

Particle Shape Dependence of Rheological Behavior for Colloid-polymer Mixtures*

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Abstract The effect of particle shape on the rheological behavior of small particle-large polymer chain mixture solutions has been investigated with two model colloidal silica dispersions, one of which is ellipsoidal (BINDZIL20/440) and the other is spherical (TM40). It was found that BINDZIL20/440 series showed shear-thickening at lower shear rates and had a lower upper limit in PEO concentration to demonstrate shear-thickening phenomena. The particle shape was identified as the major factor accounting for these differences. This work enables one to control the rheological behavior of colloid-polymer mixture through simply changing particle geometry instead of performing surface modifications, which could be especially useful in cases where only certain chemicals are allowed, for example *in vivo* applications.

Keywords: Silica colloid; Rheology; Nanoparticle; PEO.

INTRODUCTION

It is well known that colloidal particles can interact with polymers. Different particle-polymer complexes may form depending on the relative dimension and concentration of the particle and the polymer. With small polymer coils and relatively large particles, polymer adsorption on colloidal interface takes place^[1–4]. In this case, if polymers are insufficient, bridging of particles by polymer chains will happen and bridging flocculation is observed^[5, 6]. Oppositely, when polymer coils are well larger than the particles, particles adsorbed on polymer coils are expected thus the so-called nano necklace are produced^[7–9]. This long chain polymer-small particle system shows very interesting rheological behaviors. At different polymer and particle concentrations, Newtonian, shear-thinning and shear-thickening have all been observed^[9–15].

It is globally accepted that shear-thinning occurs with structural destruction or orientation, while shear-thickening is accompanied by larger scale structure formation^[14]. Shear-thickening may happen if the particle surfaces are not saturated by polymers, while if the particle surfaces are saturated by polymers, shear-thinning are normally expected^[9, 10, 16]. The microstructural changes in particle-polymer systems must be related to the

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particle-polymer interactions, thus the adsorption strength has been proposed as a key factor to determine the rheological behaviors^[9–13]. This might be true for spherical particles since polymer chains only form concentric “coronas” on the particles, thus the adsorption strength directly determines the corona thickness under otherwise same conditions. On the other hand, when non-spherical particles are used instead, polymer chain densities are not evenly distributed across particle surface, for example, polymer chains adsorb differently at the face and edge of laponite particles, a disc like colloidal particle^[17, 18]. Indeed, for two model systems, spherical silica and laponite, when mixed with PEO in water, very different rheological behaviors have been observed^[9–15]. Because laponite and silica have different surface properties, their interactions with PEO may also be different, thus, it is hard to distinguish the shape effect and interaction effect on rheological behaviors. In the current study, two silica particles with similar surface properties and hydrodynamic sizes are used as model particles to blend with PEO solutions. Through detailed study of their rheological behaviors, we expect to isolate the particle shape effect. Although control over surface property of colloidal particles can be facily achieved through chemical modifications, in certain situations where chemical modification is not allowed, for example *in vivo* applications, using the particle shape strategy becomes obviously more advantageous.

EXPERIMENTAL

Materials

Two types of aqueous colloidal silica dispersions were used as received. LUDOX-TM40 was purchased from Sigma-Aldrich Co. and Eka-BINDZIL20/440 was kindly donated by AkzoNobel Ltd. Taiwan. The DLS measurements showed hydrodynamic radii (R_h) of 15.7 nm and 14.5 nm for TM40 and BINDZIL20/440, respectively. And the BET specific surface areas were 120 and 128 m²·g⁻¹ for TM40 and BINDZIL20/440, respectively. Two poly(ethylene oxide) (PEO) polymers with molecular weights of $M_n = 95000$ g·mol⁻¹ (Polymer Source Inc., $M_w/M_n = 1.08$) and $M_v = 1000000$ g·mol⁻¹ (Sigma-Aldrich Co.) were used as received. Pure water (generated by an ELGA Purelab system) with a resistivity of 18.2 MΩ·cm was used for all samples.

Samples Preparation

Samples for rheology study were prepared by mixing silica dispersions with PEO-H₂O solution, followed by shaking gently on a rolling device for 3 days before measurements. PEO used in rheology experiments has a quoted molecular weight $M_v = 1000000$ g·mol⁻¹. Samples for ¹H solvent relaxation study were prepared by the same procedure but with the lower molecular weight PEO ($M_n = 95000$ g·mol⁻¹).

