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Soft magnetorheological polymer gels with controllable rheological properties

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Abstract

A series of magnetorheological (MR) gels consisting of plastic polyurethane matrix swollen by nonvolatile solvent in different weight fractions and carbonyl iron particles were prepared. Their magnetorheological properties, both under oscillatory and rotational shear rheometry, were systematically tested. The results demonstrate that except for the significant influence on the magnetorheological performance, the state of these MR gels can also be easily switched from solid-like (the solvent content is less than 10 wt%) to liquid-like (the solvent content exceeds 25 wt%) by adjusting the solvent content. The huge differences in magnetorheological properties of different MR gels (for example, the G' of MR gels without solvent is three orders of magnitude larger than that of MR gels with 45 wt% of solvent in the absence of a magnetic field) and movements of iron particles in the presence of a magnetic field were analyzed, which are helpful in thoroughly understanding the mechanical–magnetic coupling mechanism between the magnetic particles and the polymer matrix and promoting the application of MR polymer gels. In addition, the stability of MR gels was also investigated. A gravity yield parameter was introduced to quantitatively describe the relationship between particle sedimentation and material characteristics. When the solvent content is lower than 25 wt% or the gravity yield parameter is larger than 0.865, the particle settling phenomenon can be effectively avoided.

(Some figures may appear in colour only in the online journal)

1. Introduction

Since magnetorheological (MR) gels were first reported by Shiga *et al* in 1995 [1], they have been investigated extensively as an important branch of MR materials. As an intermediate system between magnetorheological (MR) fluids and MR elastomers, MR gels show more flexible controllability of the MR properties. Generally, MR gels are regarded as a type of composite consisting of magnetic particles, partially crosslinked polymer gels, and other additives. A variety of polymer gels were tried to serve as the matrix of MR gels and the magnetorheology of these MR polymer gels (MRPGs) was also characterized [2–14]. The early MR gels presented a liquid-like state in the absence of a magnetic field, which is actually an imitation of MR fluids with higher yield stress and lower particle settling behavior [3–5]. A kind of solid-like MR

gel has been developed recently [15–17]. The most fascinating characteristic of these solid-like MR gels is that the magnetic particles are movable under an external magnetic field and form chain-like or column-like structures along the direction of the magnetic field driven by the magnetic forces. After the magnetic field is removed, the ordered microstructure can still be retained.

Because the polymers are themselves a huge class of functional materials with various mechanical, thermal, and optical responsive properties [18], new properties may be found in MR gels in addition to the magneto-controllable property [8, 19]. Different from MR fluids, the viscosity of MR gels in the absence of a magnetic field can be controlled by adjusting the component of the carrier matrix, which gives the preparation of MR gels a great deal of flexibility. In addition, adding polymer gels into a low viscosity liquid

carrier media can efficiently preclude the particles from settling [20, 21]. The above analysis indicates MR gels have great potential to replace MR fluids in some applications (such as dampers [22, 23], MR isolators [24], MR brakes [25], vibration control [26], and so on) with superior performance, or to be applied in new fields. In short, the appearance of MR gels fills the gap in magnetorheological performance between MR fluids [22] and MR elastomers [27–29] and provides more choice for the application of MR materials.

To our knowledge, most papers related to MR gels focus on their preparation and the rheological properties. The mechanical–magnetic coupling mechanism between magnetic particles and the polymer matrix is rarely mentioned, though it can provide significant guidelines for the performance optimization of MR gels. The huge differences in magnetorheological properties between liquid-like and solid-like MR gels may originate from two aspects: the viscosities or moduli of the polymer gels and the interactions between the magnetic particles and the matrix. If a series of MR gels with different viscosities—which make MR gels change from liquid-like to solid-like in the absence of a magnetic field—can be prepared, we can quantitatively characterize their magnetorheological performance and the appropriate type of MR gel for a specific application can be easily chosen accordingly. Meanwhile, the mechanical–magnetic coupling mechanism can be further explored by comparing the magnetic response behaviors of MR gels under the same magnetic field.

Adding nonvolatile solvent into the polymer gels can easily change their viscosities. In this study, a kind of plastic polyurethane was synthesized first. After carbonyl iron particles and nonvolatile solvent in different weight fractions were evenly mixed with the polyurethane matrix, a series of polyurethane based MR gels with different viscosities were then obtained. The magnetorheological properties of MR gels under oscillatory and rotational shear rheometry were tested, respectively. At the same time, the mechanical–magnetic coupling mechanism was analyzed based on the experimental results. In addition, the stability of MR gels was investigated and the reason for particle sedimentation was also discussed.

