

# Rheological Behavior of Hydrophilic Silica Dispersion in Polyethylene Glycol

Jong-Hwan Park,<sup>1</sup> Ho-gyum Kim,<sup>1</sup> Dong-Hee Han,<sup>2</sup> Jeong-Cheol Lim,<sup>3</sup>  
Dae-Hee Oh,<sup>4</sup> Kyung-Eun Min<sup>1</sup>

<sup>1</sup>Department of Polymer Science, Kyungpook National University, Daegu, Korea, 702-701

<sup>2</sup>Advanced Electrical Materials Group, Korea Electrotechnology Research Institute, Changwon, Korea, 644-120

<sup>3</sup>Division of textile fashion Industry, Yeoungnam College of Science and Technology, Daegu, Korea, 705-703

<sup>4</sup>Division of Chemical Engineering, Pukyong National University, Pusan, Korea, 608-739

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**ABSTRACT:** The rheological properties of hydrophilic fumed silica dispersed in polyethylene glycol (PEG) were investigated. The dispersion was prepared by dispersing the fumed silica in PEG with various concentrations. The reversible sol-gel transition was observed over 5 wt % of silica concentration as a function of temperature. The gelation temperature was found to depend on the applied shear stress and silica concentration, and the high shear

stress was found to lead to the decrease of sol-gel transition temperature of the dispersion with the same silica concentration. As the silica concentration increases, the sol-gel transition shifts to the lower temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2481-2486, 2007

**Key words:** fumed silica; polyethylene glycol; sol-gel transition

## INTRODUCTION

Composite electrolytes for use in rechargeable lithium batteries have undergone considerable investigation. It is known that a solid such as like polyethylene oxide (PEO) as organic media has ability of ion conduction and of forming a stable complex with lithium ion.<sup>1</sup> But it has also reported that the characteristic crystallinity of liquid deteriorates the ion conductivity at room temperature.<sup>2</sup> For this reason, Weston and Steele<sup>3</sup> offer the addition of inorganic filler, silica, into the polymeric liquid, which ensures the enhanced mechanical properties of electrolytes. The fumed silica is widely used particular forming of silica, which has the function of forming sol/gel structure in solvent.<sup>4,5</sup> Accordingly, the behavior of hydrophobic fumed silica in low-molecular-weight polyethylene glycol (PEG) has also been investigated in recent years. Issues elucidate that the gel formation of fumed silica in PEG is influenced directly by surface chemistry of silica. In general cases, the hydrophilic fumed silica has been confirmed to establish the sol structure. On the other hand, fumed silica with hydrophobicity by attaching nonpolar groups to its surface intends to build up the gel network structure in PEG.<sup>6</sup>

Since the electrolytes are obtained by dispersing inorganic particles into polymeric liquid, it is impor-

tant to determine the colloidal interaction between components. Several investigations have focused on the effect of fumed silica surface chemistry on the conductivity of a composite electrolyte.<sup>7,8</sup> However, very few studies have dealt with the effect of temperature and shear stress on the formation of sol structure in hydrophilic PEG liquid. The motivation of our study is to investigate the rheological behavior of electrolyte obtained from hydrophilic fumed silica and PEG at a given experimental condition.

## EXPERIMENTAL

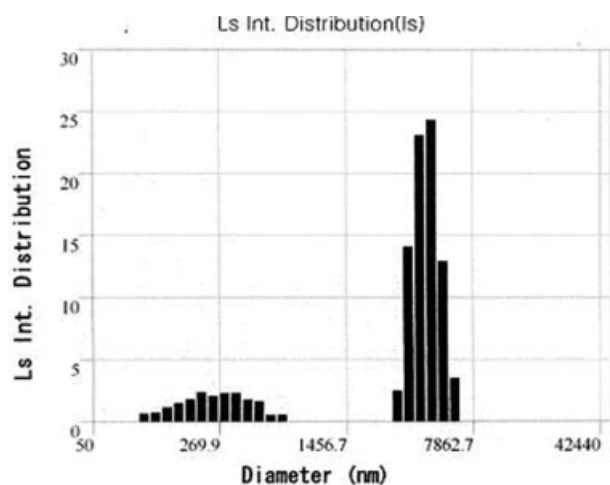
### Materials

PEG with a molecular weight of 400 was purchased from Korea Polyo (Ulsan, Korea). Hydrophilic fumed silica (Aerosil 200, Degussa, Orange, CA) of unmodified surface was allowed to dry at 120°C in vacuum oven for 12 h before mixing.<sup>9</sup>