Characterizations

Rheology measurements

Rheological measurements were performed with a stress-controlled rheometer (Thermo Scientific HAAKE MARS III) at 25 °C. Cone and plate (60 mm diameter, 1 degree cone), parallel plate (35 mm diameter, 0.8 mm gap) were used to ensure reproducibility.

¹H solvent relaxation NMR

¹H spin-spin relaxation measurements were performed on a 300 MHz NMR spectrometer (Bruker DMX300) using the CPMG^[19] pulse sequence. The spin-spin relaxation time constant (T_2) was extracted from the measured magnetization (M) relaxation decay curves by fitting the data to a single-exponential decay and the specific relaxation rate constants (R_{2sp}) were calculated from $T_2^{[2, 3, 20]}$.

$$R_{2sp} = \frac{T_2^0}{T_2} - 1$$

where T_2^0 is the relaxation time constant of a reference species.

DLS measurements

Dynamic light scattering (DLS) measurements were performed on a commercial LS spectrometer (ALV/DLS/SLS-5022F) at 25 °C, which was equipped with a multi-τ digital time correlator (ALV5000) and a

cylindrical 22 mW UNIPHASE He-Ne laser ($\lambda = 632.8$ nm). The scattering angle was fixed at 90° . Samples for DLS measurements were filtered through a $0.22\ \mu\text{m}$ pore-sized membrane directly into cylindrical optical glass cuvettes, which had been extensively cleaned over an acetone steamer before use.

RESULTS

Properties of the Colloidal Silica Dispersions

As mentioned above, in this study, we aim to investigate the effect of particle shape of colloids on the rheological behaviors of their complexes with PEO. Therefore, it is very important to ensure that their differences in other aspects are minimized. First the viscosity-shear profiles of the two colloidal silica dispersions were checked (Fig. 1). It can be seen that at a similar solid content, the two dispersions have similar viscosity and shear rate dependence. Both silica dispersions did not show any non-Newtonian behavior at this concentration for the whole shear rate range explored. Although their zeta potentials were different, -27 mV and -39 mV for TM40 and BINDZIL20/440, respectively, this similarity in shear profile does suggest that the interparticle interactions do not affect the structural changes under shear. The similar viscosity also suggests the two colloidal silica particles have similar hydrodynamic sizes, which was also confirmed by DLS results (Please see the Experimental section). The particle morphologies were further observed by TEM (JEM-2200FS) as shown in the inset of Fig. 1. It can be seen that both silica colloidal particles are similar in size. The measured specific surface area by BET for the two colloidal dispersions (Please refer to the Experimental section) are also similar and more importantly, are close to those calculated from particle sizes and solid contents, indicating these two colloidal silica particles are nonporous too. However, there is a striking difference between these two colloidal silica dispersions: BINDZIL20/440 particles are ellipsoidal, while the TM40 particles are nearly spherical.

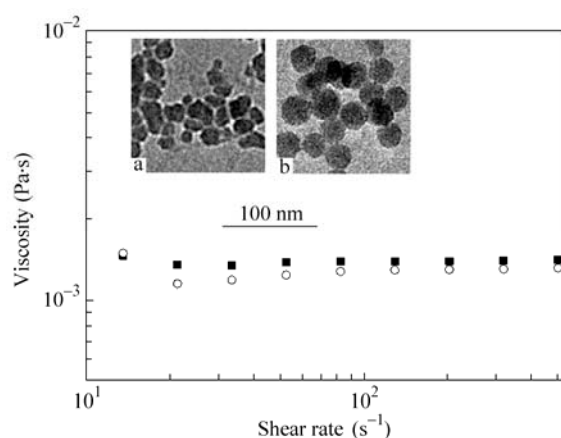


Fig. 1 Shear rate dependence of viscosity for bare silica dispersions at silica concentration of 17 wt%: ■ BINDZIL20/440, ○ TM40 (Insets are the TEM images of silica particles: (a) BINDZIL20/440, (b) TM40.)

^1H solvent spin-spin relaxation NMR was used to check their surface affinities to water. In principle, the specific relaxation rate constant ($R_{2\text{sp}}$) reflects the restriction of water by colloidal particle surface, thus representing the strength of water bound to surface. The results for bare silica dispersions are shown in Fig. 2, where one can see that the interactions between water and the two colloidal silica particles are very similar, in other words, they have a similar hydrophilicity.

