# Improving the Magnetorheological Properties of Polyurethane Magnetorheological Elastomer Through Plasticization

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**ABSTRACT:** The highly filled anisotropic polyurethane (PU) magnetorheological elastomers (MREs) were prepared through an *in-situ* one-step polycondensation process under a magnetic field. The carbonyl iron formed chain-like structure, which was fixed in the PU matrix. The plasticizer diisooctyl phthalate (DOP) was incorporated into PU to soften the matrix and improve the MR effect. The influence of DOP on the microstructure and properties of PU MREs were investigated. The incorporation of DOP reduced the viscosity of the prepolymer and made the carbonyl iron align more easily in the PU matrix. The aligned chain-like structure of carbonyl iron in PU greatly enhanced the thermal conductivity and the compressive properties of PU MREs. The incorporation of DOP reduced the modulus of PU MREs and the glass transition temperature of the soft segments of PU. But highly filled carbonyl iron and DOP led to a decrease in the thermal stability to some extent. The MR test showed that DOP plasticization significantly enhanced both absolute and relative MR effect simultaneously. With 70 wt% carbonyl iron and 15 wt% DOP (the weight ratio of Fe: PU: DOP is 70 : 15: 15), the absolute and relative MR effects of anisotropic PU MREs were $\sim$ 1.16 MPa and $\sim$ 386.7%, $\sim$ 3.5 and $\sim$ 58 times of the PU MRE without the plasticizer at the same iron content. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2476–2484, 2012

**Key words:** polyurethane; magnetorheological elastomer; *in-situ* polymerization; plasticizer

## INTRODUCTION

Magnetorheological elastomers (MREs) are a family of smart materials comprised of magnetic particles embedded in an elastomer matrix, whose elastic modulus or stiffness can be controlled continuously, rapidly, and reversibly by the application of external magnetic field. MREs can be divided into two types: isotropic MREs and anisotropic MREs. For the isotropic, the magnetic particles are dispersed randomly in the matrix; while for the anisotropic, they are oriented under a magnetic field, formed chain chain-like structure and locked in the matrix during its curing process. The matrixes for MREs include soft silicon rubber,[1–6] natural rubber,[7–10] synthetic rubber like nitrile rubber,[11,12] polyurethane (PU),[13–17] and so on.

The main factors influencing the magnetorheological (MR) effect are shapes, sizes, contents and the orientation of the magnetic particles, as well as the hardness of the matrix. Lokander *et al.*[11,12] have shown experimentally, that the particle size and shape have an influence on MR effect for isotropic nitrile rubber MREs. For ASC300 iron (particle size < 60 μm), the MR effect of the material was larger than that for carbonyl iron (particle size 3.9–5.0 μm). For even larger particles than 60 μm, the measured MR effect appeared to be slightly smaller. Lockette[18] and Li[19] have shown that a certain ratio of bimodal magnetic particles mixture can enhance the MR effect of silicone based MREs. Researchers[1,9,10] also have found that curing the particles under a magnetic field results in an enhancement of MR effect. Chen et al.[10] investigated the influence of the external magnetic flux density on the MR effect of MREs. As the external magnetic flux density for the orientation of iron increased from 0 to 900 mT, the absolute MR effect enhanced $\sim$ 0.6 MPa due to the orientation of iron. The hardness of the matrix also has great influence on the MR effect. MREs with a soft matrix have a higher relative MR effect for that zero-filed modulus is lower. Moreover, magnetic

particles in soft matrix can get more close under a magnetic field and produce a stronger interaction to antideformation. Plasticization is a common method to reduce the hardness of polymer and has been used to prepare MREs. Lokander et al.[12] introduced plasticizer di-2-ethylhexylphthalate to isotropic nitrile rubber based MREs and obtained a slight improvement of the relative MR effect. Chen et al.[10] investigated the influence of plasticizer contents on the MR effect of anisotropic natural rubber based MREs. At an iron content of 60 wt %, a variation of plasticizer from 10 to 20 wt %, the absolute MR effect increased from 0.2 to 0.7 MPa, the relative MR effect increased from 14 to 78%.

Recently, researchers have paid much attention on PU MREs due to it easy preparation and good mechanical properties.[13–17] The lower relative MR effect for highly filled magnetic particles system is the key problem of MREs.[9,11] Previously, we prepared the isotropic and anisotropic PU MREs through an *in-situ* polycondensation method.[16,17] The MR test showed that the relative MR effect is not ideal and needs to be improved to meet some practical requirement. In this study, the plasticizer diisooctyl phthalate (DOP) was incorporated into PU to soften matrix and improve the MR effect for the first time. The influence of DOP on the microstructure and properties of PU MREs were studied in detail.

## EXPERIMENTAL

### Materials

Carbonyl iron particles were bought from BASF (model OM) with size distribution of $d_{10} \sim 2$ μm, $d_{50} \sim 4$ μm, and $d_{90} \sim 9$ μm. 4, 4′-methylene-di (phenylene isocyanate) (MDI), supplied by Yantai Wanhua Polyurethanes Co., Ltd., China, was used as received without further treatment. Polytetramethylene ether glycol (PTMEG, the $\bar{M}_n$ is 1000), produced by Mitsubishi Chemical Holdings Co., was dehydrated in a vacuum oven at 110°C for 2 h prior to use. 1, 4-butanediol (BDO), purchased from Chengdu Kelong Chemical Factory, China, was redistilled to remove water prior to use. Plasticizer diisooctyl phthalate (DOP), obtained from Tianjin Bodi Chemical Holding Co., Ltd., China, was vacuum dehydrated in an oven at 110°C for 4 h prior to use. The catalyst Dabco-33LV was obtained from Air Products and Chemicals. The antifoam agent BYK-A 525 was provided by Sino Composite Co., Ltd., China.

