

DISPERSION STABILITY AND RHEOLOGICAL BEHAVIOR OF SUSPENSIONS OF POLYSTYRENE COATED FUMED SILICA PARTICLES IN POLYSTYRENE SOLUTIONS*

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Abstract Polystyrene coated silica (SiO₂@PS) core-shell composite particles with averaged diameter of about 290 nm were prepared by *in situ* emulsion polymerization of styrene on the surface of γ -methacryloxypropyltrimethoxysilane grafted SiO₂ nanoparticles of 20–50 nm in diameter. Rheological behavior and dispersion stability of SiO₂@PS suspension in 10 wt% PS solution were compared with suspensions of untreated SiO₂ and silane modified SiO₂ nanoparticles. Suspensions of the untreated and the silane modified SiO₂ exhibited obvious shear thinning. The SiO₂@PS suspension exhibits shear viscosity considerably smaller than suspensions of untreated and silane modified SiO₂ at low shear rates. Transmission electron microscopy showed that the composite particles can uniformly and stably disperse in PS solution compared to other suspensions, implying that the PS shell can effectively enhance the particle compatibility with PS macromolecules in solution.

Keywords: Fumed SiO₂; Polystyrene; Composite particles; Suspension; Steady rheology.

INTRODUCTION

During the last decade, much attention has been paid to the preparation of polymer/nanoparticle composites due to their excellent mechanical^[1–4], thermal^[5], optical^[6, 7], electrical^[8] and magnetic properties^[9] and their potential applications in polymer reinforcement, coatings, catalysis and diagnostics. Properties of nanocomposites are greatly related to dispersion of nanoparticles in the matrix and interfacial adhesion between inorganic and organic components. Unfortunately, so far it is very difficult to obtain well dispersed nanocomposites using traditional compounding techniques because of organic/inorganic immiscibility and aggregation of nanoparticles^[10].

Many chemical approaches have been developed for preparing well dispersed nanocomposites. Encapsulation of inorganic particles with polymers to form core-shell structured nanocomposite particles is desirable in many applications in order to alter the surface characteristics of the inorganic cores, to enhance the stability of the dispersions, and to improve the dispersibility in organic media. Core-shell structured nanocomposite particles can be prepared by carrying out emulsion^[11–17], dispersion^[18–22] and graft polymerizations^[23–25] on the surface of inorganic particles. Among these methods, emulsion polymerization is

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the most frequently used. Surface initiated polymerization may yield covalently bonded polymer on inorganic particles, which has been reviewed recently^[26, 27]. Monodispersed core-shell composite particles of silica coated with polystyrene (SiO₂@PS) have been prepared by *in situ* emulsion polymerization of styrene from chemically modified SiO₂ particles in the presence^[28] or absence of emulsifier^[29]. Daisy-shaped^[30], multipod-like^[30] and raspberry-like^[31] SiO₂@PS core-shell colloidal particles have also been prepared using emulsion polymerization^[32, 33].

Suspensions of fumed silica have been widely employed in academic and application fields^[34, 35]. Chemical modification of silica with coupling agents^[36] such as γ -methacryloxypropyltrimethoxysilane (γ -MPS)^[37] is effective to enhance the dispersion stability. Silica particles grafted with long tethered *n*-alkyl chains at high surface coverage may gel in polar organic media^[38].

Many works on rheological behavior of fumed silica in polymer solutions have been published recently. In chitosan solution in the concentrated regime, addition of fumed silica leads to formation of an entangled network reinforced by silica aggregates^[39]. Silica suspensions flocculated by associating polymer undergo cooperative micelle formation^[40]. Nanoparticle suspensions flocculated by polymer bridging exhibit shear-thickening flow associated with the three-dimensional network developed by polymer coils connecting several nanoparticles^[41]. Suspension of hydrophobically modified fumed silica in polyethylene glycol-lithium salt solution forms a network structure due to aggregate interacting through van der Waals forces between nonpolar surface of silica^[42]. Suspensions of the untreated and the hexyltrimethoxysilanes treated fumed silica in epoxy resin show Newtonian behavior even at 7 wt% silica while those of longer alkyl silane modified silica exhibit strong shear thinning behavior due to interaction of hydrophobic groups on silica surface^[43].

