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SiO₂/PEG 分散体系动态剪切流变行为

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摘要：　在动态应变条件下, SiO₂/PEG200(聚乙二醇, 平均分子量为200)分散体系出现了剪切增稠现象. 剪切流变实验表明, 在两种情况下都出现了剪切增稠: 一种是在不同的恒定频率下应变扫描, 在临界应力 γ_c 出现的剪切增稠; 另一种是恒定的应变(γ_0=500%)条件下频率扫描, 在临界频率 $\omega_c \approx 10$ rad·s⁻¹ 出现的剪切增稠. 在不同的恒定频率应变扫描条件下, 实验研究了储能模量(G')和耗能模量(G'')与应变的关系, 同时初步探讨了应变与不同恒定频率的函数关系. 在线性粘弹性区域内, G' 和 G'' 满足 $G' \propto \omega^{0.57}$ 和 $G'' \propto \omega^{0.7}$ 指数关系. 在恒定的应变条件下, 发现模量和复数粘度与扫描频率具有强烈的依赖关系, 这些现象可以定性地通过"粒子簇"理论来解释. "粒子簇"理论认为这种剪切增稠的发生是由于形成了亚稳定、流动所导致的"粒子簇", 使得粘度上升.

关键词：　雾化二氧化硅分散体系；　剪切增稠；　储能模量；　耗能模量；　频率
中图分类号：　O648；　O631

Rheological Behaviors of SiO₂/PEG Suspension under Dynamic Shear

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Abstract：　Fumed silica suspensions in polyethylene glycol (PEG200) exhibited shear-thickening behavior under dynamic oscillatory strain amplitude. Two regimes of shear-thickening behavior were obtained: the first occured at critical strain amplitude γ_c and different constant frequencies, and the second occured at critical frequency and constant strain amplitude γ_0=500%. For the first, the relationships of both of the moduli (G' and G'') *versus* strain amplitude were investigated. The strain amplitude as a function of different constant frequencies was observed. In the linear viscoelastic region, the storage (G') and the loss (G'') moduli depended strongly on frequency with the power-law: $G' \propto \omega^{0.57}$, $G'' \propto \omega^{0.7}$. In the second regime, the moduli (G' and G'') and complex viscosity η^* showed strong dependence on frequency. The behaviors could be qualitatively explained using the cluster theory, which attributed the phenomena to the formation of metastable, flow induced clusters.

Key Words：　Fumed silica suspensions；　Shear-thickening；　Storage modulus；　Loss modulus；　Frequency

Fumed silica is an extremely versatile material in various industries such as paints, foodstuffs and paper. Fumed silica dispersed in different polar liquids such as water[1], polypropylene glycol (PPG)[2] and tetrahydrofurfuryl alcohol (THFFA)[3] exhibits shear-thickening at a particular stress σ_c or strain γ_c. In USA, recently, some researchers[4,5] have used the shear-thickening properties of silica suspensions in ethylene glycol, polyethylene glycol (PEG) and water to make advanced body armor materials. These materials can offer equivalent ballistic performance of existing body armor materials, but with significantly more compactness and flexibility.

Researches[1−3] have been done on the silica suspensions in polypropylene glycol (PPG), tetrahydrofurfuryl alcohol (THFFA) and water under steady and dynamic oscillatory shear. Shear-thickening has been observed during the experiments and the cluster theory can explain the phenomena. Many aspects play important roles on the occurrence of shear-thickening, such as the polarity of the continuous phase[6], considerable volume frac-

tion[7,8], particle size[9] and medium[10,11] of dispersed phase. But few works[2,12] do investigation on frequency influence under dynamic shear, in particular, for suspensions of fumed silica in PEG. In this study, we investigated the rheological properties of SiO$_2$/PEG suspension under dynamic oscillatory shear. Especially, we focused on the frequency influence on the rheological properties. The experiments were carried out twofold: one was that the strain amplitude sweep was performed at constant frequency; the other was that the frequency sweep was conducted at constant stain amplitude.

