

Shear-thickening behavior of polymethylmethacrylate particles suspensions in glycerine–water mixtures

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Received: 11 May 2010 / Revised: 26 July 2010 / Accepted: 27 August 2010 / Published online: 19 September 2010
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Abstract The rheological behavior of polymethylmethacrylate (PMMA) particles suspensions in glycerine–water mixtures has been investigated by means of steady and dynamic rheometry in this work. The shear rheology of these suspensions demonstrates a strong shear thickening behavior. The variations of shear viscosity with the volume fraction and ratios of glycerine to water are discussed. The effect of volume fraction can be qualitatively explained using a clustering mechanism, which attributes the phenomena to the formation of temporary, hydrodynamic clusters. The influence of interactions between glycerine–water mixtures and PMMA particles on shear thickening is investigated by varying the ratio of glycerine to water. In addition, the reversible and thixotropic properties of suspensions of PMMA dispersed in glycerine–water (3:1) mixtures are also investigated, and the results

demonstrate the excellent reversible and thixotropic properties of PMMA particle suspensions.

Keywords Shear thickening fluid (STF) · Reversibility · Thixotropy · Glycerine–water mixtures · Polymethylmethacrylate (PMMA)

Introduction

Shear thickening behavior, accompanied with significant, discontinuous steep increase in viscosity, is a generic phenomenon existing in concentrated colloidal suspensions when they are subjected to applying stress (Barnes-and-Bebington 1989; Lee et al. 2003; Brown et al. 2010). In industrial situations, shear thickening is believed to be a severe problem, because it leads to such issues as failure of mixer motors due to overloading, mixer blade damage, and others (Barnes and Bebington 1989).

The early investigations of shear thickening behavior were to mitigate the damages on processing equipments that the shear thickening transition caused (Hoffman 1998; Bischoff White et al. 2010). However, because of their property of exhibiting a nonlinear steep rise in viscosity with increasing stress, shear thickening fluids (STF) have become attractive and been used in several specific applications for a few decades, especially in ski boot cushioning, liquid couplings, shock absorber fillings, rotary speed limiters, and body armors (Barnes and Bebington 1989; Galindo-rosales et al. 2009). Therefore, much of the effort has been focused on its mechanism recently, including rheo-optical experiments (D’Haene et al. 1993; Bender and Wagner

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1995), neutron scattering, and others (Laun et al. 1992; Bender and Wagner 1996; Maranzano and Wagner 2001, 2002). It has been demonstrated that reversible shear thickening in concentrated colloidal suspensions is due to the formation of jamming clusters resulting from hydrodynamic lubrication forces between particles, often denoted by the term “hydroclusters” (Bossis and Brady 1989; Foss and Brady 2000; Catherall and Melrose 2000; Galindo-rosales et al. 2009).

A versatile model describing the shear thickening behavior of dilute polymer solutions in high shear flows has been presented, and the model predictions are in well agreement with experimental data reported in the literature (Hatzikiriakos and Vlassopoulos 1996). The parameters, such as particle size, volume fraction, polydispersity, and medium viscosity, controlling the onset of shear thickening have been studied exhaustively (Frith et al. 1996; Hoffman 1972; Boersma et al. 1990; Shenoy and Wagner 2005). It is worth mentioning that two different methods have been taken to investigate the influence of medium viscosity on the onset of shear thickening of PMMA dispersions by varying the sample test temperature (Boersma et al. 1990; Shenoy and Wagner 2005) and varying the molecular weight of an oligomeric medium (Shenoy and Wagner 2005; Galindo-rosales et al. 2009). However, the concomitant change in particle interaction with sample temperature and medium type should be considered.

In this work, the excellent reversible and thixotropic shear thickening micron PMMA particles suspensions were prepared, which were more practical in the absorption of energy during some low-stress conditions because of their low critical rates. To choose glycerine and water as the dispersion medium reduces cost and decreases the initial viscosity of the suspensions. At the same time, it also avoids the pollution of organic solution and eliminates the effect of the change in particle–particle interaction that heating caused. Therefore, the influence of interactions between glycerine–water mixtures and PMMA particles on shear thickening can be investigated by varying the ratio of glycerine to water, and the similar results are also obtained as the change of intermediate chain length and heating.

