Study on the Properties of Magnetorheological Gel Based on Polyurethane

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ABSTRACT: Magnetorheological gels (MRGs) known as a new kind of magnetorheological material are composite gels containing magnetic particles suspended in polymer gels. In this study, a category of MR polymer gels based on polyurethane (PU) were prepared. The microstructures of these MRGs were observed with a digital microscope. Their rheological properties under both steady shear and oscillation testing were characterized by using a MR rheometer. The viscosity of the PU MRG decreased with the increment of NCO/OH ratio and increased with the increment of the weight concentration of carbonyl iron particles, molecular mass of poly propylene glycol, and applied magnetic field. The storage modulus increased gradually with the increment of applied magnetic field and weight concentration of carbonyl iron particles. The PU MRG exhibits high static shear yield stress (60.8 kPa, at 573 mT) and dynamic shear yield stress (83.9 kPa, at 573 mT) and wide variation range (static shear yield stress: 6–62 kPa, dynamic shear yield stress: 15–85 kPa). These advantages indicate that PU MRG is able to satisfy wide applications. In addition, both static and dynamic shear yield stresses of the MRG samples increase with the increment of molar mass of polypropylene glycol. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2765–2771, 2010

Key words: magnetorheological gel (MRG); polyurethane (PU); viscoelastic property; static yield stress; dynamic yield stress

INTRODUCTION

Magnetorheological (MR) materials, including MR fluids, MR elastomers, and MR foams, are functional and smart materials, as their rheological or mechanical properties can be controlled continuously, rapidly, and reversibly by an applied magnetic field.[1–6] As an important branch of MR materials, MRFs are suspensions of ferrous particles such as carbonyl iron particles, which are micrometer sized and dispersed in a carrier medium.[7] The mechanical behavior of MRFs changes from a fluid-like state to a solid-like state within milliseconds by tuning the strength of an external magnetic field,[8] and this mechanical behavior is so-called controllable MR effect. Based on the this unique characteristic, MRFs have recently found many applications, including dampers,[9–11] vibration control,[12] MR polishing,[13] MR isolator,[14] MR fluid based haptic device,[15] brakes,[4] and so on.

Because of the high density of micrometer size magnetic particles in MR fluids, the magnetic particles will sedimentate definitely. The sedimentation of magnetic particles in MR fluids leads to a notable decrease of MR effect and influences the application stability. This problem may preclude some applications of MR fluids. This problem can be overcome by replacing the carrier fluid with a much more viscous material (e.g., gel or lubricant).[16–18] Magnetorheological gel (MRG), which is a composite fluid of magnetic particles suspended in polymer gels, is known as a new generation of MRFs and used in vibration control and damping devices.[19] These fluids have the advantages of being able to control off-state viscosity and to reduce the settling rate of the magnetic particles in the fluid.[20] And with the precipitation of polymeric gel on the surface of the iron particles, the stability of the system can be improved.[17]

In this study, MR gels based on polyurethane (PU) were fabricated. The different properties of polymer can be achieved by changing raw material ratio with the same composition.[21] The PU carrier fluids of MRG were synthesized by using toluene diisocyanate (TDI) and polypropylene glycol (PPG) (PPG-1000, $M_n = 1000$; PPG-2000, $M_n = 2000$), which have different properties by adjusting the molar ratio of TDI to poly propylene glycol (NCO/OH) and the molecular mass of poly propylene glycol. PU-based MRG samples, with different reaction molar ratios of NCO/OH and the molecular mass of poly propylene glycol, were prepared. Their performances were characterized.

