Study on off-state characteristics of polyurethane based magnetorheological gels

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Abstract. Magnetorheological gel(MRG) has variable off-state viscosity and it’s anti settling performance is very good. Four different ratios of polyurethane based MRGs were prepared (The mass fraction of iron particles was 10%, 25%, 50%, 75%, respectively), and at room temperature (25 °C) flow characteristics and viscosity characteristics of off-state of samples was tested. The results indicated that both in the rising and falling stages there is a linear relationship between shear rate and shear stress except shear rate above 110 s⁻¹ of MRG. The shear stress increases with the increase of particle content. All samples shown obvious shear thinning characteristics, and the viscosity increases with the increase of particle content.

1. Introduction

Magnetorheological (MR) materials are type of smart material with their unique rheological properties can be changed almost continuously, rapidly and reversibly in the case of a changing magnetic field. Therefore, they can be used in variety of applications which include MR dampers, vibration absorber, engine mount and MR clutches. With the further study of MR technology, other applications such as aspherical optical lens polishing, artificial skin and muscle and various sensors come into being[1-3].

MR materials include MR fluid, MR elastomers (MRE), MR gel (MRG), MR grease and MR foam. Up to present, there have been a lot of researches on the development of MRF[4-7]. Many studies show that when a magnetic field is applied, mutual attraction will produce between particles due to a dipole moment is induced in the particles in the MRF. Therefore, this drives the particles to align “head-to-tail” and form chains of particles parallel to the direction of the field. With the increase of magnetic field strength, the chain continues to absorb the neighboring particles and becoming thicker, so the MRF becomes more and more weak viscoelastic and ultimately like solid. It is interesting to note that when the magnetic field is removed, the MRF return to the Newtonian fluid. The above corresponding process is rapidly, continuous and reversible[8,9].

MRG as a kind of magnetorheological materials, the response process is similar to that of MRF. MRF has a wide relative magnetic rheological effect, which extends the engineering application of MRF. However, the problems such as particle sediment, stability and leakage in application device hinder its further development. These shortcoming are particularly evident in the following applications: gun
recoil damping, bridge cable vibration and building seismic device. By contraries, MRE as a kind of magnetorheological materials, with relatively low magnetorheological effect compare MRF, about 133% and 3.6MPa of the magneto-induced storage modulus. And MRE have no problems such as particle sediment, stability and leakage in application device\cite{10-14}.

To solve the problems such as particle sediment, stability and leakage of MRF and with relatively low magnetorheological effect of MRE, polymer matrices with high viscosity are employed to carry ferromagnetic particles and was named MRG, which will be better applied to vibration control and damping devices\cite{15,16}. It was worthy noted that another attraction is MRG have the advantage of providing controllable viscosity of the carrier fluid by changing the ratio of polymer components, which reducing the setting of magnetic particles in the fluid. In this study, firstly four different ratios of polyurethane based MRGs were prepared (The mass fraction of iron particles was 10%, 25%, 50%, 75%, respectively), and polyurethane without particles as a set of reference object. Secondly, the experimental device was designed and fabricated according to the off-state characteristics of MRG. Lastly, study on the relationship between viscosity and shear rate, shear stress and shear rate, viscosity and particle content, shear stress and particle content under off-state of polyurethane based MRGs.

2. Methodology

2.1. Raw materials

Polyurethane was produced by the polymerization of Toluene diisocyanate (TDI: 2.4-≈ 80%, 2.6-≈ 20%, Sinopharm Chemical Reagent Co., Ltd, China) and polypropylene glycol (PPG-100, $M_n = 1000$ , The Third Petrochemical Factory, Tianjin Petrochemical Inc, China). In the first step, the polypropylene glycol (PPG-100, $M_n = 1000$) was distilled at 90°C–100°C in a vacuum for about 2 hours before used. In order to make the rheological effect more remarkable, 1,4-Butanediol (BDO, Sinopharm Chemical Reagent Co., Ltd, China) was used as a chain extender and stannous octoate was used as the catalyst. Acetone (Sinopharm Chemical Reagent Co., Ltd, China) was selected as solvent when needed. Carbonyl iron particles with the average size is 5 μm was used as the magnetic particles despersed in the matrix.

The ratio of TDI and PPG was calculated by the following Eq.1:

$$\frac{n_{\text{NCO}}}{n_{\text{OH}}} = \frac{m_{\text{TDI}} / 174.15 \text{g.mol}^{-1}}{m_{\text{PPG}} / 1000 \text{g.mol}^{-1}}$$

(1)

Where $n_{\text{NCO}}$ and $n_{\text{OH}}$ present the mol of -NCO group and -OH group repectively, $m_{\text{TDI}}$ and $m_{\text{PPG}}$ present the weight of TDI and PPG, repectively.

The weight of the BDO added at the phase of chain extension was calculated by the Eq.2 below:

$$\frac{n_{\text{NCO}}}{n_{\text{OH}}} = \left(\frac{m_{\text{BDO}} / 174.15 \text{g.mol}^{-1}}{1000 \text{g.mol}^{-1}} \times 2 + \frac{m_{\text{BDO}} / 90.12 \text{g.mol}^{-1}}{90.12 \text{g.mol}^{-1}} \times 2\right)$$

(2)

2.2. Synthesis of the polyurethane magnetorheological gel

There are six steps in the synthesis of the samples, the specific process is shown in Fig.1.
Toluene diisocyanate (TDI; 2,4-=80%, 2,6-=20%)
Polypropylene glycol (PPG-1000, Mn=1000)
PPG was distilled at 90-100°C in a vacuum for about 2 h.

