Rheological Behavior and Microstructure of Bimodal Suspensions of Core-Shell Structured Swollen Particles

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Received 19 October 2005; accepted 3 February 2006
DOI 10.1002/app.24330
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The rheological behavior and microstructure of bimodal suspensions of core-shell structured swollen particles have been examined with changing volume ratio of two different sized particles. As the volume fraction of large particles increases, the viscosity, degree of shear-thinning, and the critical shear stress σ_c decreases, while the interparticle distance ξ of the microstructure increases. The suspensions exhibit single mode rheological behavior and have a single diffraction peak in the SAXS profiles. These results suggest that the bimodal suspensions of the core-shell structured swollen particles behave likely to unimodal suspensions of hard spheres with alloy like single mode microstructure composed of hypothetical intermediate size particle. The relationship between σ_c and ξ can be represented as $\sigma_c = 3kT/4\pi\xi^3$, which corresponds to the dynamics of the Brownian hard sphere model with ξ being the particle diameter. These findings indicate that the shear-thinning of the suspensions can be attributed to dynamical competition between the thermal motion and the hydrodynamic motion under shear flow and that the mechanism can be applied to bimodal suspensions of the swollen particles as well as unimodal suspensions of hard spheres. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2212–2217, 2006

Key words: suspension rheology; bimodal suspension; core-shell particle; swollen particle; carboxylated group; critical shear stress; interparticle distance; Brownian dynamics

INTRODUCTION

Core-shell structured latex particles, with a mantle core polymer and a shell polymer layer having carboxyl groups, swell in an aqueous medium when a base is added.[1] Aqueous suspensions of the swollen particles show shear-thinning flow for relatively low concentrations, while suspensions of non-swelling particles show Newtonian flow for high concentrations.[2–4] This characteristic rheological behavior makes possible the control of the rheological behavior of paints, inks, and other substances.[5–7]

It is well known that when a polymer latex containing an acrylic acid is neutralized to an alkaline pH, the viscosity of the suspension of particles increases markedly.[7–11] In our previous work, we have found that suspensions of the core-shell structured swollen particles with carboxyl groups in the shell polymer show shear-thinning flow and exhibit elastic solid-like behavior in dynamic rheological tests. Moreover, from small angle X-ray scattering (SAXS) measurements, we found that the suspensions have pseudo-lattice-like microstructure made up of swollen core-shell particles. However, the lattice-like microstructure was not a permanent structure but was metastable and deformed by thermal motion, with the behavior represented by a time–temperature conversion with the Arrhenius equation.[12] This behavior derives from the fact that the suspension of the core-shell particles behaves similarly to that of hard spheres or polymerically stabilized particles.[13–20] The shear-thinning rheological behavior of polymer-stabilized colloidal suspensions is usually predicted and correlated based on data and scaling laws for the Brownian hard sphere model. In the Brownian hard sphere model, the rheological behavior is explained through the correlation between the bulk mass transfer and diffusive mass transfer. If the applied fields are smaller than the diffusion of the particles, the viscosity does not change; however if the applied field dominates, the viscosity falls. At the critical shear stress σ_c, the bulk mass transfer due to the applied field is greater than the diffusion of the particles in the system.

On the other hand, the dynamics of core-shell suspensions consisting of two kinds of spherical monodisperse particles with different particle size, a bimodal suspension, remains an open question. Because most disperse systems used in industrial applications have broad distributions of particle size and shape, this issue is of fundamental importance in problems relating to industrial rheological applications.

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TABLE I
Monomer Compositions of Core-Shell Particles

	Weight ratio	
	First stage (core)	Second stage (shell)
MMA	47	24
n-BA	50	38
AMA	3	
MAA		18
HEA		20

In this article, the rheological behavior and microstructure of bimodal aqueous suspensions of the core-shell structured swollen particles is examined for various concentrations of bimodal particles. The dynamics of shear-thinning has been analyzed by Brownian hard sphere models using the correlation between critical shear stress σ_c.