### Preparation of polyurethane magnetorheological elastomers

PU with a hard segment content of 26 wt % and ─NCO/OH ratio of 1.1 : 1 is used as matrix for MREs. Typically, the synthesis of PU MREs was conducted by the one-step polycondensation process. Preheated PTMEG and DOP (100°C) were mixed with carbonyl iron through ball milling for 30 min. The obtained PTMEG/DOP/carbonyl iron (PTMEG/DOP/Fe) dispersion was heated at 100°C again before blending with MDI and chain extender BDO. The detailed procedure for anisotropic plasticized PU MREs with 70 wt % carbonyl iron (the weight ratio of Fe : PU : DOP is 70 : 21 : 9) are as follows: the melted PTMEG (20.00 g), the plasticizer DOP (11.58 g) and carbonyl iron (90.09 g) were added to the jar, and mixed by ball milling for 30 min to obtain PTMEG/DOP/Fe dispersion. The dispersion was blended with 6.65 g of melted MDI, 0.38 g of BDO, 0.03 g of Dabco-33LV, and 0.1 g of BYK A-525 at room temperature for ~ 2 min. Then the mixture was vacuum degassed for 3–5 min to remove the bubbles. After that, the viscous prepolymer was poured into a hot O-ring mold preheated at 120°C and oriented under a magnetic field for 1 h. For MR test, the samples with a thickness of ~ 3 mm were prepared under a magnetic field of 1.2 T along the thickness direction. For compressive test, the anisotropic PU MREs cylinder samples with dimensions of 12.5 mm in height and 29.0 mm in diameter were prepared under a magnetic field of 0.9 T along the height direction. Finally, the prepolymer was cured at 120°C for 24 h, and cooled to room temperature and kept for two weeks to obtain the anisotropic PU MREs. As a contrast, isotropic PU MREs were prepared with the same procedure without a magnetic field. For the purpose of easy identification, PU MREs samples with different carbonyl iron and DOP contents are designated as Iso-xxyy or Aniso-xxyy (the weight percentage of Fe/(PU+DOP+Fe) is xx, the weight percentage of DOP/(PU+DOP) is yy, if not specified, the DOP content is based on the matrix PU in this study). For example, isotropic PU MREs at an iron content of 70 wt % without plasticizer is designated as Iso-7000; anisotropic PU MREs with 70 wt % iron and 30 wt % DOP is designated as Aniso-7030. Correspondingly, the PTMEG/DOP/Fe dispersion for preparing sample Iso/Aniso-xxyy is designated as D-xxyy.

## CHARACTERIZATION

### Viscosity measurement

The rheological properties of PTMEG/DOP/Fe dispersion with different iron and DOP contents were investigated by a RH7D rheometer (Bohlin Instruments) using 40-mm diameter parallel plate. The gap between the plates is 0.15 mm during measurement. The sample was allowed to equilibrate for at least 3 min at the test temperature before steady
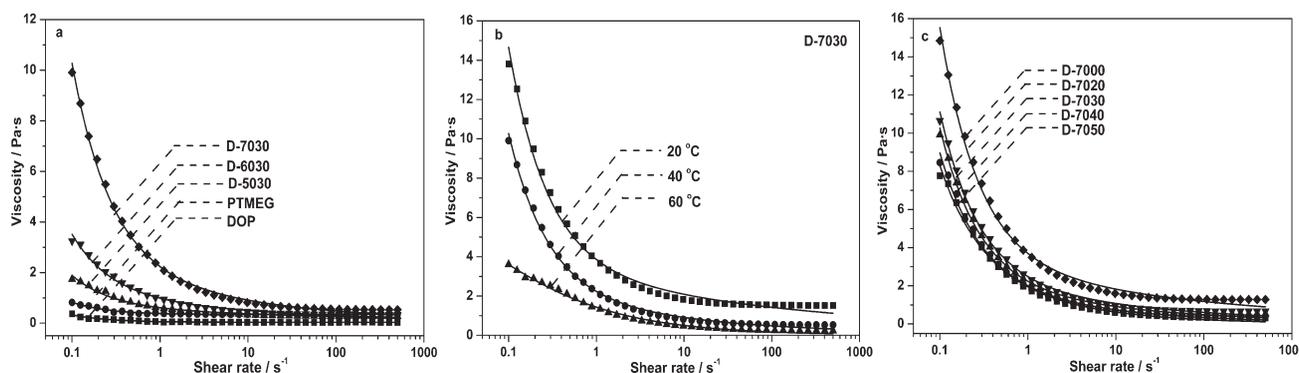
**Figure 1** (a) The influence of iron content on the viscosity of PTMG/DOP/Fe dispersion at 40°C; (b) the influence of temperature on the viscosity of D-7030; (c) the influence of DOP contents on the viscosity of PTMG/DOP/Fe dispersion at 40°C.

shear measurement. The relationship between viscosity and shear rate for each dispersion was obtained at a shear rate range of 0.1-500 s$^{-1}$ at 20, 40, and 60°C, respectively.

### Scanning electron microscope

An Inspect F SEM instrument (FEI Company) was used to observe the morphology of the fractured surface and the dispersion of carbonyl iron particles in the matrix with an acceleration voltage of 20 kV. The samples were cryogenically fractured in the liquid nitrogen and coated with a thin gold layer prior to observation.

### Thermal conductivity measurement

The thermal conductivity of PU and PU MREs was measured on a Hot Disk 2500 thermal constant analyzer, which was based on a transient technique. The measurement was performed by putting a sensor (3 mm in diameter) between two smooth slabs of specimens (50 mm × 50 mm × 3 mm). The sensor supplied a heat pulse of 0.03 W for 10 s to the sample at room temperature and the associated change of temperature was recorded.

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out on a Q600 equipment (TA Instrument) in the nitrogen to characterize the thermal stability of samples with different carbonyl iron contents. The sample was heated from 30°C to 700°C at a heating rate of 10°C/min.

### Compressive properties measurement

The cylinder specimens were compressed to the maximum stain of 25% at a rate of 10 mm/min according to the China standard GB/T 7757-1993.

Four compression cycles were carried out and the last cycle was selected to determine the compressive properties.