Core-shell SiO₂ nanoparticles are superior in modifying surface wetting and improving dispersion of naked nanoparticles^[44]. However, rheology of core-shell SiO₂ nanoparticle suspensions is rarely investigated. The nanoparticles grafted with polyacrylates form transparent dispersions without sediment in tetrahydrofuran^[45] while those grafted with polybutadiene form a stable colloidal dispersion in xylene^[46]. Ultrafine core-shell nanoparticles formed from silica crosslinked, individual block copolymer micelles exhibit significantly higher stability resistant to dilution in comparison with pure polymeric micelles^[47]. In the present article, rheological behavior and dispersion stability of fumed SiO₂, silane modified SiO₂, and SiO₂@PS composite particles suspended in 10 wt% PS/xylene solution were systematically investigated.

EXPERIMENTAL

Materials

Fumed silica particles with an average primary particle size of 20–50 nm were purchased from Zhoushan Mingri Nanomaterials Co., China. Chemical pure grade styrene was purified by distillation under reduced pressure before use. Coupling agent γ -methacryloxypropyltrimethoxysilane (γ -MPS) was purchased from Organic Silicon Co. in Wuhan University, China. Polystyrene (PS) (weight averaged molecular weight $M_w = 1.5 \times 10^5$) was purchased from Dow Chem. Co., USA. Other reagents were of chemical pure grade.

Surface Modification of SiO₂ with γ -MPS

Dried fumed SiO₂ particles were treated using γ -MPS in ethanol/deionized water (4/1 by weight) mixture under stirring for 12 h at 50°C. The amount of γ -MPS was 3% based on SiO₂ amount. After reaction, the SiO₂ suspension was centrifuged at 10000 r/min for 30 min. The precipitates were carefully washed three times with ethanol and further three times with deionized water in order to remove excess γ -MPS. The washed particles were dried overnight in a vacuum oven at 60°C.

Preparation of SiO₂@PS Core-Shell Nanoparticles

Core-shell composite particles were synthesized through emulsion polymerization^[16]. One hundred milliliters deionized water, 1.5 g modified SiO₂ particles, 10 mL styrene monomer, 0.2 g sodium dodecyl sulfonate (SDS) emulsifier and 0.15 g sodium bicarbonate buffer agent were added to a 500 mL glass reactor vessel. The suspension was stirred ultrasonically at 50°C for 30 min and was then heated under stirring until reaction

temperature reached 85°C. Aqueous solution of potassium persulfate preheated to 85°C was added into the reactor to initiate polymerization reaction in an atmosphere of nitrogen. The amount of potassium persulfate was 2 wt% of the monomer. After demulsification and centrifugation, the final product was washed with deionized water, tetrahydrofuran and ethanol in turn for three times, and was dried at 60°C in vacuum. The washing process allowed removing SDS and other reagents used in the *in situ* emulsion polymerization. The products were further extracted with toluene for 48 h in a Soxhlet apparatus to remove any ungrafted polymer and were finally dried to constant weight in vacuum.

Preparation of SiO₂/PS Suspensions and Films

Suspensions were prepared by dissolving 3 g PS in 27 g xylene followed by adding untreated or modified SiO₂ particles or SiO₂@PS composite particles in the solution under ultrasonication for 30 min. The suspensions were poured into glass dishes and were dried at 60°C in vacuum to remove xylene solvent to form composite films.

Characterization

Molecular weight was characterized by size exclusion chromatography (SEC, Aligent 1100 HPLC, America) equipped with a 79911GP-MXC column and an RI detector at 25°C in tetrahydrofuran solution at an elution rate of 1.0 mL/min against PS standards. M_w and polydispersity index of the PS shell after dissolving SiO₂ cores of the SiO₂@PS particles using hydrofluoric acid solution were determined as 3.3×10^5 and 1.91, respectively.

