

Rheological Behavior and Microstructure of Aqueous Suspension of Carboxylated Core-Shell Structured Latex Particle

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ABSTRACT: Core-shell type carboxylated particles form a flocculated structure in aqueous suspension with neutralization of carboxyl groups. Rheological behaviors of the suspension have been studied at various temperatures, and microstructures of the suspension have been discussed from the rheological behaviors and SAXS measurements. At 25°C, G' is larger than G'' in all ω regions, and G' is almost independent of ω , and the diffraction peak is detected by SAXS. These results mean that a three-dimensional network of interconnected lattice-like flocculated structure is formed. With increasing temperature, ω dependency of G' becomes stronger and distance of the particles of the structure does not change. These mean the network linkage is disrupted partially by thermal motion, and the interconnected lattice-like flocculated structure changes to an isolated lattice-like one with increasing temperature. With increasing the degree of neutralization, an isolated structure changes to an interconnected three-dimensional structure decreasing the thermal motion just like decreasing temperature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1627–1633, 2001

Key words: core-shell particle; rheological behavior; shear thinning flow; three-dimensional network; lattice-like structure

INTRODUCTION

The “soft sphere,” which is composed of a rigid spherical particle “hard sphere” and an adsorbed polymer layer, is stabilized by repulsive forces and attractive forces in the suspension, but the attraction is not as strong as to cause a permanent bond between the particles. As a result, these particles made metastable structures that are disrupted by shear fields and recover within a reasonable experimental time scale. The metastable structures affect the rheological behavior of the suspension of the soft spheres,^{1–9} while in the

suspension of noninteracting hard spheres no structure is made, and the rheological behaviors are dominated by Brownian dynamics.^{10–13} The soft-sphere suspensions studied are about poly(methyl methacrylate) particles with adsorbed poly(hydroxystearic acid) dispersed in hydrocarbon medium,^{2–5} and polystyrene particles with adsorbed poly(ethylene oxide) in aqueous medium.^{7–9}

A core-shell structured latex particle consisted of mantle core polymer and shell polymer is a kind of soft-sphere. Aqueous suspension of carboxylated core-shell particles that contain a carboxyl groups in a shell polymer indicates shear thinning flow in relatively low concentration with addition of base.^{14–17} The rheological behavior is sensitive to the microstructure of the suspension,

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making it a useful probe for the microstructure. Steady shear measurements at relatively large stresses give the strength of the microstructure, while dynamic oscillatory shear measurements at small deformations elucidate the dynamics of the unperturbed microstructure. In our previous works, it was found by dynamic oscillatory shear measurements that there is a flocculated structure that indicates elastic response and is disrupted by large stresses.^{18–20} Moreover, it was elucidated from the small-angle X-ray scattering method the flocculated structure is ordered.

In this article, rheological behaviors of aqueous suspension of a carboxylated core-shell particle have been investigated at various temperatures, and microstructures of the suspension have been measured by small-angle X-ray scattering measurements.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA) allyl methacrylate (AMA), methacrylic acid (MAA), 2-hydroxyethyl acrylate (HEA), potassium persulfate (KPS) as an initiator, sodium dodecyl sulfate (SDS) as an emulsifier, and 2-dimethylaminoethanol (DMAE) as a neutralizer were all reagent grade obtained from Wako Junyaku, and used without further purification. Deionized water with a conductivity of ca. 1 $\mu\text{mho/cm}$ was used in all the experiments.

Carboxylated Core-Shell Particle

The carboxylated core-shell particle was obtained by semicontinuous two-stage feed emulsion polymerization.^{21–24} 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 monomer composition is presented in Table I. Crosslinked core polymer was synthesized from MMA, *n*-BA, and AMA, and linear shell polymer was from MAA, HEA, *n*-BA, and MMA. Weight ratio of monomers of core polymer/shell polymer was 100/29.5. KPS and SDS were added at 0.2 and 0.3 wt %, respectively, based on total monomers. 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

Table I Monomer Composition of Core-Shell Particle

	Weight	
	First Stage (Core Part)	Second Stage (Shell Layer)
MMA	47	24
<i>n</i> -BA	50	38
AMA	3	
MAA		18
HEA		20

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 microscope 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. The diameter of core of the particles in diluted suspension (0.1 wt %) measured with a dynamic light-scattering equipment (Otsuka Electronics ELS-800) was 90 nm. The diameter of the entire particle was 180 nm as calculated fully neutralized by DMAE. The amount of carboxyl groups is 2.14 mmol per shell polymer.