### Dispersion preparation

The dispersion of fumed silica in polymeric glycol was prepared by continuously stirring at 150 rpm for 2 h using a high-speed mixer (RZR2041, Heidolph, Cinnaminson, NJ). The solution was then mixed again at 200 rpm for 30 min to enhance the homogeneity. The resulting dispersion was kept at room temperature for several hours to remove entrapped bubbles. The particle size and its distribution of

Correspondence to: K.-E. Min (minkyee@knu.ac.kr).



**Figure 1** Particle size distribution of silica dispersions. Light scattering intensity distribution is plotted as a function of diameter.

fumed silica were determined by electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka Electronics Co., Ltd., Osaka, Japan).

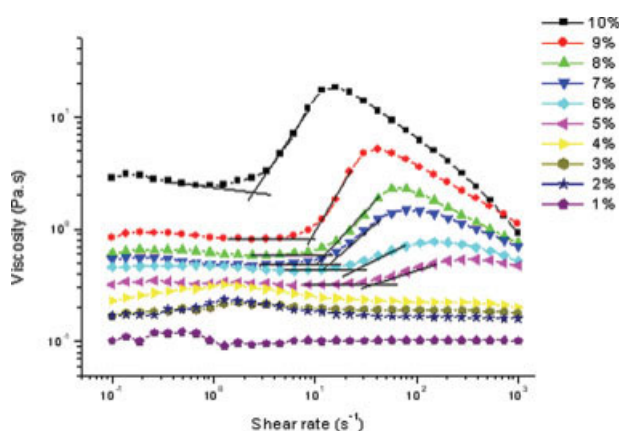
### Rheological measurements

The various dynamic measurements were performed using a UDS-200 rheometer (Anton-Paar-Str.20, Austria). The viscoelastic strain behaviors of the sample under the sinusoidal deformation ( $\gamma$ ) at a specific frequency ( $\omega$ ) and maximum strain amplitude ( $\gamma_0$ ) can be determined as

$$\gamma = \gamma_0 \sin(\omega t). \quad (1)$$

Since the resulting stress is sinusoidal, so the equation can be expressed as

$$\sigma(t) = \gamma_0(G' \sin \omega t + G'' \cos \omega t), \quad (2)$$



**Figure 2** Steady shear viscosity of silica dispersions as a function of shear rate. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

where the elastic modulus  $G'$  is related to the stored energy, and  $G''$  is linked to the viscous dissipation energy in the system. To evaluate the modulus of sample as a function of strain, the strain sweep test at constant frequency was examined. The angular frequency sweep measurements were also performed within a frequency range of 0.1–100  $\text{rad s}^{-1}$  at the fixed shear rate ( $100 \text{ s}^{-1}$ ), using the same cone and plate, with a diameter of 50 mm and a cone angle of  $4^\circ$ , within a temperature range of 25–60°C.

To acquire data concerning the effect of temperature on viscoelastic properties in fixed silica concentration, temperature sweep tests were performed under the shear stress corresponding to a strain rate range of 10–30  $\text{s}^{-1}$ .

## RESULTS AND DISCUSSION

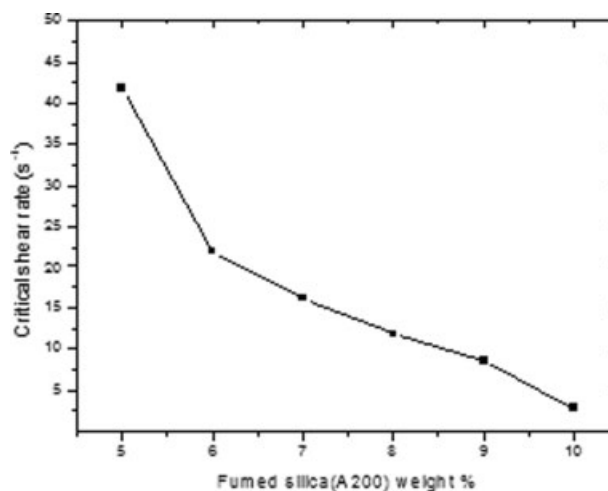
### Average particle size of fumed silica

Figure 1 displays the average particle size distribution of fumed silica used in this study. As shown, there are two distinct diameter spreads: a broad range of  $\sim 270 \text{ nm}$  and a relatively narrow range of  $\sim 7862 \text{ nm}$ . The test is carried out only to check the particle size, as we use only one selected fumed silica.