Toluene diisocyanate (TDI; 2,4-=80%, 2,6-=20%)
Polypropylene glycol (PPG-1000, Mn=1000)
TPDI and PPG were added to a 250 mL three-necked round bottom flask with a stirrer agitating the reactants all the time, the temperature of reaction system is 75°C.

Temperature was reduced to 65°C and this phase lasted about 1 h.

Stannous octoate (0.15 g) was added into flask at 60°C
During the reaction, moderate acetone was added to avoid gelation

The iron particles were added into the matrix by vigorously stirring until the matrix and iron particles were well mixed

Fig.1. Manufacturing process of polyurethane based MRGs
From this manufacturing process, four kinds of samples with 10wt%, 25wt%, 50wt%, 75wt% of iron particle content were prepared, and was named as MRG-10, MRG-25, MRG-50, MRG-75 repectively. In addition, the polyurethane without any iron particles (contrast component) for comparison purposes.

Samples with ratio of iron particles content of 10wt%, 25wt%, 50wt%, 75wt% and the polyurethane without iron particles is shown in Fig.2.

Fig.2. Samples with ratio of iron particles content of 10wt%, 25wt%, 50wt%, 75wt% and the polyurethane without iron particles for comparison

Fig.3. The schematic diagram of the experimental setup

2.3. Experimental setup
The experimental device is composed of five parts, including temperature controller, motor and driver, shear cylinder, water bath, shear rate regulating switch, and the schematic diagram of the experimental setup is shown in Fig.3.

The temperature of the experimental environment is controlled at 25 °C (at room temperature), therefore, temperature controller and water bath was used to provide room temperature at 25 °C. After electrify, motor and driver can drive the cylinder rotate, and then the samples were sheared, during the process of shear, shear rate can be controlled by adjusting the shear rate regulating switch.

3. Results and discussion

At the room temperature, the relationship between viscosity and shear rate, shear stress and shear rate, viscosity and particle content, shear stress and particle content of polyurethane based MRGs under off-state was studied respectively.

Experiments were carried out on MRG-10, MRG-25, MRG-50, MRG-75 and contrast component, and the shear rate was controlled varied from 2.509 s⁻¹ to 163.1 s⁻¹. first let the shear rate increasing gradually, and then decreasing gradually, during this period, the relationship between shear stress and viscosity with shear rate is shown in Fig.4 and Fig.5 respectively.
Fig. 4. Relationship between shear stress and shear rate of MRG-10, MRG-25, MRG-50, MRG-75 and contrast component.

To understand the influence of shear rate on the shear stress of MRGs, the off-state properties under continuous uniform shear were first investigated. It is easy to determine the trend of shear stress with shear rate by using the shear rate sweeping. From Fig. 4(a-d), the results show that in the rising stage of shear rate, the shear stress increases linearly with the increase of shear rate, contrary, in the decline stage of shear rate, the shear stress decreases linearly with the decreases of shear rate.

However, from Fig. 4(e), as for sample of MRG-75, the relationship between shear stress and shear rate is nonlinear when the shear rate is beyond 110 s⁻¹, showing that it slows down with increasing shear rate. Therefore, it can be predicted that with the further increase of shear rate, the shear stress will tend to a stable value.

From Fig. 4(f), in the case of constant shear rate, the shear stress increases with the increase of particle content. The reason for this is that the increase in particle content lead to an increase in the probability of collision between the particles, which requires greater force to flow.

From Fig. 4(a-e), it also can be concluded that the flow curve is basically same both in the rising and falling stages.
From the Fig. 5(a-d), it is indicated that when the shear rate is less than 20 s\(^{-1}\), the viscosity is very unstable with the change of shear rate. However, when the shear rate is greater than 20 s\(^{-1}\), the viscosity decreases with the increase of shear rate, shown obvious shear thinning characteristics. However, from the Fig. 5(e), as for sample of MRG-75, the viscosity varies stable with the whole rate range. Similarly, the viscosity decreases with increasing shear rate, shown obvious shear thinning characteristics.

From the Fig. 5(f), in the case of constant shear rate, the viscosity increases with the increase of particle content. The reason for this is that the increase in particle content lead to an increase in the probability of collision between the particles, which produced greater internal friction resistance. From Fig. 5(a-e), it can be concluded that the flow curve is basically the same in both the rising and falling stages.

4. Conclusions
To solve the problems such as particle sediment, stability and leakage of MRF and with relatively low magnetorheological effect of MRE, polymer matrices with high viscosity are employed to carry ferromagnetic particles and was named MRG, four different ratios of polyurethane based MRGs were prepared (The mass fraction of iron particles was 10%, 25%, 50%, 75%, respectively), and then study on the relationship between viscosity and shear rate, shear stress and shear rate, viscosity and particle content, shear stress and particle content of polyurethane based MRGs under off-state, respectively. The
results shown that both in the rising and falling stages there was a linear relationship between shear rate and shear stress except shear rate above 110 s⁻¹ of MRG-75. The shear stress increases with the increase of particle content. All samples shown obvious shear thinning characteristics, and the viscosity increases with the increase of particle content.

Acknowledgements
This work was financially supported by the Zhejiang Provincial Natural Science Foundation (LY13E050006); Zhejiang Provincial Natural Science Foundation (LY15E050009); National Natural Science Foundation of China (51275483); Innovative and Entrepreneurship Training Program for College Students of China(201610345033)

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