Fourier transform infrared (FTIR) spectra were recorded using a spectrometer (Vector 22, Bruker, Germany) using KBr pellet technique.

Thermogravimetric analyses (TGA) from 30°C to 800°C were performed on a thermogravimetric analyzer (Pyris 1, Perkin-Elmer, USA) at a heating rate of 10 K/min in nitrogen atmosphere.

Diameters of the untreated SiO₂ and the SiO₂@PS particles suspended in 10 wt% PS solution were investigated at 25°C on a particle size analyzer (BI-90 plus, Brookhaven Instruments, USA). The particle concentration was 0.5 wt%.

A scanning electron microscope (SEM, S4800, Hitachi, Japan) was used to observe particle morphology at an acceleration voltage of 5.0 kV. The observation was done after scattering the particles on carbon conducting resin and spraying a thin gold layer. Transmission electron microscopy (TEM, JEM 1200EX, Electron, Japan) was used to observe the particle morphology and dispersion in PS film. The particles were dispersed into ethanol at a concentration of 0.1 wt% and the suspension was ultrasonicated at 25°C for 1 min. Two or three drops of the obtained suspension were dried on carbon-coated copper grids before examination. Film samples were microtomed and sections of 100 nm were obtained for TEM observation.

UV-Vis transmission spectra of suspensions with 0.3 wt% SiO₂ were measured using a spectrophotometer (UV-1800PC, Shanghai Mei-Pu-Da Instrument Corp. Ltd., China).

Steady rheological measurements were performed in shear rate range from 0.001 s⁻¹ to 1000 s⁻¹ using a rheometer (AR G2, TA Instruments, USA) at 25°C in parallel-plate geometry.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 1 shows FTIR spectra of the untreated and the γ -MPS modified SiO₂ particles and the SiO₂@PS composite particles. The absorption bands at 1100 and 956 cm⁻¹ are assigned to Si—O and Si—OH stretching vibrations of SiO₂, respectively. The broad band at 3700–3000 cm⁻¹ represents absorption of hydroxyl groups on the surface of SiO₂ particle, which does not vary markedly upon γ -MPS modification. Two absorption bands at 2867 and 2970 cm⁻¹ corresponding to C—H stretching vibrations of methyl and methylene groups of γ -MPS^[48] appear in the spectrum of modified SiO₂ particles. In the spectrum of SiO₂@PS composite particles, the bands at 1450, 1492, and 1604 cm⁻¹ are assigned to C=C stretching vibration and the bands at 760 and 693 cm⁻¹ to C—H bending vibration of benzene ring of PS^[49], revealing that PS molecules are successfully grafted onto the surface of modified SiO₂ particles.

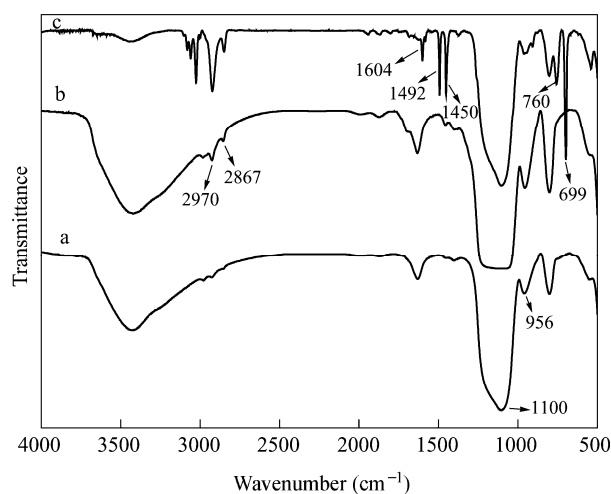


Fig. 1 FTIR spectra of the untreated (a) and the modified SiO₂ particles (b) and the SiO₂@PS composite particles (c)