### Dynamical mechanical analysis

The normal dynamical mechanical tests were performed on a Q-800 instrument (TA Instruments, USA) by using a dual cantilever mode. The storage modulus ($E'$) and loss factor (tan δ) were measured in the temperature range of −100 to 80°C at a heating rate of 3°C/min. The strain amplitude used was 50 μm and the test frequency was 1 Hz.

### The magnetorheological effect analysis

The MR effect were conducted on a modified dynamic mechanical analyzer (DMA) (Triton Technology, UK, model Tritec 2000B) at room temperature.[16] The samples have dimensions of 10 mm × 10 mm × 3 mm. During the test, a magnetic field which can vary from 0 to 1000 mT is applied to the sample. The dynamic strain amplitude was set as 0.3%. The test frequencies are 1, 5, and 10 Hz.

## RESULTS AND DISCUSSION

### The rheological behavior of PTMEG/DOP/Fe dispersion

The incorporation of plenty of micron-sized carbonyl iron and plasticizer DOP into PTMEG has a significant influence on the viscosity of the dispersion. The effects of carbonyl iron content, temperature, and DOP content on the viscosity of PTMEG/DOP/Fe dispersion are shown in Figure 1(a-c), respectively. The experimental data (dot in Figure 1) can be fitted well with the Herschel–Bulkley model (solid line in Figure 1). The viscosity data (η) of suspensions can be fitted according to the equation: $\eta = \tau_0/\dot{\gamma} + k\gamma^{n-1}$,[20,21] where $\dot{\gamma}$ is the shear rate, $k$ and $\tau_0$ are constants, and $n$ is the

**TABLE I**
**The Viscosity of PTMEG/DOP/Fe Dispersion at a Low Shear Rate of 1.10 s$^{-1}$ ($\eta_L$) and a High Shear Rate of 70.00 s$^{-1}$ ($\eta_H$) and Shear Thinning Parameter $n$**

| Dispersion | Test temperature/°C | $\eta_L$/Pa s | $\eta_H$/Pa s | $n$ |
|---|---|---|---|---|
| DOP | 40 | 0.05 | 0.03 | 1.01 |
| PTMEG | 40 | 0.38 | 0.34 | 1.02 |
| D-5030 | 40 | 0.58 | 0.27 | 0.86 |
| D-6030 | 40 | 0.93 | 0.35 | 0.80 |
| D-7000 | 40 | 3.48 | 1.30 | 0.83 |
| D-7020 | 40 | 2.31 | 0.69 | 0.78 |
| D-7030 | 20 | 3.67 | 1.56 | 0.85 |
| D-7030 | 40 | 2.08 | 0.57 | 0.75 |
| D-7030 | 60 | 1.34 | 0.27 | 0.52 |
| D-7040 | 40 | 1.81 | 0.43 | 0.69 |
| D-7050 | 40 | 1.72 | 0.35 | 0.58 |

flow behavior index. The viscosity at a low shear rate of 1.10 s$^{-1}$ and a high shear rate of 70.00 s$^{-1}$, and the shear thinning parameter $n$ fitted based on Herschel–Bulkley model are shown in Table I. The PTMEG/DOP/Fe dispersion shows a shear-thinning behavior. With the increase of the iron content, the viscosity of the PTMEG/DOP/Fe dispersion increase. For example, at a shear rate of 1.10 s$^{-1}$, the viscosity of the samples DOP, PTMEG, D-5030, D-6030, and D-7030 are 0.05, 0.38, 0.58, 0.93, and 2.08 Pa s at 40°C, respectively. At the same time, the shear thinning parameter $n$ shows an obvious decrease from 1.02 to 0.75. So, for PTMEG/DOP/Fe dispersion, the higher the carbonyl iron content is, the more obvious the shear-thinning behavior is. From Figure 1(b), it can be known that temperature also has great influence on the viscosity of the dispersion. A variation of temperature from

20°C to 60°C, the viscosity of D-7030 at a shear rate of 70.00 s$^{-1}$ decreases sharply from 1.56 to 0.27 Pa s, the shear thinning parameter $n$ also decreases significantly. The influence of plasticizer content on the viscosity of PTMEG/DOP/Fe dispersion is shown in Figure 1(c). It can be seen that both viscosity and shear thinning parameter $n$ decrease with increasing the DOP content. The higher the DOP content is, the more obvious the shear-thinning behavior is. The sensitivity of PTMEG/DOP/Fe viscosity to the shear rate and temperature was utilized in the sample preparation. The dispersion was heated to 100°C before mixing with other raw material. At the same time, the mixture was stirred at a high agitation speed to assure the complete mixing of the raw material.