Rheological Measurements

Rheological behaviors of a fully neutralized 20 wt % aqueous suspension (pH = 8.5) of carboxylated core-shell particle were examined at 25, 45, and 65°C. Relative viscosity was measured from shear rate $\dot{\gamma} = 1 \times 10^{-2} \text{ s}^{-1}$ to $1 \times 10^3 \text{ s}^{-1}$. Storage modulus G' and loss modulus G'' were measured from strain amplitude $\gamma = 1 \times 10^{-2}\%$ to $5 \times 10^2\%$ at $1 \times 10^1 \text{ rad} \cdot \text{s}^{-1}$, and from angular frequency $\omega = 1 \times 10^{-2} \text{ rad} \cdot \text{s}^{-1}$ to $1 \times 10^2 \text{ rad} \cdot \text{s}^{-1}$ in a linear region. Recovery time of G' was estimated with skipped from $\gamma = 5 \times 10^2\%$ (nonlinear region) to $1 \times 10^{-1}\%$ (linear region) at $1 \times 10^1 \text{ rad} \cdot \text{s}^{-1}$. A rheometer (Rheometrics ARES) was equipped with a conical-cylinder (quette) fixture. About the suspensions with different degree of neutralization, viscoelastic measurements carried out in same way.

Small-Angle X-ray Scattering Measurements

Microscopic structures of aqueous suspension of carboxylated core-shell particle were estimated

Table II Condition of SAXS Measurement

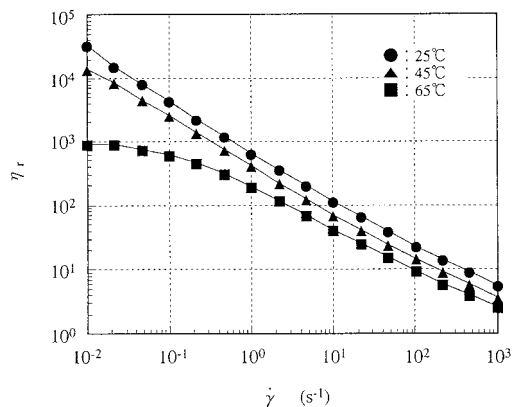
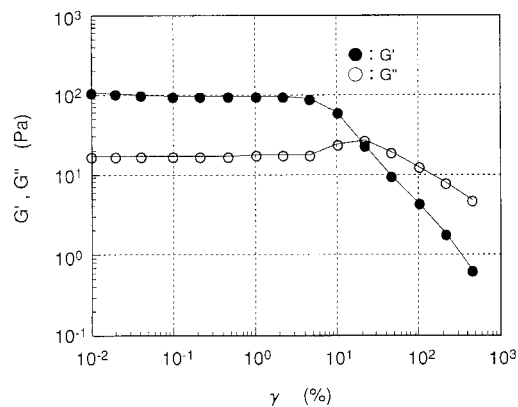
Target	Cu
K β Filter	Ni
Voltage, current	50 kV, 300 mA
Angle range	0.015–0.15 deg
Step angle	0.003 deg
Slits	Entrance slit 0.015 mm Receiving slit 0.02 mm Scatter Slit 0.08 mm Height limiter 25 mm
Sampling time	50 s (10 s \times 5)

by small-angle X-ray scattering, SAXS, measurements. Condition of the SAXS measurements was shown in Table II. Radial distribution function of the suspension was derived from Fourier transform of intensity. Distance of center to center of the particles in the lattice-like flocculated structure was evaluated from the first peak position by the Bragg equation.^{25,26}