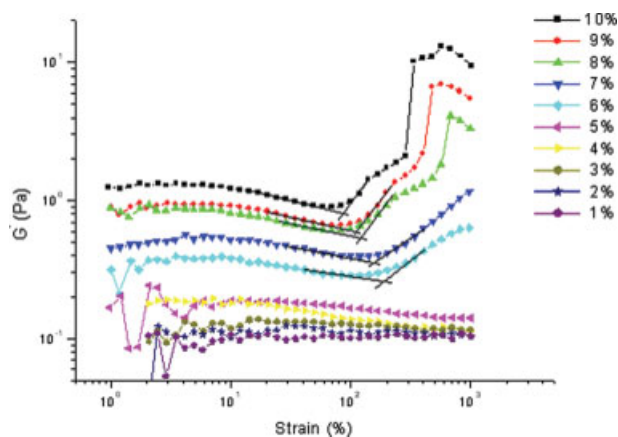
### Rheological behavior under steady shear

The viscosity of silica dispersion against shear rate is plotted in Figure 2. The transition from Newtonian flow to non-Newtonian flow behavior is observed over 5% of silica concentration. The characteristic shear-thickening behavior begins at the same concentration.

The critical shear rate corresponds to a transition from a favorable flowing state where the particles are ordered into layers to an unfavorable disordered state



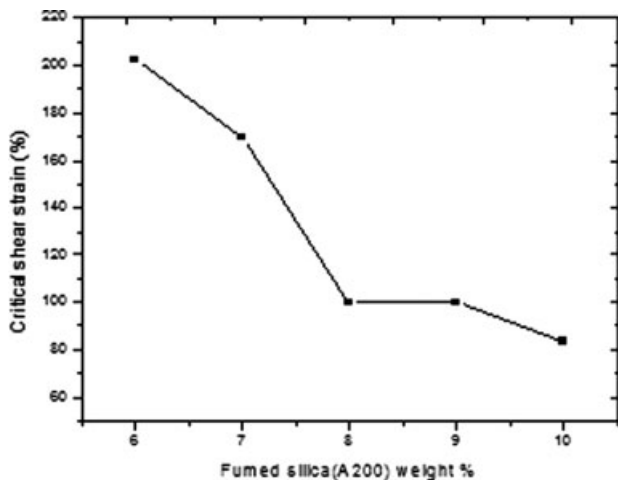
**Figure 3** Critical shear rate as a function of silica concentration.



**Figure 4** Storage modulus  $G'$  of silica dispersions with as a function of shear strain. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

where this ordering is absent.<sup>3</sup> The critical shear rate as a function of silica concentration is plotted in Figure 3. It is observed that the critical shear rate decreases almost linearly with the silica loading. The observation of shear thickening over 5% of the silica concentration may be explained by the well-known cluster formation theory.<sup>10</sup> According to this theory, it is assumed that the aggregation of silica particles is created by the high silica loading.

Figure 4 shows the plot of modulus of the silica dispersion against shear strain at 25°C. The remarkable increase of storage modulus is obtained at critical shear strain, whose pattern is very similar to that of the shear-thickening behavior, as mentioned above.<sup>10</sup> The critical shear strain can be mentioned as the onset of strain-thickening behavior. These values decrease with the particle concentration, as shown in Figure 5.



