Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Polymer Testing 24 (2005) 324–329
POLYMER TESTING
www.elsevier.com/locate/polytest

Material Behaviour

# New magnetorheological elastomers based on polyurethane/Si-rubber hybrid

Y. Hu[a,*], Y.L. Wang[a,b], X.L. Gong[c], X.Q. Gong[b], X.Z. Zhang[b], W.Q. Jiang[c], P.Q. Zhang[b], Z.Y. Chen[c]

[a]*State Key laboratory of Fire Science, University of Science and Technology of China (USTC), Hefei 230026, China*
[b]*CAS Key Laboratory of Mechanical Behavior and Design of Materials, Department of Mechanics and Mechanical Engineering, USTC, Hefei 230027, China*
[c]*Department of Chemistry, USTC, Hefei 230026, China*

Received 21 September 2004; accepted 9 November 2004

**Abstract**

A type of magnetorheological elastomer based on polyurethane (PU)/silicone rubber (Si-rubber) hybrid was fabricated without applying a magnetic field. The MR effect was improved by optimizing preparation conditions, in particular by adjusting the PU/Si-rubber ratio, and improving compatibility between PU and Si-rubber. The influences of the preparation conditions and the relationship between the microstructure and MR effect of this kind of magnetorheological elastomer are discussed in detail. The results show that this kind of MR elastomer has better MR effect than that of MR elastomers based on pure Si-rubber or PU matrix with the same testing conditions. SEM analysis indicates that the former forms a peculiar interpenetrating microstructure in the presence of PU in the matrix. The maximum increase in shear modulus of this kind of MR elastomer can be up to 0.5 MPa when exposed to a magnetic field of about 0.2 T.


*Keywords:* Magnetorheological elastomers; Polyurethane/rubber hybrid; Microstructure

## 1. Introduction

Magnetorheological (MR) materials are a group of smart materials whose rheological properties can be controlled by the application of an external magnetic field. MR fluids are the most common MR materials which exhibit Newtonian-like behavior in the absence of a magnetic field and become a weak viscoelastic solid with a certain yield stress when a magnetic field is applied [1]. MR elastomers can be thought of as a new generation of MR materials and have distinct properties relative to MR fluids because the matrix is a rubber-like solid material rather than liquid oil. MR elastomers have controllable field-dependent modulus while MR fluids have a field-dependent yield stress. The obvious advantage of MR elastomers is that the particles are not able to settle with time and hence have stable MR performance. MR elastomers hold promise in adaptive tuned vibration absorbers, stiffness tunable mounts, and automobile suspensions [2].

MR elastomers can be classified into two kinds: anisotropic MR elastomers and isotropic MR elastomers. Anisotropic MR elastomers have a special chain structure of magnetic particles in the matrix because the curing of the matrix is performed under a strong magnetic field. This kind of MR elastomer with special chain structure of magnetic particles has long attracted the interest of the researchers and materials have been fabricated based on different matrices, i.e. silicone elastomers [3–5], poly (vinyl alcohol) [6], gelatin [7], hard natural or synthetic rubber [8]

* Corresponding author. Tel./fax: +86 551 3601664.
*E-mail addresses:* yuanhu@ustc.edu.cn or gongxl@ustc.edu.cn (Y. Hu).

0142-9418/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymertesting.2004.11.003

and polyurethane sealant [9]. However, the typical magnetic fields needed to prepare them are very strong, about $8\times10^6$ A/m [4], which makes the manufacture complicated and difficult to be broadly applied.

The preparation of isotropic MR elastomers is almost the same as that of anisotropic MR elastomers except that the curing of the matrix is not performed under a magnetic field. Hence, the magnetic particles disperse uniformly in the matrix and the manufacture is greatly simplified. Recently, Lokander and Stenberg [10,11] have studied isotropic MR rubber. They have made MR elastomers by embedding large irregular particles into nitrile rubber without using a magnetic field to align the particles, and these MR elastomers have a large absolute MR effect. However, in order to achieve such a substantial MR effect, the amount of the magnetic particles needed is too large which results in a high zero-field modulus and a low relative effect.