RESULTS AND DISCUSSION

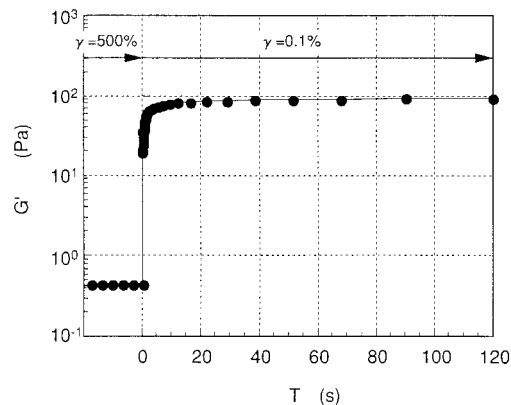
Viscosity of the Suspension at Various Temperatures

In Figure 1, relative viscosity η_r of the fully neutralized suspension is plotted against the shear rate $\dot{\gamma}$ at 25, 45, and 65°C. With increasing temperature, η_r in all $\dot{\gamma}$ region and degree of shear thinning from $1 \times 10^{-2} \text{ s}^{-1}$ to $1 \times 10^0 \text{ s}^{-1}$ region decreased. These suggest the microstructure of the suspension changes with temperature.

**Figure 1** Relative viscosity η_r plotted against shear rate $\dot{\gamma}$ for suspension at 25, 45, and 65°C.**Figure 2** Storage modulus G' and loss modulus G'' of the suspension plotted against strain amplitude γ of $1 \times 10^1 \text{ rad} \cdot \text{s}^{-1}$ at 25°C.

Viscoelastic Behavior and Microstructure of the Suspension

In Figure 2, storage modulus G' and loss modulus G'' of the suspension are plotted against strain amplitude γ of $1 \times 10^1 \text{ rad} \cdot \text{s}^{-1}$ at 25°C. G' and G'' stay constant up to a critical strain γ_c (4%) and G' is larger than G'' in $\gamma < \gamma_c$. These results mean that a flocculated structure that indicates elastic response is in the suspension. With increasing γ in $\gamma > \gamma_c$, G' decreases monotonously, because of disruption of the flocculated structure by shear fields, G'' decreases after going through a maximum. The maximum peak in G'' suggests that the flocculated structure is a lattice-like structure,^{19,20} because the maximum peak is caused by increasing the size of lattice-like structure with large stress.²⁷ The lattice-like flocculated structure is a metastable structure because G' recovers immediately when γ decreases, as shown in Figure 3.

**Figure 3** Recovery of storage modulus G' after large strain amplitude γ at 25°C.

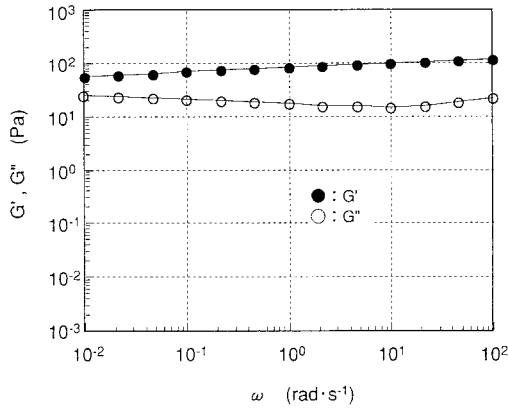


Figure 4 Storage modulus G' and loss modulus G'' of the suspension plotted against angular frequency ω of linear region at 25°C,

In Figure 4, G' and G'' are plotted against angular frequency ω at 25°C. G' is larger than G'' in all region, and G' and G'' are almost independent of ω . These behaviors result from a gel-like structure that is a three-dimensional network composed of elastic bondings. From these results it is found that the lattice-like flocculated structure which is metastable and gel-like formed in the suspension at 25°C.

