

# Preparation and Properties of Magnetorheological Elastomers Based on Silicon Rubber/Polystyrene Blend Matrix

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**ABSTRACT:** Magnetorheological (MR) elastomers, which are mainly composed of magnetic particles and elastic polymer, are a new kind of smart materials whose modulus can be controlled by changing the strength of magnetic fields. In this article, MR elastomers based on immiscible silicon rubber/polystyrene (SR/PS) blend matrix were fabricated successfully via cosolvent method and the MR effect, electric and mechanical properties, and the microstructures of the corresponding materials were studied. SEM studies showed that the dispersion of iron particles in blend matrix were different from that in single polymer, which could be further proved by the different electric

conductivity. The MR effect of MR elastomers based on blend matrix varied with the different ratios of SR and PS, which was discussed in detail from the special dispersion of iron particles and of zero-modulus of MR elastomers. In addition, the MR elastomers based on SR/PS blend matrix had enhanced mechanical properties, which made them more hopeful to be applied in practice. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3143–3149, 2007

**Key words:** magnetorheological elastomers; silicon rubber/polystyrene blend matrix; MR effect; microstructure; mechanical properties

## INTRODUCTION

Magnetorheological (MR) materials are a group of smart materials whose rheological properties can be controlled by applying 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 applying a magnetic field.<sup>1</sup> MR elastomers can be thought of a new generation of MR materials and have distinct properties from MR fluids, because the matrix of them is rubber-like solid materials 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 then have stable MR performance. And it has sensi-

tive response to magnetic fields for the time of response of MR elastomers is less than 10 ms.<sup>2</sup> MR elastomers hold promise in adaptive tuned vibration absorbers, stiffness tunable mounts, and automobile suspensions.<sup>2</sup>

MR elastomers basically consist of two components: elastic matrix and magnetic particles. The magnetic particles commonly have been aligned by an applied magnetic field prior to the curing of the matrix. And they have been fabricated based on different matrix, i.e., silicone elastomers,<sup>3–5</sup> poly(vinyl alcohol),<sup>6</sup> gelatin,<sup>7</sup> hard natural or synthesized rubber,<sup>8</sup> and polyurethane sealant.<sup>9</sup> However, the typical magnetic fields needed to align the magnetic particles are very strong and about  $8 \times 10^6$  A/m, which makes the manufacture complicated and difficult to be broadly applied.<sup>4</sup>

Recently, Lokander and Stenberg<sup>10,11</sup> have studied the isotropic MR rubber. They have made MR elastomers by embedding large irregular particles into the nitrile rubber without using the magnetic fields to align the particles, and these MR elastomers have a large absolute MR effect. However, to achieve such a substantial MR effect, the amount of the magnetic particles needed is too large which result in a high zero-field modulus and a low relative effect.

Polymer blends containing functional particles have different properties from that of single polymer for

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**TABLE I**  
**Composition of the Analyzed Samples**

Samples	Silicon rubber/g	Polystyrene/g	Carbonyl iron particles/g	BPO/g
1	50	0	150	1.00
2	47.5	2.5	150	0.95
3	45	5	150	0.90
4	40	10	150	0.80

their special microstructure.<sup>12–14</sup> Compared with single polymer, polymer blend have lower percolation threshold<sup>12,13</sup> and sensing properties of liquids.<sup>14</sup> In our recent investigation,<sup>15</sup> it was found that the MR elastomers-based PU/SR (silicon rubber) blend matrix have better MR effect than the MR elastomers based on single matrix.

It is well known that SR is a polymer with good elasticity, and polystyrene (PS) is a plastic with high modulus. Their blends may bring these properties together, and result in materials with good elasticity and strong modulus. Liu et al.<sup>16</sup> has synthesized composites of SR and PS, which have enhanced mechanical performances, using supercritical CO<sub>2</sub> as a swelling agent.

To get MR elastomers with better MR effect and mechanical properties, the MR elastomers based on SR/PS blend were fabricated via cosolvent method. The MR effects and electric properties and mechanical properties were studied. The microstructure of was characterized by SEM, which provided a good explanation for the better properties.

