



Effect of particle/polymer number ratio on the structure and dynamics of complex between large polymer and nanoparticle



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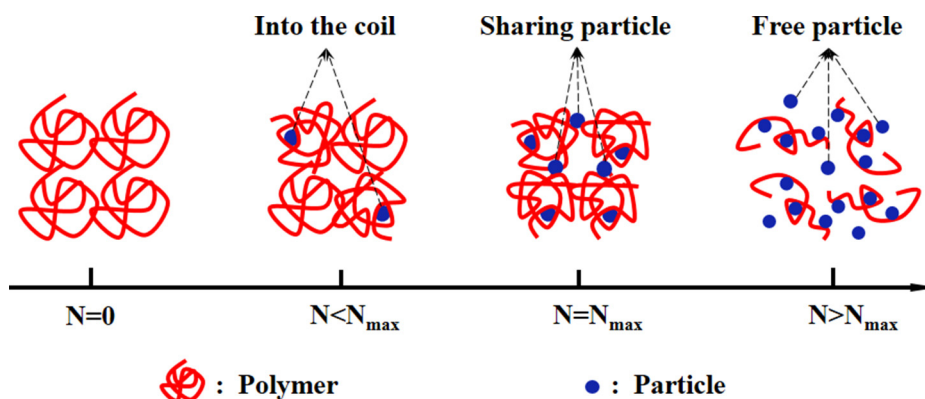
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HIGHLIGHTS

- The particle/polymer number ratio has a great effect on the structure and dynamics of such complexes at constant polymer concentration.
- The zero-shear viscosity of silica-PEO1 M mixture exposed an interesting decrease when much more particles were added.
- The interaction between particle and polymer chains leads to the microstructure evolution of colloid-polymer mixture.

GRAPHICAL ABSTRACT



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ABSTRACT

The effect of particle/polymer number ratio on the structure and dynamics of particle-polymer complexes at a fixed polymer concentration has been investigated. Mixtures of poly(ethylene oxide) (PEO, $M_v = 1,000,000 \text{ g mol}^{-1}$, $R_h \sim 39 \text{ nm}$) aqueous solution and colloidal silica dispersion ($R_h \sim 10 \text{ nm}$) were used as models. By adding silica particles, both zero-shear viscosity and R_h of the silica-PEO complexes increased with particle/polymer number ratio. The maximum zero-shear viscosity was reached when the PEO coils were saturated by silica particles. After that, a decrease in zero-shear viscosity and R_h was observed. SAXS results showed that PEO had a great effect on the inter-particle correlations before the PEO chains were saturated with silica particles, however, this effect diminished when even more silica particles were introduced. The reversible bridging interaction and inter-particle electrostatic repulsion were identified as the major factors accounting for the change in zero-shear viscosity and hydrodynamic size, and a tentative mechanism was proposed based on the spatial distribution of silica particles in the mixtures.

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1. Introduction

Mixtures of colloidal particle and polymer are widely used in many fields, such as hydrogels [1], wastewater treatment [2] and drug delivery [3]. Colloidal particles can adsorb polymer chains,

and the polymer conformation on a surface can be described in terms of train, loop and tail [4]. Depending on the final applications, polymers with different properties can be chosen to mediate the colloidal interactions. For example, a large amount of adsorbed or grafted polymers on colloid surfaces can provide steric repulsions to prevent colloidal particles aggregation [5–9]. In this case, the radius of colloidal particles is usually large compared with R_g of the polymer. Another application is to tune the rheological or mechanical property of the composite materials by adding colloidal particles to polymer solutions or melts [10–21], where the R_g of polymer may be significantly greater than the particle size.

Numerous studies [22–26] have been carried out to understand the interaction between colloidal particle and polymer, especially in the case of polymer chain with a smaller R_g compared to particle size. Cosgrove et al. [22] have shown increasing the particle size and therefore decreasing the surface curvature rendered the adsorbed polymer less mobile by facilitating a more strongly bounded, dynamically restricted train layer. The opposite situation, however, where polymer coils are much larger than particles, is less documented. Some theoretical predictions based on the interactions between large polymers and small particles have been made by Alexander [27,28], Pincus et al. [29], Marques and Joanny [30]. Lafuma, Wong, Spalla, Cabane and coworkers also experimentally investigated the bridging flocculation of nanoparticles by long polymer chains [31–36]. These previous studies have shown that when large polymers were mixed with nanoparticles, some flocs or necklace-like structures are expected. These large polymer-small particle systems could display a variety of rheological behaviors or mechanical properties [10–21,37], thus may lead to new applications. There is an intimate relationship between microstructure and property of composite materials. Therefore, the structural details of large polymer-small particle flocs may provide a more comprehensive understanding of ways to control the mechanical property of colloid-polymer composite materials. In this study, our interest is to investigate the effect of particle/polymer number ratio on the structure and dynamics of such complexes at constant polymer concentration. The spatial distribution of colloidal particles obtained by small-angle scattering through the elucidation of structure factors is used as a clue to infer the microstructures in the polymer-colloid mixture.