In Figure 5, G' and G'' of the suspension are plotted against γ at various temperatures. At every temperature, G' and G'' stay constant up to the critical strain γ_c (4%) and G' is larger than G'' in $\gamma < \gamma_c$. These results also noted that all suspensions have the flocculated structure. With increasing temperature, the maximum peak of G'' in the high γ (nonlinear viscoelastic) region decreases. This result suggests that the number of

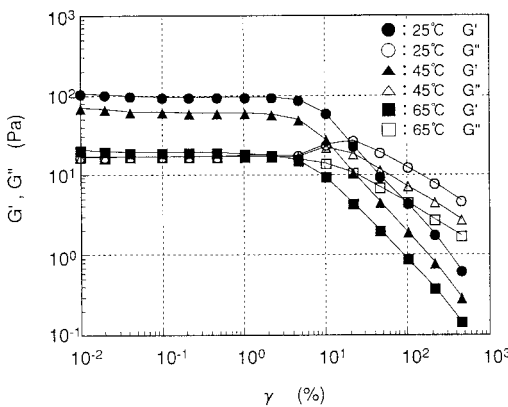


Figure 5 Storage modulus G' and loss modulus G'' plotted against strain amplitude γ of $1 \times 10^1 \text{ rad} \cdot \text{s}^{-1}$ for the suspension at 25, 45, and 65°C.

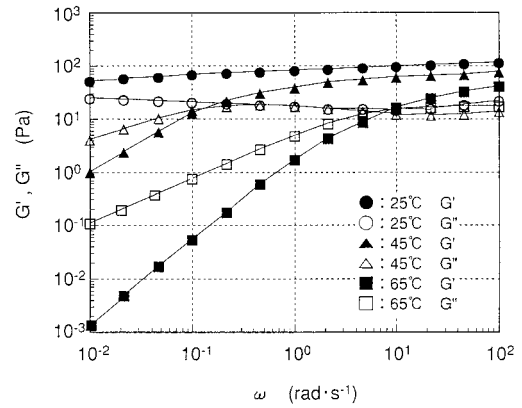


Figure 6 Storage modulus G' and loss modulus G'' plotted against angular frequency ω of linear region for the suspension at 25, 45, and 65°C,

the particles forming the lattice-like flocculated structure decreases with increasing the temperature. This hypothesis is supported by the fact that G' decreases in all γ regions with increasing the temperature.

In Figure 6, G' and G'' of the suspension are plotted against ω at various temperatures. With increasing temperature, G' and G'' decrease in all ω regions and ω dependencies of G' and G'' become stronger. At 65°C, viscoelastic behavior between G' , G'' , and ω is just liquid like. It is concluded from γ and ω dependencies of G' and G'' that there is isolated lattice-like flocculated structure in the suspension at 65°C.

Figure 7 demonstrates a master curve derived from Figure 6 by applying time-temperature superposition techniques.^{23,24} Data at different temperatures can be superimposed by horizontal translation along the log ω axis. No further vertical translation reveals that chemical potential

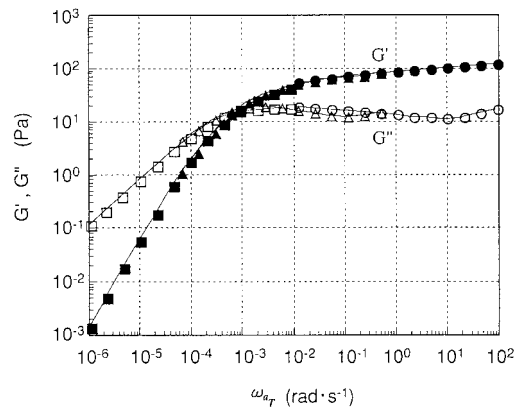


Figure 7 Master curve of G' and G'' .