2. Experimental details

2.1. Preparation

The preparation process of MR gels is illustrated in scheme 1. Preformed polymer was first synthesized by mixing toluene diisocyanate (TDI, 2,4-~80%, 2,6-~20%, Tokyo Chemical Industry Co., Ltd, Japan) and polypropylene glycol (PPG-1000, $M_n = 1000$, Sigma-Aldrich (Shanghai) Trading Co., Ltd, China) into a three-necked round bottom flask and the mixture was stirred for 2 h at 70 °C. Then the mixture was cooled to 40 °C and the dipropylene glycol (as a chain extender, Sigma-Aldrich (Shanghai) Trading Co., Ltd, China) was added into the flask at the same time. 20 min later, the mixture was divided among six beakers, and 1-methyl-2-pyrrolidone (nonvolatile solvent, vapor pressure: 0.99 mmHg (40 °C), Sinopharm Chemical Reagent Co., Ltd,

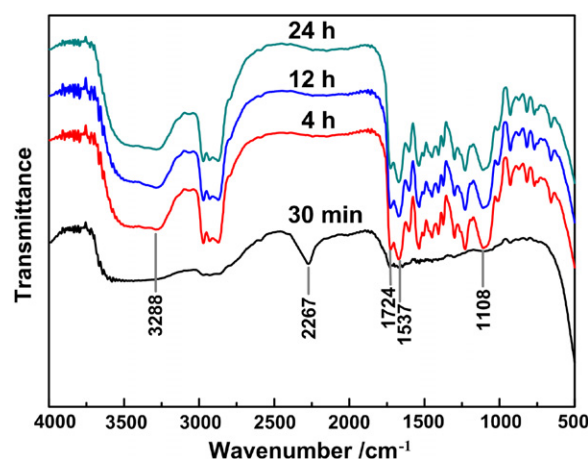


Figure 1. FTIR spectra of the reaction mixture without solvent and iron particles after the reaction ended (i.e. the time after ‘stirring at 40 °C for 20 mins’ in scheme 1) for 30 min, 4 h, 12 h, and 24 h in the range of 4000–500 cm^{-1} .

China) with different weight ratio to the mixture (0 wt%, 10 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, and 45 wt%) and carbonyl iron particles (type CN, provided by BASF in Germany, with an average radius of 6 μm) with weight fraction of 70% to the matrix (mixture of polymer gels and solvent) were added in these beakers respectively. After vigorously stirring the mixture for 30 min, the beakers were placed in an oven at 40 °C for 12 h. Finally, MR gels, swollen by solvent, in different weight fractions with 70 wt% iron particle content were prepared.

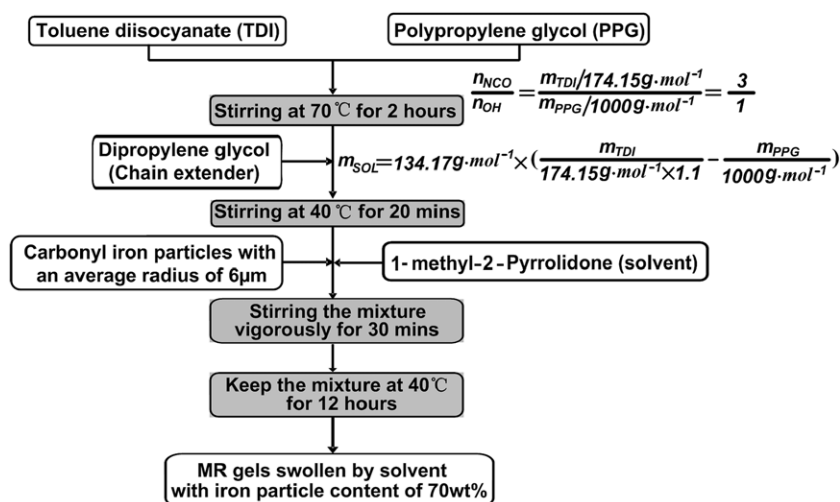
2.2. Component analysis of the matrix

To determine the chemical groups of the matrix and further speculate the component of the matrix, Fourier transform infrared spectroscopy (FTIR) spectra of the reaction mixture in the range of 4000–500 cm^{-1} at room temperature were measured by a Bruker FTIR (EQUINOX55) spectrometer. The measurements were carried out at various times after the reaction: 30 min, 4 h, 12 h, and 24 h, respectively.

As shown in figure 1, the peak located at 2267 cm^{-1} (–NCO group, only existing in TDI) disappears after 4 h, indicating that the synthetic reaction still proceeded during the first 4 h and that TDI was completely reacted 4 h later. An ether C–O–C group appearing at 1106 cm^{-1} also proves that TDI and PPG have taken part in the reaction. Three characteristic bands of polyurethane (PU) located at 1537, 1724, and 3288 cm^{-1} can be observed in the FTIR spectra after 4 h, giving evidence that PU was successfully synthesized after a reaction of 4 h. In addition, the FTIR spectra collected after 4, 12, and 24 h are almost coincident, from which it can be concluded that the PU matrix is stable after it is synthesized.

2.3. Magnetorheology characterization

Rotational and oscillatory shear tests are the most frequently used measurement methods to investigate the rheological



Scheme 1. The preparation process of MR gels swollen by solvent in different weight fractions. n_{NCO} is the mol of the $-\text{NCO}$ group while n_{OH} is the mol of the $-\text{OH}$ group, m_{TDI} , m_{PPG} , and m_{SOL} represent the weight of toluene diisocyanate, polypropylene glycol, and dipropylene glycol, respectively. The weight of reactants can be calculated according to the formulas in the scheme.

properties of materials for the parallel-plate rheometer. The magnetorheological properties of MR gels were measured by a parallel-plate rheometer (Physica MCR 301, Anton Paar Co., Austria) with a magneto-controllable accessory, named MRD 180, in which the magnetic field can be changed from 0 to 930 mT by adjusting the coil current from 0 to 4 A. An oscillatory shear test can give information about viscoelastic properties such as storage stability, elasticity and energy dissipation of viscoelastic materials, with which the structure of these materials at rest can be analyzed. In this study, the strain amplitude sweep, the transient response under a stepwise magnetic field and the magnetic field sweep for the MR gels under oscillatory shear rheometry were all tested (the temperature and oscillatory frequency were set as 25 °C and 5 Hz, respectively). The rheological properties under large shear deformation for liquid-like materials under rotational shear rheometry can be obtained. Three control modes (shear rate, strain, and stress control) can be chosen for different purposes. In this study, the shear rate control mode under rotational shear rheometry was used to investigate the stress response of liquid-like MR gels under different magnetic fields in the shear rate range 0–100 s^{-1} .