1 Experimental

1.1 Materials

The fumed silica used was Aerosil A200 supplied by Degussa Corporation. The fumed silica, with a primary spherical particle size of 12 nm and a specific surface area of 200 m^2·g^{-1}, was prepared by flame hydrolysis of silicon tetrachloride (SiCl$_4$) in flame of H$_2$ and O$_2$. Fumed silica primary spherical irreversibly fused into larger particle called aggregate because of high specific surface area. These aggregates are hydrophilic owe to the presence of hydroxyl groups (Si—OH) on the surface[13].

The continuous phase used in our studies is polyethylene glycol (PEG), which is a polar liquid with an average molecular weight of 200. The viscosity of PEG, a Newtonian liquid, is 0.03 Pa·s at temperature of 25 ℃.

1.2 Suspension sample preparation

The suspensions were prepared by adding the powder into the liquid in a blender and mixing for about 30 min. Because of the refractive-index matching the solvent, the suspensions were transparent. The samples were made in batches for 80 mL and placed in vacuum at room temperature for more than 24 h to remove air bubbles.

1.3 Dynamic rheological experiment

The experiments were carried out on a stress controlled rheometer AR2000 (USA: TA Company). A cone-and-plate fixture having a cone angle of 1° and a diameter of 40 mm was used. Experiments were carried out under dynamic oscillatory shear strain at room temperature of 25 ℃. Dynamic experiments were twofold: strain sweeps, where the frequency was fixed and frequency sweeps performed at constant strain amplitude, with the frequency being increased in discrete steps.

2 Results and discussion

2.1 Shear-thickening behavior under various constant frequencies

Fig.1 shows the dynamic complex viscosity (η^*) as a function of strain amplitude (γ) for the suspension of 12% (w) fumed silica in PEG at different frequencies. As can be seen from Fig.1, the complex viscosity slightly decreases with increasing of strain amplitude at lower strain amplitude. But once the strain amplitude gets the critical strain (γ_c), the complex viscosity shows an abrupt discontinuous jump to higher level, which marks the transition to shear-thickening behavior. It is noted that shear-thinning behavior becomes so unclearly with the frequency of the deformation increasing that shear-thinning behavior can hardly be observed at
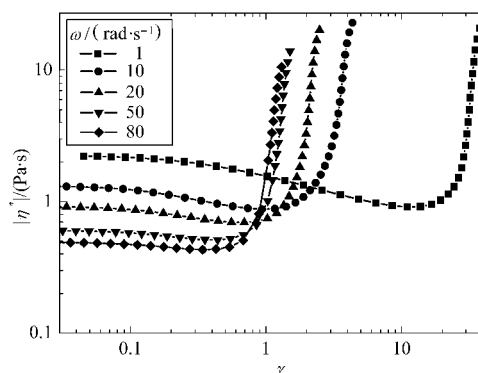

Fig.1   Complex viscosity (η^*) as a function of strain amplitude (γ) for the suspension of 12% (w) fumed silica in PEG

The complex viscosity sweeps were conducted at different frequencies with increasing of strain amplitude. PEG: polyethylene glycol

higher frequency. On the other hand, the data in Fig.1 indicate that the transition to shear-thickening behavior occurs at smaller strain as the frequency of the deformation is increased. The critical strain for shear-thickening is observed to decrease with the increase of frequency. The relationship between critical strain and frequencies is plotted in Fig.2. It can be observed that the critical strain is scaled inversely with frequency. The critical strains of different mass fractions almost overlap at higher frequency and get to a plateau, but at lower frequency the lower volume needs higher critical strain to get shear-thickening behavior.