EXPERIMENTAL

Raw materials

Polypropylene glycol (PPG-1000, $M_n = 1000$; PPG-2000, $M_n = 2000$) (The Third Petrochemical Factory, Tianjin Petrochemical, China) was distilled at 110°C under a vacuum for 1 h before use. TDI (TDI-80; Bayer Co.), 1,4-butanediol (BDO, Sinopharm Chemical Reagent Co.), tin(II) octoate (Sinopharm Chemical Reagent Co.), and acetone (Sinopharm Chemical Reagent Co.) were used as received. The 1-methyl-2-pyrrolidone(NMP;Sinopharm Chemical Reagent Co.) was used as additives. The magnetic particles were carbonyl iron bought from BASF (German, model CN) with the size distribution: d10 = 3.5 μm, d50 = 6 μm, d90 = 21 μm.

Synthesis of polyurethane

Poly propylene glycol and TDI were mixed in a 250 mL three-necked round-bottom flask fitted with mechanical stirrer, thermometer, and condenser. The temperature of a reaction system was heated to 80°C and kept at this temperature for about 2 h under agitation. The mole ratio of TDI to poly propylene glycol was calculated according to:

$$\frac{n_{NCO}}{n_{OH}} = \frac{m_{TDI}/174 \text{ g.mol}^{-1}}{m_{PPG}/2000 \text{ g.mol}^{-1}} \tag{1}$$

where n_{NCO} is the mol of NCO group, n_{OH} is the mol of OH group, m_{TDI} is the weight of TDI, and m_{OH} is the weight of poly propylene glycol.

Four categories of MRG samples with different mole ratios were prepared. The selective mole ratios for these five samples were listed in Table I.

1,4-Butanediol used as a chain extender was then added to the reactor, and chain extension was performed at 70°C for the next 2 h. During the reaction, suitable amount of acetone was added to reduce the system viscosity. Then, tin (II) octoate (0.015 g) was added dropwise into the flask, and the reaction temperature was kept at 70°C for about 1 h under agitation.

Preparation of MRG materials

The 1-methyl-2-pyrrolidone was added as additive under agitation. Then, the iron particles were added
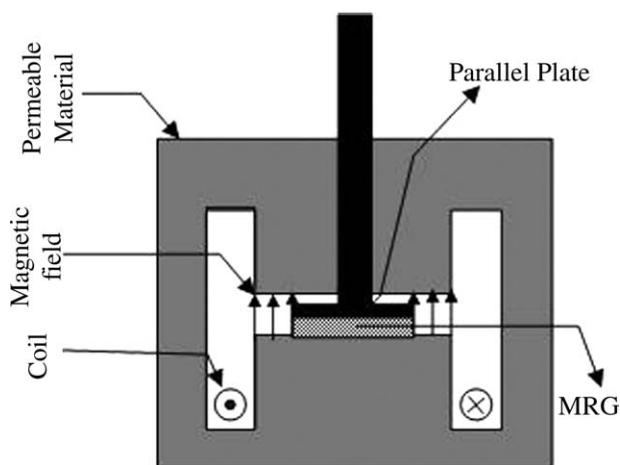

Figure 1 Principle of MR-device.

to PU under stirring. In this study, five MRG samples based on PU had the different compositions (carbonyl iron particle: 60, 70, and 80 wt %). Then, the sample was put into an oven at 50°C for 72 h to vaporize acetone.

Characterization and measurement

FTIR

Fourier Transform Infrared (FTIR) spectra of PU were collected on a Bruker FTIR (EQUINOX55) spectrometer in the range of 4000–500 cm^{-1} at an ambient temperature.

Observation of microstructure

The microstructure of MRG based on PU was observed by using a digital microscope (VHX-200, Keyence Co., Japan). The sample was spread on the surface of slide glass and observed with and without magnetic field.

MRG rheology testing

An Anton Paar Physica MCR301 rheometer, operated in either a stress- or a strain-control mode, with an accessory of MR device MRD180, was used to study rheological properties of MRG under different magnetic fields. Figure 1 shows the schematic of the MRD-device. A parallel-plate measuring system with a diameter of 20 mm was used at a constant gap of 1 mm. The viscosity were measured by rotation tests with and without magnetic field, and the shear stress, static shear yield stress, and dynamic shear yield stress were measured when the external magnetic field was applied. Oscillation tests were taken to investigate the viscoelastic properties. All the tests were conducted at the room temperature of 25°C.