3. Results and discussion

3.1. Dynamic properties under oscillatory shear rheometry

To understand the influence of solvent on the magnetorheology of MR gels, the dynamic properties under oscillatory shear rheometry were first investigated. The linear viscoelastic (LVE) range is important for viscoelastic materials. Within the LVE range, the dynamic properties (storage modulus, loss modulus, and loss factor) have specific physical meanings and the microstructure rupture of viscoelastic materials induced by external actuating signals can be ignored. In other words, if the actuating strain amplitude is set within the LVE range, the possibility of strain-induced microstructure

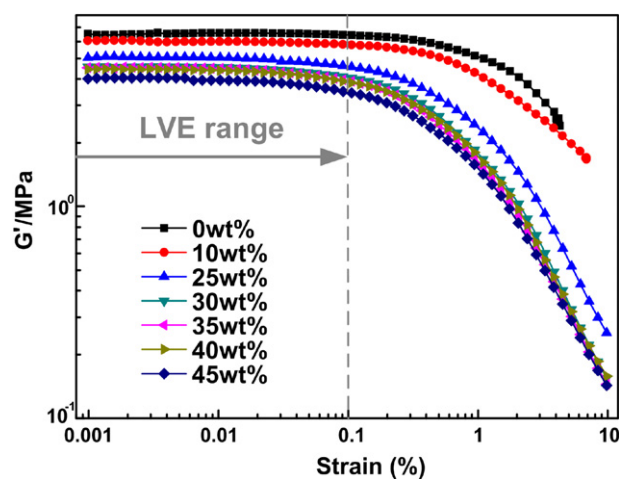


Figure 2. G' of MR gels swollen by solvent in different weight fractions at different strain amplitudes. Each product was exposed to a 930 mT magnetic field for 5 min before the test and the 930 mT magnetic field was kept on during the measurement process.

rupture can be excluded (this proposition will be used in our subsequent analysis), which is helpful to further understand the relationship between the changes of dynamic properties and microstructure evolution. It is easy to determine the LVE range from the strain amplitude sweeping results. Normally, it is believed that the dynamic properties are independent of the strain amplitude for linear viscoelastic materials. When the dynamic properties change dramatically with increasing strain amplitude, then strain-induced nonlinearity is generated. The strain dependent behavior of the dynamic properties of particle-filled polymers is called the Payne effect, and has been investigated extensively [17, 30]. Figure 2 shows the strain amplitude dependence of MR gels with different solvent contents on the storage modulus (G') under a 930 mT magnetic field. It can be seen from figure 2 that the solvent has almost no influence on the LVE range of MR gels, though

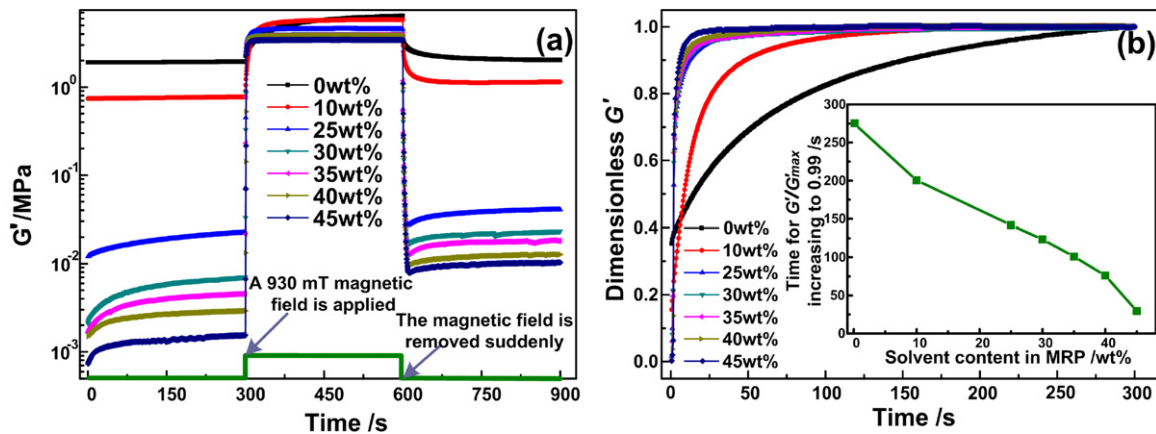


Figure 3. G' of MR gels swollen by solvent in different weight fractions in response to stepwise magnetic field (there was no magnetic field during the first 300 s, a 930 mT magnetic field was instantaneously applied to the sample at 300 s and was removed suddenly at 600 s) (a) and the dimensionless transient response of G' under a 930 mT magnetic field (the inset shows the time for dimensionless G' of MR gels with different solvent contents to increase to 0.99) (b).