TGA Analysis

Figure 2 shows TGA curves of the untreated and the γ -MPS modified SiO₂ particles and the SiO₂@PS composite particles. The untreated SiO₂ exhibits a weight loss of 5.7 wt% from 32°C to 200°C, which could be ascribed to the elimination of adsorbed water and dehydration of silanols^[50]. The modified SiO₂ exhibits a weight loss higher than naked SiO₂ from 256°C, which is related to decomposition of γ -MPS. The composite particles show a weight loss (3.5 wt%) from 32°C to 300°C smaller than that of the untreated and the γ -MPS modified silica due to the improved hydrophobicity. The composite particles have a sharp weight loss of 48.4 wt% from 380°C to 466°C owing to the thermal oxidation and decomposition of PS grafted onto silica particles^[28]. Based on the TGA residues at 800°C^[50], the weight content of γ -MPS in the modified silica is determined as 8.2% and that of grafted PS in the composite particle is 52.3%.

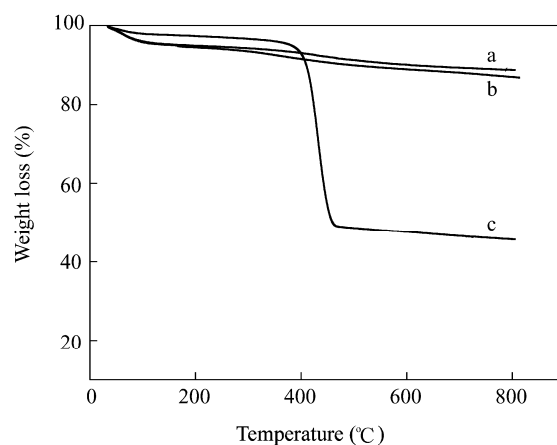


Fig. 2 TGA curves of the untreated (a) and the modified SiO₂ particles (b) and the SiO₂@PS composite particles (c)

Morphological Observation

TEM micrographs and size distributions of the untreated SiO₂ particles and the SiO₂@PS composite particles are shown in Fig. 3 and Fig. 4, respectively. The untreated particles agglomerate significantly to form large agglomerates with a wide size distribution of 460–850 nm (Fig. 3a). An averaged diameter of about 600 nm is determined by using light scattering (Fig. 4). The composite particles appear approximately spherical (Fig. 3b) with a diameter of about 290 nm and a size distribution of 250–330 nm (Fig. 4). It is noted that the size of composite particles is much larger than that (20–50 nm) of the primary nanoparticle of bare SiO₂. Figure 3(b)

shows that the composite particles do not have a simple core-shell structure but contain multiple SiO_2 cores connected by PS chains penetrating the shell of individual cores^[51]. During γ -MPS modification, the aggregates composing of several primary SiO_2 nanoparticles could not be broken down completely. The PS grafting polymerization reaction proceeds in the presence of these modified aggregates. Consequently, the modified aggregates act as the multiple cores for deposition of the polymer in the shell^[52]. On the other hand, the PS grafting improves the hydrophobicity of SiO_2 , leading to a further particle aggregation in the emulsion *via* PS shell bridging. The grafting polymerization is thus accompanied with particle aggregation and results in composite particles of several times larger than the primary SiO_2 nanoparticles. Similarly, emulsion polymerization of methyl methacrylate in the presence of γ -MPS modified nanosize magnesium hydroxide yields composite particles with multiple aggregated cores^[53]. Figure 5 shows SEM micrographs of the untreated SiO_2 and the $\text{SiO}_2@\text{PS}$ composite particles. The untreated particles seriously aggregate to form irregularly shaped agglomerates (Fig. 5a). On the other hand, the $\text{SiO}_2@\text{PS}$ particles form spherulites with clear boundaries (Fig. 5b). It is no doubt that the hydrophobic PS shell could effectively reduce the interfacial tension of the SiO_2 particles in organic solvent, which thereby restrains the agglomeration and promotes the dispersibility^[54].