The change in the viscosity of the silica suspension is assumed to be the result of the micro-structural change. The clustering theory can be used to explain the phenomena mentioned above. The fumed silica particles are colloidal particles whose physico-chemical properties are known. Just as mentioned earlier, the fumed silica A200 was prepared by flame hydrolysis of silicon tetrachloride (SiCl$_4$) in flame of H$_2$ and O$_2$. A lot of silanol groups are generated on its surface during the preparation process and irreversible aggregates, linked by hydroxyl groups (Si—OH) which are too strong to be broken, are formed. When dispersed in parlor PEG, the hydroxyl groups (Si—OH) on fumed silica aggregates surface can bond with the polar liquid, which has —OH. Due to adsorption of PEG chains on the silica aggregates, by mean of hydrogen bonds between the hydroxyls on the
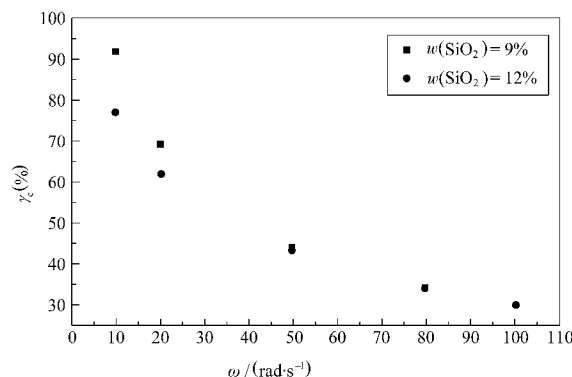

Fig.2   Correlations of critical strain amplitude (γ_c) and the frequencies (ω) for 9% and 12% fumed silica suspensions in PEG
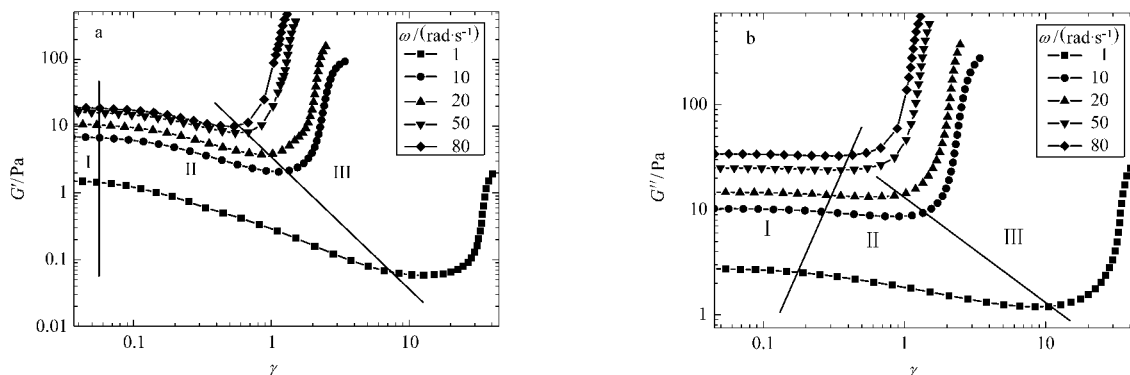
Fig.3　The moduli (G' and G'') as functions of the strain amplitude (γ) of 12% fumed silica in PEG

The strain sweeps are conducted at different frequencies. The storage G' as a function of strain is shown in (a).

The loss G'' as a function of strain is shown in (b). The linear viscoelastic region is investigated.