TABLE I
Five Samples Classified from Different Reaction Molar Ratios of TDI to PPG

PPG (M_n)	2000			1000	
$n_{NCO} : n_{OH}$	1 : 1	2 : 1	3 : 1	2 : 1	3 : 1
Sample	1	2	3	4	5
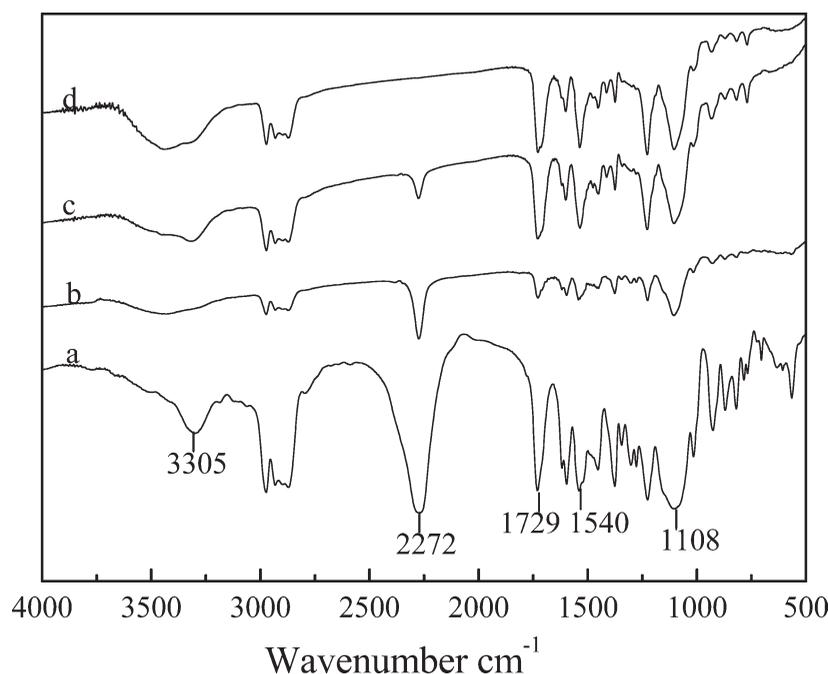
Figure 2 FTIR spectra of the PU: (a) 3 min, (b) 2 h, (c) 4 h, and (d) 5 h.

RESULTS AND DISCUSSION

Characterization of the polyurethane

Figure 2 shows the infrared spectrum of the PU in the range 500–4000 cm^{-1} at different reaction time. The urethane group signals, such as 3305 cm^{-1} (—NH stretching), 1729 cm^{-1} (C=O stretching), and 1540 cm^{-1} (—NH deformation vibration), were observed. The absorption at 2272 cm^{-1} is due to —NCO group (curve a). However, for curves b to d, this peak disappears generally. This result indicates that —NCO group was reacted completely, and the formation of PU was confirmed. A peak at 1108 cm^{-1} is ascribed to an ether (C—O—C) group. The above results indicate that PU has been successfully prepared.

Microscopy of the MRG based on polyurethane

The optical microscopy images of the sample 4 (carbonyl iron particle: 60 wt %) were obtained by the digital microscope when the magnetic field was 0 mT and 600 mT, as shown in Figure 3(a,b), respectively. As can be seen in Figure 3(a), the carbonyl iron particles, which are light spots in the images, are randomly dispersed in the PU when the magnetic field was 0 mT. Compared Figure 3(b) with Figure 3(a), it can be apparently observed that the carbonyl iron particles are oriented into chainlike columns along the direction of applied magnetic field. This phenomenon is because that the magnetic interaction dipole forces, which were induced by the applied magnetic field, drive the particles to form chainlike structures in the polyurethane. These chainlike structures can resist the mechanical deformation such as shear or compression, and the effective stiffness of the material is increased in the magnetic field.