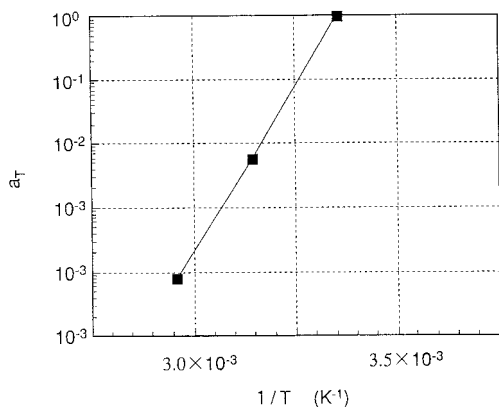


Figure 8 Shift factors a_T plotted against reciprocal temperature T^{-1} .

between the particles in the structure does not change with temperature. Apparent activation energy that is derived from the Arrhenius equation (1)

$$\ln a_T = A + \frac{E_V}{RT} \quad (1)$$

a_T : Shift factor
 E_V : Activation energy
 R : Gas constant
 T : Temperature
 A : Constant

using the shift factors a_T and a reciprocal temperature $1/T$ (Fig. 8) is 130 kJ/mol. This value will correspond to the depth of potential minimum between the particles in the lattice-like flocculated structure.

From these results it is found that the metastable lattice-like flocculated structure made of the carboxylated core-shell particle changes from three-dimensional network to the isolated one by the thermal motion with increasing temperature.

SAXS Measurements and Microstructure of the Suspension

SAXS profiles of the suspension at various temperatures are shown in Figure 9. At every temperature, a broad diffraction peak that suggests liquid-like paracrystal,^{25,26} is detected, and the height of the diffraction peak decreases with temperature. As the diffraction peak is generated from lattice-like flocculated structures, de-

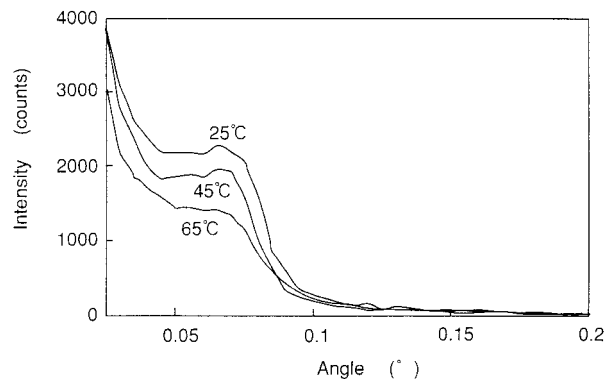


Figure 9 SAXS profiles of the suspension at 25, 45, and 65°C.

ing the height supports strongly that number of the particles in the lattice-like flocculated structures decrease with increasing the temperature. At every temperature, distance of center to center of the particles of the lattice-like flocculated structure was about 130 nm. This means the distance does not change with temperature, and the shell overlapped each other in the lattice-like flocculated structure (Fig. 10) because the diameter of the fully neutralized particle is 180 nm and that of the core is 100 nm.

Rheological behaviors and SAXS profiles clarify the microstructures in the aqueous suspension made of the carboxylated core-shell particle (Fig. 11). A three-dimensional network of interconnected lattice-like flocculated structure is formed in the suspension at 25°C [Fig. 11(a)]. With increasing the temperature, the network linkage disrupted partially by the thermal motion, and the interconnected lattice-like flocculated structure changed to the isolated lattice-like flocculated one. The isolated lattice-like flocculated one exists in the suspension at 65°C [Fig. 11(b)].

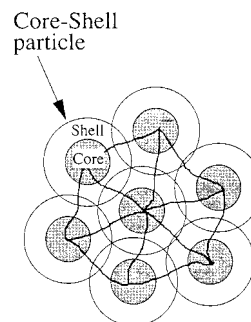


Figure 10 Schematic illustration of lattice-like flocculated structure of particles.