## EXPERIMENTAL

### Materials

The spherical carbonyl iron particles were FTF-4 type with size range of 3–5 μm bought from Hebao Nanomaterial. The polymers used in this study were methyl vinyl gum, 110-2, the content of vinyl = 0.7% (Dong Jue Fine Chemicals, Nanjing) and HIPS, 492-J (Hefei KeYan). Benzoyl peroxide (BPO) was produced by Shanghai Zhongli Chemical Plant (C.R. grade). Toluene was purchased from Shanghai Suyi chemical reagent Company (A.R. grade).

### Preparation of SR/PS MR Elastomers

SR/PS MR elastomers were prepared by cosolvent method. First methyl vinyl silicon gum was dissolved in toluene at 90°C. And then carbonyl iron particles were dispersed in this viscosity solution by stirring. After that, PS with different content were added into the mixture and stirred until the three phases became uniform gel-like black mixture. Then the mixture was dropped and placed in an oven at 80°C to get rid of solvent. When the special odor of toluene disappeared and the mass of the samples could not change any

more, we think that toluene had been got rid of. To make the mixture more uniform, the mixture was further mixed on a two-roll blending machine at 25°C, and at this processing, BPO were added into the mixture. The linear velocity of the two-roll mixer was 9.8 m/min and the diameter of the rolls was 160 mm. The velocity-ratio of two rolls was 1:1.22 and gauge between two rolls was about 2 mm. At last, the mixtures were vulcanized in a mold with the size 100 × 100 × 3 mm<sup>3</sup> at 140°C and 14 MPa for half an hour.

The composition of the analyzed compounds was given in Table I. BPO was the crosslinking agent of SR so the ratio of SR to BPO was kept constant at 50 : 1.

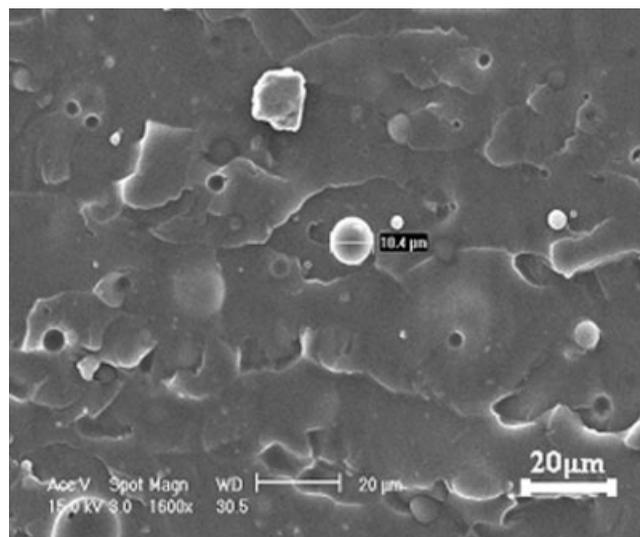
### Morphological characterization

The samples were cut into small pieces and scanning electron microscopy of cut surfaces was performed with a XL30 ESEM at an accelerating voltage of 10–15 kV depending on the samples. Samples were gold-sputtered before observation.