EXPERIMENTAL

Preparation of suspension of carboxylated core-shell particles

Carboxylated core-shell particles CS-1 and CS-4 were obtained by semicontinuous two-stage feed emulsion polymerization with sodium dodecyl sulfate as an emulsifier.[1,12,21] In each of the types of particles, the mantle core polymers were crosslinked and the shell polymers were linear and grafted to the core. The crosslinked core was synthesized with methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA), and allyl methacrylate (AMA) and the linear shell was synthesized with methacrylic acid (MAA) containing carboxyl groups, 2-hydroxyethyl acrylate (HEA), *n*-BA, and MMA. The weight ratio of the monomers of the core polymer and shell polymer was 100/29.5. The monomer compositions are shown in Table I. The particles swelled with addition of a base in an aqueous medium. The equipment used was a 1-L four-neck reactor, fitted with a reflux condenser, a mechanical stirrer, a nitrogen inlet, and a dropping funnel, and kept in a water bath. The polymerization temperature was 80°C. The first stage mixture was fed into a flask, which was then purged with nitrogen gas and heated to 80°C. After polymerization at 80°C for 1 h to obtain conversion of 95% or more, the second stage feed mixture was added at constant rate over 1.5 h, and the flask was then maintained at 80°C for an additional 5 h. It was confirmed by a light-scattering measurement and electron microscopic observation that the first-stage feed monomers formed polymer seed particles and that the second-stage feed monomers were polymerized without forming additional new particles. The particle was passed through a glass filter to remove coagulum. Though the core and shell particle compositions of the particles CS-1 and CS-4 were the same, their diameters were different, being controlled by the initiator (potassium persulfate) weight. Table II shows the core diameter and core-shell diameter with un-neutralized and fully neutralized diameters of the two types of particles measured with dynamic light scattering equipment (Otsuka Electronics ELS-800, Osaka, Japan) in a dilute suspension (0.1 wt %). The neutralizing alkaline agent was 2-dimetylaminoethanol (DMAE).

Suspensions of the core-shell particle were prepared with a 20 wt % particle concentration and 100% neutralized by DMAE. The volume ratios of CS-1/CS-4 in the suspensions were 100/0, 90/10, 75/25, 50/50, 25/75, 10/90, and 0/100.

Measurements of rheological behavior and microstructure of the suspension

The steady shear rate viscosity η of the suspensions was measured with a changing shear rate $\dot{\gamma}$ from 10^{-2} to 10^3 s^{-1}. The critical shear stress σ_c at which the suspensions changed their flow behavior from Newtonian to shear-thinning was estimated as the intersection point of the low shear rate Newtonian region and the shear-thinning region in a plot of η versus σ ($= \eta\dot{\gamma}$). The shear modulus G′ was measured with an oscillation frequency ω from 10^{-2} to 10^3 rad s^{-1} in the linear region using a rotational type rheometer (Rheometrics ARES) equipped with a conical-cylinder fixture.

The microstructure of the suspensions of core-shell particles was estimated by SAXS measurements. The voltage and current were 50 kv and 300 mA. The angle range was 0.015–0.15° and step angle was 0.003°. The slits were 0.015 mm (entrance), 0.02 mm (receiving), 0.08 mm (scatter), and 25 mm (height). Sampling time was 50 s (10 s × 5). The radial distribution function of the suspensions was derived from a Fourier transform of the intensity. The interparticle distance ξ from the center to center of the particles in the lattice-like microstructure was derived from the first peak position of the radial distribution function. Rheological behaviors and SAXS profiles were measured at 25°C.

TABLE II
Diameters of Core-Shell Particles with Non-Neutralized (d_0) and fully-neutralized (d_{100}) by 2-Dimetylaminoethanol Measured by Dynamic Light Scattering

	Diameter (nm)		
	d_{core}	d_0	D_{100}
CS-1	90	109	176
CS-4	165	191	291

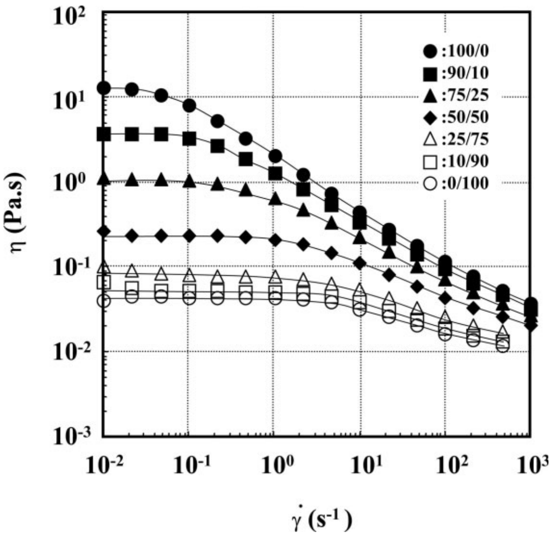

Figure 1 Steady shear rate viscosity η as a function of shear rate $\dot{\gamma}$ for various volume ratios of small-to-large particles in bimodal suspensions of the core-shell particles: ●,100/0; ■, 90/10; ▲, 75/25; ◆, 50/50; △, 25/75; □,10/90; ○, 0/100.