silica surface and the hydroxyl end groups, the three-dimension aggregates networks are formed, which prevent the suspension flocculating. Applied lower stress the silica aggregates in suspension are prevented from further association by weak steric repulsive force and Brownian forces, at the same time, some of the broken aggregates networks are able to restore the structure to the equilibrium value through the Brownian motion[15]. Linear viscoelastic region can be observed when the broken aggregates are equal to the new restored structure and shear thinning occurred when the broken aggregates are slightly more than new restored aggregates, which cause the viscosity to decrease. But if the hydrodynamic force predominates at critical strain amplitude point $\gamma=\gamma_c$, the metastable clusters, which are composed of compact groups of particles formed when strain or shear forces drive particles nearly into contact[15], are formed[16] and then the viscosity shows dramatic increase. The reasons for the metastable clusters increasing the viscosity are twofold[13]. One is that the formation of clusters causes an increase of the effective volume fraction of disperse phase. The metastable clusters are silica aggregates, which have a lot of holes. These holes would be occupied by the liquid phase, the whole structures deform as a single entity, which leads to the increase of volume fraction. On the other hand, the shapes of the clusters are believed to be oval, nonsperical structures. According to the clustering theory[17], the hydrodynamic force is proportional to the cube of the larger dimension, which leads to higher viscosity than spherical ones. But the metastable clusters are not stable. Upon cease of hydrodynamic force, the clusters are dispersed in the liquid

phase, making the shear thickening reversely[10,18].

Some papers[2,19,20] have reported the relationship between critical strain and the frequencies. The relationships between critical strain amplitude and frequency are plotted in Fig.2 in our experiment. It can be seen that the higher mass fraction (12%) gets γ_c easier, but with the increasing of frequency the critical strain points get to a plateau. The reason maybe is that the lower mass fraction has less dispersed phase and the distance of disperse phase is longer than that in higher mass fraction, which make the formation of clusters difficult at lower frequency. Raghavan and Khan[2] have reported that at high frequencies the shear thickening transitions are independent of frequencies, which is agreed with our experiment.

The moduli (G' and G'') as functions of strain are shown in Fig.3. It can be seen from Fig.3 that three regions can be divided: I linear viscoelastic region, II shear thinning region, III shear thickening region. It can also be learned from Fig.3 that in linear viscoelastic region with constant frequencies increasing the system gets more and more viscous and more and more dissipated. In the shear thinning region, both of the moduli show a slight decrease, but the storage modulus G' decreases more rapidly than the loss modulus G'' which can hardly be observed in Fig.3b under higher frequency. And in the shear-thickening region both of the moduli increase steeply, but the storage modulus is also lower than the loss modulus. In a word, the loss modulus G'' is higher than the storage modulus G' in the whole frequency range investigated. In this study, we mainly focus on the linear viscoelastic region.
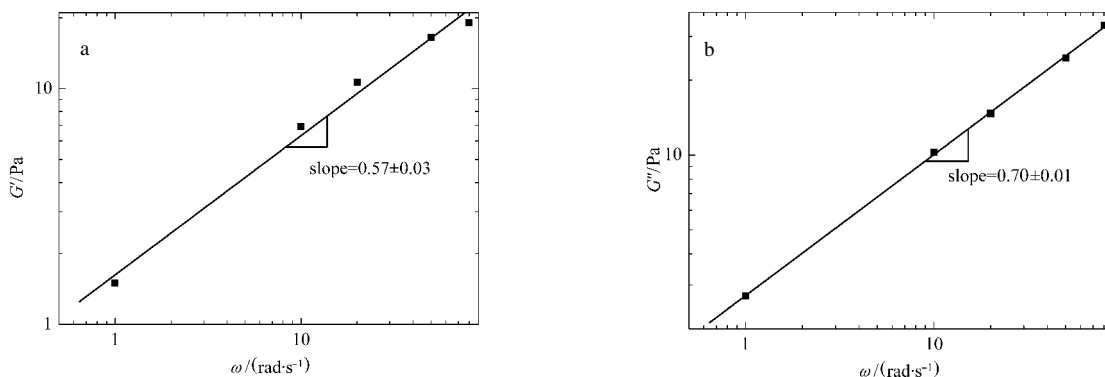

Fig.4　Plots of storage modulus G' and loss modulus G'' at linear viscoelastic *versus* frequency ω

Fig.4 shows the correlations between the storage modulus G', the loss modulus G'' and frequency ω. In Fig.4a the slope of the storage modulus *versus* frequency ω is $G' \propto \omega^{0.57\pm0.03}$ and the slope of the loss modulus *versus* frequency ω is $G'' \propto \omega^{0.7\pm0.01}$ in Fig.4b, which indicates that in the linear visoelastic region the loss modulus G'' increases more rapidly than the storage modulus G'.