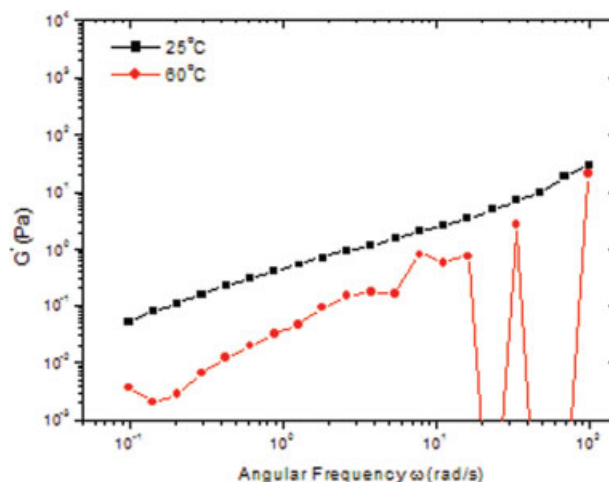
**Figure 5** Critical shear strain as a function of silica concentration.

### Angular frequency sweep test

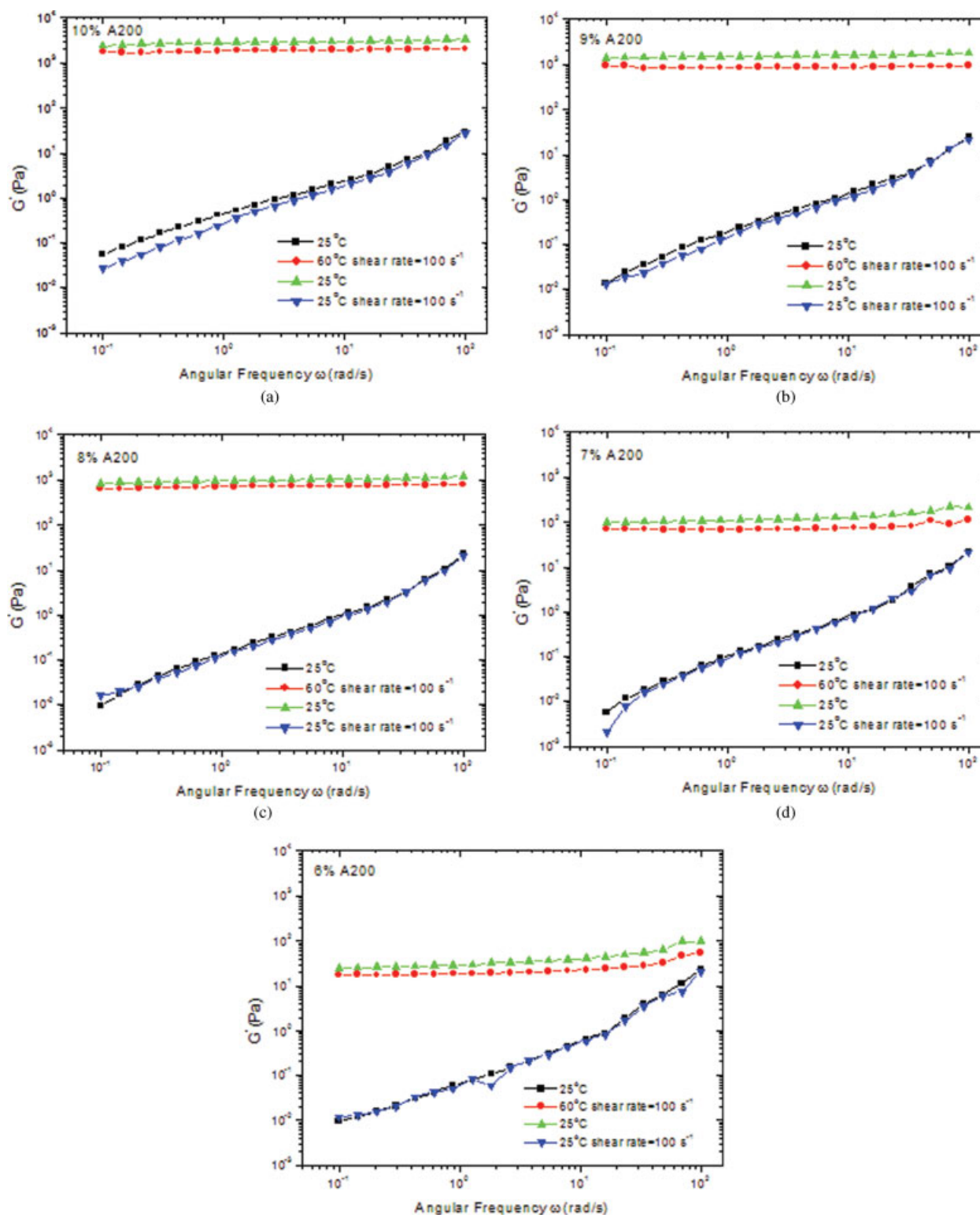
Generally, the polymer exhibits the dependence of modulus on angular frequency; in particular, the prompt response of the polymer is observed at a lower angular frequency.<sup>11</sup> The strong hydrogen bonding between PEG and the particle offers stable dispersion, known as silica "sol," mainly due to the electrostatic repulsion between particles.<sup>4-6</sup> The sol structure can contribute to an enhanced modulus, but the robust physical network in the silica "gel" produces frequency-independent behavior.<sup>11,12</sup>