Up to now, there are no reports about MR elastomers based on a blend of polymers, especially an immiscible polymer matrix. According to the literature [12], when iron particles are dispersed in a two-polymer blend, a special interpenetrating structure can be formed and the system becomes conductive at lower average filler content compared to the single matrix. In this paper, a type of isotropic MR elastomer based on polyurethane/Si-rubber hybrid is fabricated by curing without applying a magnetic field. The influences of the preparation conditions and the relationship between the microstructure and MR effect for this type of MR elastomer are also discussed in detail.

## 2. Experimental

### *2.1. Materials*

The spherical carbonyl iron particles were FTF-4 type with size range of 3–5 μm bought from Hebao Nanomaterial Co., Ltd. The one-composition Si-rubber was RTV 704 from the Xida Adhesives Factory. Dimethyl-silicon oil was 201–500 Si-oil from Shanghai Resin Factory. The polyurethane was synthesized in our laboratory using reactions between poly (butadiene polyol) and isocyanate. The poly (butadiene polyol) was hydroxy-terminated (Shandong Qilu Ethylene Chemical Industry Stock Co. Ltd) with an equivalent molecular weight of 2300 and a functionality of 0.80–1.0. The isocyanate was TDI (Tolune Diisocyanate) with a functionality of 2.0. The molar ratio of the TDI/poly (butadiene polyol) was 0.6. After the reaction at 80 °C for about 1 h, a viscous liquid (polyurethane) was synthesized.

### *2.2. Common procedure for preparing MR elastomers based on PU/Si-rubber hybrid*

Firstly, carbonyl iron particles were mixed with Si-oil followed by this mixture being mixed with Si-rubber. The synthesized polyurethane was added and thoroughly mixed. Then the mixture was poured into a mold and cured in an oven at 80 °C for 17 h.

In all samples containing Si-oil and Si-rubber, the weight ratio of Si-oil to Si-rubber was kept constant as 8/9.

### *2.3. MR elastomers based on pure Si-rubber or PU matrix for comparison*

The procedure for preparing this kind of MR elastomers was almost the same as that of MR elastomers based on PU/Si-rubber hybrid, except that comparative sample based on pure Si-rubber matrix was cured at room temperature. The weight ratio of Si-oil to single matrix was also kept constant as 8/9.

### *2.4. MR measurements*

The magnetorheological effect was evaluated by measuring the dynamic shear modulus with and without an applied magnetic field The schematic equipment set-up is shown in Fig. 1. The principle of the tests can be found in [13].

The magnetic field was produced by an electromagnet and the magnetic induction through samples was kept at 0.2 T. The test samples were about $28\times7\times4$ mm and sandwiched between a brass and an aluminium plate.

### *2.5. Morphological characterization of elastomers*

The samples are cut into pieces and scanning electron microscopy of cut surfaces performed with a XL30 ESEM at an accelerating voltage of 10–15 kV depending on the sample.

## 3. Results and discussions

The key factors, which directly affect the microstructure and the final MR effect, are discussed below.

### *3.1. Way of mixing materials*

Two different ways to mix materials for fabricating PU/Si-rubber hybrid were attempted. The first way was to mix PU, Si-rubber and iron particles at the same time and then to cure the mixture. The other way was to mix the Si-rubber and PU uniformly, then to add the iron particles to the blend polymer and finally to cure the mixture. The typical SEM micrographs of MR elastomers obtained by different ways of mixing materials are shown in Figure 2. Fig. 2(a) depicts the morphology of MR elastomers obtained by the first method. Si-rubber inlays in the PU matrix and the iron particles are preferentially located in the PU phase. Fig. 2(b) shows the morphology of MR elastomers prepared by the second method. In Fig. 2(b), the two polymers intercross uniformly and the iron particles mainly disperse in the surface of the PU phase. Their mechanical performances