## The morphology of PU MREs

The cryogenically fractured surface morphology of isotropic and anisotropic PU MREs is shown in Figure 2. Figure 2(a) shows the original spherical carbonyl iron particles with an average size of $\sim$ 4 µm. For isotropic PU MREs with 50 wt % carbonyl iron, the carbonyl iron particles are dispersed randomly in the PU matrix [Fig. 2(b)]; no big aggregates can be seen in the fractured surface. For the anisotropic PU MREs oriented under a magnetic field of 1.2 T, the carbonyl iron particles formed chain-like structure along the direction of the magnetic field. When the magnetic field is applied to the prepolymer, the interaction among the iron particles makes them align along the magnetic field. As the curing reaction goes on, the chain-like structure of the carbonyl iron is fixed in the matrix. SEM images of anisotropic PU MREs with iron contents of 50, 60,
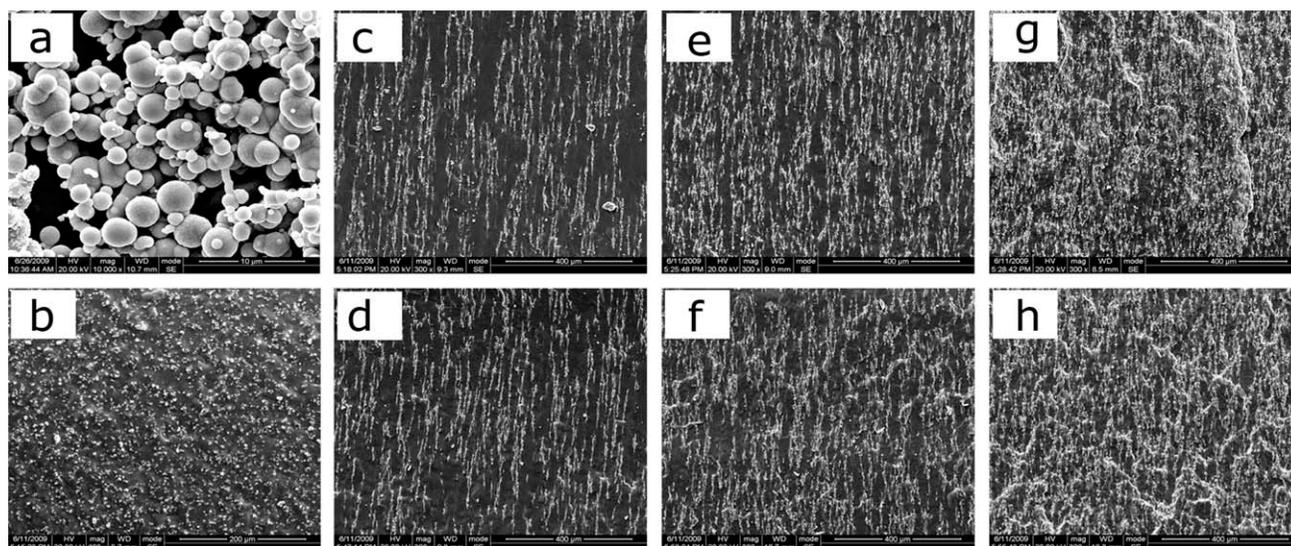


**Figure 2** SEM images of (a) carbonyl iron, (b) isotropic PU MREs with 50 wt % carbonyl iron, anisotropic PU MREs oriented under 1.2 T without (c, e, g) and with (d, f, h) DOP plasticizer (the DOP/(PU+DOP) is 30 wt %), the carbonyl iron content are 50 wt % in (c) and (d), 60 wt % in (e) and (f), 70 wt % in (g) and (h).
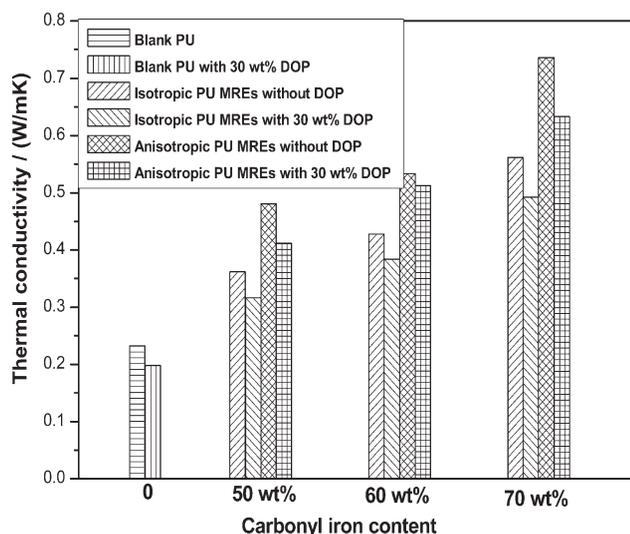
**Figure 3** Thermal conductivity of PU and PU MREs without and with DOP plasticizer (DOP/(PU+DOP) is 30 wt %).

and 70 wt % are shown in Figure 2(c,e,g), respectively. As the iron content increases from 50 to 70%, the iron chains get dense and the gap between the adjacent chains decreases. SEM images of DOP plasticized anisotropic PU MREs (DOP/(PU+DOP) is 30 wt %) are shown in Figure 2(d,f,h). It can be seen that the chain-like structure of DOP plasticized PU MREs is a little more obvious than that of PU MREs without plasticizer. From the rheological behavior of PTMEG/DOP/Fe dispersions, it can be seen that the incorporation of DOP reduced the viscosity of the dispersions. Thus, the resistance of orientation of carbonyl iron in the prepolymer reduced, which results in a more obvious chain-like structure.
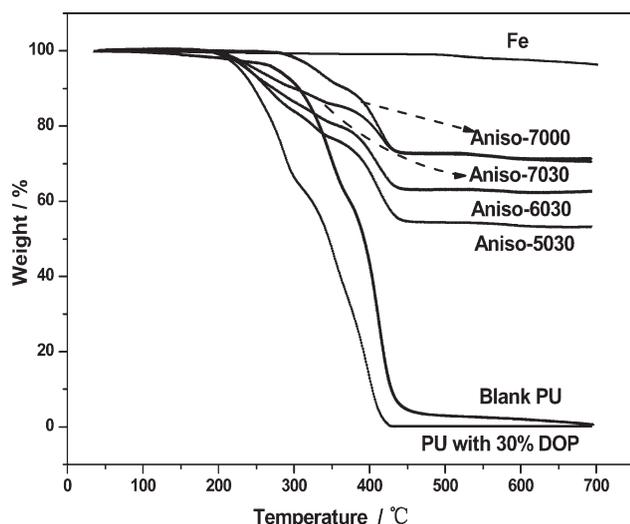


**Figure 4** TGA curves of PU and anisotropic PU MREs in the nitrogen atmosphere.

## Thermal properties

Figure 3 shows the thermal conductivity of PU, isotropic and anisotropic PU MREs. The thermal conductivity of blank PU is only $\sim 0.23$ w/mk. With increasing the carbonyl iron content, the thermal conductivity of isotropic PU MREs increases. When the iron content is 70 wt %, the thermal conductivity of isotropic PU MREs increases to $\sim 0.56$ W/mk, by $\sim 140\%$ compared with the blank PU. This is the direct result of incorporation of carbonyl iron with thermal conductivity of 80.2 W/mk.[22] For anisotropic PU MREs, the thermal conductivity increases more than that for isotropic PU MREs with the same carbonyl iron content. The thermal conductivity of sample Aniso-7000 reaches $\sim 0.74$ W/mk. After orientation, the carbonyl iron formed chain-like structure in the PU matrix, which can act as heat transfer pathway. After incorporation of 30 wt % plasticizer DOP, the thermal conductivity of PU, isotropic and anisotropic PU MREs all decrease to some extent.

