastomers (MREs). MREs have been prepared from silicone RTV and two different types of iron particles; noncoated particles and surface coated particles. The MREs which were prepared with surface coated iron particles have superior mechanical properties respect to oxidation stability test. MREs with surface coated iron particles required only 3% higher force to achieve 20% strain after 72 h oxidation when the magnetic field was applied at 0.62 Tesla. On the other hand, the

TABLE I
The Summary of Percentage Change of Required Force to Achieve 20% Strain for Each Supplied Current Before and After 72 Hrs Oxidation Processes of MRE

Magnetic field (Tesla)	Type of MRE	
	Non surface coated (%)	Surface coated (%)
0	(24 ± 0.48)	(4 ± 0.60)
0.46	(17 ± 0.63)	(3 ± 1.10)
0.62	(17 ± 0.59)	(3 ± 0.55)

required force for MREs with nonsurface coated iron particles changed up to 17% to achieve 20% strain after 72 h oxidation test. Based on this work, MREs have potential to be used as intelligent materials for vibration isolation.

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