Experimental methods

The preparation of PMMA particles

Methyl alcohol (analytical reagent), polyvinylpyrrolidone k-30, and NaOH (analytical reagent), used directly, were all purchased from Sinopharm Chemical

Reagent Co., Ltd. All polymerizations were conducted in a 500-mL three-necked flask. The flask was fitted with a mechanical stirrer, a reflux condenser, and a nitrogen inlet. First, the reactor was charged with pretreated methylmethacrylate, methyl alcohol, and polyvinylpyrrolidone k-30. And then, azobisisobutyronitrile, recrystallized by ethanol before use, was added into the mixture. After 30 min of mixing at room temperature, the reactor was heated to 60°C in a bath for 8 h. All runs were conducted under nitrogen atmosphere. The emulsion obtained was centrifuged and then the PMMA sediment was redispersed in deionized water and then the emulsion was sonicated for 30 min. This procedure was iterated three times. At last, the PMMA particles obtained were dried in a vacuum oven at 50°C.

The preparation of shear thickening fluids

Typically, the STF were prepared by adding the PMMA powders to glycerine–water mixtures and afterwards they were mixed in a ball crusher and rub for 24 h in order to obtain a uniform distribution of PMMA particles within the suspension and to insure the particles were not aggregated. The samples were sonicated for an hour for the purpose of removing the air bubbles. In order to study the variation of shear viscosity with the volume fraction and ratio to glycerine–water mixtures, high concentration suspensions with different PMMA particles volume fraction of 45%, 50%, 52%, and 55% dispersed in glycerine–water mixtures (3:1) were prepared, and suspensions with 52% PMMA particles dispersed in glycerine–water mixtures with different ratios: 2:1, 5:2, 7:2, and 4:1 were also prepared.

Rheological measurements

The experiments were performed primarily in a stress and strain controlled rheometer (Anton-Paar MCR 301) at 25°C with cone-plate geometry having a cone angle of 0.2° and a diameter of 25 mm. Both steady-shear and oscillatory-shear tests were conducted on each sample. A standard procedure was used for all rheological measurements. Angular frequency sweep experiments were performed to determine the dynamic shear thickening behaviors (Li et al. 2003, 2004). For the steady-shear experiment, an equilibration time of 90 s was given at each shear rate to allow the system to reach steady state. The oscillatory and steady tests were performed in an Anton-Paar MCR301 rheometer with a gap size of 0.05 mm.

Results and discussion

Characterization of PMMA particles

The synthesized monodisperse PMMA particles were spherical and the average particle diameter, as measured using scanning electron microscope (SEM, Sirion 200) was determined to be about 2.5 μm . The SEM images of these PMMA particles are given in Fig. 1.

Influence of PMMA volume fraction in colloidal dispersions on suspension shear rheology

It can be observed from Fig. 2a that each sample shows shear thickening behavior and the degree of the shear thickening is also increased with the increasing PMMA volume fraction. Explanation can be proposed that the reversible shear thickening is caused by the shear-induced self-organization of particles into stress bearing clusters. This self-organized microstructure is thought to be a consequence of the dominance of short-range hydrodynamic lubrication forces. The formation of the jamming clusters induces the increase in shear viscosity at a critical shear stress (Maranzano and Wagner 2002). Volume fraction is one of the most important parameters of the nature of shear thickening. In the very high phase volume situations, the average separation of the particles is very small and is strongly affected by the relative positions of the particles. Therefore, high phase volume situations make the hydrodynamic forces easier to move the particles from the equilibrium position and form the jamming clusters once shear stress was put on the suspensions. At the same time, larger clusters will be formed (Barnes and Bebington 1989; Zaman et al. 2000; Wu et al. 2006).

The steady shear sweep plots in Fig. 2b demonstrate that the shear thickening will be more drastic with the increase of PMMA volume fraction. The results can also be explained that the increase of volume fraction

shortens the distance between the particles, so it is easier to form clusters and exhibit shear-thickening behavior. High phase volume will form more clusters and the clusters formed will be larger.