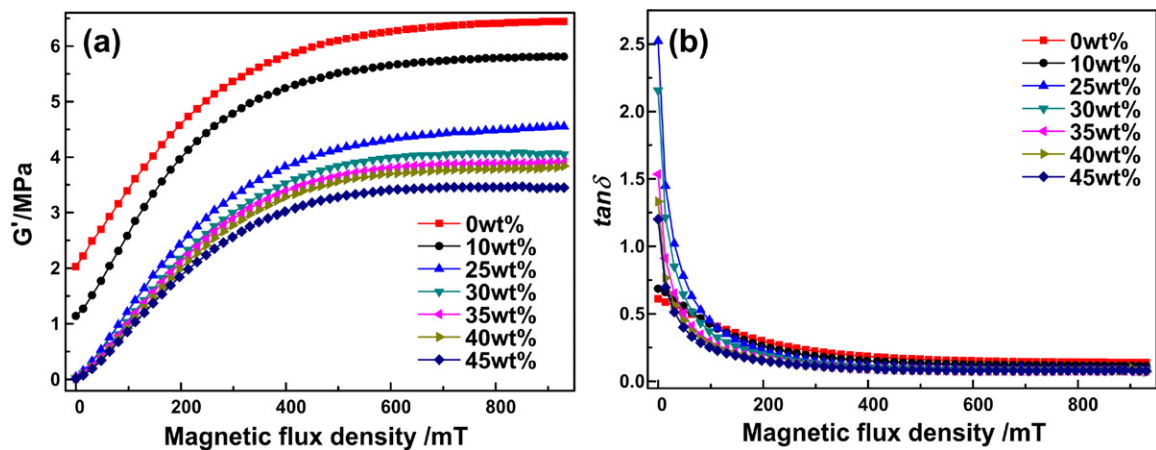


Figure 4. G' (a) and $\tan \delta$ (b) of MR gels swollen by solvent in different weight fractions under different magnetic fields. A 930 mT magnetic field is applied to every product for 5 min before the test to make sure the chain-like microstructures can be generated.

the magnitude of G' can be greatly changed by the solvent content. Our previous work indicated that the magnetic field strength also has no influence on the LVE range of MR gels [10, 31]. As a result, the LVE range of MR gels with different solvent contents can be regarded as 0–0.1%. Based on the above analysis, the strain amplitude was set as 0.1% in figures 3 and 4 to ensure that the actuating strain will be unlikely to destroy the microstructure of the MR gels when an oscillatory shear test is implemented.

The physical state of MR gels can be decided by the solvent content added in the matrix. The MR gels with 0 wt% and 10 wt% of solvent are solid-like while the MR gels with solvent contents larger than 25 wt% present a liquid state in the absence of a magnetic field (the MR gels with solvent content between 10 wt% and 25 wt% are similar to a kind of glue with sticky characteristics, which cannot be easily classified as solid or liquid). In fact, the PU in MR gels is a plasticine-like product without sufficient crosslinking. Therefore, the solid-like MR gels can be changed into various shapes and the shapes can be retained after the external force is removed. We named this kind of solid-like plastic PU

based MR gels as MR plastomers (MRPs) [32]. The magnetic response behaviors of solid-like MR gels are far different from those of liquid-like MR gels, as can be found from figures 2–4.

The transient response of MR fluids and MR elastomers under a stepwise magnetic field have been investigated by Ulicny *et al* [33] and Mitsumata *et al* [15], respectively. Here, G' of different MR gels in response to a stepwise magnetic field were also tested (figure 3(a)), from which we can further deduce the microstructure evolution process of MR gels driven by an external magnetic field. It can be seen from figure 3(a) that less solvent content in MR gels will lead to larger G' . In particular, the G' of MR gels without solvent in the absence of a magnetic field is three orders of magnitude larger than that of MR gels with 45 wt% of solvent, which indicates that the solvent can also greatly change the dynamic properties of MR gels.

It is found from figure 3(a) that the G' of MR gels after being exposed to an external magnetic field (time range of 600–900 s) is larger than that without a magnetic field (time range of 0–300 s). The differences of G' for the same MR gel cannot be ascribed to the microstructure rupture

Table 1. The main parameters of magnetorheological properties for different MR gels.

Solvent content	0 wt%	10 wt%	25 wt%	30 wt%	35 wt%	40 wt%	45 wt%
G'_0 (MPa)	2.03	1.14	0.0406	0.0233	0.0182	0.0127	0.0103
$\Delta G'$ (MPa)	4.41	4.67	4.06	4.03	3.89	3.83	3.44
$\tan \delta_0$	0.6105	0.6855	2.523	2.156	1.534	1.332	1.201
τ_{y0} (kPa)	—	—	—	7.247	1.78	0.583	0.179
$\Delta \tau_y$ (kPa)	—	—	—	90.788	63.831	47.015	46.98

induced by actuating strain according to our previous analysis, so it is deduced that the iron particles can be rearranged by applying an external magnetic field and the movements of particles will change the MR performance of MR gels. Our previous work proved that by exposure to an external magnetic field for a long enough time, the iron particles dispersing randomly in the solid-like MR gels will rearrange to form chain-like or column-like microstructures in the direction of a magnetic field [31]. Figure 3(a) also indicates that the microstructure of liquid-like MR gels can be changed by an external magnetic field and the microstructure can be retained for a period of time (the G' of MR gels remains constant for at least 300 s after removing the magnetic field). This characteristic is different from MR fluids (MR fluids present good redispersibility [34–36]) because the iron particles can suspend well in the PU network as long as the viscosity of the matrix is not too low. Stable chain-like microstructures can give MR gels excellent MR performance, which is important for some specific applications.