TGA curves of PU and anisotropic PU MREs with different carbonyl iron contents are shown in Figure 4. The thermal characteristic decomposition temperature of PU and PU MREs in the nitrogen atmosphere is shown in Table II. $T_{onset}$ and $T_{end}$ represent the temperature at which the degradation of PU matrix start and end. $T_{max1}$ is the temperature with the maximal thermal degradation rate of DOP. $T_{max2}$ and $T_{max3}$ are two temperatures with the maximal thermal degradation rate of PU. For blank PU, $T_{max2}$ and $T_{max3}$ are closed to that of PU with hard segment of 35 wt % (352.3 and 433.0°C) in the literature.[23] In the nitrogen atmosphere, the mass of carbonyl iron particles is almost constant during heating. So, it can be deduced that the mass loss of PU MREs is entirely due to the thermal degradation of PU matrix and DOP. After adding 30 wt % DOP, the $T_{onset}$ decreases from 308.8°C to 230.9°C, which suggests that DOP has great influence on the characteristic temperature of PU. The similar trend of $T_{onset}$ can be seen from the samples Aniso-7000 and Aniso-7030. Also, it can be noted that $T_{onset}$, $T_{max1}$, and $T_{max2}$ of PU MREs with 30 wt % DOP all decrease

**TABLE II**
**The Thermal Decomposition Temperature of PU and Anisotropic PU MREs in the Nitrogen**

| Sample | $T_{onset}/$ °C | $T_{max1}/$ °C | $T_{max2}/$ °C | $T_{max3}/$ °C | $T_{end}/$ °C |
|---|---|---|---|---|---|
| Blank PU | 308.8 | – | 354.1 | 416.8 | 432.6 |
| PU with 30% DOP | 230.9 | 286.3 | 352.6 | 397.1 | 415.6 |
| Aniso-7000 | 283.5 | – | 337.1 | 412.4 | 435.5 |
| Aniso-5030 | 214.1 | 256.8 | 328.2 | 412.7 | 437.0 |
| Aniso-6030 | 206.2 | 244.2 | 327.1 | 409.7 | 435.0 |
| Aniso-7030 | 205.3 | 241.1 | 323.3 | 415.6 | 434.5 |
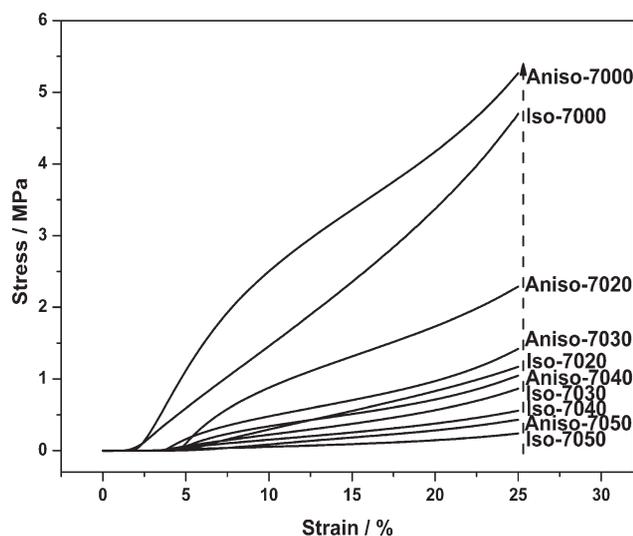
**Figure 5** The compressive stress–strain curves of PU MREs with different plasticizer contents.

with increasing the iron content. The possible explanations are as follows: on one hand, the increase in the thermal conductivity of composite leads to the faster degradation of PU matrix; on the other hand, iron and the iron ions can catalyze the decomposition and thereby accelerate the oxidation.[24] Since $T_{max3}$ is affected by the soft segment content,[23] the carbonyl iron has little effect on the $T_{max3}$ and $T_{end}$. In summary, highly filled carbonyl iron and the incorporation of DOP lead to a decrease in the thermal stability of the PU MREs.

## Mechanical properties

The effect of DOP content on the compressive properties of isotropic as well as anisotropic PU MREs with 70 wt % carbonyl iron are shown in Figure 5.
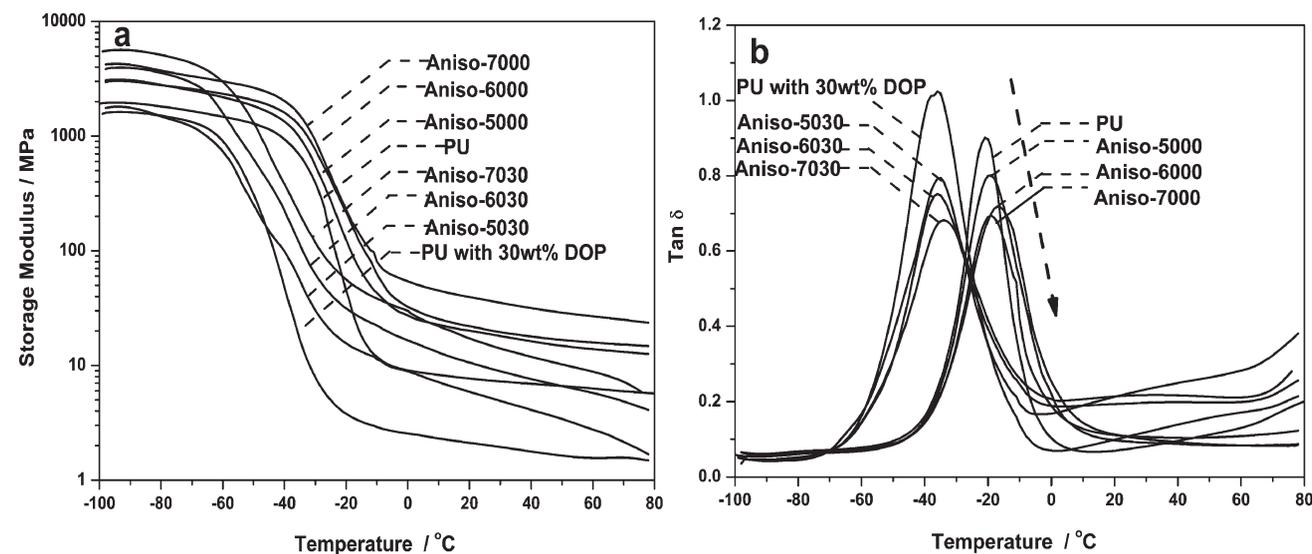
The incorporation of DOP reduces the compression stress greatly. A dramatic decrease in the stress at 20% strain, from 3.38 to 0.15 MPa, can be seen as the increase of DOP from 0 to 50 wt % for isotropic samples. Compared with the isotropic PU MREs, the anisotropic sample with the same DOP content has a higher compression stress. The orientation of iron particles along the direction of compression enhances the stiffness of the anisotropic sample, which results in a higher compression stress.