2.2 Frequency sweep at the constant strain amplitude

Fig.5 shows the relationship between the complex viscosity, the moduli (G' and G'') and the frequency at the constant strain is γ_0=500%. It is indicates from Fig.5 that the moduli and complex viscosity are strongly dependent on frequency. The complex viscosity decreases slowly at lower frequency and makes an abrupt jump at critical frequency $\omega_c \approx 10$ rad·s^{-1}, which indicates that shear-thickening behavior occurs. The dramatic increase of the complex viscosity is so obvious that it is much higher than the initial viscosity. From Fig.5 it can also be learned that the moduli (G' and G'') show strongly dependence on frequency. Over the entire frequency range investigated the moduli are to be monotone increasing function of frequency and show steep increase to higher level at critical frequency. Although the storage modulus increases more rapidly than the loss modulus, in the range of frequency investigated the loss modulus G'' is higher than the storage modulus G', which means that the system is viscous and dissipated. Note that at higher frequency the complex viscosity and both of the moduli show a slight decrease. It can also be observed in Fig.1 and Fig.3 the increasing rate of the viscosity and moduli also get slowly. The reason may be that the clusters are mestable, when applied higher frequency or higher strain some clusters are broken.

The effects that the complex viscosity gets from shear-thinning to shear-thickening transition with the increasing of frequency at constant strain amplitude can also be explained by the cluster theory. At the lower frequency some aggregates networks are broken, but with the increasing of the frequency the new restored aggregates networks are suspended and then obvious shear thinning behavior occurs. At critical frequency $\omega_c \approx 10$ rad·s^{-1}, the hydrodynamic force predominates and the clusters are formed, which leads to the complex viscosity increase just as mentioned before.
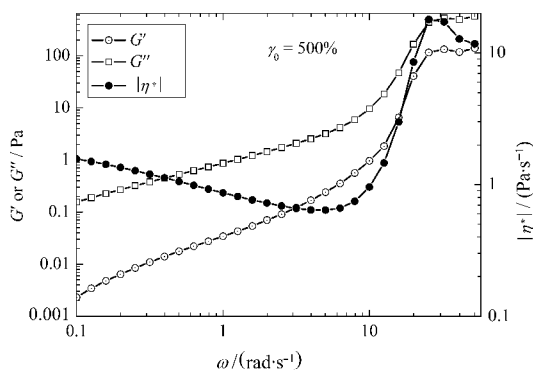

Fig.5 Moduli (G' and G'') and the complex viscosity η^* as a function of frequency at the constant strain amplitude γ_0= 500% of 12% fumed silica in PEG

3 Conclusions

1) The fumed silica suspensions in PEG exhibited shear-thickening behavior in different frequencies under dynamic oscillatory strain amplitude. The phenomena can be explained by the cluster theory. At critical strain amplitude, the presence of the mestable, flow-induced clusters lead to the complex viscosity increase dramatically. The critical strain amplitude increased inversely with frequency and get to a plateau at higher frequency.

2) The moduli (G' and G'') were dependent on the strain amplitude at different constant frequencies. The relationships of the moduli *versus* frequency were $G' \propto \omega^{0.57}$ and $G'' \propto \omega^{0.7}$ in the linear viscoelastic region. The loss modulus G'' was higher than the storage modulus G' over the whole range investigated, which meat that the systems were viscous and dissipated.

3) The moduli and complex viscosity were dependent on frequency and made an abrupt jump at critical frequency under constant strain amplitude γ_0=500%. The shear-thickening phenomena were so notable that the viscosity could be much higher than the initial value. Because the loss modulus G'' was higher than the storage modulus G', the system was viscous and dissipated.

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