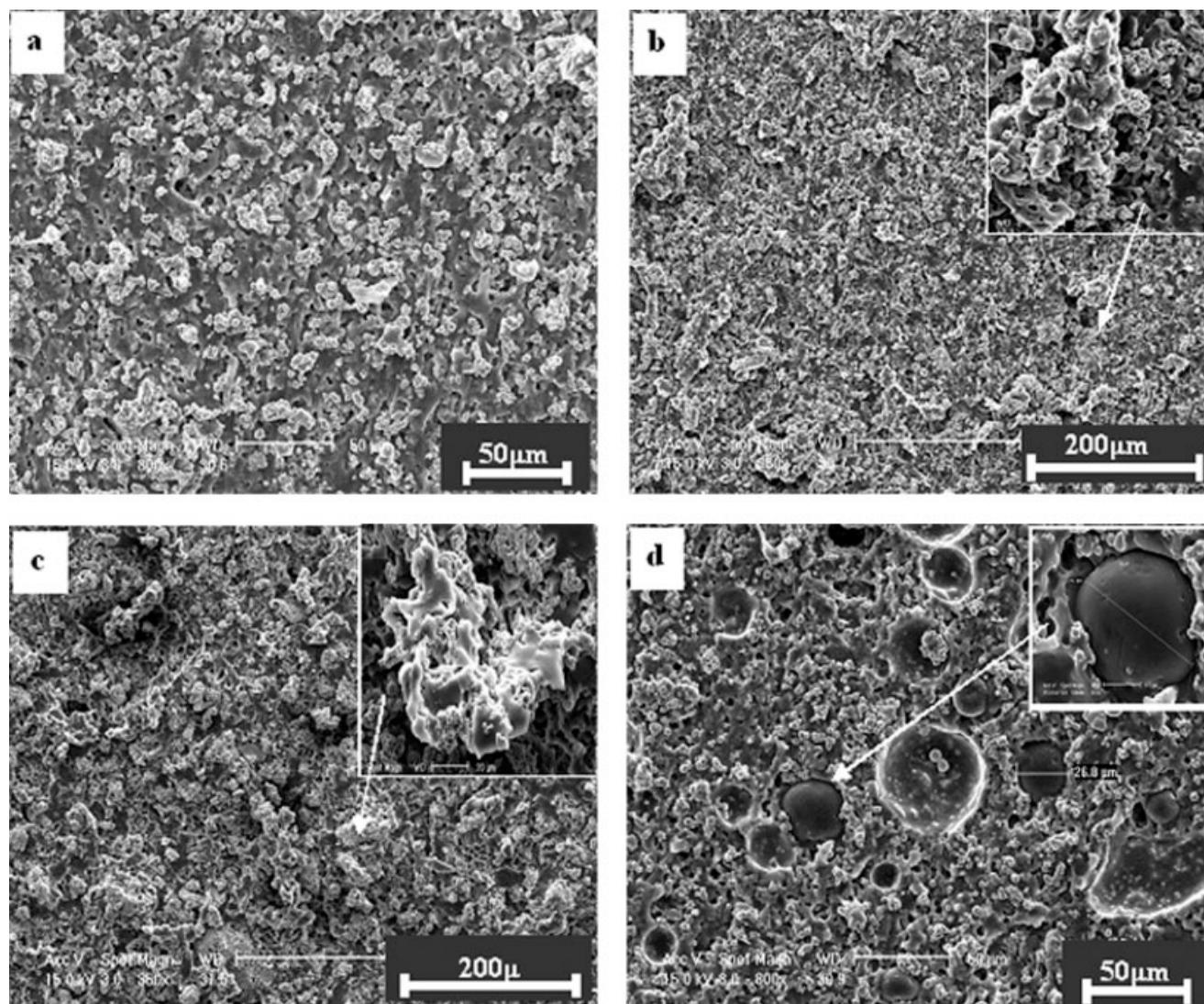
### MR measurements

The MR effect was evaluated by measuring the dynamic shear modulus with and without an applied magnetic field at room temperature. The schematic equipment set-up and the principle of the tests could be found in our previous work.<sup>17,18</sup> The analyzer provided three columns of data. They were lists of frequency, real and imaginary parts of the transfer function. The correlation coefficient was about 0.97. And to make the reliability of the data be good enough, every curve was averaged for 30 times.

The magnetic field was produced by an electromagnet and the magnetic flux density through sam-



**Figure 1** SEM micrographs of SR/PS blends without iron particles.



**Figure 2** SEM micrographs of MR elastomers based on SR/PS with different content of PS: (a) 0%; (b) 5%; (c) 10%; and (d) 20%.

ples could be turned from 0 to 1000 mT. The test samples were about  $30 \times 6 \times 3 \text{ mm}^3$  and sandwiched between a brass and an aluminum plate. The experiment could be carried out in a wide range of frequency and the shear modulus of sample was got at its resonance frequency.