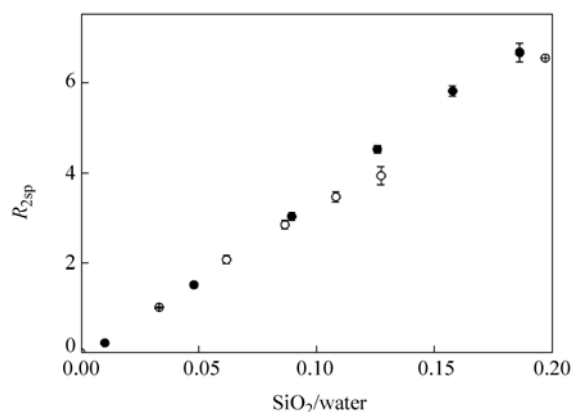


Fig. 2 R_{2sp} of silica dispersions as a function of silica concentration (W/W), $\circ$: BINDZIL20/440, $\bullet$: TM40 (Pure water was used as reference.)

The PEO-particle Interactions

As both silica dispersions have similar hydrodynamic sizes and surface properties, it is reasonable to assume that they would have similar direct interaction strength with PEO, which is the bounding strength between particle surface and PEO segments directly in contact with particle surface, *i.e.* segments presented as “trains”^[21]. A monodisperse PEO (Polymersource Inc. $M_n = 95000 \text{ g}\cdot\text{mol}^{-1}$) was used, differently from that used for rheological measurements. This is just for the convenience of measuring interaction strength, because in this case it is PEO absorbed onto silica particles rather than the reverse case when large molecular weight PEO is used. Although polymer adsorption changes with molecular weight, it is mainly due to entropy rather than enthalpy, thus the interaction strength measured with this lower molecular weight PEO should still be valid. The direct interaction forces between PEO and particle were also measured by ^1H spin-spin solvent relaxation NMR, monitoring the enhancement of R_{2sp} with increasing polymer concentration (Fig. 3). It can be seen that for both systems, with increase in PEO surface coverage, R_{2sp} increased until a maximum at $0.51 \text{ mg}\cdot\text{m}^{-2}$ and $0.52 \text{ mg}\cdot\text{m}^{-2}$ for BINDZIL20/440-PEO and TM40-PEO, respectively, after which a plateau was observed, suggesting very similar PEO-silica interactions for both types of silica.

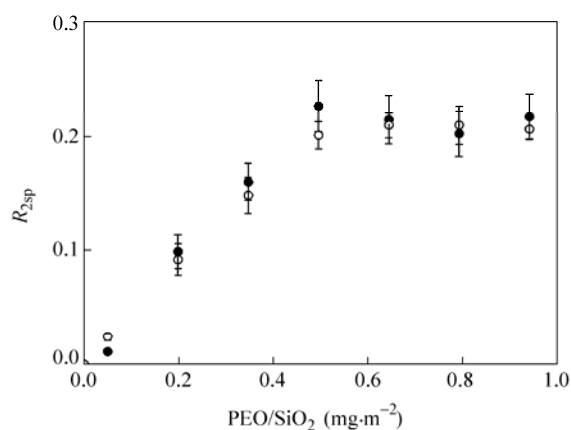


Fig. 3 R_{2sp} of PEO/silica dispersions as a function of nominal PEO surface coverage at a fixed particle concentration of 3 wt%, $\circ$: BINDZIL20/440-PEO, $\bullet$: TM40-PEO (Bare silica dispersions were used as references.)

Rheological Behaviors of PEO and Colloidal Silica Complexes

Figure 4 shows the shear rate dependence of viscosity for BINDZIL20/440-PEO and TM40-PEO dispersions. Silica concentration was fixed at 17 wt%, while overall PEO concentration varied from 0.2 wt% to 0.8 wt%. As expected, with increasing polymer concentration, the viscosity of both TM40-PEO and BINDZIL20/440-PEO

increased, but generally, for similar compositions, BINDZIL20/440-PEO showed higher viscosity than TM40-PEO series. This is probably due to stronger electrostatic repulsions between BINDZIL20/440 colloidal silica particles since the zeta potentials were measured to be -39 mV for BINDZIL20/440 and -27 mV for TM40. In our systems, there were more silica particles than polymer chains and the silica particles were much smaller than polymer coils. Therefore, many silica particles would adsorb on one polymer chain to form a small local flocculation^[9–13]. When BINDZIL20/440 particles are adsorbed on PEO chains, PEO chains will be more extended due to this stronger electrostatic repulsion.