RESULTS AND DISCUSSION

Rheological behavior of bimodal suspensions of the core-shell particle

Figure 1 shows the steady shear rate viscosity η of bimodal suspensions of the core-shell structured swollen particles as a function of the shear rate $\dot{\gamma}$ for various volume ratios of small-to-large particles. With increasing volume ratio of large particles, both η and the degree of shear-thinning decreased. This behavior is often observed for bimodal suspensions of hard spheres and is the result of more efficient packing of polydisperse spheres, as indicated by earlier studies.[22–24] In these systems, small particles can fit into the spaces between the larger particles and if small enough, they act like a larger sea for the large particles along with the suspending fluid. At a fixed total volume fraction of the particles, it was observed that binary mixtures of particles of larger size ratios give lower viscosities than suspensions containing smaller size ratio particles. As mentioned earlier, in polydisperse suspensions, smaller particles can fit into the spaces between the larger ones, resulting in more efficient packing, but can also act as a lubricant for the larger particles. This rheological behavior indicates a single mode shear rate dependence, suggesting that bimodal suspensions of the core-shell structured swollen particles showed rheological behavior and microstructure similar to those of an unimodal (monodisperse) suspension of hard spheres. Figure 2 shows the storage modulus (G') of suspensions of core-shell particles as a function of frequency ω with various volume ratios of small-to-large particles. With increasing volume ratio of large particles, G' decreased and degree of ω dependence increased likely to more liquid-like behavior. This change also indicates a single mode rheological behavior. Shikata has suggested that a bimodal suspension with ratio of the radii of large and small particles (R_l/R_s) up to 3.3 behaves as a monodisperse suspension consisting of hypothetical particles with the average radius.[22] When the ratio R_l/R_s is not too large, the relaxation modes of the Brownian motions for the two particles cannot be distinguished as two separate modes, but the suspension will show relaxation modes that can be attributed to the Brownian motion of the hypothetical average-radius particle. In our case, $R_l/R_s = 1.5$ and the bimodal suspension behaved as a monodisperse suspension. These results suggest that the bimodal suspensions of the core-shell structured swollen particles behave likely to unimodal suspensions of hard spheres with having alloy like single mode microstructure composed of hypothetical intermediate size particle.

Microstructure of bimodal suspensions of the core-shell particles

Figure 3 shows SAXS profiles of bimodal suspensions of the core-shell particles. Diffraction peaks originating from a psudo-lattice-like microstructure made of the particles.[12] In each SAXS profile, a single peak indicates a single mode lattice-like microsturucture in spite of a bimodal suspension. With increasing volume ratio of large particles, the height of the peak

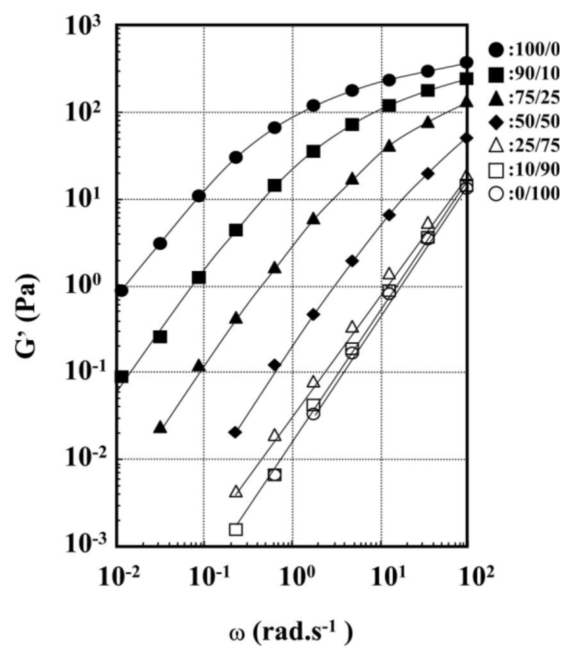

Figure 2 Dynamic shear modulus G' as a function of angular frequency ω for various volume ratios of small-to-large particles in bimodal suspensions of the core-shell particles: ●,100/0; ■, 90/10; ▲, 75/25; ◆, 50/50; △, 25/75; □,10/90; ○, 0/100.