### Mechanical test

All the samples were standard dumb-bell test pieces with an effective area of  $4 \times 20 \text{ mm}^2$ . Tensile tests were performed on a Universal Testing Machine (WD-5D, Changchun, China) with a crosshead speed of 50 mm/min at 25°C. The average of five tests was reported here.

### Resistivity measurements

The electrical resistance of the conducting MR elastomers was measured with a two-probe technique by

ohmmeter at room temperature and the volume resistivity was calculated according to  $\rho = R \frac{A}{l}$ .

Here,  $\rho$  is the volume resistivity;  $A$  is the area of the samples,  $l$  is the distance of the probe, and  $R$  is the resistance.

Resistance was measured at different parts of the same sample and averaged to ensure reliable results.

## RESULTS AND DISCUSSIONS

### Morphology and resistivity

SR/PS blends had been firstly prepared via cosolvent method. The morphology of the blend without iron particles was depicted in Figure 1. It was clear that PS phase disperses in SR matrix as spherical particles with the diameter of a few micrometers. SR and PS are incompatible because they were very different in many properties. In Figure 1, the spherical

**TABLE II**  
**Surface Resistivity and Volume Resistivity**  
**of MR Elastomers Based on SR/PS Blend with**  
**Different Content of PS**

No. of sample	Content of PS (%)	Surface resistance ( $\Omega$ )	Volume resistivity ( $\Omega$ cm)
1	0	$1.2 \times 10^6$	$6.78 \times 10^5$
2	5	$2.4 \times 10^5$	$2.1 \times 10^4$
3	10	$3.6 \times 10^5$	$6.5 \times 10^4$
4	20	$1.1 \times 10^6$	$1.3 \times 10^5$

cavities resulting from the detaching of PS particles proved the weak adhesion of PS and SR.

Figure 2 displayed the microstructure of the MR elastomers based on SR/PS with different content of PS, respectively. In Figure 2(a), the matrix was pure SR, and iron particles uniformly dispersed in it. In Figure 2(b,c), PS dispersed in the SR as big irregular conglomeration, and iron particles were located in the SR and in the surface of PS conglomeration. It could be seen that the iron-containing blend morphology was different from that of neat blend. When the content of PS was 20%, the morphology of the system in Figure 2(d) was different from that in Figure 2(b,c). There were some spherical particles of about 30  $\mu\text{m}$  in diameter dispersed in the matrix. The iron particles used were 3–5  $\mu\text{m}$ -sized; those large particles must be PS particles formed in the processing and iron particles preferentially located in SR.

The morphology of MR elastomers could be reflected by the electrical conductivity. The resistivity of the SR/PS/iron particles composites was given in Table II. The resistivities of SR/PS/iron particles composites were all lower than that of SR/iron particles. Especially when the content of PS was 5 and

10%, the resistivity decreased to approximately one order of magnitude. The improvement of the conductivity in the ternary systems meant the more efficient formation of the conductive pathways, because the iron particles preferentially dispersed in one polymer and the interface of two polymers. For MR elastomers with the content of PS 20%, the improvement of the conductivity may mean the increasing of local concentration of iron particles in SR. However, in Table II, the volume resistivity at 20% of PS content increased compared to 5 and 10% of PS content, and the reason may be that too much PS particles limit the formation of the conductive pathways to some extent.