Figure 3 shows the transition from continued shear thickening to discontinued shear thickening. As can be seen from Fig. 3, at low volume fraction, the maximum complex viscosities observed from Fig. 2a increase gently with the increase of volume fractions, the slope of the viscosity curve becomes steeper and steeper, which indicates the tendency of the transition from continuous to discontinuous shear thickening. Once the volume fraction reached a critical value, the suspensions will exhibit discontinued shear thickening.

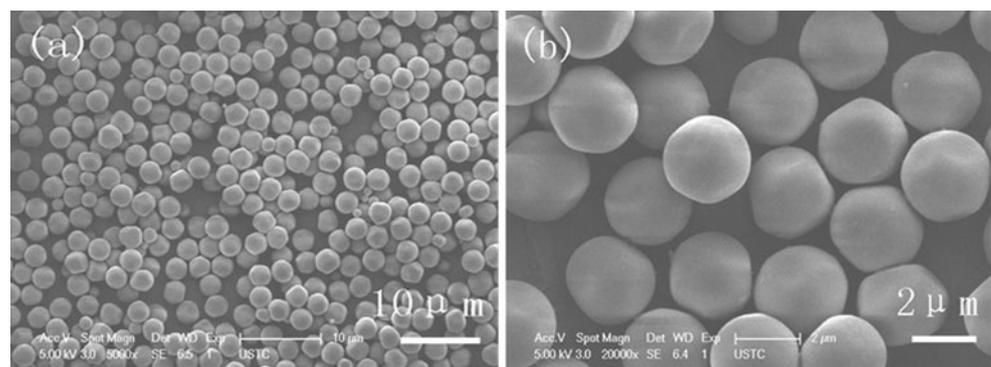
Reversible shear thickening behavior of PMMA suspensions

The complex viscosity was measured for both ascending and descending dynamic strain sweeps as shown in Fig. 4. The dispersion viscosity is nearly constant at the beginning. At a critical shear rate, the viscosity increased quickly with increasing shear rate. As soon as the shear rate is decreased, the viscosity immediately decreases. It is important to note that the complex viscosities are in good agreement at the same shear rate. It can be concluded that shear thickening behavior of the suspensions is reversible. The jamming clusters formed in the shear thickening period are unstable, the clusters will be decomposed and the particles will be dispersed in the dispersed phase again with the decrease of the shear rate (Barnes and Bebington 1989; Lee and Wagner 2003; Lee et al. 2003; Wu et al. 2006).

Thixotropic property of suspensions of PMMA dispersed in glycerine–water (3:1) mixtures

The critical shear thickening strain γ_c of 52% PMMA dispersed in glycerine–water (3:1) mixture for dynamic