Mechanical properties

Rheology under steady shear

Figure 4 shows the viscosities of the PU MRG samples (carbonyl iron particle: 0 wt %, 60 wt %) with different NCO/OH ratio, which were measured under various shear rates (from 0 to 50 s^{-1}) when the external magnetic field strength was 0 mT. As can be observed from this figure, the PU MRG has high viscosity without magnetic field. By replacing the carrier fluid with a much more viscous material, the problem of sedimentation was overcome.[16] The PU gel, which has no magnetic particles, is Newtonian fluid. As the addition of magnetic particles, the material shows non-Newtonian behavior and higher viscosity. This result is in a good agreement with Fuchs' report.[22]

From this figure, it can also be seen that the viscosities of PU MRG samples decreased with the increment of NCO/OH ratio. This result is due to the change of PU carrier as the NCO/OH ratio increased. The hard segments of PU are composed of TDI, and the soft segments are composed of poly propylene glycol. The amount of soft segments increased when the NCO/OH ratio decreased, and the number of chain entanglement per unit volume is enhanced. This phenomenon may result in the increment of viscosity of PU carrier, and the viscosity of PU MRG (with the same weight concentration of
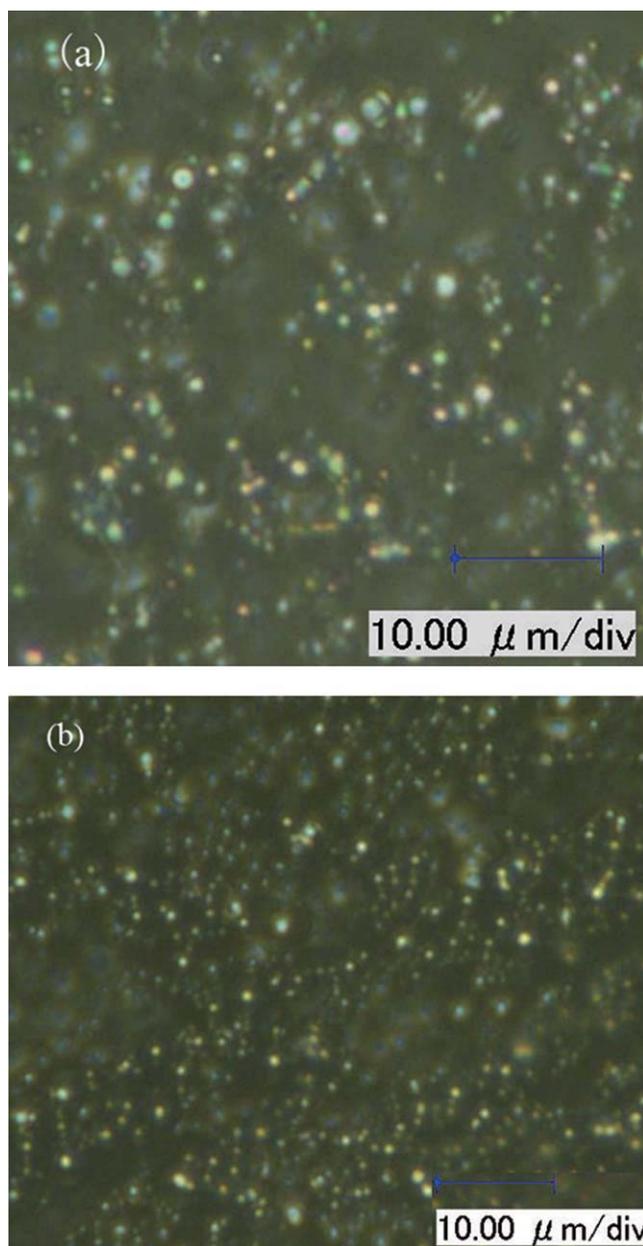
Figure 3 Optical microscopy images of the sample 4 (carbonyl iron particle: 60 wt %) observed by digital microscope: (a) 0 mT and (b) 600 mT. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

carbonyl iron particles) increases with the decrease of NCO/OH ratio under test.