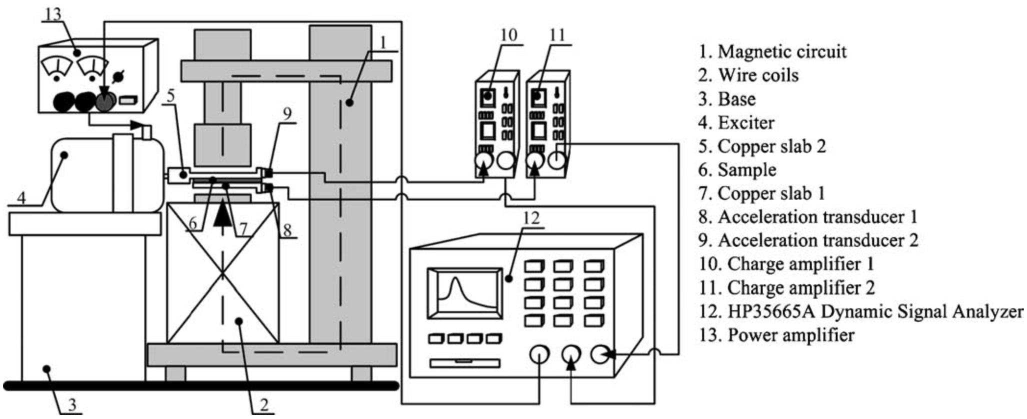


Fig. 1. Sketch of the measurement apparatus for MR elastomers.

show that the MR elastomers with microstructure (a) have better MR effect than MR elastomers with microstructure (b). The relative MR effect of the former is about 25% and the latter only 2%. However, the physical properties of MR elastomers by the first way are not so good. Therefore, the first mixing method for preparing hybrids was improved as described in Section 2: to firstly mix iron particles with one polymer, then to add the other polymer into the mixture and finally to mix them thoroughly. The morphology of MR elastomers by this way is similar to that in Fig. 2(a).

### 3.2. Si-oil additive

When preparing the MR elastomers, extra additive is very important. Fig. 3(a) is a typical SEM micrograph for PU/Si-rubber hybrid without Si-oil additive.

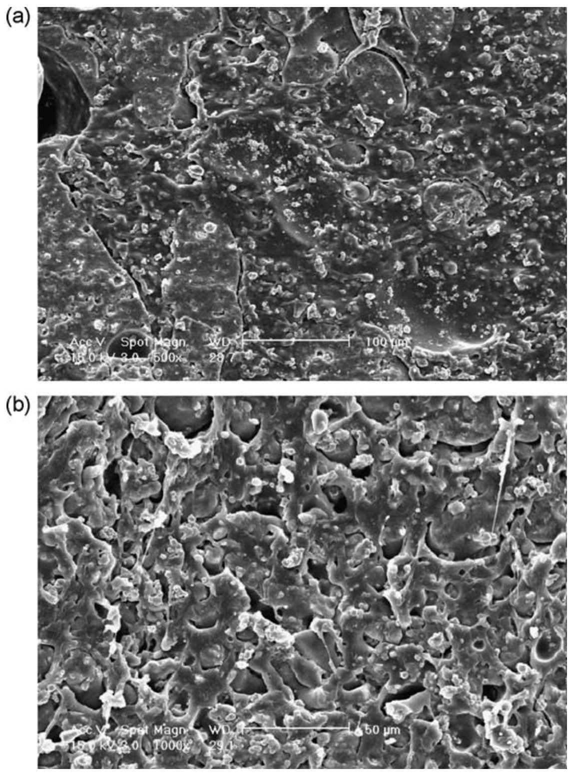


Fig. 2. SEM micrographs of MR elastomers fabricated by different way of mixing materials.

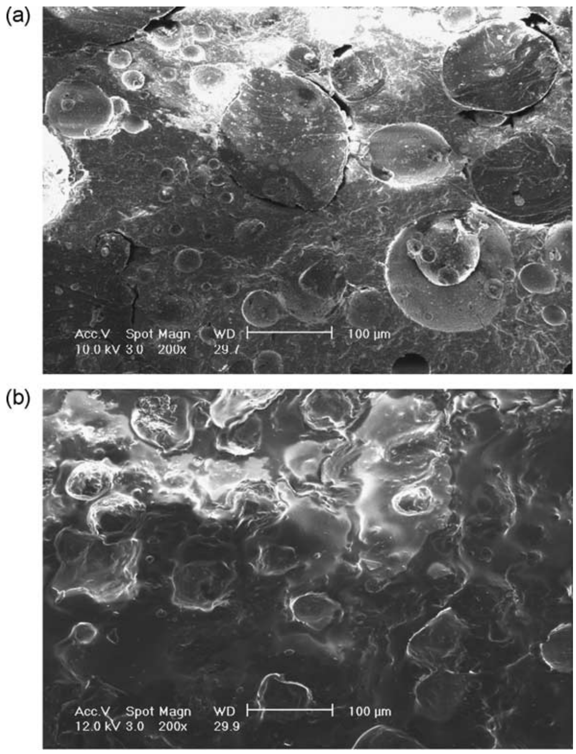


Fig. 3. SEM micrographs of PU/Si-rubber hybrid (a) without or (b)with Si-oil additive (weight ratio for all PU/Si-rubber hybrids is 1/1).