2. Experimental

2.1. Materials

Colloidal silica dispersion was kindly donated by AkzoNobel (under the commercial name BINDZIL 1440) and used as received. The hydrodynamic radius of the silica particle was ~ 10 nm as measured by DLS and the BET specific surface area was about $162 \text{ m}^2 \text{ g}^{-1}$. Poly(ethylene oxide) (PEO) with a nominal molecular weight $M_v = 2 \text{ Mg mol}^{-1}$, 1 Mg mol^{-1} , 300 Kg mol^{-1} and 100 Kg mol^{-1} (Sigma-Aldrich) were used as received. Pure water (generated by an ELGA Purelab[®] system) with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ was used for all samples.

2.2. Sample preparation

Samples were prepared by mixing silica dispersions with PEO aqueous solution, followed by shaking gently on a rolling device for 3 days before measurements. The pH of the samples was adjusted to 10 by adding dilute NaOH/HCl solutions. System studies were mainly based on PEO of $M_v = 1 \text{ Mg mol}^{-1}$ with the final PEO concentration fixed at 0.2 wt% and silica concentration in the range of 2–12 wt% (Table 1).

Table 1
Sample Information.

| Sample code | Silica Concentration | Particle/Polymer Number Ratio |
|-------------|----------------------|-------------------------------|
| BP-2 | 2 wt% | 3.4 |
| BP-4 | 4 wt% | 6.7 |
| BP-6 | 6 wt% | 10.1 |
| BP-8 | 8 wt% | 13.4 |
| BP-10 | 10 wt% | 16.8 |
| BP-12 | 12 wt% | 20.2 |

2.3. Characterizations

2.3.1. Viscometry and rheological measurements

Viscosities of polymer aqueous solution at different concentrations were measured at 25°C by using an Ubbelohde viscometer with a flow time longer than 300 s for pure water, so that the kinetic energy correction could be neglected. When the viscosity was measured at different polymer concentration, the intrinsic viscosity can be obtained by extrapolation of the concentration to zero by two methods [38]. Both methods are based on the fact that, in extremely dilute polymer solutions, the contribution of each polymer coil can be added up linearly. The first one is by using Huggins equation as

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c \quad (1)$$

where η_{sp} is the specific viscosity defined by $\eta_{sp} = (\eta - \eta_s)/\eta_s$, k_H , c and $[\eta]$ is the Huggins constant, polymer concentration, and intrinsic viscosity, respectively. The second method is by using Kraemer equation as

$$\frac{\ln \eta_r}{c} = [\eta] - \beta[\eta]^2 c \quad (2)$$

where η_r is the relative viscosity defined by $\eta_r = \eta/\eta_s$ and β is the Kraemer constant. When η_{sp}/c and $\ln \eta_r$ were plotted against the polymer concentration, these two lines shall meet at the same intercept, which is the intrinsic viscosity. Rheology properties were investigated with a stress-controlled rheometer (Thermo Scientific HAAKE MARS III) at 25°C . Steady-shear measurements were performed in a cone-and-plate (60 mm diameter, 1° cone) geometries by gradually changing the steady shear rate from low to high, if not specially noted. The equipment waited 10 s for equilibrium at each step gradient. Each sample was measured at least 5 times to check the reproducibility.

2.3.2. Dynamic light scattering (DLS) measurements

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 ($\lambda = 632.8 \text{ nm}$). The scattering angle was fixed at 90° . Samples for DLS measurements were filtered through a $0.45 \mu\text{m}$ pore-sized membrane directly into cylindrical optical glass cuvettes, which had been extensively cleaned over an acetone steamer before use. In DLS, the baseline normalized intensity-intensity time correlation function $g^{(2)}(t, q)$ in the self-beating mode was measured. CONTIN program supplied with the correlator was used to calculate the hydrodynamic radius [39]. The hydrodynamic radius (R_h) can be acquired by using the Stokes-Einstein equation,

$$R_h = \frac{k_B T}{6\pi\eta_0 D} \quad (3)$$

where k_B , T and η_0 are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively.

2.3.3. Small angle X-ray scattering (SAXS) measurements

The SAXS measurements were carried out on BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of X-rays was 1.24 \AA . Rectangular metal cells covered by Kapton films with

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