Figure 5 shows the viscosity of the PU MRG (carbonyl iron particle: 70 wt %, 80 wt %) with different molar mass of PPG at zero field strength. It can be seen that the viscosity of the PU MRG increased with the increment of molar mass of PPG and the weight concentration of carbonyl iron particles. Compared with PPG-1000 (M_n = 1000), PPG-2000 (M_n = 2000) has longer soft segment, which may result in the high degree of chain entanglement.
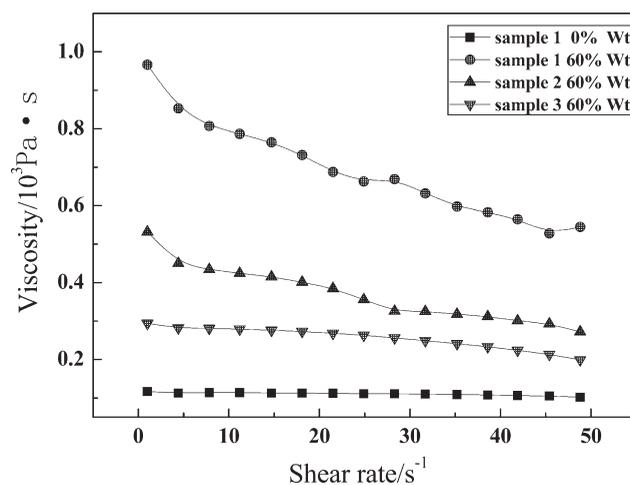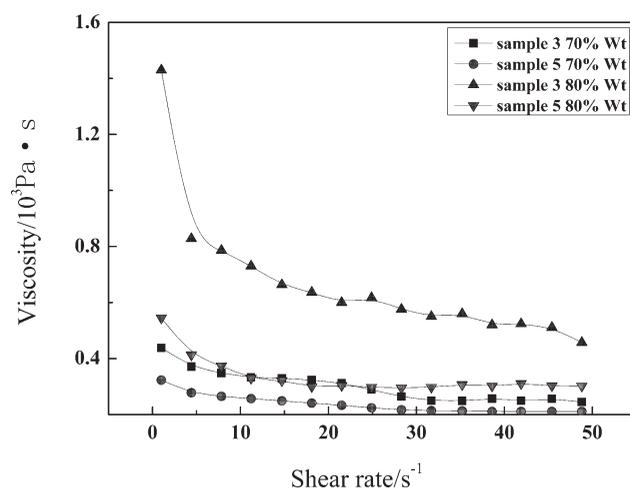
Figure 4 The viscosity of the samples for different reaction molar ratio in PU MRG.

On the other hand, as the weight concentration of carbonyl iron particles increased, the interaction force between particles and the PU carrier is enhanced under steady shear test. This interaction force also causes the increment of composite viscosity.

The above results indicate that the viscosity of PU MRG is influenced by both particles and carrier. Thus, the viscosity can be controlled by adjusting weight concentration of carbonyl iron particles, molar ratio of TDI to poly propylene glycol, and the molar mass of PPG to satisfy different applications.

Figure 6 shows the viscosity of the sample 1 (carbonyl iron particle: 60 wt %) with the same weight concentrations of carbonyl iron particles under various magnetic fields. The phenomenon of the decreasing apparent viscosity with increasing shear rate is known as shear thinning behavior and is due to the presence of micrometer-size particles.[22] The