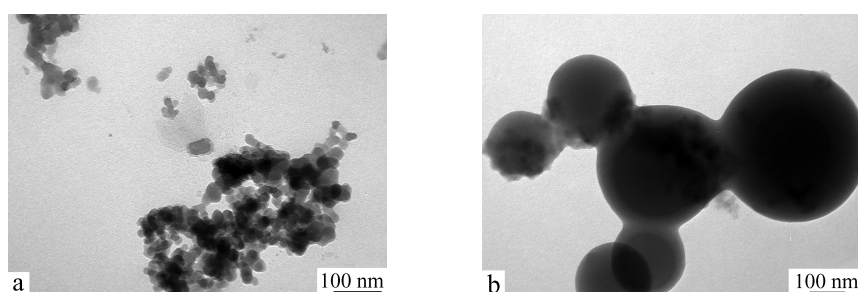


Fig. 3 TEM micrographs of the untreated SiO_2 (a) and the $\text{SiO}_2@\text{PS}$ composite particles (b)

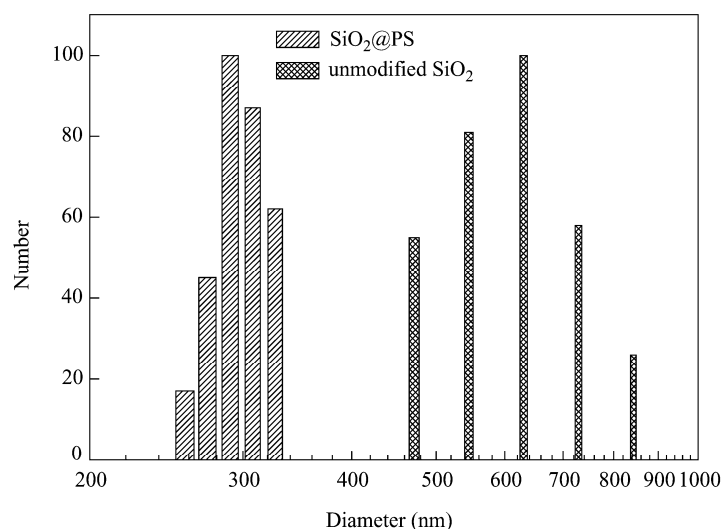


Fig. 4 Particle size distributions of the untreated SiO_2 and the $\text{SiO}_2@\text{PS}$ composite particles

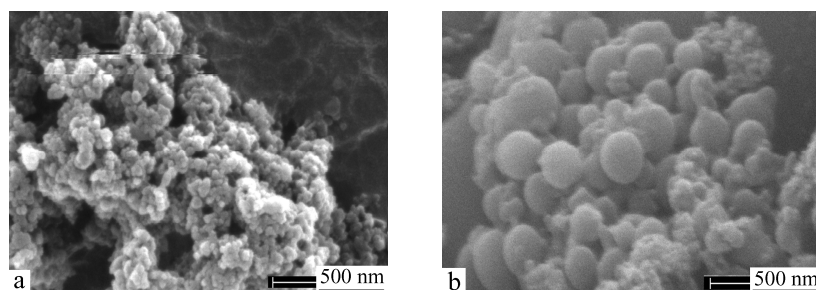


Fig. 5 SEM micrographs of the untreated SiO₂ (a) and the SiO₂@PS composite particles (b)

The particle morphologies were also assessed in the solidified films prepared from suspensions containing 0.5 wt% untreated SiO₂ or SiO₂@PS particles. Figure 6 shows TEM micrographs of the films. The untreated particles form large agglomerates with a size above 2 μm along with well dispersed small aggregates. The SiO₂@PS particles are rather homogeneously dispersed in the film, and the size of aggregates is considerably smaller than that in the film containing untreated SiO₂ particles.