Fig. 1 SEM images of PMMA particles prepared



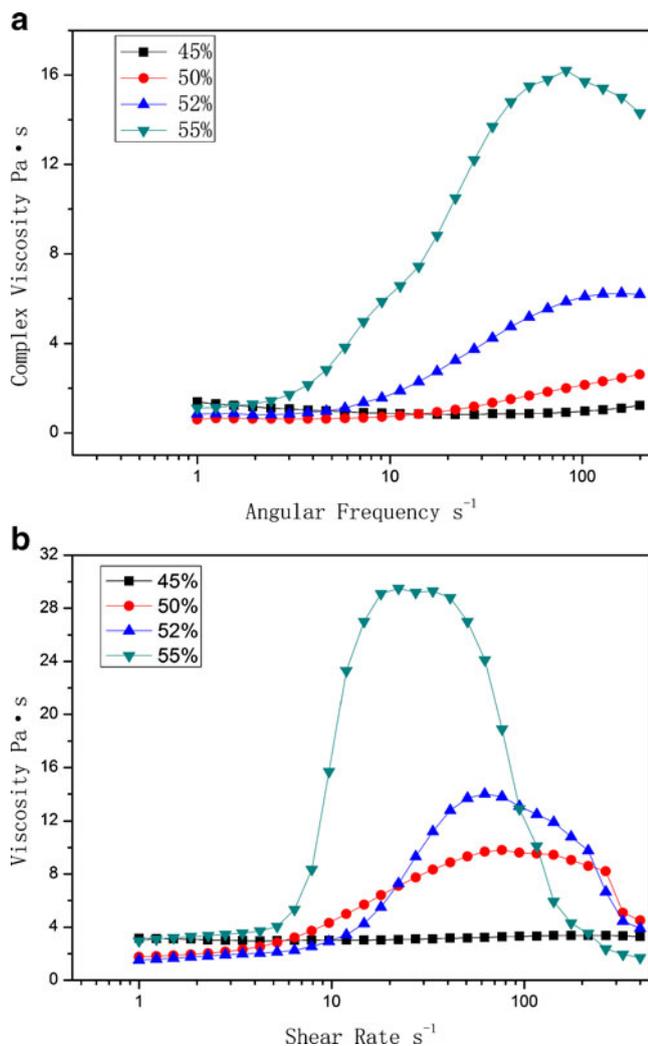


Fig. 2 **a** Complex viscosity versus angular frequency for different PMMA volume fraction suspensions: 45%, 50%, 52%, and 55%. Dynamic frequency sweeps at $T = 25^\circ\text{C}$, $\gamma = 100\%$, and $\omega = 1\text{--}200\text{ s}^{-1}$. **b** Viscosity versus shear rate for different PMMA volume fraction suspensions: 45%, 50%, 52%, and 55%. Steady shear sweeps at $\dot{\gamma} = 1\text{--}400\text{ 1/s}$

shear strain sweep observed from Fig. 2b is about 86.3%. Therefore, $\gamma_1 = 1\%$ ($\gamma_1 < \gamma_c$) and $\gamma_2 = 600\%$ ($\gamma_2 > \gamma_c$) are selected to study the thixotropic property of the PMMA particles suspensions. Dynamic shear strain sweep was processed at $\gamma_1 = 1\%$ in the first step, the value of the complex viscosity keeps at about 0.71 Pa·s during this period. And then the value of the strain changes to $\gamma_2 = 600\%$, and the value of the complex viscosity is nearly constant about 19.5 Pa·s. In the third period, the strain sweeps is carried out at $\gamma = 1\%$ again, and the complex viscosity is maintained at about 0.83 Pa·s. It can be concluded that when the value of the shear strain is constant, the value of the complex viscosity keeps nearly a constant, once the

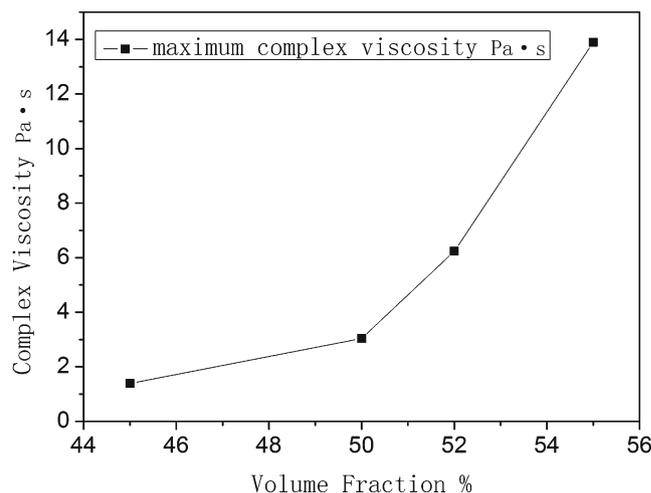


Fig. 3 Maximum complex viscosity versus volume fraction in dynamic frequency sweep

strain is higher than $\gamma_c = 86.3\%$, the shear thickening phenomenon will appear immediately, and the value of the complex viscosity keeps constant. After the shear strain gets back to the initial value, the complex viscosity comes back to a constant nearly the same as the initial value. The thixotropic property indicates that the suspension is sensitive to shear strain, once the shear strain reached the critical value, the suspension will behave shear thickening, and the shear thickening behavior is reversible. It can also be explained by the instability of the jamming clusters formed in the shear thickening period as the reversible property (Fig. 5).