Figure 5 The viscosity of the samples for different molar mass of PPG in PU MRG.
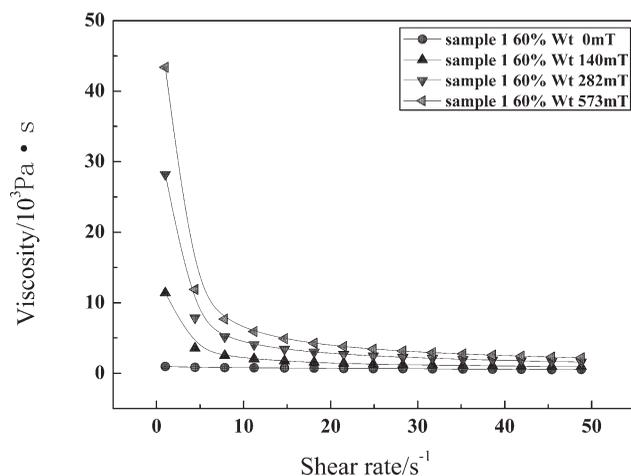
Figure 6 The viscosity of the sample1 under various magnetic fields.

constant value of viscosity increased with the increment of magnetic field when the shear rate is high. This phenomenon may result from the higher magnetic interaction force between particles when the magnetic field is raised.
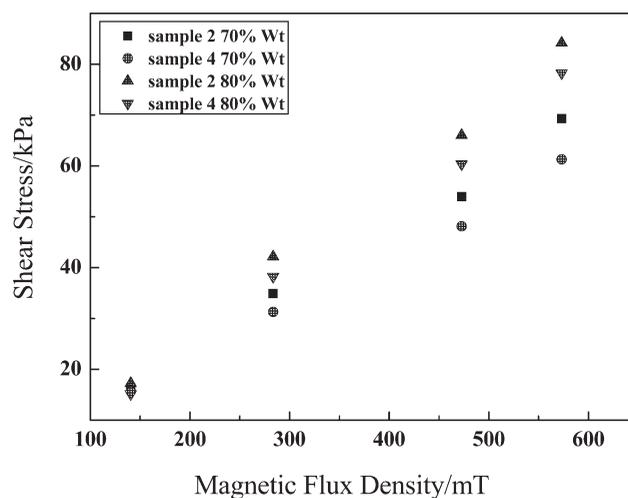
Static shear yield stress and dynamic shear yield stress

The static shear yield stress of different molar mass of PPG in PU MRG was measured with Anton Paar Physica MCR301 rheometer under various magnetic fields, as shown in Figure 7. A stress sweep test was taken to investigate the static shear yield stress from the curve of stress–strain. Figure 8 shows the dynamic shear yield stress of the samples for different molar mass of PPG in PU MRG, which was measured under the shear rate sweep (from 0 to 100 s^{-1}) at 25°C.

As can be seen in Figures 7 and 8, the PU MRG exhibits high static shear yield stress (60.8 kPa, at 573 mT) (83.9 kPa, at 573 mT) and wide field-dependence
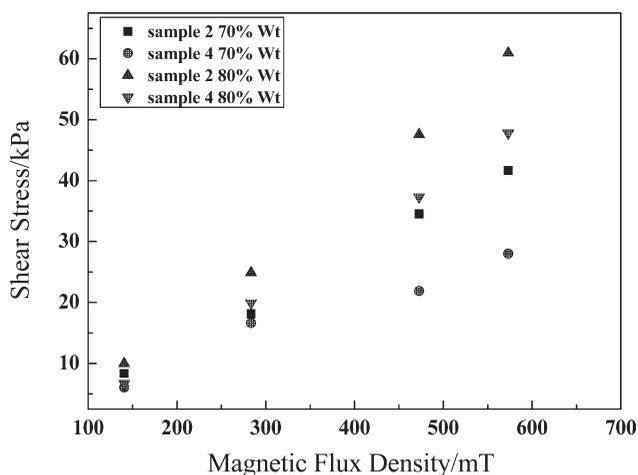
Figure 7 The static shear yield stress of the samples for different molar mass of PPG in PU MRG.

Figure 8 The dynamic shear yield stress of the samples for different molar mass of PPG in PU MRG.

stress range. For example, the static shear yield stress of PU MRG can be changed from 6 to 60 kPa, whereas the dynamic shear yield stress can be changed from 15 to 80 kPa. This advantage indicates that PU MRG is able to satisfy wide applications.