Table 1
Relationship between Si-oil additive and MR effect

| No. of samples | Composition | Relative MR effect (%) | Absolute MR effect (MPa) |
|---|---|---|---|
| 1 | 4.5 g PU +9 g silicon rubber +36 g carbonyl iron particles without Si-oil | 9 | 0.34 |
| 2 | 4.5 g PU +9 g silicon rubber +36 g carbonyl iron particles with 8 g Si-oil | 35 | 0.44 |

The morphology consists of round PU agglomerates, about 100 μm in diameter, inlayed within the silicon rubber matrix. The adhesion between PU and the silicon rubber is rather weak as depicted by the gaps between the two polymers. This means that compatibility between PU and Si-rubber is poor because PU and Si-rubber occupy their own fields. To improve the compatibility, a variety of additives were tested. The experimental results show that Si-oil additive gives the best result. Fig. 3(b) is a typical SEM micrograph for PU/Si-rubber hybrid with Si-oil additive. The diameter of PU agglomerates becomes smaller and the distribution of the PU agglomerates becomes more uniform. Also, the gap between the two polymers cannot be seen clearly. This may be explained by Si-oil having good compatibility with the Si-rubber and able to reduce its viscosity and the interfacial tension of the PU/Si-rubber.

Table 1 shows the results of MR measurements for samples with and without Si-oil additive. From Table 1, it can be seen that the addition of Si-oil additive greatly improves the relative MR effect. The reason may be that Si-oil improves the compatibility between PU and Si-rubber and decreases the zero-field modulus of the blend polymer. However, the absolute MR effect seems independent of the matrix materials.

### 3.3. Concentration of carbonyl iron particles

Generally, the concentration of carbonyl iron particles in the prepared elastomers has a large influence on the MR effect. Table 2 shows the relationship between MR effect and concentration of carbonyl iron particles (wt%, i.e. $w_{Fe}/(w_{Fe}+w_{PU}+w_{Si\text{-}rubber})$) when PU/Si-rubber by weight ratio was 0.5.

Table 2
Relationship between MR effect and concentration of carbonyl iron particles

| No. of samples | $w_{Fe}/(w_{Fe}+w_{PU}+w_{Si\text{-}rubber})$ (wt%) | Relative MR effect (%) | Absolute MR effect (MPa) |
|---|---|---|---|
| 3 | 67 | 29 | 0.15 |
| 4 | 73 | 35 | 0.44 |
| 5 | 79 | 31 | 0.26 |

The weight ratio for PU/Si-rubber is 0.5/1.

It can be seen from Table 2 that there is a maximum in the relative MR effect when the concentration of carbonyl iron particles reaches 73%. A similar result has been obtained in isotropic MR elastomers based on nitrile rubbers [10]. The new MR elastomers based on PU/Si-rubber also have a 'Critical Particle Weight Concentration' (CPWC). Excessive increase of filler content in the samples will increase the stiffness of the elastomers but the absolute MR effect will not increase much, or even decrease (in our experiment) with iron particles content increase. Hence, the relative MR effect will show a maximum value.

### 3.4. Weight ratio of PU/Si-rubber

Table 3 shows the relationship between weight ratio of PU/Si-rubber in the prepared samples and corresponding MR effect. Fig. 3 is their relevant SEM analyses.

It can be seen from Table 3 that MR elastomers based on PU/Si-rubber have higher MR effect compared to the MR elastomers based on single Si-rubber or PU matrix. The MR effect for the elastomers based on pure PU matrix is larger than for the elastomers based on pure Si-rubber matrix.

In Fig. 4(a), iron particles disperse uniformly in the matrix of single pure Si-rubber. However, it can be seen in Fig. 4(d) that pure PU has poor compatibility with Si-oil, and there are many voids. Also, iron particles mainly disperse in the edge and interior of the holes. When a magnetic field is applied, the iron particles interact with a hole as a unit. This behavior is equal to increasing the size of iron particles. According to the literature [7], MR elastomers using iron particles with larger size have higher MR effect.