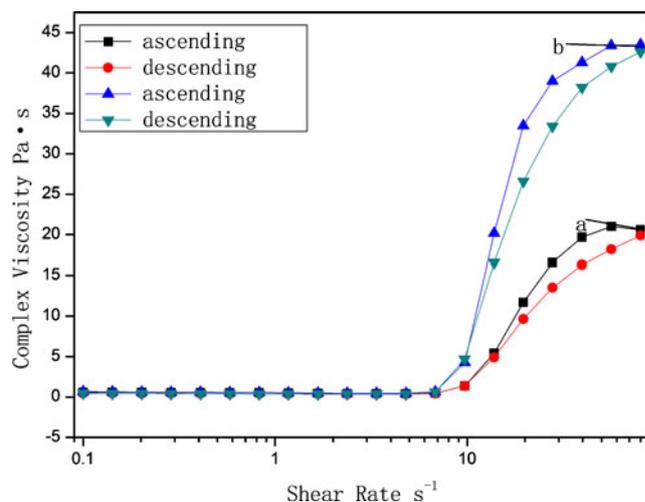


Fig. 4 Reversible shear thickening behavior of **a** 52 vol.%; **b** 55 vol. % PMMA dispersed in glycerine–water (3:1) mixtures

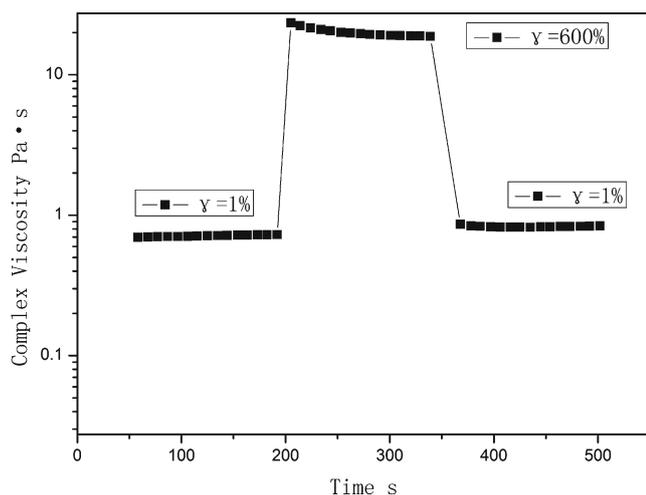


Fig. 5 Thixotropic shear thickening behavior of 52% PMMA dispersed in glycerine–water (3:1) mixtures at $T = 25^\circ\text{C}$, $\omega = 10 \text{ s}^{-1}$

Influence of variation of ratios of glycerine–water mixtures in PMMA colloidal dispersions on suspension shear rheology

In this section, the influence of the medium viscosity is investigated by changing the ratio of glycerine–water in colloidal dispersions at a fixed PMMA volume fraction. As indicated in Fig. 6a, the plots show the varying trends of the complex viscosity of different ratios of glycerine to water in colloidal dispersions. It can be seen that, with the increase of the proportion of glycerine, the medium viscosity increases, and the degree of the increase is becoming higher and higher. The results can be explained that: the complex viscosity η^* is almost always a direct function of the solvent viscosity η_s . This relationship can be formed: $\eta^* = \eta_s f n$ (phase volume, size shape, and particle size distribution; Barnes and Bebington 1989). The experimental results presented in Fig. 6a is approximately consistent with the relationship.

Figure 6b presents plots of the change of the relative viscosity $\eta_\gamma = \eta^*/\eta_s$ (Andrew et al. 1991; Wolf et al. 2001), where η_s being the solvent viscosity, as a function of angular frequency by varying the ratio of glycerine to water in 52% PMMA volume fraction colloidal dispersions. It can be observed from Fig. 6b that the critical shear-thickening angular frequency values decrease with the increase of the ratio of glycerol–water (Lee and Wagner 2003; Lee et al. 2003). It is supposed that there are two main reasons that have caused the change. On the one hand, water has more hydroxyl groups than glycerine when with the same volume. The increase of the proportion of glycerine in the same