It can also be seen that both the static and dynamic yield stresses of PU MRG increased with the increment of molar mass of PPG and weight concentrations of carbonyl iron particles. When the samples are exposed to an applied magnetic field, the aligned particle chains can be formed during test, which are along the direction of magnetic field. As the weight concentrations of carbonyl iron particles increased, the aligned particle chains are tremendously enhanced and the magnetic interaction force between particles increased. The change of particle chains may result in the high static and dynamic shear yield stresses.

The effect of the weight concentrations of PPG on the yield stresses MRGs can be obtained from these figures. For the sample weight concentrations of carbonyl iron particles, the yield stress increased with the increment of molar mass of PPG. This result may be due to the different dispersion stabilities of samples. The dynamic shear yield stress is higher for fluids with better dispersion stability.[19] As can be observed from Figure 5, the viscosity of the sample 2 (PPG-2000, M_n = 2000) is higher than sample 4 (PPG-1000, M_n = 1000). When the system viscosity increased, the dispersion stability of sample 2 is better than that of sample 4.
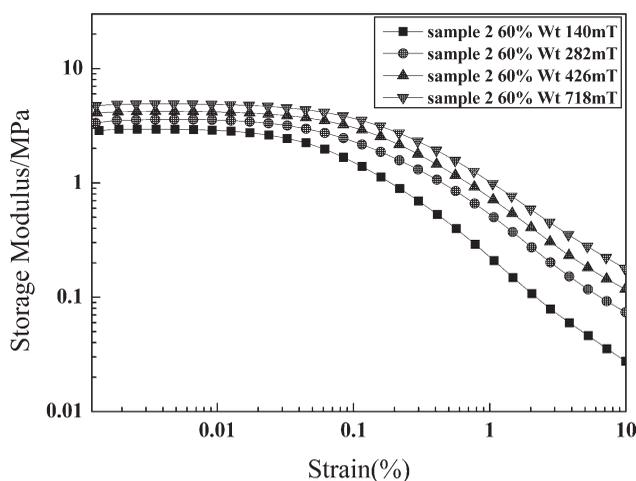
Rheology under oscillatory shear

Figure 9 shows the storage modulus (G') of the sample 1 with different weight concentrations of carbonyl iron particles under various magnetic fields, which were measured under various shear strain (from 0.001 to 10%) at the angular frequency of 10 s^{-1}. As can be seen in Figure 9, the storage modulus of the sample
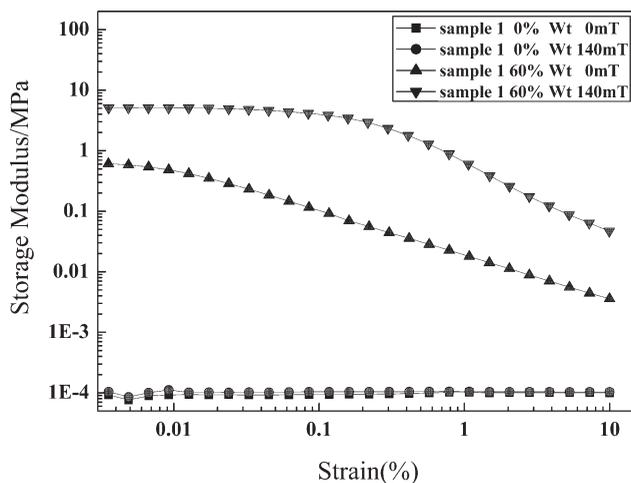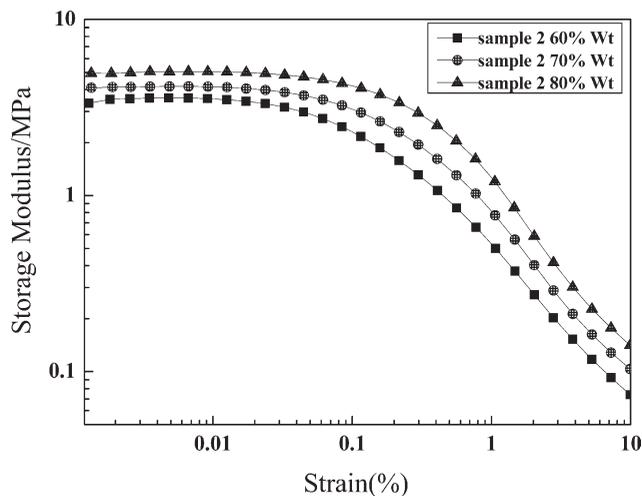
Figure 9 The storage modulus (G') of the samples under different magnetic fields.