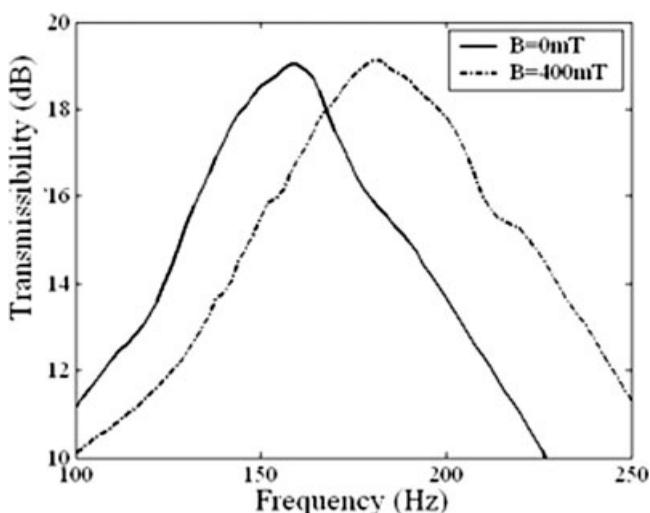
### Magnetorheological effect

MR elastomers had adjustable shear modulus by changing the magnetic flux density. The frequency-dependent transmissibility of MR elastomers based on pure SR at magnetic flux density  $B = 0$  and 400 mT was shown in Figure 3. It could be seen that the resonance frequency was 158 Hz at  $B = 0$  mT and 180 Hz at  $B = 400$  mT.

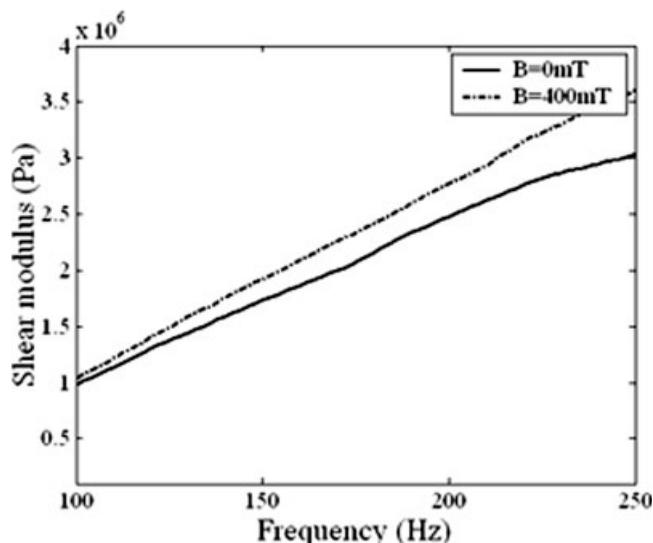
$$f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (1)$$

where  $k$  is the dynamic stiffness and  $m$  is the mass of MR elastomers.

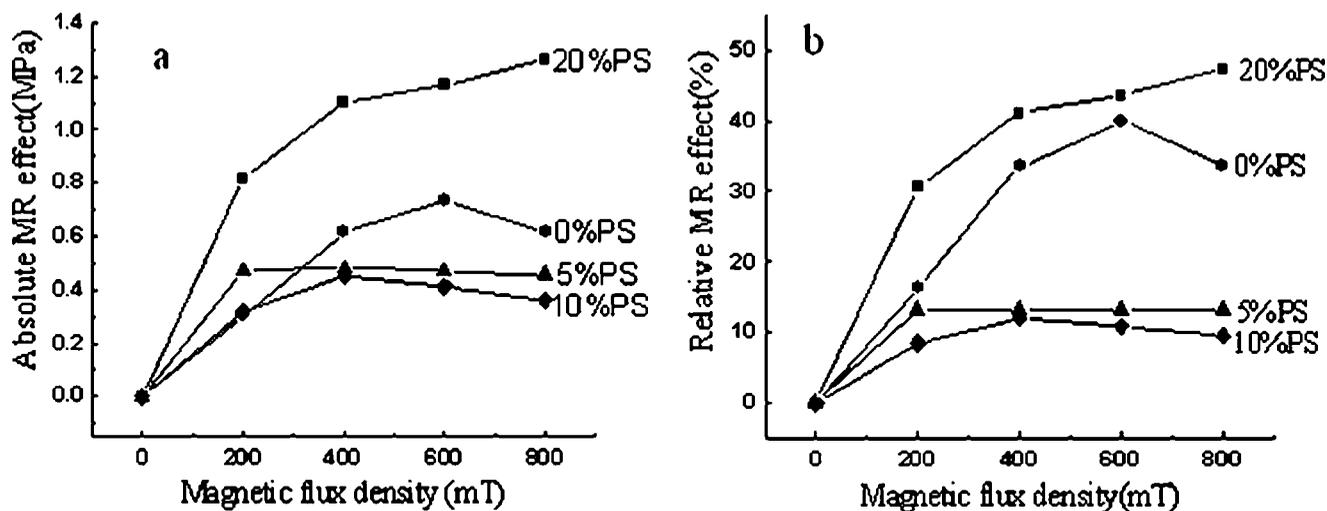
According to the eq. (1), the resonance frequency shifted up word which meant that the stiffness increased with the magnetic flux density. Figure 4 showed the shear modulus as a function of frequency at different magnetic flux fields. The shear modulus ( $G$ ) increased with the frequency. The shear modulus