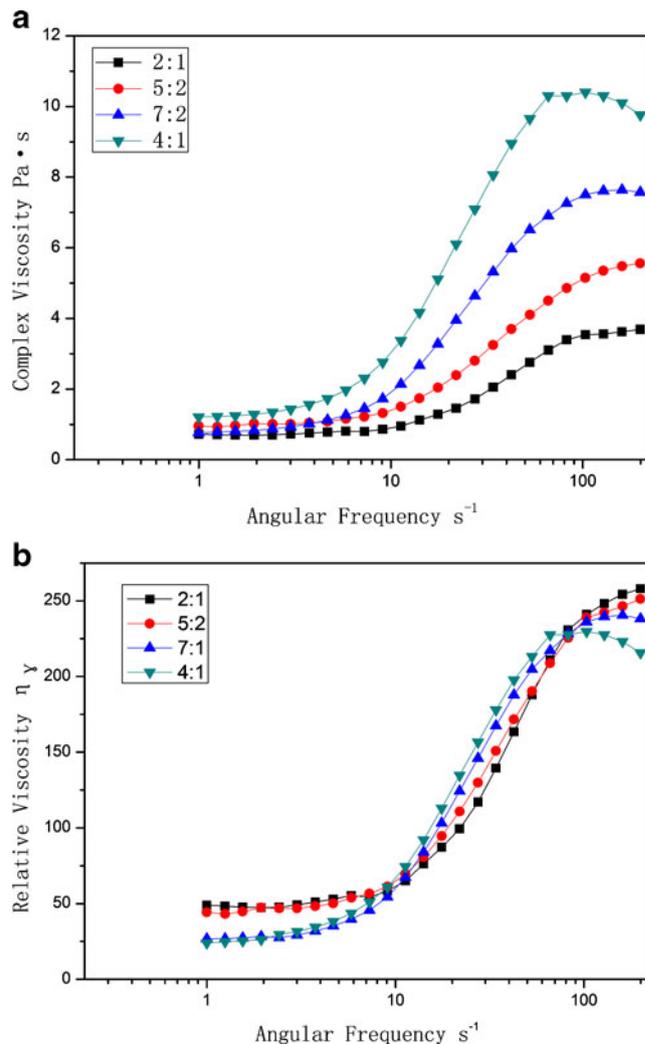


Fig. 6 a Complex viscosity versus angular frequency for PMMA volume fraction 52% dispersed in glycerine–water mixtures with different ratios: 2:1, 5:2, 7:2, and 4:1. Dynamic frequency sweeps at $T = 25^\circ\text{C}$, $\gamma = 100\%$, and $\omega = 1\text{--}200 \text{ 1/s}$. **b** Relative viscosity versus angular frequency for PMMA volume fraction 52% dispersed in glycerine–water mixtures with different ratios: 2:1, 5:2, 7:2, and 4:1. Dynamic frequency sweeps at $T = 25^\circ\text{C}$, $\gamma = 100\%$, and $\omega = 1\text{--}200 \text{ 1/s}$

medium volume leads to the decrease of the amount of the hydroxyl groups, which weakens the hydrogen bond interactions between the medium and the PMMA particles. And thus, it is easier to exhibit shear-thickening behavior for the lower proportion of water medium suspensions. On the other hand, as the glycerine has molecular chains longer than water, the glycerine has a higher viscosity value than water, so PMMA particles primary agglomerates moving through them suffer much more difficulties in dispersion medium contained a higher proportion of glycerine. Therefore, the amount of liquid phase trapped into the clusters is higher for the