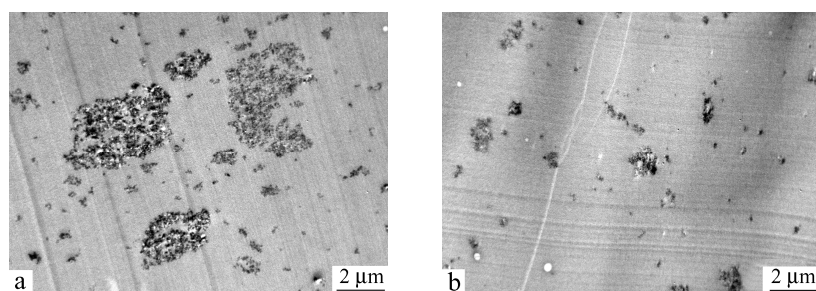


Fig. 6 TEM micrographs of films prepared from suspensions with 0.5 wt% untreated SiO₂ (a) and SiO₂@PS particles (b)

Transparency and Stability of Suspensions

Figure 7 shows UV-Vis absorption spectra of the suspensions with 0.3 wt% SiO₂. Suspension of the composite particle exhibits translucency considerably higher than the other two suspensions, retaining 80% transmittance at wavelength of 550 nm. γ -MPS modification of SiO₂ does not improve the transparency of the suspension in comparison with the untreated SiO₂. The high transparency of the SiO₂@PS suspension is related to the fine dispersion of the composite particles.

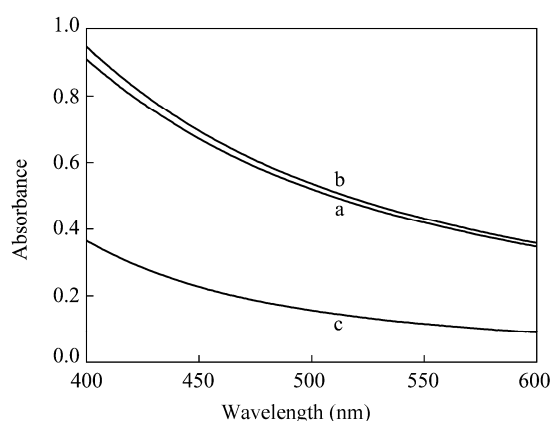


Fig. 7 UV-Vis absorption spectra for suspensions of 0.3 wt% untreated SiO₂ (a), modified SiO₂ (b) and SiO₂@PS composite particles (c)

Figure 8 shows photographs of the suspensions containing 0.5 wt% SiO₂. All the particles can be well-dispersed in the suspensions upon sonication for 30 min. Suspensions of the untreated and the γ -MPS modified SiO₂ are slightly turbid while that of the SiO₂@PS particle is highly transparent. After storage at room temperature for 30 days, white sediments and a clear solution separate in the suspensions of the untreated and the modified SiO₂. On the other hand, the SiO₂@PS suspensions only form a little sediments, most of the composite particles remained suspending stably in PS solution. The ratio of sedimentation is about 95.0%, 85.0%, and 17.9%, respectively, for suspensions of the untreated and the modified SiO₂ and the composite particles. Conventional inorganic particles have a tendency to precipitate easily in original solvents, because of their high density and low compatibility. The phase stability of colloid-polymer mixtures is related to interaction between the colloidal particles expressed in terms of an effective potential^[55, 56]. In the suspension of the untreated and the γ -MPS modified SiO₂ particles, the interaction potential can develop an attractive well because the free PS molecular chains in the solution could be expelled from the interparticle region. This depletion effect leads to an unbalanced osmotic pressure difference pushing the particles together. The effective attraction large enough gives rise to phase separation in the suspensions. Grafting modification of SiO₂ using silanes could restrict the particles from aggregation^[34, 36, 37, 39, 57] while the long term dispersion stability in PS solution does not improve markedly. On the other hand, polymer coating with formation of core-shell structure is effective in reducing sedimentation^[58] and improving dispersion stability of SiO₂ in PS solution.

