Effect of surfactant adsorption on the rheology of suspensions flocculated by associating polymers

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Abstract

Associating polymers act as flocculants in colloidal suspensions, because the hydrophobic groups (hydrophobes) can adsorb onto particle surfaces and create intermolecular cross-linking. The steady-shear viscosity and dynamic viscoelasticity were measured for suspensions flocculated by multichain bridging of associating polymers. The effects of surfactant on the suspension rheology are studied in relation to the bridging conformation. The surfactant molecule behaves as a displacer and the polymer chains are forced to desorb from the particle surfaces. The overall effect of surfactant is the reduction of suspension viscosity. However, the additions of a small amount of surfactant to suspensions, in which the degree of bridging is low, cause a viscosity increase, although the number of chains forming one bridge is decreased by the forced desorption of associating polymer. Since the polymer chains desorbed from one bridge can form another bridge between bare particles, the bridging density over the system is increased. Therefore, the surfactant adsorption leads to a viscosity increase. The surfactant influences the viscosity in two opposing ways depending on the degree of bridging.

Keywords : suspension rheology, associating polymer, bridging flocculation, surfactant adsorption, shear-thickening flow

1. Introduction

Associating polymers are hydrophilic long-chain molecules which contain a small amount of hydrophobic groups. The hydrophobic groups (hydrophobes) can be randomly distributed along the water-soluble backbone or incorporated as terminal groups. In aqueous solution, the hydrophobes tend to aggregate and create a bond between polymer chains by associating interactions. The associating polymers end-capped with hydrophobes form flowerlike micelles beyond a critical micellar concentration(Wang and Winnik, 1990). One micellar cluster is built up by 10~80 molecules (Pham et al., 1999). In dilute solutions of multisticker polymers, intrachain associations cause a reduction in chain size and a decrease in intrinsic viscosity(Lau et al., 2002). When the polymer concentration is increased, two flowerlike micelles are connected by bridging for polymers with hydrophobic endgroups. In solution of multisticker polymers, the aggregation of two or more hydrophobes from different chains takes place. Thus a three-dimensional structure of association network can be

constructed in semidilute solutions of associating polymers. Due to interchain associations, the solutions of associating polymers exhibit peculiar rheological properties. The most interesting effect is a shear-thickening flow curve(Jenkins et al., 1991; Jimenez-Regalado et al., 2000; Tan et al., 2000). Witten and Cohen (1985) have explained that the shear-thickening flow of solutions of multisticker polymers arises from the shear-induced formation of interchain associations at the expense of intrachain association.

The addition of low concentrations of polymer often leads to flocculation in colloidal suspensions by bridging, in which one polymer chain simultaneously adsorbs onto two particles (Iler, 1971; Fleer and Lyklema, 1974). The hydrophobes can adsorb onto the particle surfaces. Therefore, the associating polymers act as flocculants in colloidal suspensions. In the presence of associating polymers at low concentrations, the suspensions are flocculated by bridging (Sperry et al., 1987). At relatively high concentrations, the associating polymers can induce depletion flocculation in similar manner that the suspensions containing nonadsorbing polymer are flocculated (Santore et al., 1990a; 1990b). Depending on the population of hydrophobes per molecule and adhesion energies for hydrophobe-hydrophobe and hydrophobe-surface, the suspen-

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sions are flocculated by different mechanisms. The associating polymers are very attractive as thickeners for paints and inks. For accurate control of rheological properties in application to coating and printing technology, it is essential to understand the associating interactions between polymer chains and particle surfaces.

In a previous paper (Horigome and Otsubo, 2002), we studied the rheological properties of suspensions flocculated by bridging of associating polymers and discussed two important features. One is the Newtonian flow at very low shear rates. No yield stress is generated irrespective of degree of flocculation and the suspensions behave as liquids in the limit of zero shear rate. The other is the complicated effect of polymer concentration. The degree of flocculation and in turn the viscosity of suspensions are expected to monotonously increase with polymer concentration, because the polymer chains contribute to the bridging of particles. However, the rheological values such as viscosity, elasticity, and relaxation time, are not given by a simple function of polymer concentration. The particle-particle interactions resulting in these unique rheological properties can be coupled with the weak adsorption affinity of polymer chains for particle surfaces. It is of interest to examine the relation among the adsorption affinity, bridging conformation and suspension rheology. In the present study, the effect of surfactant on the rheological properties is discussed for suspensions flocculated by bridging of associating polymers.

2. Experimental

2.1. Materials

The suspensions were composed of styrene-methyl acrylate copolymer particles, associating polymer, surfactant, and water. The polymer particles with a diameter of 250 nm were formed by emulsion polymerization. The stock suspension without polymers was electrostatically stabilized. The associating polymer was hydrophobically modified ethoxylated urethane (HEUR) (RM-825 from Rohm and Haas), the molecular weight of which was about 2.5×10^4. The hydrophobes are incorporated on the ends of molecule as terminal groups. The suspensions were prepared at a particle concentration of 30% by volume. The polymer and surfactant concentrations were in the range of 0−1.5% by weight based on the water. The rheological measurements were carried out after the suspensions were stored under gentle shear on a rolling device for one week. Because of initial conditioning prior to measurements, the results were highly reproducible.