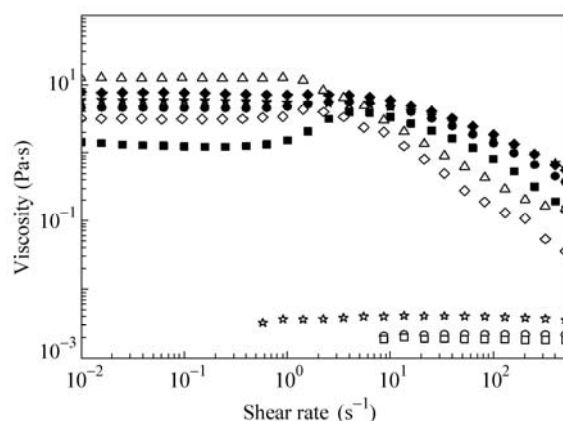


Fig. 4 Shear rate dependence of viscosity for silica-PEO at a silica concentration of 17 wt% and different PEO concentrations

The solid symbols were BINDZIL20/440-PEO series, while the open symbols were TM40-PEO series.

■□: PEO = 0.2 wt%; ●○: PEO = 0.4 wt%; ★☆: PEO = 0.6 wt%; ◆◇: PEO = 0.8 wt%; △: PEO = 1.0 wt%.

Simple salts can reduce electrostatic repulsions between colloidal particles through screening effect, thus may reduce the floc size. If the argument above was valid, the viscosity should also decrease with salt concentration. Viscosity-shear curves of BINDZIL20/440-PEO at different NaCl levels were measured (Fig. 5). From Fig. 5, one can see that the low-shear viscosity does decrease with NaCl concentration, supporting the argument made earlier. However, the shear-thickening region was not affected by NaCl concentration, indicating that shear-thickening behavior may not merely determined by the floc size.

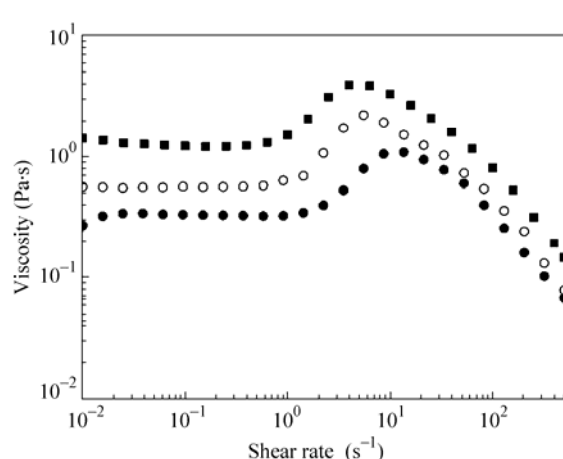


Fig. 5 Shear rate dependence of viscosity for BINDZIL20/440-PEO dispersions at different NaCl levels:

■: 0 mmol·L⁻¹; ○: 1 mmol·L⁻¹; ●: 2 mmol·L⁻¹ (PEO = 0.2 wt%, BINDZIL20/440 = 17 wt%)

Besides the viscosity, BINDZIL20/440-PEO series also showed different rheological behaviors from TM40-PEO series (Fig. 4). Obvious shear-thickening and shear-thinning was observed for BINDZIL20/440-PEO systems. However, in the explored shear rate range, TM40 series did not show significant shear-thinning or shear-thickening behavior. Only at the PEO concentration of 0.8 wt%, slight shear-thickening was observed. However, when shaken violently, the TM40-PEO dispersion (PEO = 0.6 wt% and silica = 17 wt%) showed shear-thickening or even shake-gelling^[10] (Fig. 6), indicating that shear thickening may take place at even higher shear rates. Thus, we may conclude qualitatively that with the increase in PEO concentration, both silica dispersions change from shear-thickening into shear-thinning fluids: BINDZIL20/440-PEO turns from shear-thickening into shear-thinning at 0.4 wt% PEO, while TM40-PEO at 1.0 wt% PEO. However, TM40-PEO series can only demonstrate shear-thickening behavior at much higher shear rates.