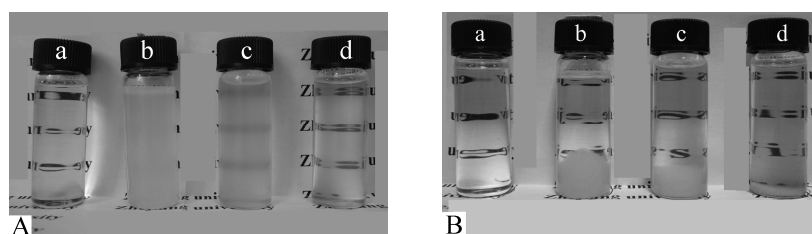


Fig. 8 Photographs of pure PS solution (a) and suspensions of 0.5 wt% untreated SiO₂ (b), modified SiO₂ (c), and SiO₂@PS composite particles (d): (A) sonication for 30 min; (B) storage for 30 days

Rheology of Suspensions

Figure 9 shows steady shear viscosity as a function of shear rate for the untreated and the modified SiO₂ suspensions. Rheological behaviors of suspensions may be very complicated in comparison with homogeneous fluid^[37]. The PS solution is a Newtonian fluid at shear rates above 1 s⁻¹. In the suspensions with less than 0.5 wt% untreated SiO₂, the presence of particles hardly influences apparent viscosity at shear rates from 10 s⁻¹ to 10³ s⁻¹ while viscosity increment is significant at low strain rates. Marked deviations from Newtonian behavior are induced by the combined contributions of the hydrodynamic and non-hydrodynamic interparticle interactions and random Brownian motions under a uniform shear field. Increasing particle content leads to a reduction in interparticle distance, resulting in considerable changes in flow properties of the suspension. PS molecules adsorbed on the aggregate surface can bridge several aggregates. The suspensions with more than 0.3 wt% SiO₂ particles exhibit shear thinning related to breakdown of the particle-particle and the particle-polymer interactions. At high shear rates, the adsorbed macromolecules are desorbed, the aggregates are broken down and the particles tend to arrange along the flow direction, resulting in the marked shear thinning either reversible or irreversible frequently observed in heterogeneous systems like flocculated suspensions^[59, 60]. Chemical modification of SiO₂ by γ -MPS leads to a reduction in viscosity as illuminated in the suspensions with 1.0 wt% and 1.5 wt% particles, which could be ascribed to the weakened particle-particle interaction.

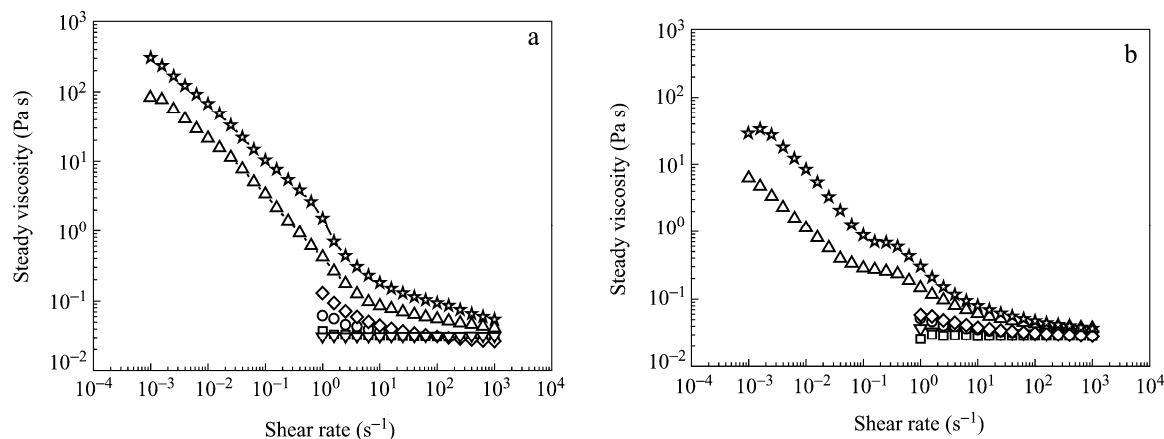


Fig. 9 Steady viscosity as a function of shear rate for suspensions of untreated (a) and modified (b) SiO₂ of 0 wt% (∇), 0.1 wt% ($\square$), 0.3 wt% ($\circ$), 0.5 wt% ($\diamond$), 1.0 wt% ($\triangle$) and 1.5 wt% ($\star$), respectively