**Figure 3** Frequency-dependent transmissibility of MR elastomers based on pure SR at magnetic flux density  $B = 0$  and 400 mT.



**Figure 4** The shear modulus as a function of frequency at different magnetic flux fields.



**Figure 5** Absolute (a) and relative (b) MR effect as a function of the applied magnetic field for MR elastomers with different content of PS.

was higher at  $B = 0$  mT than that at  $B = 400$  mT. The modulus changed at the resonance frequency of every sample.  $\Delta G$  and  $\frac{\Delta G}{G_0} \times 100\%$  was respectively, named as absolute MR effect and relative MR effect.

The absolute and relative MR effect as a function of the applied magnetic field for different content of PS was shown in Figure 5(a,b). As can be seen, MR effect increased with the increasing of magnetic field strengths. However, at high magnetic field, the increasing of the MR effect became invisible. This indicated that the materials started to saturate magnetically at this magnetic field level. This behavior was similar to that reported for anisotropic MR elastomers.<sup>8</sup> However, the saturated magnetic field strength was seemingly different when the content of PS varies.

From Figure 5(a,b), it can be seen that the absolute MR effects of SR/PS blend MR elastomers were all larger than that of pure SR MR elastomers at 200 mT. At higher magnetic fields, the absolute and relative MR effect had the same marked tendency, which namely increased in the order 10% PS-5% PS-pure SR-20% PS.

The research about the mechanism of isotropic MR elastomers had not been seen in the literature. We think that the magnetic particles dispersed in the matrix and form a network of them. When applying magnetic fields, the neighboring iron particles assembled in the direction of magnetic fields, which increased the modulus of the MR elastomers. It was expected that the higher the concentration of iron particles in the elastic matrix, the easier to form the network of iron particles and the higher the MR effect. For MR elastomers based on single elastic matrix, the formation of network of iron particles could be characterized by the electrical conductivity,

namely the higher the electrical conductivity, the higher the MR effect. However, for MR elastomers based blend matrix, this relationship did not exist. When the content of PS was 5 and 10%, the resistivity of MR elastomers based on SR/PS was quite low, namely the electrical conductivity was better. However, the corresponding MR effect was smaller than others.

This could be explained from the morphology. When the MR elastomers were based on SR/PS blend, PS acted as the rigid phase and SR as elastic phase. It should be pointed out that the shear modulus increased by magnetic fields is mainly due to the elastic part in the blend matrix. And the MR effect was affected by the concentration of iron particles in the SR.

For MR elastomers with the content of PS 5 and 10%, iron particles were located mostly in the surface of rigid PS and limited by PS, which contribute nothing to the MR effect. Compared to the MR elastomers based on single SR, the concentration of iron particles in the elastic phase became smaller, which would reduce the MR effect.