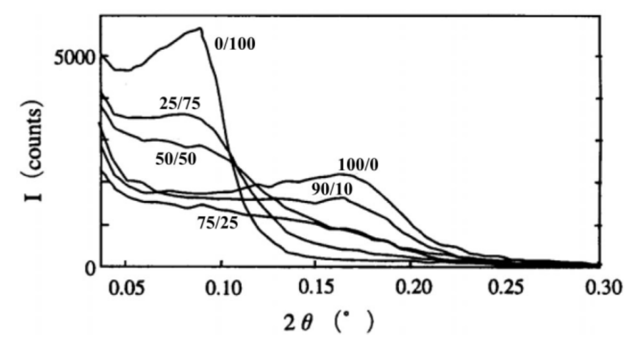

Figure 3 SAXS profiles for various volume ratios of small-to-large particles in bimodal suspensions of the core-shell particles.

decreased for ratios below 75/25 and increased for ratios above 50/50, while the angle of the peak decreased. Values of ξ, the center-to-center distance between neighboring particles in the suspensions, derived from the radial distribution function of Figure 4, are listed in Table III. These results indicate that the bimodal suspension have an alloy like (Fig. 5) unimodal microstructure composed of binary core-shell particles.

Dynamics of bimodal suspensions of the core-shell particles

We consider that the rheological dynamics of suspensions of the core-shell particles can be explained by the relationship between σ_c and ξ, via the scaling for the Brownian hard sphere model.[13–20]

To clarify the relationship between the rheological behavior and the microstructure, we plotted η against the shear stress σ, shown in Figure 6. As the volume

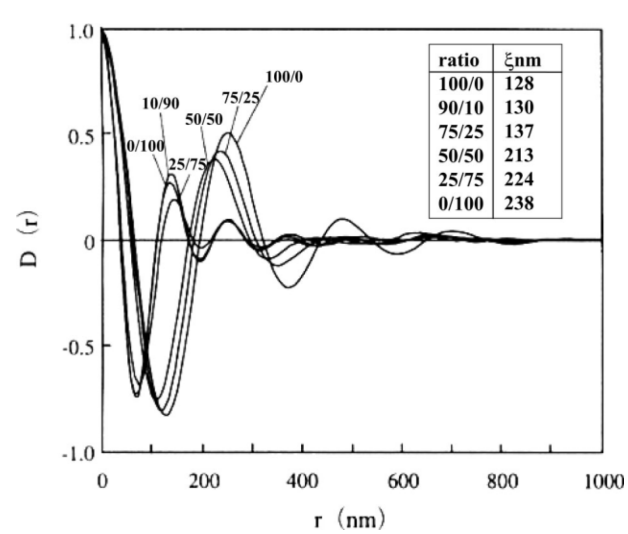

Figure 4 Radial distribution function profiles derived from SAXS profiles (Fig. 3) for various volume ratios of bimodal suspensions of the core-shell particles.

TABLE III
InterParticle Distance ξ, Critical Shear Stress σ_c, and Particle Radius a Calculated from Brownian Dynamics with Stokes–Einstein Condition

	Diameter (nm)		
	Inter-particle Distance ξ (nm)	Critical shear stress σ_c (Pa)	Particle radius from Brownian dynamics a (nm)
CS-1	128	1	60
CS-4	238	0.1	113

ratio of large particles increased, η decreased, as did the critical shear stress σ_c at which the suspension changes its flow behavior from Newtonian to shear-thinning. The flow mechanism changes markedly around the critical shear stress σ_c. Below this value a creeping motion seems to occur, caused by structural rearrangement. At the critical stress the microstructure ruptures and regular macroscopic flow sets in. This critical stress can be considered a yield stress. At higher stresses isolated microstructure exist, which gradually erode with increasing shear.

The ratio of the bulk mass transfer to the diffusive mass transfer is the Peclet number *Pe*. In the low stress regime, the stress does not perturb the system until σ_c is reached and the viscosity falls. At this stress, the bulk mass transfer due to the applied field is greater than the Brownian movement in the system and the existing order in the suspension is disrupted.