The movements of iron particles in PU based MR gels under a stepwise magnetic field can be further investigated by analyzing the time evolution of G' in response to an instantaneously applied magnetic field. Figure 3(b) shows the dimensionless G' (G'/G'_{\max} , where G'_{\max} is the maximum G' for each MR gel in the time range of 300–600 s in figure 3(a)) of MR gels with different solvent contents under a 930 mT magnetic field, which is actually another form of the data in figure 3(a) ranging from 300 to 600 s. It is easy to compare the time that the MR performance of MR gels with different solvent contents takes to stabilize from the dimensionless G' under a stepwise magnetic field. It can be seen from figure 3 that the evolution of G' is highly dependent on the solvent content added in MR gels. Furthermore, the time for iron particles to change from a random distribution to stable chain-like structures can be obtained. The inset of figure 3(b) shows the time for the dimensionless G' of MR gels with different solvent contents to increase to 0.99, which can be regarded as the chain formation time of iron particles under an external magnetic field. It should be noted that after the dimensionless G' exceeds 0.99, the dimensionless G' will fluctuate between 0.99 and 1. This phenomenon actually reflects a series of rupture and reformation processes of particle chain-like structures caused by oscillatory shear strain under a magnetic field. After the particle chain structures are partly destroyed by oscillatory shear strain, the magnetic interactions will drive the iron particles to reconstruct complete chain-like structures. However, the influence of oscillatory shear strain on G' can be

ignored (the change of G' is less than 1%), so it is believed that the stable particle chain-like structures have formed when the dimensionless G' increases to 0.99. In addition, it can be deduced from figure 3(b) that the iron particles will move more easily in MR gels with a higher solvent content under the same magnetic field. This is because the iron particles will encounter less resistance from a matrix with a lower viscosity. An *et al* have compared the transient response of three kinds of MR materials with a different matrix under the same stepwise magnetic field and a similar conclusion was drawn [37]. In particular, the response time of MR gels with high solvent content for iron particles changing from randomly distribution to stable chain-like structures is close to that of MR fluids, indicating that solvent can effectively improve the movement speed of iron particles under a magnetic field. This will make it possible to substitute this kind of MR gels swollen by a nonvolatile solvent for MR fluids in some applications because of their good stability and rapid response to stepwise magnetic fields.

The response of G' and loss factor ($\tan \delta$) of different MR gels to a continuously increasing magnetic field are shown in figures 4(a) and (b), respectively. As expected, the solvent does have a significant influence on the dynamic properties of MR gels under different magnetic fields. On the one hand, the differences of dynamic properties in value between solid-like MR gels (solvent content is lower than 10 wt%) and liquid-like MR gels (solvent content is higher than 25 wt%) are great, as can be seen in table 1. For example, the initial storage modulus (G'_0 , the G' value in the absence of a magnetic field) of solid-like MR gel with 10 wt% of solvent content is 28 times larger than that of liquid-like MR gels with 25 wt% of solvent content, whereas the initial loss factor ($\tan \delta_0$, the $\tan \delta$ value in the absence of a magnetic field) of liquid-like MR gels with 25 wt% of solvent content is 3.68 times larger than that of solid-like MR gels with 10 wt% of solvent content. These results prove again that the addition of solvent will greatly affect the magnetorheology of MR gels. On the other hand, the magnetic dependent behaviors of dynamic properties changing with solvent content for solid-like MR gels and liquid-like MR gels are different in some cases. The magneto-induced modulus $\Delta G'$ (the difference between G' under a 930 mT magnetic field and G'_0) and $\tan \delta_0$ of solid-like MR gels increase with increasing solvent content while the two parameters decrease with increasing solvent content for liquid-like MR gels, which indicates that different mechanisms are involved for the solvent in MR gels with different physical states.

In the absence of a magnetic field, the dynamic properties of MR gels are mainly decided by the matrix. It is not difficult