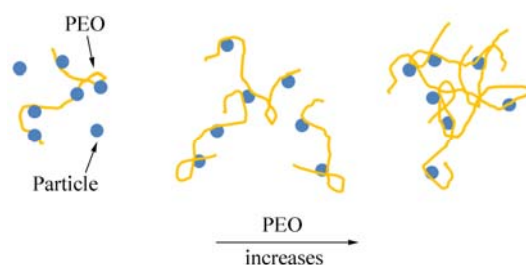


Fig. 6 Photographs of TM40-PEO (PEO = 0.6 wt%, TM40 = 17 wt%) in a quiescent state (a) and after violent shaking (b)

DISCUSSION

Shear-thinning or shear-thickening is related to structural orientation-destruction or formation, respectively. There are many previous studies dealing with shear-thinning behavior in colloid-polymer mixtures, however, shear-thickening behaviors are relatively less documented. In this study, we mainly focused on the difference in shear-thickening behavior imposed by particle shape. As we have shown earlier, these two model silica systems have similar hydrodynamic sizes, specific surface areas and direct interactions with PEO *etc.* They are only different in particle shape and zeta potentials. Thus we can preliminarily propose the differences in silica-PEO mixture shear-thickening behaviors may be raised by these two variants. Although for both series, shear-thickening behaviors disappear with increasing PEO concentration (Fig. 4), the major differences in shear-thickening behaviors can be summarized into two points (Fig. 4): i) BINDZIL20/440 series show shear-thickening at lower shear rate; ii) BINDZIL20/440 series have a lower upper limit in PEO concentration to demonstrate shear-thickening phenomena.

Previous studies^[9–16, 22–24] showed that, when shear was applied, some polymer segments may desorb from the nanoparticle surfaces and the released bare surface might adsorb segments from other polymer chains, leading to the formation of larger structures through bridging effect, thus shear-thickening is observed. In Otsubo's model^[11–13], one polymer chain can adsorb several particles to form a small floc. In this study, there are more particles than polymer chains thus there would be more than one particle adsorbs on one polymer chain. When polymer concentration increases, polymer coils will need to share colloidal particles thus become crosslinked, leading to an increase in floc size. The evolution of floc structure is illustrated in Scheme 1.



Scheme 1 Illustration of silica-PEO floc structure evolution with PEO concentration

Previous studies^[11–13] have found that if the flocs are smaller, they may store more energy by changing polymer chain conformation under shear, thus, a higher shear rate was required to show shear-thickening behavior. According to static viscosity, BINDZIL20/440 systems do form larger flocs with PEO chains due to its higher zeta potential, which seems having explained the observed differences in shear-thickening very well (Fig. 4). However, a series of control experiments proved this not to be true. A simple salt, NaCl was added to screen the electrostatic repulsions between BINDZIL20/440 colloidal particles, therefore to reduce the floc size (Fig. 5). It can be seen that, the viscosity of BINDZIL20/440-PEO decreased as adding NaCl to dispersions. In contrast, viscosity of PEO solution did not change significantly with similar NaCl concentration (Fig. 7). This means adding NaCl to dispersions does reduce the floc size in BINDZIL20/440-PEO mixture, leading to a decrease in viscosity. However, the shear-thickening behavior was not affected by adding NaCl (Fig. 5): the shear-thickening took place at similar shear rate, suggesting the explanation of shear-thickening behavior in terms of floc sizes may not be applicable in our case. These control experiments also suggest that difference in zeta potential between these two silica dispersions may not be the major reason accounting for differences in shear-thickening behaviors, thus, the shape effect becomes the only possible candidate.

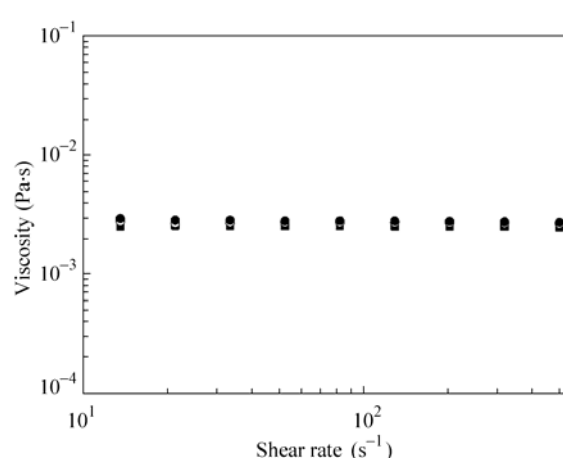
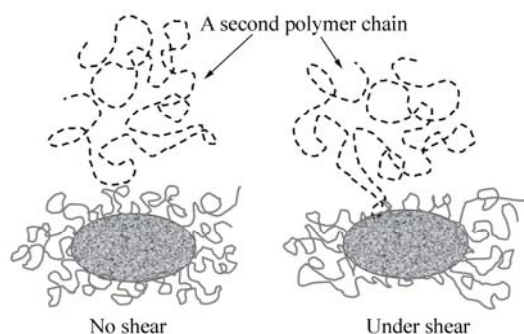