In Fig. 4(b) and (c), when the matrix is hybrid polymer, iron particles disperse selectively in the Si-rubber phase. At the same average concentration, such a structure will result in improving the local concentration of iron particles in this polymer phase, and bring about irregular agglomeration of magnetic particles. Both of these two aspects are helpful to increase the MR effect for the hybrid elastomers. Thus, the MR elastomers based on PU/Si-rubber have higher MR

Table 3
Relationship between weight ratio of PU/Si-rubber and MR effect

| No. of samples | Weigh ratio of PU/Si-rubber | $w_{Fe}/(w_{Fe}+w_{PU}+w_{Si\text{-}rubber})$ (wt%) | Relative MR effect (%) | Absolute MR effect (MPa) |
|---|---|---|---|---|
| 6 | 0:1 | 73 | 33 | 0.03 |
| 7 | 0.5:1 | 73 | 35 | 0.4 |
| 8 | 1:1 | 73 | 26 | 0.5 |
| 9 | 2:1 | 73 | 33 | 0.4 |
| 10 | 1:0 | 73 | 7 | 0.2 |

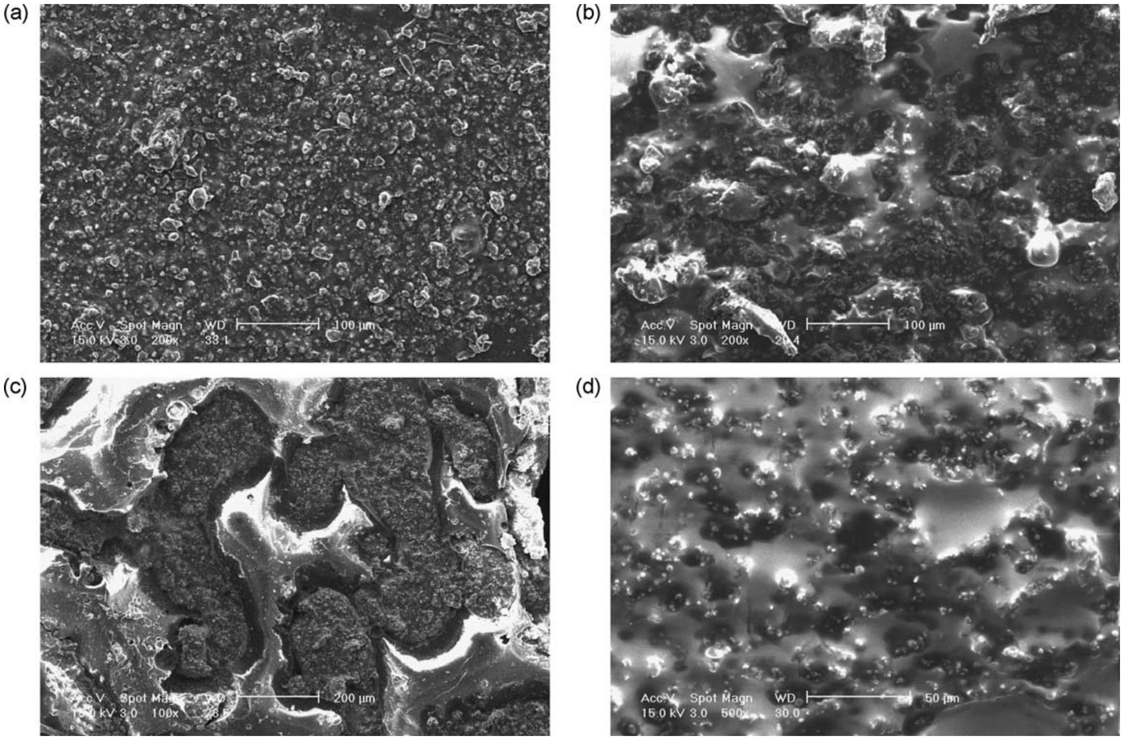


Fig. 4. SEM micrographs for MR elastomers prepared with different weight ratio of PU/Si-rubber: (a) 0/1, (b) 1/1, (c) 2/1, (d) 1/0, respectively.

effect compared to those based on only one rubber. It can be seen from Table 3 that there are some differences in absolute MR effects when the weight ratio of PU/Si-rubber changes. This may be due to the different dispersion morphology of PU in the Si-rubber. When the weight ratio of PU/Si-rubber reaches 1/1, PU disperses in the Si-rubber matrix with irregular islands of iron particle agglomerates and the highest MR effect of 0.5 MPa is achieved.