To investigate the effect of temperature on the storage modulus of silica dispersion, the angular frequency sweep is performed at 0.1–100  $\text{rad s}^{-1}$  at 25°C and 60°C, with a maximum shear strain of 5%. The results are shown in Figure 6. The fluctuation of modulus data at 60°C indicates the disordered state of silica dispersion. It appears that the dependence of storage modulus on the frequency is observed over the entire frequency range; similar behavior is also observed at an elevated temperature under no shear strain conditions, suggesting that the sol structure is formed in dispersion.

We are interested in seeing whether the sol-gel transition is observed in dispersion with a different silica concentration by altering the temperature and shear stress. Accordingly, the frequency sweep tests are performed again in four steps at different temperatures. The angular frequency sweep test is carried out at 25°C (first step); the same test is also performed continuously at 60°C of the elevated temperature with 100  $\text{s}^{-1}$  of single shear rate for 30 s (second step). Shortly afterward, the temperature of the system is decreased to 25°C (third step), and the sample is placed under 100  $\text{s}^{-1}$  of the shear rate for 30 s (fourth step). The sol structure is clearly affected by this applied stress. From the results shown in Figure 7, it



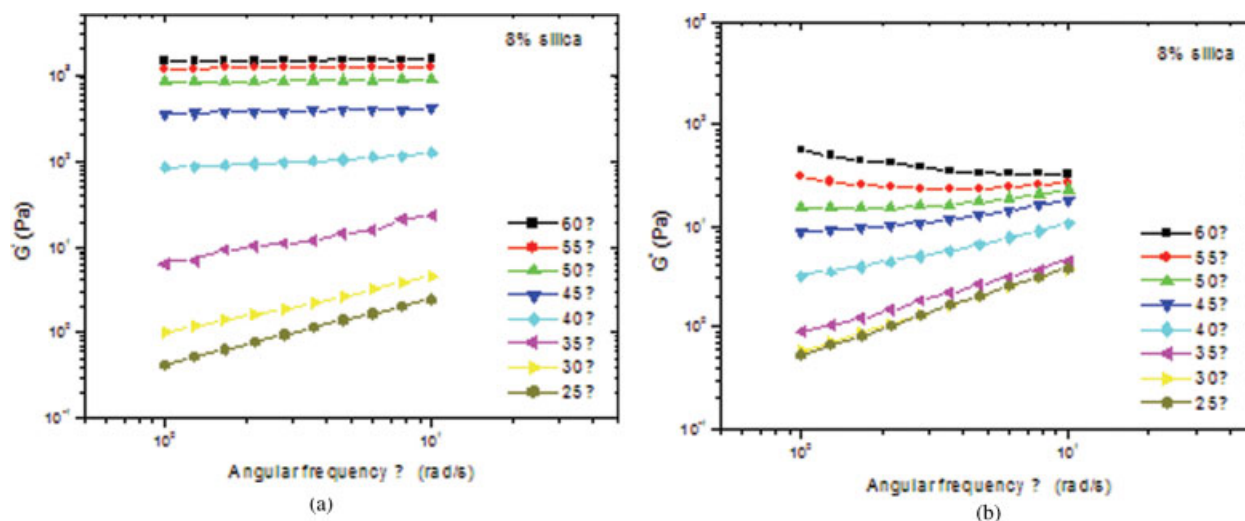
**Figure 6** Dynamic storage modulus  $G'$  of silica dispersions as a function of frequency (silica concentration: 10 wt %). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 7** Dynamic storage modulus  $G'$  of dispersions as a function of frequency: ■, first step; ●, second step; ▲, third step; ▼, fourth step. (a) silica concentration: 10 wt %; (b) silica concentration: 9 wt %; (c) silica concentration: 8 wt %; (d) silica concentration: 7 wt %; (e) silica concentration: 6 wt %. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

can be seen that instant gel formation occurs at the second step. The weak physical network between particles may be a contributing factor toward the immedi-

ate sol-gel transition under shear stress. In the third step, the gel-like response is still observed because the structure cannot be disrupted if sufficient shear stress