Figure 10 shows steady shear viscosity as a function of shear rate for the SiO₂@PS suspensions. It is rather surprising that addition of 0.1 wt% to 1.0 wt% composite particles does not influence apparent viscosity obviously and the suspensions still exhibit Newtonian behavior like pure PS solution. Shear viscosity increases with increasing SiO₂@PS concentration above 1.0 wt% and marked shear thinning appears at 1.5 wt% and 2.0 wt% SiO₂@PS concentrations.

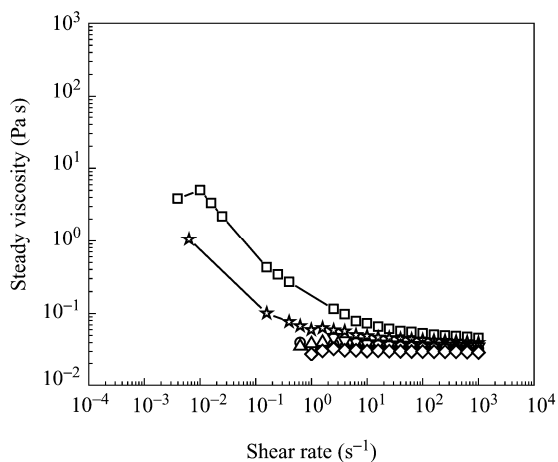


Fig. 10 Steady viscosity as a function of shear rate for suspensions with SiO₂@PS composite particles of 0.1 wt% ($\circ$), 0.3 wt% ($\triangle$), 0.5 wt% (∇), 1.0 wt% ($\diamond$), 1.5 wt% ($\star$) and 2.0 wt% ($\square$), respectively

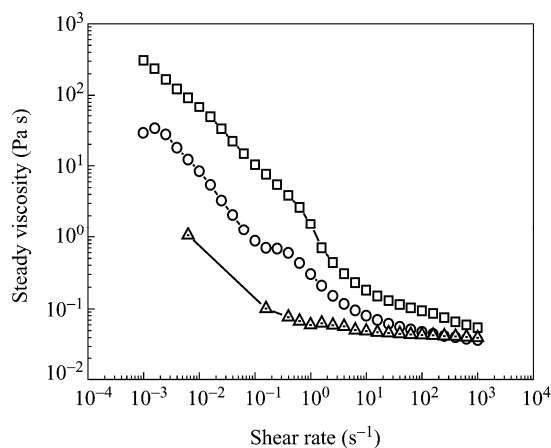


Fig. 11 Steady viscosity as a function of shear rate for suspensions containing 1.5 wt% untreated SiO₂ ($\square$), modified SiO₂ ($\circ$) and SiO₂@PS particles ($\triangle$)

Figure 11 compares steady shear viscosity as a function of shear rate for the suspensions with 1.5 wt% untreated and modified SiO₂ particles and SiO₂@PS composite particles. Hydrophobic modification with γ -MPS lowers apparent viscosity and weakens the shear thinning due to suppressing of polymer absorption and particle aggregation. Grafting polymerization modification further reduces apparent viscosity of the suspension because the PS shell layer on SiO₂ surface does not only hinder the free PS molecular chains to bridge the particles but also enhance the SiO₂ particle compatibility with PS molecules in solution.

CONCLUSIONS

In comparison with the untreated and the γ -MPS modified SiO₂ particles, SiO₂@PS core-shell composite particles synthesized through *in situ* emulsion polymerization show significantly improved dispersion stability in suspensions of 10 wt% PS solution. Suspensions of the composite particles exhibit reduced viscosity and weakened shear thinning at low shear rates in comparison with those of the untreated and the γ -MPS modified SiO₂ particles. The rheological difference is related to restriction of particle aggregation as demonstrated in morphological observations.

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