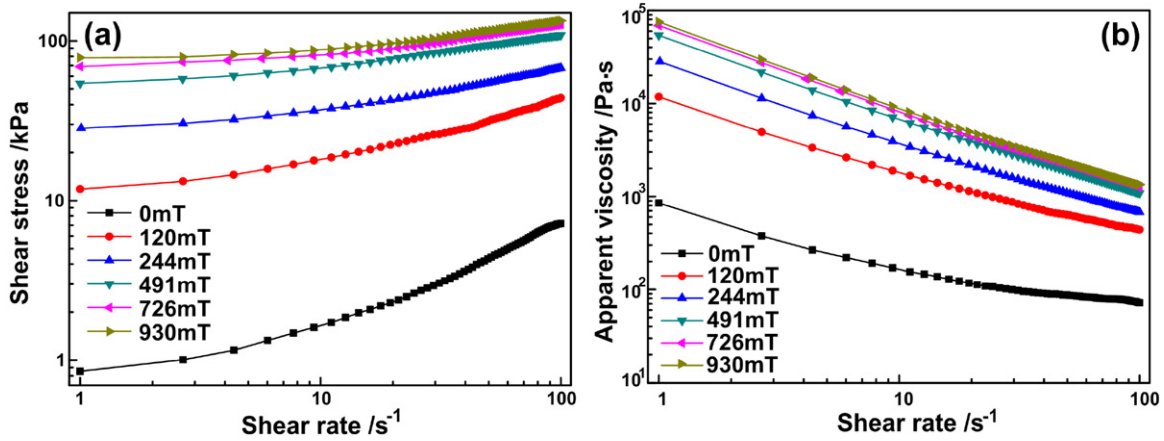


Figure 5. Shear stress (a) and apparent viscosity (b) as a function of shear rate for MR gels with 30 wt% of solvent content under different magnetic fields.

to understand that G'_0 will decrease with increasing solvent content. A high solvent content will make the matrix become soft and a small G'_0 can be tested. The damping of MR gels mainly comes from the movements of the soft segments in PU and the energy dissipation caused by interfacial slipping between iron particles and the matrix [33]. For solid-like MR gels, interfacial slipping hardly occurs, so the movements of the soft segments in PU are the main source of damping. The soft segments will move more easily in the matrix due to the addition of solvent, therefore the $\tan \delta_0$ of MR gels with 10 wt% of solvent content is larger than that of MR gels without solvent content. In liquid-like MR gels, the soft segments will move freely without being blocked. In addition, interfacial slipping between iron particles and the matrix should be taken into account. In this situation, the solvent plays the role of a lubricant, and the friction between iron particles and a matrix with high solvent content is small. That is to say, liquid-like MR gels with higher solvent content will show smaller $\tan \delta_0$. The damping of liquid-like MR gels consists of two parts, with the part coming from the movements of soft segments being larger than that of solid-like MR gels. For this reason, the $\tan \delta_0$ of liquid-like MR gels is larger than that of solid-like MR gels. Many models of magneto-sensitive materials based on classical magnetic dipole theories believe that magnetic field is the only influential factor on $\Delta G'$ if the type and content of magnetic particles are fixed [38–40]. However, $\Delta G'$ of MR gels in this study can also be changed by the solvent content added in the matrix (table 1), which cannot be explained by the classical magnetic dipole theories. According to our experimental results, the interaction between iron particles and the matrix should be taken into account when considering the magneto-induced behaviors of MR materials. The theoretical analysis for this interesting phenomenon needs to be further investigated.

3.2. Magnetorheology under rotational shear rheometry

Figure 5 shows the shear stress and apparent viscosity of MR gels (with 30 wt% of solvent content) as a function

of shear rate under different magnetic fields (the other data of MR gels with 35 wt%, 40 wt%, and 45 wt% of solvent content show similar trends, and their main parameters under rotational shear rheometry can be found in table 1). The flow curves of MR gels are very different from those of the matrix in the absence of a magnetic field (figures 5(a) and 8(a)). As we will mention in section 3.3, matrices without iron particles are Newtonian viscous fluids. Interestingly, after the iron particles are dispersed into the matrix (i.e. MR gels), a yield stress is generated. In particular, the yield stress will increase accordingly with increasing magnetic field (figure 5(a)). This flow behavior can be described well by the Bingham equation [41–43].

$$\tau = \tau_y + \eta\dot{\gamma} \quad (1)$$

where τ and $\dot{\gamma}$ represent the shear stress and shear rate, respectively. τ_y is the field dependent dynamic yield stress and η is the plastic viscosity. In this work, τ_y was obtained by fitting the Bingham equation to the flow curves of liquid-like MR gels under various magnetic fields when $\dot{\gamma}$ is higher than 25 s^{-1} .

It can be found from figure 6 that the dynamic yield stress is mainly determined by the magnetic field and solvent content. τ_y will increase with increasing magnetic field but decrease with increasing solvent content. The initial shear yield stress τ_{y0} (the value of τ_y of MR gels in the absence of a magnetic field) and magneto-induced shear yield stress $\Delta\tau_y$ (the difference between τ_y under a 930 mT magnetic field and τ_{y0}) also decrease with increasing solvent content (table 1). It is easy to understand that τ of MR gels will be enhanced by a magnetic force under rotational shear rheometry. The addition of solvent can decrease not only the viscosity of the matrix but also the friction between the iron particles and the matrix, which will induce a smaller τ and τ_y under rotational shear rheometry. For the same reason, the microstructures of MR gels with lower solvent content will be destroyed with more difficulty when a steady shear flow occurs. A larger magnetic force will be generated for MR gels with a more ordered microstructure under the same magnetic field, thus larger $\Delta\tau_y$ will be tested accordingly.