Figure 6 shows the influence of iron and plasticizer contents on the storage modulus ($E'$) and mechanical loss factor (tan δ) of anisotropic PU MREs. The tan δ peak is associated with glass transition temperature ($T_g$) of the soft segment of PU. Below $T_g$, the effect of iron content on the storage modulus is not obvious. Above room temperature, the storage modulus increases with increasing the iron content. The incorporation of rigid iron particles and the formation of chain-like structure enhance the stiffness of the composites. But the addition of the plasticizer leads to a decrease in the storage modulus. The tan δ of blank PU elastomer is as high as ∼ 0.90. The peak value of tan δ of the PU MREs decreases with increasing the iron content. This is attributed to the reduced chain mobility during dynamic mechanical deformation with high filler contents. The result is consistent with the usually observed behavior in filled rubber composites.[25] Also, the introduction of 30 wt % DOP results in a slight decrease in $T_g$, from −20 to −35°C. It should be attributed to the reduced interaction of PU molecules with the addition of plasticizer DOP.[26]

## The magnetorheological effect

The relative MR effect can be defined as $\Delta G/G_0 \times$ 100%. Here, $G_0$ is the zero-field shear modulus; $\Delta G$



**Figure 6** Storage modulus (a) and loss factor (b) of anisotropic PU MREs and DOP plasticized anisotropic PU MREs.
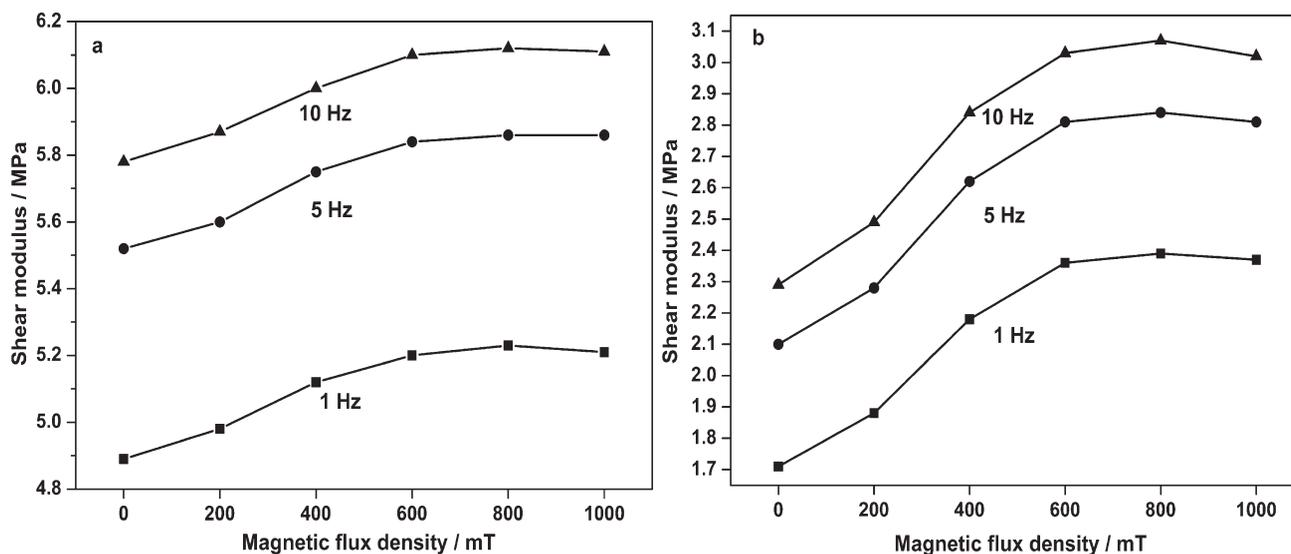
**Figure 7** Magnetic field induced shear modulus increment of anisotropic PU MREs without plasticizer (a) and with 30 wt % plasticizer (b) at 1, 5, and 10 Hz, the carbonyl iron content is 70 wt %, shear stain amplitude is 0.3%.

is the increment of field-induced shear modulus, i.e., absolute MR effect. In this study, the test frequency, the test amplitude of shear stain, the magnetic particles content and the plasticizer content, on the MR effect of the PU MREs were studied.

The motion of polymer molecular chain is frequency dependent, so the MR effect of MREs is also frequency dependent.[27] The MR effect of Aniso-7000 and Aniso-7030 at 1, 5, and 10 Hz is shown in Figure 7. It can be noted that the zero-field modulus increases with increasing the test frequency. With increasing the frequency, the motion of PU molecular chains can not keep up with the external stimuli, so molecular chains tend to be rigid and result in an enhancement of zero-field modulus. At the three test frequencies, the absolute MR effect of the samples Aniso-7000 and Aniso-7030 are ∼ 0.33 and ∼ 0.68 MPa, respectively. The absolute MR effect is independent of the test frequency, while the relative MR effect decreases with increasing the test frequency.