**Figure 8** Storage and loss modulus of dispersion with 8 wt % of fumed silica as a function of frequency. (a) Storage modulus; (b) loss modulus. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

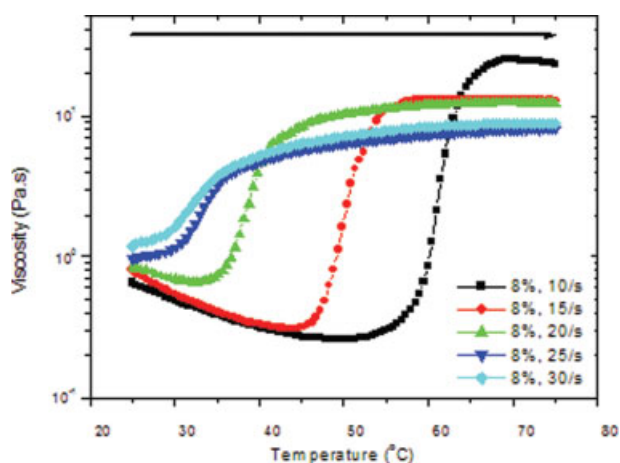
is not applied. The collapse of the structure in the fourth step verifies the sol structure.

Further evidence of temperature and shear stress effect on the modulus of silica dispersion as a function of angular frequency is studied. The shear stress corresponding to  $100 \text{ s}^{-1}$  of the shear rate was applied to the same sample at different temperatures. The frequency range is controlled at  $1\text{--}10 \text{ rad s}^{-1}$ . Figure 8 illustrates that the storage modulus of dispersion does not depend on the frequency over  $55^\circ\text{C}$  of temperature. Moreover, it can be confirmed that the storage modulus begins to exceed the loss modulus at  $> 40^\circ\text{C}$ . Consequently, it can be proposed that the sol-gel transition depends on the temperature and silica concentration under sufficient shear stress.

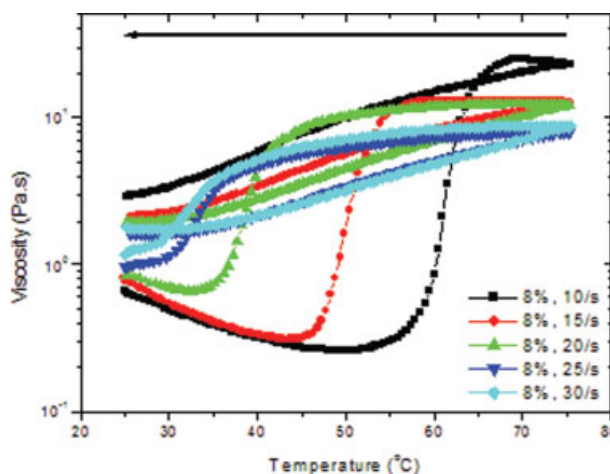
### Sol-gel transition temperature

#### Effect of shear rate

To investigate further the effect of shear rate on the sol-gel transition of silica dispersion, the steady shear viscosity of dispersion as a function of temperature is examined; the data are illustrated in Figures 9 and 10. The test is carried out at a temperature range of  $25\text{--}75^\circ\text{C}$  by heating (heating rate =  $10^\circ\text{C}/\text{min}$ ), and is also performed at a temperature range of  $75\text{--}25^\circ\text{C}$  by cooling (cooling rate =  $10^\circ\text{C}/\text{min}$ ), using the same samples. The main reason that we test the samples in the heating and cooling mode is to check the reversibility of its sol-gel transition. In Figure 9, the abrupt shear-thickening behavior is observed in all the sam-



**Figure 9** Steady shear viscosity of silica dispersion with varying shear rate as a function of temperature (condition: heating mode). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 10** Steady shear viscosity of silica dispersion with varying shear rate as a function of temperature (condition: cooling mode). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ples, indicating the gel formation in dispersion. The onset point of gel formation is increased with shear rate. Comparison of the result in the cooling mode shown in Figure 10 suggests that the sol–gel transition is reversible in all the samples, but not perfectly.