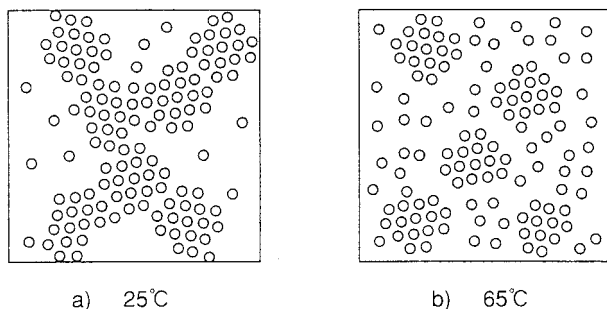


Figure 11 Schematic illustration of microstructure of suspension at 25 and 65°C,

Viscoelastic Behavior and SAXS Measurements at Various Degrees of Neutralization

In Figure 12, G' and G'' are plotted against γ for various degrees of neutralization at 25°C. With decreasing the degree of neutralization, G' decreases in all γ regions, and the maximum peak of G'' in the nonlinear viscoelastic region decreases. These results mean that changing the microstructure in the suspension with increasing the degree of neutralization is the same as that with decreasing the temperature. This is supported by G' and G'' plotted against ω (Fig. 13). With decreasing the degree of neutralization, ω dependencies of G' and G'' become stronger. Viscoelastic behavior changes from gel like to liquid like. At every degree of neutralization, the diffraction peak is detected by SAXS measurements, and the height of the diffraction peak decreases with decreasing the degree of neutralization (Fig. 14). This suggests that the number of the particles in the lattice-like flocculated structures decreases with de-

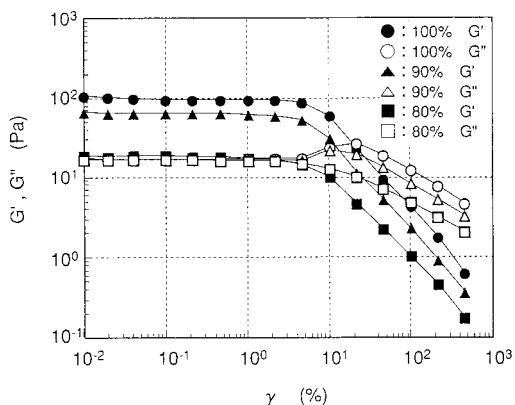


Figure 12 Storage modulus G' and loss modulus G'' plotted against strain amplitude for suspension at degree of neutralization 80, 90, and 100%.

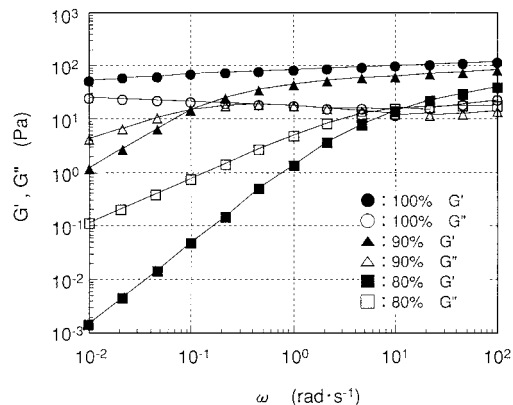


Figure 13 Storage modulus G' and loss modulus G'' plotted against angular frequency for suspension at degree of neutralization 80, 90, and 100%.

creasing the degree of neutralization. The distance of center to center of the particles of the lattice-like flocculated structure does not change with degree of neutralization.

After all, with increasing the degree of neutralization, an isolated lattice-like flocculated structure changes to a three-dimensional network of an interconnected lattice-like flocculated one with decreasing the thermal motion.

CONCLUSIONS

Core-shell type carboxylated particles form a lattice-like flocculated structure in aqueous suspension with neutralization of carboxyl groups. Microstructures made of the particle in the suspension change with temperature. A three-dimensional network of interconnected lattice-like flocculated structure formed in the suspension at

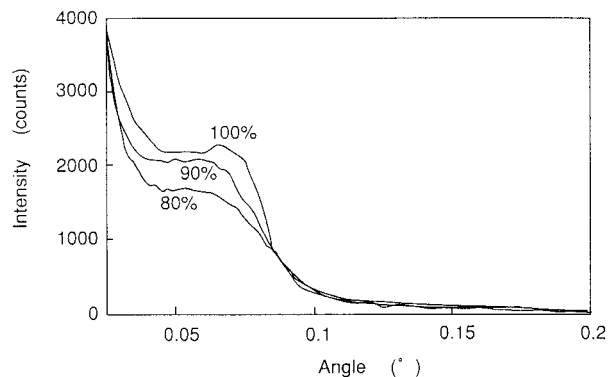


Figure 14 SAXS profiles of suspension at degree of neutralization 80, 90, and 100%.