The magnetic field induced modulus change of the sample Aniso-7030 at four different stain amplitudes is shown in Figure 8. As the strain amplitude increases from 0.1% to 1%, the zero-field modulus decreases from 1.91 MPa to 1.51 MPa. When the shear strain amplitude increases, the motion of the rubber molecule chains and the sliding between the particles and the matrix increase, consequently the interaction among molecule chains as well as between the particles and matrix may be broken. The absolute MR effects at stain amplitudes of 0.1%, 0.3%, 0.5%, and 1% are 0.74, 0.68, 0.59, and 0.48 MPa, respectively. A decrease in the MR effect with increasing the test strain amplitude can be noted. With increasing the strain amplitude, the distance between particles within MREs increases, and this

will lead to the decrease of interactive forces between particles which results in the decrease of the magneto-induced modulus. This is in agreement with previous results.[10,12]

Figure 9 shows the MR effect of isotropic and anisotropic PU MREs with different carbonyl iron contents. For isotropic PU MREs, the MR effects are quite low. Even at an iron content of 80 wt %, the absolute MR effect is only ∼ 0.28 MPa. For anisotropic PU MREs, the MR effect appears when the content of carbonyl iron particles is 50 wt %, and become relatively pronounced at an iron content of 70 wt %. The absolute MR effects of Aniso-5030, Aniso-6030 Aniso-7030 and Aniso-8030 are 0.19, 0.32,
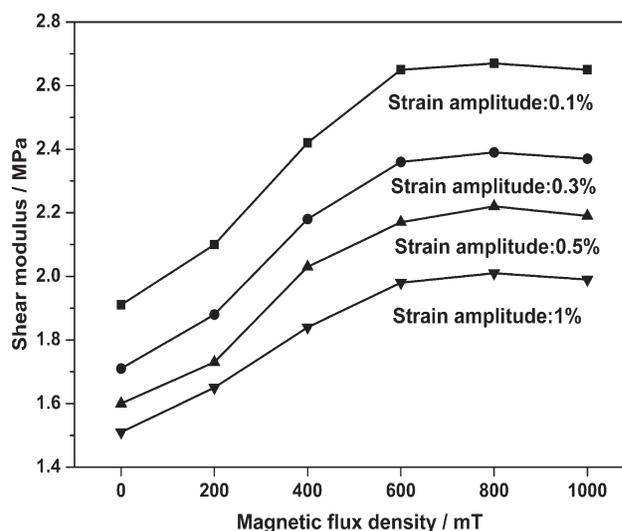


**Figure 8** Magnetic field induced shear modulus increment of anisotropic PU MREs with 70 wt % carbonyl iron at different strain amplitudes, the DOP is 30 wt %, test frequency is 1 Hz.
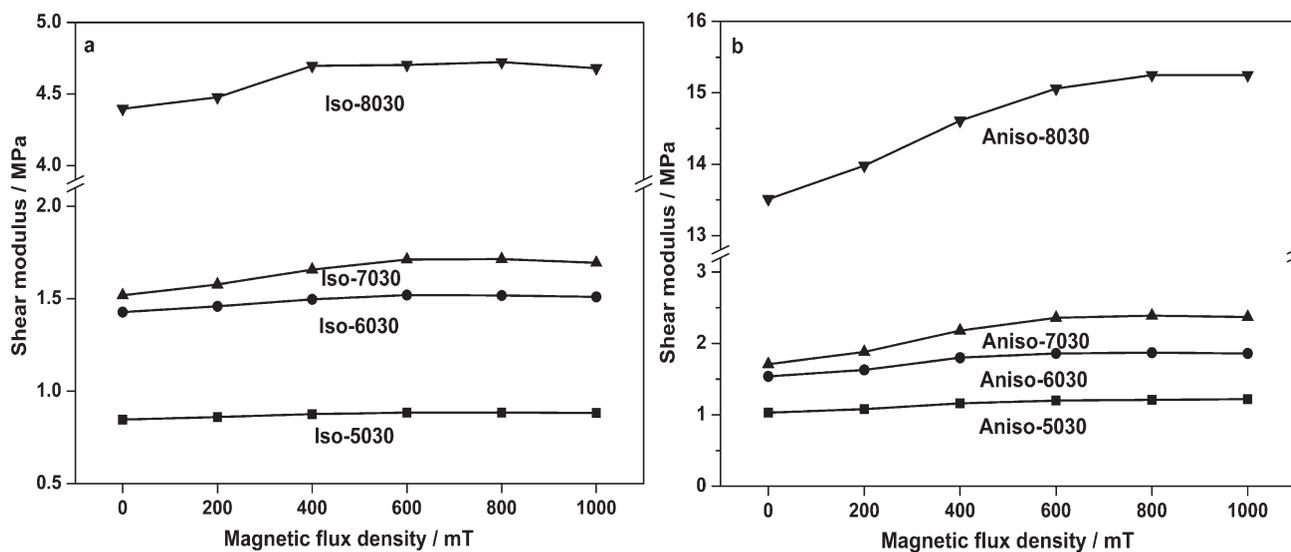
**Figure 9** Magnetic field induced shear modulus increment of isotropic PU MREs (a) and anisotropic PU MREs (b) with different carbonyl iron contents, the DOP content is 30 wt %, test frequency is 1 Hz, shear stain amplitude is 0.3 %.

0.68, and ~ 1.74 MPa, respectively. The orientation of the iron particles in PU matrix can greatly improve the MR effect. After orientation, the iron particles form chain-like structure which is fixed in the PU matrix. The formed chain-like structure reduced the distance of the iron particles, so the interaction of iron particles under magnetic field is enhanced.