Pe is expressed by

$$Pe\ a^2\dot{\gamma}/D, \tag{1}$$

where a is the radius of the particle, γ is the shear rate, and D is the diffusion coefficient of the particles. For a diffusion coefficient expressed as $D = kT/6\pi\eta_0 a$, Pe is expressed as

$$Pe\ 6\pi\eta_0\dot{\gamma}a^2/kT. \tag{2}$$

Pe should be 1 at the critical shear stress and σ_c can be expressed as

$$\sigma_c = kT/6\pi a^3. \tag{3}$$

However, this equation is concerned with dilute suspensions exhibiting Stokes–Einstein diffusion of particles. The diffusion constant of particles in a shear-thinning suspension is unknown. Scaling eq. (3), we derived the particle radius from Brownian dynamics. This value does not agree with ξ, but with $\xi/2$ indicating that the diffusion coefficient of particle in the suspension must correlate with ξ and is likely to represent the diffusion coefficient of a three dimensional gel corresponding to the correlation length.[25,26] These

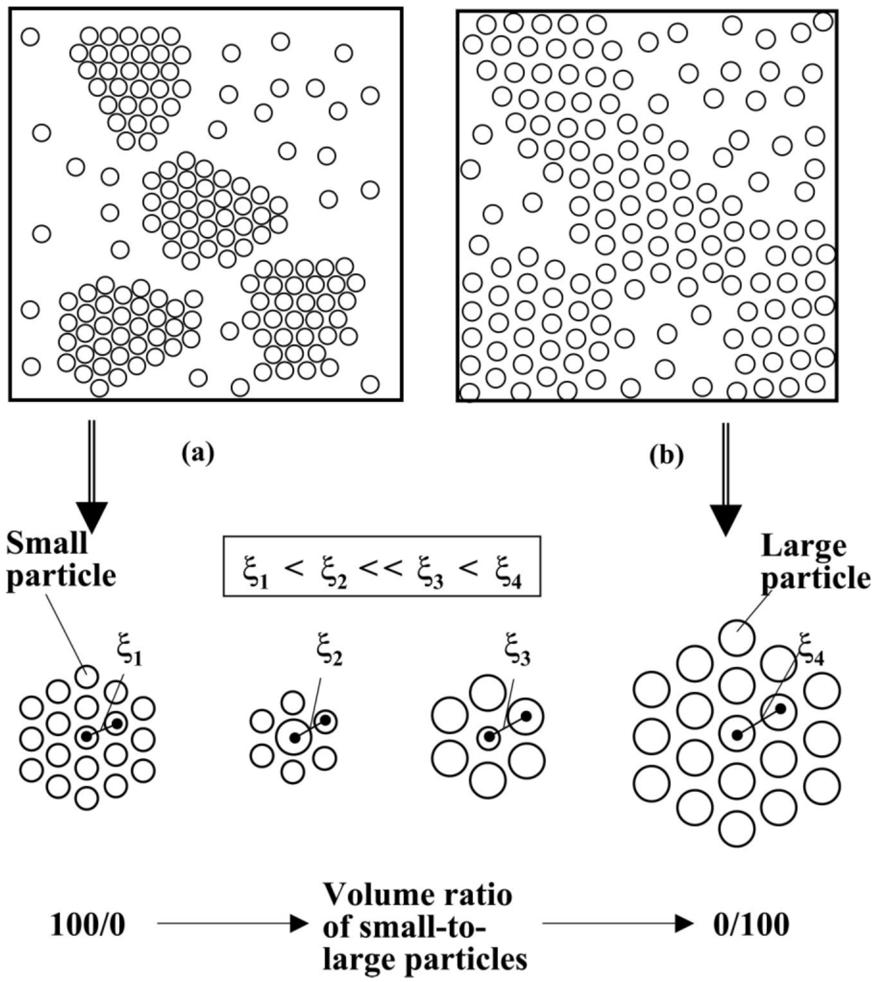

Figure 5 Schematic illustrations of alloy structures of bimodal suspensions of the core-shell particles.

results indicate that the dynamics of the core-shell particles in shear-thinning suspension can be expressed by the scaling of Brownian dynamics of hard spheres and that the diffusion of the particles corresponds to that of hard spheres with diameter ξ. We have derived an expression for σ_c that depends on ξ, expressed as

$$\sigma_c = 3kT/4\pi\xi^3. \tag{4}$$

We examined the correlation between σ_c and ξ in the microstructure for not only unimodal systems but also bimodal systems. Figure 7 shows the relationship between $1/\text{xî}^3$ and σ_c for various volume ratios of small-to-large particles. In the log-log plot, σ_c is proportional to $1/\xi^3$; and the slope of the relationship is $3kT/4\pi$. This shows that the diffusion coefficient of particles in the suspension corresponds to that of particles of diameter ξ for bimodal suspensions as well as unimodal suspensions.