25°C. With increasing the temperature, the network linkage was disrupted partially by thermal motion, and the interconnected lattice-like flocculated structure changes to the isolated lattice-like flocculated one. The isolate lattice-like flocculated structure exists in the suspension at 65°C.

The microstructure of the suspension with increasing the degree of neutralization is the same as that with decreasing the temperature.

REFERENCES

1. Jones, D. A. R.; Leary, B.; Boger, D. V. *J Colloid Interface Sci* 1991, 147, 479.
2. Jones, D. A. R.; Leary, B.; Boger, D. V. *J Colloid Interface Sci* 1992, 150, 84.
3. Mewis, J.; Frith, W. J.; Strivens, T. A.; Russel, W. B. *AIChE J* 1989, 35, 415.
4. Frith, W. F.; Strivens, T. A.; Mewis, J. *J Colloid Interface Sci* 1989, 139, 55.
5. Buscall, R.; McGowan, J. I.; Morton-Jones, A. J. *J Rheol* 1993, 37, 621.
6. Buscall, R. *Colloids Surfaces A* 1994, 83, 33.
7. Goodwin, J. W.; Ottewill, R. H. *J Chem Soc Faraday Trans* 1991, 87, 357.
8. Liang, W.; Tadros, Th.F.; Luckham, P. F. *J Colloid Interface Sci* 1992, 153, 131.
9. Liang, W.; Tadros, Th. F.; Luckham, P. F. *J Colloid Interface Sci* 1993, 155, 156.
10. Liang, W.; Tadros, Th. F.; Luckham, P. F. *J Colloid Interface Sci* 1993, 158, 152.
11. Shikata, T.; Pearson, D. S. *J Rheol* 1994, 38, 601.
12. Wagner, N. J.; Russel, W. B. *Phys A* 1989, 155, 475.
13. Bossis, G.; Brady, J. F. *J Chem Phys* 1989, 91, 1866.
14. van der Werff, J. C.; de Kruif, C. G.; Blom, C.; Mellema, J. *Phys Rev A* 1989, 39, 795.
15. Van Beelen, D.C.; Metzger, W.; Buter, R.; Lichtenbelt, J. W. Th. *Proc 15th IntConf in Org Coat Sci Technol* 1989, 39.
16. Vachlas, Z. *J Oil Color Chem Assoc* 1989, 77, 139.
17. Quadrat, O. *J Appl Polym Sci* 1988, 35, 1.
18. Quadrat, O.; Mrkvickova, L.; Snuparek, J. *J Colloid Interface Sci* 1988, 123, 35.
19. Nakamura, H.; Tachi, K. *J Soc Rheol Jpn* 1996, 24, 133.
20. Nakamura, H.; Tachi, K. *J Soc Rheol Jpn* 1996, 25, 283.
21. Nakamura, H.; Tachi, K. *J Soc Rheol Jpn* 1996, 26, 95.
22. Muroi, S.; Hashimoto, H.; Hosoi, K. *J Appl Polym Sci* 1984, 22, 1365.
23. Hoy, K. L. *J Coat Technol* 1979, 51, 27.
24. O'Callaghan, K. J.; Paine, J.; Rudin, A. *J Polym Sci A* 1995, 33, 1849.
25. Devon, M. J.; Gardon, J. L.; Roberts, G.; Rudin, A. *J Appl Polym Sci* 1990, 39, 2119.
26. Matsuoka, H.; Murai, H.; Ise, N. *Phys Rev B* 1988, 37, 1368.
27. Matsuoka, H.; Tanaka, H.; Hashimoto, T.; Ise, N. *Phys Rev B* 1987, 36, 1754.
28. Butera, R. J.; Wolfe, M. S.; Bender, J.; Wagner, N. J. *Phys Rev Lett* 1996, 77, 2117.