Fig. 7 Shear rate dependence of viscosity for PEO/H₂O solutions at different NaCl levels, ■: 0 mmol·L⁻¹; ○: 1 mmol·L⁻¹; ●: 2 mmol·L⁻¹ (PEO = 0.2 wt%)

The distribution of polymer segments on particle surface might give us a handle to understand the differences in shear-thickening behaviors between these two colloidal silica dispersions. As suggested by a previous study on Laponite, a disc like colloidal particle, adsorbed polymer thickness on the edge is much higher than on the face^[17, 18]. We therefore suspect the same situation may take place in the ellipsoidal colloidal particles. Although these two kinds of silica particles have similar interactions with PEO, polymer segments may enrich on the two poles of the ellipsoid particles and the faces of particles are less covered (Scheme 2). Upon shear, the less covered part may be easily exposed due to the deformation of adsorbed polymer ‘corona’, thus polymer segments from a second chain may adsorb onto the exposed particle surface to form crosslinked

network through the shared particle and an increase in viscosity will be observed (shear-thickening). For those spherical colloidal particles (TM40), polymer segments will be evenly distributed across particle surface, thus no such “weak part” exists. To release particle surface, higher shear rate will be required, which can deform the adsorbed polymer ‘corona’ to a much higher degree. Therefore, BINDZIL20/440 series show shear-thickening behaviors at relatively lower shear rate than TM40 series do (the first difference summarized *vide supra*).



Scheme 2 Illustration of mechanism for shear-thickening in BINDZIL20/440-PEO systems

Based on the proposed distribution of adsorbed polymer segments across particle surface, it is also easy to understand the phenomena that BINDZIL20/440-PEO series have much higher viscosity than their TM40 counterparts. If the faces of BINDZIL20/440 particles are less covered with PEO segments, with increase in PEO concentration, there is a better chance for segments from other PEO chains being adsorbed onto the same silica particles, thus forming locally crosslinked network flocs. Therefore the higher viscosity in BINDZIL20/440-PEO systems is not only because of the higher expansion of single polymer coils due to the stronger electrostatic repulsions between silica particles, but also because of the formation of locally crosslinked flocs (Scheme 1). With this argument, it is not surprising that even at higher salt concentrations, the viscosity of BINDZIL20/440-PEO is still much higher than TM40 counterparts (Figs. 4 and 5). Since more locally crosslinked flocs are formed in BINDZIL20/440/PEO systems with increasing PEO concentration, it becomes more and more difficult to release silica surfaces for further crosslinking by PEO under shear, thus only at low PEO concentrations, BINDZIL20/440-PEO systems show shear-thickening behaviors, which explains very well the lower upper limit in PEO concentration to demonstrate shear-thickening phenomena in BINDZIL20/440-PEO systems (the second difference summarized *vide supra*).

We have to admit that although the above models interpreted the experimental observations very well, at this stage, all the explanations based on polymer segment distribution across ellipsoidal particle surface are still speculative. Direct measurements on the real distribution of polymer segments may provide better support, which might be achieved by small-angle neutron scattering measurements, as has been demonstrated in Nelson's work^[17, 18].

CONCLUSIONS

The effect of particle shape on the rheological behavior of small particle-large polymer chain mixture solutions has been investigated. Two model colloidal silica dispersions were used to blend with PEO, which is much larger than the particles themselves. These two types of silica particles have similar particle size, surface property and interactions with PEO, but one of which is ellipsoidal (BINDZIL20/440), the other is spherical (TM40). It was found that i) BINDZIL20/440 series show shear-thickening at lower shear rates; ii) BINDZIL20/440 series have a lower upper limit in PEO concentration to demonstrate shear-thickening behavior. The differences in shear-thickening behaviors were explained in terms of distribution of polymer segments across colloidal particle surfaces. Due to the uneven distribution of polymer segments across the ellipsoidal BINDZIL20/440 particles, crosslinking of polymer coils by colloidal particles become more likely upon increasing shear rate or polymer

concentration, thus BINDZIL20/440-PEO demonstrates shear-thickening at lower shear rates and only at lower PEO concentrations. This work enables one to control the rheological behavior of colloid-polymer mixture through changing particle geometry instead of performing surface chemical modification, which can be very advantageous in case chemical treatments are prohibited.

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