Figure 11 The storage modulus (G') of the sample 2 under the same magnetic fields.

without iron particles varies very little with the magnetic field. When the weight concentration of carbonyl iron particles is 60%, the storage modulus is much higher than that of the sample without particles. The linear viscoelastic (LVE) of the sample (carbonyl iron particles: 60 wt %), which can be determined from the storage modulus curve because G' is almost a constant in the range of LVE,[23] immensely increased when the magnetic field is applied.

This result indicates that the elastic behavior of MRG is mainly caused by the particle chains when the magnetic field is applied. The material apparently exhibits elastic behavior and rigidity because the particles are arranged along the direction of magnetic field in the range of LVE. It also proved that viscoelastic properties of PU MRG were affected by the microstructure of iron particles. which shows a good agreement with Hu et al.[20]

Figure 10 shows the storage modulus (G') of the samples with the same weight concentrations of carbonyl iron particles under various magnetic fields, which were measured under various shear strain (from 0.001 to 10%) at an angular frequency of 10 s^{-1}. The storage modulus (G') of samples, which have the different weight concentrations of carbonyl iron particles (60, 70, and 80 wt %), were measured under the same various magnetic fields (282.4 mT), as shown in Figure 11. As can be seen in Figures 10 and 11, the storage modulus increased gradually with the increment of applied magnetic field and weight concentration of carbonyl iron particles. Moreover, the LVE also increased gradually.

This result may be due to the change of particle chain microstructure. In Figure 9, it can be seen that the LVE property of PU MRG is mainly caused by the particle chains when the magnetic field is applied. In the LVE range, the elastic behavior of MRPG fluid dominates the viscous behavior; the structure exhibits rigidity because in the preyield range, the iron chains or columns that are induced by the external magnetic field have high stiffness.[20] As can be seen in Figures 10 and 11, the interaction between particles is enhanced with the increment of applied magnetic field, and the particle chains were significantly reinforced with the increase of weight concentration of carbonyl iron particles. This change of particle chain microstructure may result in increment of storage modulus.

CONCLUSIONS

The MR gel based on PU (MRG) were prepared and experimentally studied by adjusting the molar ratio of hard segment (TDI) to soft segment (PPG) and the molecular mass of poly propylene glycol. The viscosity of the PU MRG decreased with the

Figure 10 The storage modulus (G') of the sample 2 under various magnetic fields.

increment of NCO/OH ratio and increased with the increment of molecular mass of poly propylene glycol, the weight concentration of carbonyl iron particles, and applied magnetic field.

The PU MRG exhibits high static shear yield stress (60.8 kPa, at 573 mT) and dynamic shear yield stress (83.9 kPa, at 573 mT) and wide variation range (static shear yield stress: 6–62 kPa, dynamic shear yield stress: 15–85 kPa). These results indicate that PU MRG is able to satisfy different applications.

Both the static and dynamic shear yield stress of samples, with the same weight concentrations of carbonyl iron particles, increased with the increment of molar mass of PPG. This result may be due to the different dispersion stabilities of samples.

The storage modulus gradually increased with the increment of applied magnetic field and weight concentration of carbonyl iron particles. The elastic behavior of MRG is mainly caused by the particle chains when the magnetic field is applied, and the viscoelastic properties of PU MRG were affected by the orientation of iron particles.

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