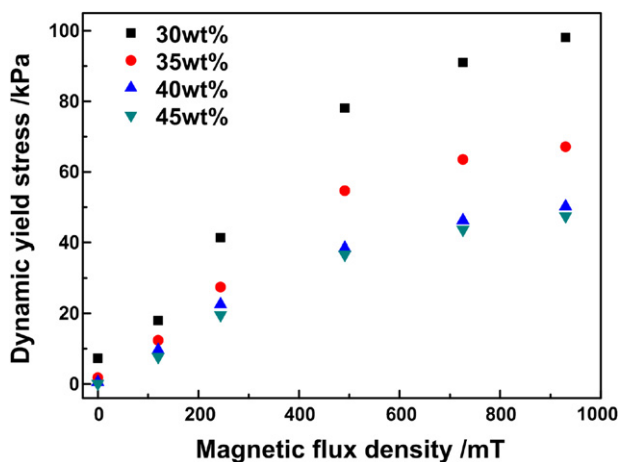


Figure 6. Dynamic yield stresses of liquid-like MR gels swollen by solvent in different weight fractions under different magnetic fields.

The apparent viscosity of MR gels can be obtained directly by dividing τ by $\dot{\gamma}$. The shear thinning effect can be observed from the apparent viscosity versus $\dot{\gamma}$ curves with double logarithmic coordinates, as shown in figure 5(b), which is a typical non-Newtonian flow property for polymer liquid materials. This phenomenon indicates that the liquid-like MR gels is a kind of pseudoplastic fluids. At the same time, the apparent viscosity of liquid-like MR gels can be greatly changed by an external magnetic field, which is defined as the magnetoviscous effect (MVE) [44]. Taking the MR gels with 30 wt% of solvent content for example, the apparent viscosity can increase by at most three orders of magnitude

when the magnetic field increases from 0 to 930 mT. In short, the PU based liquid-like MR gels not only possess complex polymer rheological properties, but also these properties can be controlled by magnetic field and solvent content. These characteristics give them great potential in some applications with reference to intelligent control.

3.3. Stability analysis of MR gels

As a magneto-sensitive intelligent engineering material, stability is an important indicator to evaluate the performance of MR gels [4, 5]. The main target of substituting polymer materials for liquid media is to overcome the particle settling problem in MR fluids. Here, MR gels swollen by different weight ratios of nonvolatile solvent (1-methyl-2-pyrrolidone) were injected into six test tubes, respectively. The stability of each kind of MR gel was observed by taking photographs at regular intervals after the MR gels were prepared (figure 7). Three days later, particle settling is obvious for the MR gels with solvent contents of 40 wt% and 45 wt%. A sedimentation phenomenon can be observed on the MR gels with 35 wt% solvent after one week. Macroscopic sedimentation is generated in the MR gels with a solvent content of 30 wt% after one month. The status of each product will no longer change after two months, which indicates that the stability of MR gels is superior to many MR fluids reported in the literature [45–47]. In particular, we found that there is almost no particle settling phenomenon for MR gels with solvent content lower than 25 wt%. In other words, there exists a threshold value for the solvent added in the MR gels and the sedimentation problem can be effectively avoided

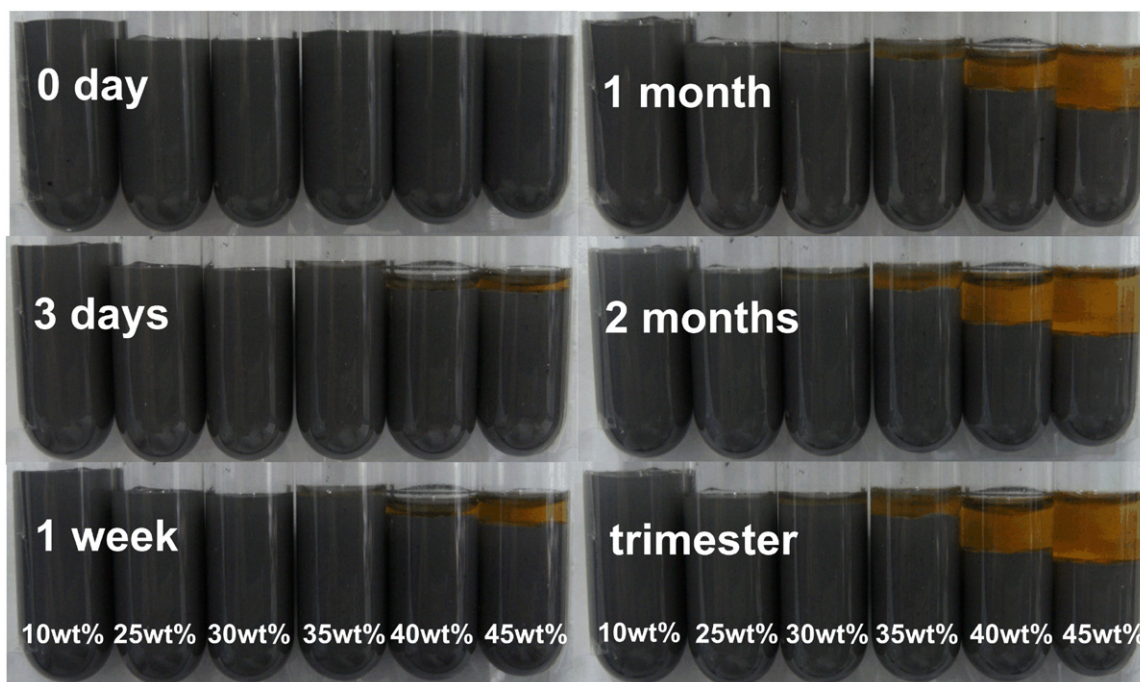


Figure 7. Sedimentation images of MR gels swollen by solvent in different weight fractions at regular intervals after the MR gels were prepared.