DOP is a kind of effective plasticizer for PU, which can reduce the molecular interaction and soften the matrix.[26] The effect of DOP content on the MR properties of isotropic and anisotropic PU MREs with 70 wt % carbonyl iron are shown in Figure 10. The related zero-fied modulus and MR effect data are summarized in Table III. For both isotropic and anisotropic PU MREs, the zero-field modulus decreases significantly with increasing DOP content. The higher the DOP content is, the lower the shear modulus is. For isotropic PU MREs, the absolute MR effect shows a slight increase trend with increasing the DOP content, while the relative MR effect increases from 3.5% to 78.6%, which should be attributed to the significant decrease in the zero-field modulus with the addition of the plasticizer. For anisotropic PU MREs, both absolute and relative MR effect increase greatly with DOP content. The absolute and relative MR effects of the sample Aniso-7050 (the weight ratio of Fe: PU: DOP is 70 : 15 : 15) reach ~ 1.16 MPa and ~ 386.7%, respectively, which are ~ 3.5 and ~ 58 times of that PU MREs without
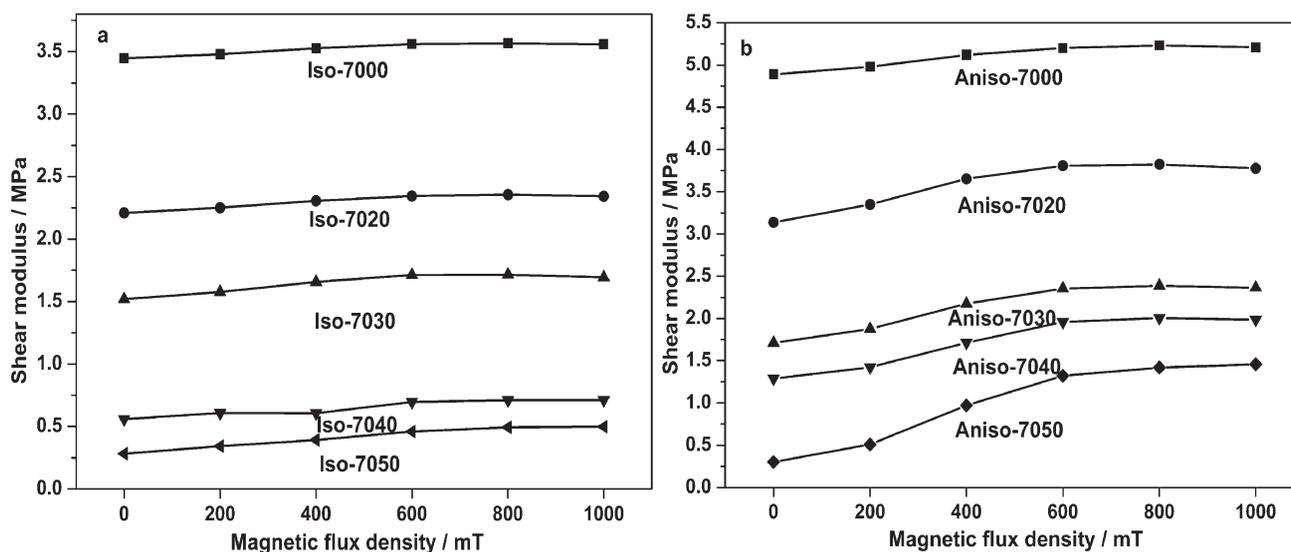


**Figure 10** Magnetic field induced shear modulus increment of isotropic PU MREs (a) and anisotropic PU MREs (b) with different plasticizer contents, the carbonyl iron content is 70 wt %, test frequency is 1 Hz, shear stain is 0.3%.

**TABLE III**
**The Zero-Field Modulus and MR Effect of PU MREs
with Different DOP Contents**

| Sample | $G_0$/MPa | Absolute MR effect/MPa | Relative MR effect/% |
|---|---|---|---|
| Iso-7000 | 3.45 | 0.12 | 3.5 |
| Aniso-7000 | 4.89 | 0.33 | 6.7 |
| Iso-7020 | 2.21 | 0.15 | 6.8 |
| Aniso-7020 | 3.14 | 0.64 | 20.4 |
| Iso-7030 | 1.52 | 0.17 | 11.2 |
| Aniso-7030 | 1.71 | 0.68 | 39.8 |
| Iso-7040 | 0.56 | 0.18 | 32.1 |
| Aniso-7040 | 1.29 | 0.70 | 54.3 |
| Iso-7050 | 0.28 | 0.22 | 78.6 |
| Aniso-7050 | 0.30 | 1.16 | 386.7 |

plasticizer. The maximum relative MR effect reported in the literature is 133% for plasticized natural rubber based MREs with 80 wt % carbonyl iron.[10] The relative MR effect of sample Aniso-7050 in this study is ∼ 3 times of plasticized natural rubber based MREs. The lower zero-field modulus and improved interaction between the aligned carbonyl iron particles with the addition of DOP are two main factors for the improvement of the MR effect. So, plasticization is an effective method to improve the MR effect, especially the relative MR effect.

## CONCLUSIONS

The plasticized polyurethane magnetorheological elastomers were prepared by *in-situ* one-step polycondensation process under a magnetic field. The microstructure, thermal, mechanical, and MR properties of PU MREs containing plasticizer were investigated.

1. By orientation of carbonyl iron in the process of polycondensation under the magnetic field, the carbonyl iron formed chain-like structure in the PU matrix. After incorporation of plasticizer to PU MREs, the viscosity of prepolymer decreased and thus made the carbonyl iron align more easily.
2. With the incorporation of carbonyl iron, the thermal conductivity of the composite increased. Highly filled carbonyl iron and plasticizer reduced the thermal stability of the composite to some extent.
3. The orientation of carbonyl iron particles enhanced the compressive strength of the com-

posite, but the addition of plasticizer reduced the compressive strength significantly.
4. Plasticization is an effective method to improve the MR effect especially the relative MR effect. With 70 wt % carbonyl iron and 15 wt % DOP content, the absolute and relative MR effect of anisotropic PU MREs were ∼ 3.5 and ∼ 58 times of that PU MRE without plasticizer at the same iron content.

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