#### Effect of silica concentration

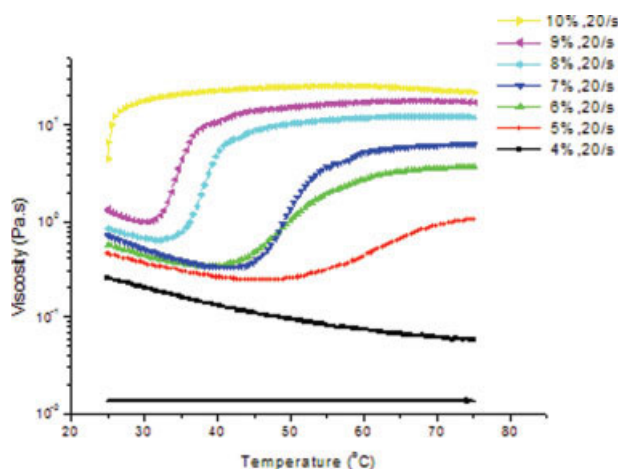
To investigate the effect of silica amount on the sol–gel transitions, the viscosity of dispersions having different silica concentration is plotted as a function of temperature. The tests are executed in the heating and cooling mode similar that in the previous experiment. The results are shown in Figure 11 (heating mode) and Figure 12 (cooling mode), respectively.

In the heating mode, the onset of sol–gel transition can be distinguished to shift to the lower temperature with silica loading. The transition occurs when 5% of silica is dispersed in PEG, as shown in Figure 11. From the rheological behavior at this temperature range, it can be concluded that increasing the silica concentration promotes the sol–gel transition when constant shear stress is applied.

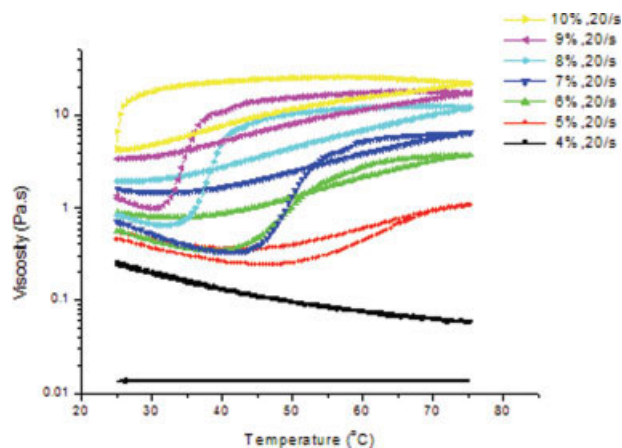
## CONCLUSIONS

In this study, the dispersions of fumed silica in PEG are prepared by mixing components in a high-speed mechanical stirrer. Some of the findings are demonstrated by the effect of shear stress and temperature on the sol–gel transition in dispersions:

1. The volume of silica has an effect on the rheological behavior of dispersion, resulting in shear thickening of samples over a 6 wt % silica concentration. The reversible sol–gel transition attributable to the temperature is also observed in sam-



**Figure 11** Steady shear viscosity of silica dispersion with varying silica concentration as a function of temperature (condition: heating mode). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 12** Steady shear viscosity of dispersion with varying silica concentration as a function of temperature (condition: cooling mode). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ples containing more than 5 wt % of silica. The gelation temperature is found to depend on both applied shear stress and silica concentration.

2. At the same silica concentration, the viscosity of dispersions is independent of the temperature as the shear stress is decreased. Moreover, it is observed that zero shear viscosity of dispersion increases with applied shear stress, which is well in agreement with the increased viscosity with shear rate, as illustrated in our results.
3. Viscosity as a function of temperature for silica dispersion is found to be nearly absent with high silica loading. The shift to a lower temperature of the sol–gel transition is observed when the silica concentration is increased. The steady shear viscosity of silica dispersion increases with silica concentration, suggesting that gel formation occurs more effectively with high silica loading.

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