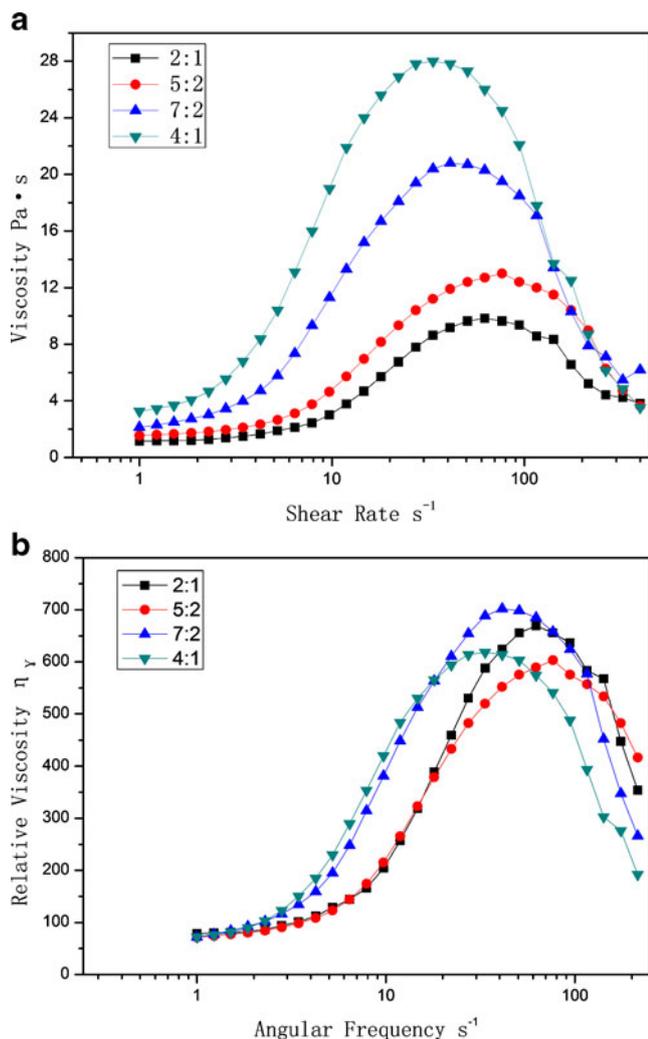


Fig. 7 **a** Viscosity versus shear rate for PMMA volume fraction 52% dispersed in glycerine–water mixtures with different ratios: 2:1, 5:2, 7:2, and 4:1. Steady shear sweeps at $\dot{\gamma} = 1\text{--}400\text{ s}^{-1}$. **b** Relative viscosity versus shear rate for PMMA volume fraction 52% dispersed in glycerine–water mixtures with different ratios: 2:1, 5:2, 7:2, and 4:1. Steady shear sweeps at $\dot{\gamma} = 1\text{--}200\text{ s}^{-1}$

case of higher proportion of glycerine medium suspension and consequently the cluster sizes are larger. The effective disperse phase volume fraction is also higher for the case of higher proportion of glycerine medium suspension (Hoffman 1998). The two reasons cause the results as the Fig. 6b presents.

Same trends can be found from Fig. 7a, b, and the same conclusions can also be made. On the one hand, the overall viscosity η is almost always a direct function of the solvent viscosity η_s . The increase of the medium viscosity leads to the increase of the degree of the shear thickening. On the other hand, because of the weakened hydrogen bond interactions between particles and medium, and higher effective disperse phase volume

fraction led by the longer molecular chains of glycerine, the critical shear-thickening shear rate values decrease with the increase of the ratio of glycerol–water.

Conclusions

In this work, the rheological behavior of micron PMMA suspensions in glycerine–water mixtures has been investigated, and four important conclusions have been obtained. Firstly, the micron PMMA particles self-prepared are monodisperse and nonfloculent, and the PMMA particles suspensions behave shear-thickening property. Secondly, the degree of shear thickening is very dependent on PMMA volume fraction, increases with the increase of the PMMA volume fraction. Thirdly, the excellent reversibility and thixotropic properties of PMMA particle suspensions are also shown in the rheological measurements. Fourthly, the complex viscosity η^* measured is approximately consistent with the relationship: $\eta^* = \eta_s f n$ (phase volume, size shape, and particle size distribution; Barnes and Bebington 1989). On the other hand, the influence of interactions between glycerine–water mixtures and PMMA particles on shear thickening investigated by varying the ratio of glycerine to water showed that the increase of the glycerine proportion weakens the hydrogen bond interactions between particles and medium, and increases the effective disperse phase volume fraction at the same time. The shear thickening will be more drastically with the increase of the proportion of glycerine in glycerine–water mixtures medium.

Acknowledgements Financial support from National Basic Research Program of China (973 program, grant no. 2007CB936800) and SRFDP of China (project no. 20093402110010) is gratefully acknowledged.

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