Table III showed dynamic zero-field modulus of all samples. It could be seen that the zero-modulus of MR elastomers with the content of PS 5 and 10% were larger than that of others, which indicated that the rigid PS phase had stronger interaction with the elastic phase and limited the deformation of the

**TABLE III**  
Zero-Field Modulus of MR Elastomers Based on SR/PS Blend with Different Content of PS

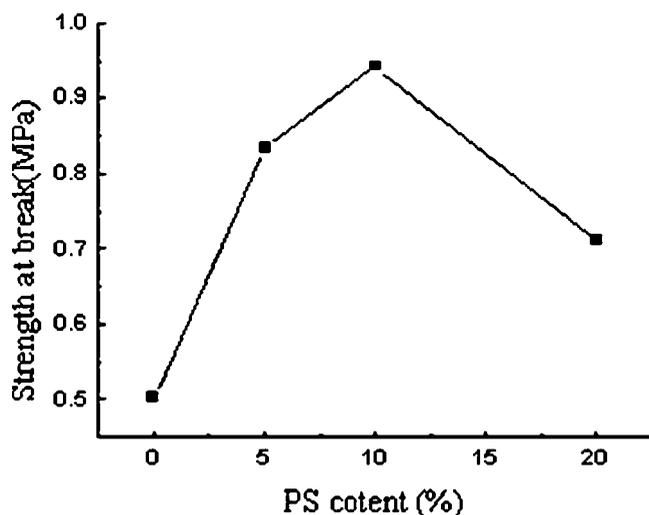
No. of sample	Content of PS (%)	Zero-field modulus (MPa)
1	0	1.84
2	5	3.60
3	10	3.78
4	20	2.67

elastic phase. Thus the change of shear modulus caused by magnetic fields was also smaller.

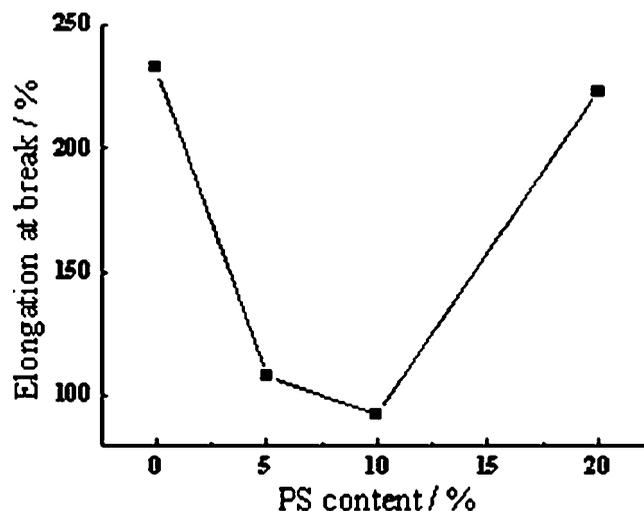
However, for the MR elastomers with the PS content of 20%, iron particles preferentially were located in SR and PS as smaller spherical particles were dispersed in the SR matrix. Thus, the concentration of iron particles in the elastic phase increased compared with that of MR based on single SR so that the MR effect of MR elastomers with the PS content of 20% was the best. The absolute MR effect of MR elastomers based on blend matrix with the content of PS 20% was 0.8 MPa at 0.2 T, which was above two times of that of MR elastomers based on pure SR and higher than that of MR elastomers based on nitrile rubber using big irregular iron particle.<sup>10</sup>

### Mechanical properties

MR elastomers based on SR/PS not only had better MR effect but also had better mechanical properties. Figure 6 displayed the tensile strength changing with the content of PS. It could be seen that the addition of PS improved the tensile strength. There was a maximum of tensile strength when the content of PS was 10%. This behavior coincided with the SR/PS blend using supercritical CO<sub>2</sub> prepared by using supercritical CO<sub>2</sub>.<sup>16</sup> It may be the poor compatibility of SR and PS that resulted in the decreasing of the tensile strength at certain concentration. Figure 7 showed that the elongation at break decreased with PS content. However, when the content of PS was 20%, the elongation at break became almost as higher as that of pure SR. This may be due to the morphology that the PS dispersed uniformly in the matrix as small particles that improved the toughness of the materials.