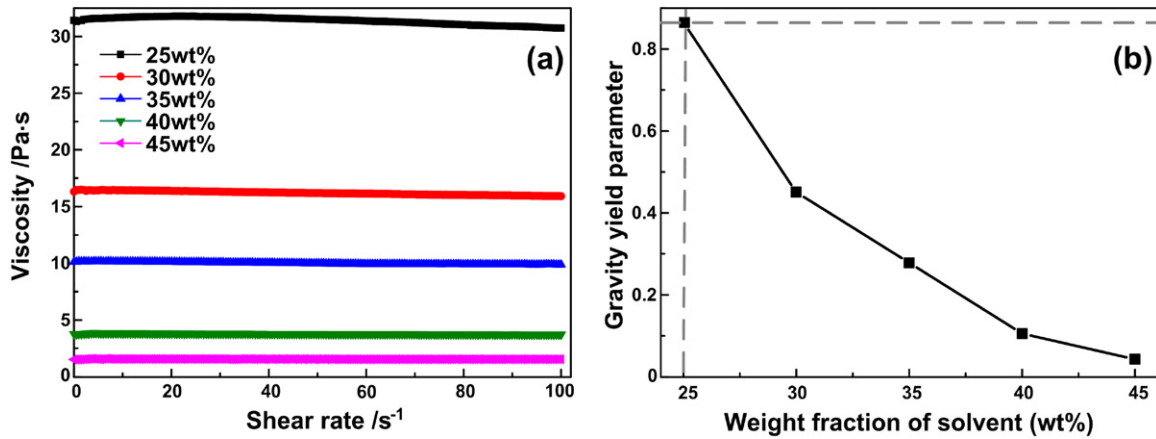


Figure 8. Viscosity versus shear rate curves (a) for the PU matrix and the gravity yield parameter (b) of MR gels swollen by solvent in different weight fractions.

when the solvent content is lower than this threshold value. In this study, the threshold value for solvent content is around 25 wt%.

Normally, the sedimentation problem is ascribed to the mismatch of density between the iron particles and the carrier medium [4, 11]. A gravity yield parameter (Y_G) was proposed by Chhabra to characterize the ability of a carrier medium to suspend the rigid particles [48].

$$Y_G = \frac{\tau_0^G}{gR(\rho_P - \rho_M)} \quad (2)$$

where τ_0^G , g , and R represent the yield stress of carrier media, the acceleration of gravity, and the particle radius, respectively. ρ_P is the particle density while ρ_M is the density of the carrier medium. Better suspending ability of a carrier medium to the particles will lead to a larger value of Y_G by analyzing the expression of Y_G (equation (2)). Rankin *et al* investigated the stability of MR suspensions using the gravity yield parameter and they believed that there is a critical value for Y_G , above which particle settling will not occur [49].

It seems that these theories can well explain the phenomenon shown in figure 7. However, when a series of rotational shear tests for the PU matrix with different solvent contents were carried out, it was found that there is no yield stress for the carrier medium. In other words, the matrix without iron particles can be regarded as a Newtonian viscous fluid. Therefore, the gravity yield parameter cannot be used to characterize these PU based MR gels directly. The viscosity of the PU matrix with different solvent contents will not change with the shear rate and will decrease with increasing of solvent content (figure 8(a)). It is obvious that the viscosity of the matrix has an important influence on the stability of MR gels, so we substitute the product of viscosity and shear rate at 0.01 for yield stress in equation (2) to characterize the ability of the matrix to suspend iron particles in MR gels, as shown in equation (3).

$$Y_G = \frac{\eta_0^G \dot{\gamma}_0}{gR(\rho_P - \rho_M)}. \quad (3)$$

In this way, the gravity yield parameters of MR gels swollen by different weight ratios of solvent were calculated

(figure 8(b)). It is clear that the gravity yield parameter decreases with increasing solvent content. Combining this with the experimental phenomena shown in figure 7, we can find the critical gravity yield parameter ($Y_G = 0.865$). In conclusion, if the solvent content is lower than 25 wt% or the gravity yield parameter is larger than 0.865, then PU based MR gels will be stable without particle settling.

4. Conclusions

Apart from the significant influence on the rheological properties, the physical state of MR gels (solid-like or liquid-like) in the absence of a magnetic field can be decided by the solvent added in the MR gels. It is found that there exists a critical value of solvent content for the polymer matrix to prevent iron particles from settling. By introducing a gravity yield parameter, the mismatch of density between the iron particles and the carrier medium, which is the essential reason for particle settling, were quantitatively described. If the solvent content is lower than 25 wt% or the gravity yield parameter is larger than 0.865, then PU based MR gels will be stable without particle settling. The transient responses of different MR gels under a stepwise magnetic field demonstrate that the chain formation time of iron particles are sensitive to the solvent content. The magneto-induced behaviors of different MR gels under a continuously increasing magnetic field indicate that the mechanisms involved for the solvent in solid-like and liquid-like MR gels are different. All the results are helpful in further understanding the magnetorheological mechanism in MR polymer gels and may provide significant guidelines for the performance optimization of MR gels.

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