From these results, the dynamics of a suspension of the core-shell structured swollen particle can be ex-

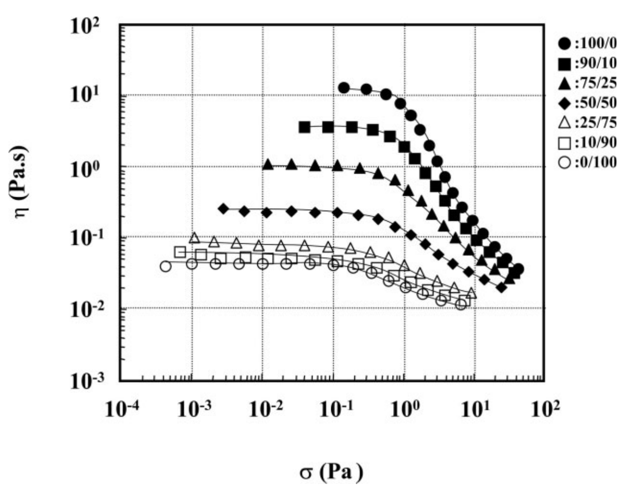

Figure 6 Steady shear rate viscosity η as a function of shear stress σ, derived from Figure 1 by substituting σ ($= \eta\dot{\gamma}$) for $\dot{\gamma}$, for various volume ratios of small-to-large particles in bimodal suspensions of the core-shell particles: ●,100/0; ■, 90/10; ▲, 75/25; ◆, 50/50; △, 25/75; □,10/90; ○, 0/100.

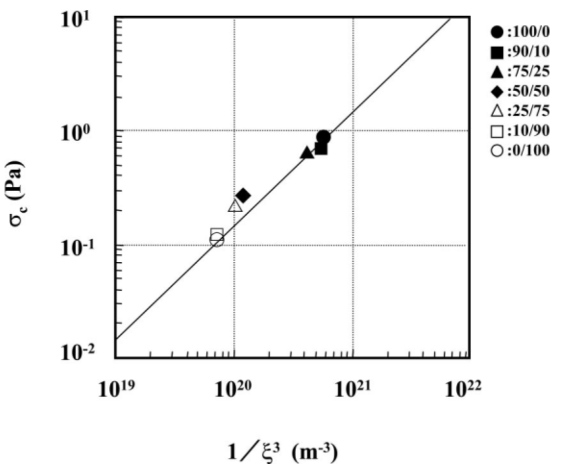

Figure 7 The relationship between 1/xî^3; and σ_c for various volume ratios of small-to-large particles in bimodal suspensions of the core-shell particles: ●,100/0; ■, 90/10; ▲, 75/25; ◆, 50/50; △, 25/75; □,10/90; ○, 0/100. The slope of the straight line is $3kT/4\pi$.

plained via scaling of the Brownian hard sphere model that describes competition between the bulk mass transfer due to the applied field and diffusion of the particles in the suspension for not only unimodal suspensions but also bimodal suspensions. σ_c depends on ξ and can be expressed as ó$_c$ = $3kT$/4xî^3, which indicates that in bimodal suspensions of the core-shell particle σ_c is dominated by the thermal motion of the particle in the same way as for unimodal suspensions of hard spheres.

CONCLUSIONS

We studied the rheological behavior and microstructure of aqueous suspensions of a bimodal core-shell structured swollen particle with changing volume fraction ratio of two different sized particles. The particle was swollen with dissociation of carboxyl group in the shell by neutralization, and the diameters of these particles in the fully neutralized state were 176 and 291 nm. We measured the steady shear flow with a conical-cylinder rheometer and estimated the critical shear stress σ_c, defined as the stress at the transition point from Newtonian flow to shear-thinning flow. The distance ξ, the center-to-center distance between neighboring particles in the suspensions was estimated with SAXS. As the volume ratio of large particles increases, the viscosity, degree of shear-thinning, and the critical shear stress σ_c decrease, while the interparticle distance ξ of the microstructure increases. The suspensions exhibit single mode rheological behavior and have a single diffraction peak in their SAXS profiles. These results suggest that the bimodal suspensions of the core-shell structured swollen particles behave likely to unimodal suspensions of hard spheres with alloy like single mode microstructure composed of hypothetical intermediate size particle. The relationship between σ_c and ξ was determined to be σ_c = $3kT$/4xî^3, which corresponds to the dynamics of the Brownian hard sphere model with ξ being the particle diameter. These findings indicate that the shear-thinning of the suspensions can be attributed to dynamical competition between the thermal motion and the hydrodynamic motion under shear flow and that the mechanism can be applied to bimodal suspensions of the swollen particles as well as unimodal suspensions of hard spheres.

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