**Figure 6** Dependence of tensile strength on the PS content in the MR elastomers based on SR/PS. Error < 0.05 MPa.



**Figure 7** Effect of PS content in the SR/PS blends on elongation at break. Error < 10.

### CONCLUSIONS

1. MR elastomers based on SR/PS had been fabricated successfully by cosolvent method. The microstructure of the MR elastomers were characterized by SEM. PS phase dispersed homogeneously in SR matrix as micrometers-sized irregular conglomeration or spherical particles, and iron particles preferentially localized in the interface of SR and PS or in the SR. The special microstructures of the MR elastomers resulted in different electrical conductivity, MR effect, and mechanical performances.
2. The resistivity of MR elastomers based on SR/PS was lower than that of MR elastomers based on pure SR especially when the content of PS was 5 and 10%; the resistivity decreased about a magnitude.
3. The mechanism of MR elastomers based on SR/PS blend matrix was discussed. It was considered that the concentration of iron particles in the SR phase was the main factor to affect the MR effect. The SR/PS MR elastomers with the content of PS 20% had better MR effect than pure SR MR elastomers for the special microstructure that resulted in the higher concentration of iron particles in the SR phase. The corresponding absolute and relative MR effect could be up to 0.8 MPa and 33% at 0.2 T.
4. Tensile test showed that the MR elastomers based on SR/PS blend had higher tensile strength and lower elongation at break than that of MR elastomers based on pure SR. There was a maximum of tensile strength when the content of PS was 10%.

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## References

1. Munoz, B. C.; Jolly, M. R. In *Performance of Plastics*; Brostow, W., Ed.; Carl Hanser Verlag: Munich, 2001; p 553.
2. Ginder, J. M.; Nichols, M. E.; Clark, S. M. *Proc SPIE* 2000, 3985, 418.
3. Shiga, T.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1995, 58, 787.
4. Jolly, M. R.; Carlson, J. D.; Munoz, B. C.; Bullions, T. A. *J Intell Mater Syst Struct* 1996, 7, 613.
5. Bossis, G.; Abbo, C.; Cutillas, S.; Laci, S. C. In *Proceeding of the 7th International Conference on ERF fluids and MR Suspensions*, Singapore, 2000; p 18.
6. Mitsumata, T.; Ikeda, K.; Gong, J. P.; Osada, Y.; Szabo, D.; Zrinyi, M. *J Appl Phys* 1999, 85, 8451.
7. Demchuk, S. A.; Kuz'min, V. A. *J Eng Phys Thermophys* 2002, 75, 396.
8. Ginder, J. M.; Nichols, M. E.; Elie, L. D.; Tardiff, J. L. *Proc SPIE* 1999, 3675, 131.
9. Shen, Y.; Golnaraghi, M. F.; Heppler, G. R. *J Intell Mater Syst Struct* 2004, 15, 27.
10. Lokander, M.; Stenberg, B. *Polym Test* 2002, 3, 245.
11. Lokander, M.; Stenberg, B. *Polym Test* 2003, 22, 677.
12. Haralampos, Z.; Lazaros, A.; Mamunya, Y. P. *Macromol Symp* 2003, 194, 351.
13. Zhang, Q. H.; Chen, D. J. *J Mater Sci* 2004, 39, 1751.
14. Segal, E.; Tchoudakov, R.; Narkis, M.; Siegmann, A. *J Polym Sci Part B: Polym Phys* 2003, 41, 1428.
15. Hu, Y.; Wang, Y. L.; Gong, X. L.; Gong, X. Q.; Zhang, X. Z.; Jiang, W. Q.; Zhang, P. Q.; Chen, Z. Y. *Polym Test* 2005, 24, 324.
16. Liu, Z. M.; Wang, J. Q.; Dai, X. H.; Han, B. X.; Dong, Z. X.; Yang, G. Y.; Zhang, X. L.; Xu, J. *J Mater Chem* 2002, 12, 2688.
17. Fang, S.; Gong, X. L.; Zhang, X. Z. *J Univ Sci Technol China* 2004, 34, 456.
18. Gong, X. L.; Zhang, X. Z.; Zhang, P. Q. *Polym Test* 2005, 24, 669.