## 4. Conclusions

1. The MR elastomers based on PU/Si-rubber hybrid were successfully fabricated by curing without applying a magnetic field. Some key factors, for example way of mixing materials, additive, concentration of carbonyl iron particles, weight ratio of PU/Si-rubber and so on, directly affect the microstructure and the final MR effect. The maximum increase in shear modulus of these new MR elastomers can be up to 0.5 MPa at a magnetic field of about 0.2 T.
2. The Si-oil additive can improve the compatibility between PU and Si-rubber, and increase MR effect of this kind of MR elastomer.
3. The MR elastomers based on PU/Si-rubber hybrid have higher MR effect compared to those based on pure Si-rubber or PU matrix. This reason may be attributed to formation of a special interpenetrating microstructure in the presence of PU at certain concentration of carbonyl iron particles.

## Acknowledgements

This work is supported by the China NKBRSF project (no. 2001CB409600) and BRJH Project of Chinese Academy of Sciences and Specialized Research Fund for the Doctoral Program of Higher Education (no.20030358014). The authors would like to thank Dr M. Gong and Mr F. Yu (Lab of Mechanical and Material Science of USTC) for their attributions to the SEM photos.

## References

[1] B.C. Munoz, M.R. Jolly, Composites with field responsive rheology in: W. Brostow (Ed.),, Performance of Plastics, Carl Hanser, Munich, 2001, pp. 553–574.
[2] J.M. Ginder, M.E. Nichols, L.D. Elie, S.M. Clark, Controllable-stiffness components based on magnetorheological elastomers, in: Proceedings of SPIE, vol. 3985, 2000, 418–425.

[3] T. Shiga, A. Okada, T. Kurauchi, Magnetroviscoelastic behavior of composite gels, J. Appl. Polym. Sci. 58 (1995) 787–792.
[4] M.R. Jolly, J.D. Carlson, B.C. Munoz, T.A. Bullions, The magnetoviscoelastic response of elastomers composites consisting of ferrous particles embedded in a polymer matrix, J. Intell. Mater. Syst. Struct. 7 (1996) 613–622.
[5] G. Bossis, C. Abbo, S. Cutillas, S.C. Lacis, Metayer, Electroactive and electrostructured elastomers, in: Proceeding of the Seventh International Conference on ERF fluids and MR Suspensions, Singapore, 2000. pp. 18–27
[6] T. Mitsumata, K. Ikeda, J.P. Gong, Y. Osada, D. Szabo, M. Zrinyi, Magnetism and compressive modulus of magnetic fluid containing gels, J. Appl. Phys. 85 (1999) 8451–8455.
[7] S.A. Demchuk, V.A. Kuz'min, Viscoelastic properties of magnetorheological elastomers in the regime of dynamic deformation, J. Eng. Phys. Thermophys. 75 (2002) 396–400.
[8] J.M. Ginder, M.E. Nichols, L.D. Elie, J.L. Tardiff, Magnerorheological elastomers: properties and applications, in: Proceedings of SPIE, vol.3675, 1999, pp. 131–138
[9] Y. Shen, M.F. Golnaraghi, G.R. Heppler, Experimental research and modeling of magnetorheological elastomers, J. Intell. Mater. Syst. Struct. 15 (2004) 27–35.
[10] M. Lokander, B. Stenberg, Performance of isotropic magnetorheological rubber materials, Polym. Test. 3 (2002) 245–251.
[11] M. Lokander, B. Stenberg, Improving the magnetorheological effect in isotropic magnetorheological rubber materials, Polym. Test. 22 (2003) 677–680.
[12] Z. Haralampos, A. Lazaros, Y.P. Mamunya, Structure-electrical properties relationships of polymer composites filled with Fe-powder, Macromol. Symp. 194 (2003) 351–359.
[13] S. Fang, X.L. Gong, X.Z. Zhang, et al., Mechanical analysis and measurement of magnetorheological elastomers, J. Univ. Sci. Technol. China 34 (2004) 456–463.