2.2. Methods

Steady-shear viscosity and dynamic viscoelasticity were measured using a parallel plate geometry on a stress-controlled rheometer (Haake Rheo-Stress RS100). The diam-
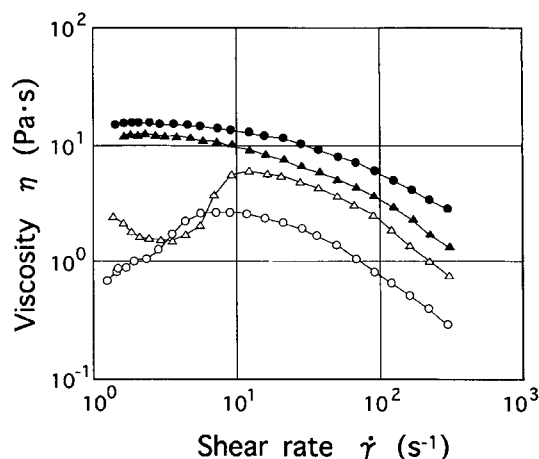

Fig. 1. Shear rate dependence of viscosity for suspensions in solutions of associating polymer at different concentrations: 0.1 (O); 0.3 (△); 0.5 (▲); 1.0 wt% (●).

eter of plates was 35 mm and the gap between two plates was 0.8 mm. The viscosity was determined in the range of shear rates from 1.1×10^0 to 3.0×10^2 s^{-1}. The dynamic viscoelastic functions (G, G") were measured as a function of frequency at small strains in the linear regions and as a function of strain at a constant frequency. The frequencies were from 6.3×10^{-2} to 6.3×10^1 s^{-1} and strain amplitude was from 2.0×10^{-3} to 2.0×10^1. The temperature was 25°C for all runs.

The suspensions were centrifuged at 1000 g for more than 20 h. The final sedimentation volume gives the concentration of the dispersed phase, from which the surface separation in the flocs can be determined. The amount of polymer adsorbed on the particles was also calculated from the viscosity of supernatant solution.

3. Results

Fig. 1 shows the shear rate dependence of viscosity for suspensions in aqueous solutions of associating polymer at different concentrations. The 30 vol% suspension without additives is electrostatically stabilized and Newtonian with a viscosity of 3.5×10^{-3} Pas. The addition of polymer causes a drastic increase in viscosity and the suspensions may be highly flocculated. In ordinary flocculated suspensions, the flow is shear-thinning in a wide range of shear rates. When the three-dimensional network of flocs is developed over the system, the flocculated suspensions show the plastic responses. The general agreement with respect to the flow curve of flocculated suspensions is that with increasing degree of flocculation, the viscosity increases and the shear-thinning tendency becomes striking. However, the viscosity behavior of sample suspensions is quite different. The interesting features can be summarized as follows. First, the suspensions prepared with dilute

polymer solutions show shear-thickening flow. The shear-thickening flow is reported for concentrated suspensions of noninteracting particles (Hoffman, 1972; Strivens, 1976; Barnes, 1989), but hardly observed for flocculated suspensions. Secondly, at polymer concentrations of 0.5wt% and above, the viscosity is constant at low shear rates. Even in highly flocculated states, the suspensions are Newtonian in the limit of zero shear rate.

Fig. 2 shows the frequency dependence of storage modulus G' for suspensions at different polymer concentrations. It is well known that the viscoelastic functions of highly flocculated suspensions show a plateau at low frequencies. The elastic responses in plateau region imply the existence of three-dimensional network structures of particles (Otsubo, 1990). However, the clear plateau was not observed for the sample suspensions. Although the shoulder is considered to be an indication of additional relax-

ation process due to the flocculated structure, the modulus rapidly decrease with decreasing frequency. The lack of plateau in frequency-dependent curve can be attributed to the rapid dissipation of strain energy stored in deformed network.

Fig. 3 shows the strain dependence of storage modulus at an angular frequency of 6.28 s^{-1} (1 Hz) for suspensions at different polymer concentrations. In many cases, the storage and loss moduli of flocculated suspensions are constant at very low strains and drastically decrease with increasing strain. The sharp decrease of moduli can be related to the breakdown of internal structures.

However, except at 0.1 wt%, the storage modulus of the sample suspensions shows an increase, as the strain amplitude exceeds some critical levels. The critical strain is in the range to 1~3. Considering that the shear-thinning flow and sharp drop of storage modulus at large strains which are generally observed for ordinary flocculated suspensions can be due to the structural rupture induced by shear, the increase of storage modulus in oscillatory shear reflects the same rheology as the shear thickening in steady shear. The suspensions flocculated by associating polymers are highly elastic under large strains.

In typical associating polymers, the hydrophobes consist of long alkyl chains (C_{12}~C_{18}), the molecular structures of which are very similar to nonionic surfactants. The surfactant molecules can create micelles and adsorb onto the solid surfaces in solution. Since the association and adsorption processes of associating polymers may be strongly affected by surfactant, it is important to examine the rheological properties of suspensions in the presence of surfactant.

Fig. 4 shows the shear rate dependence of viscosity for suspensions in 0.5 wt% polymer solutions containing sur-
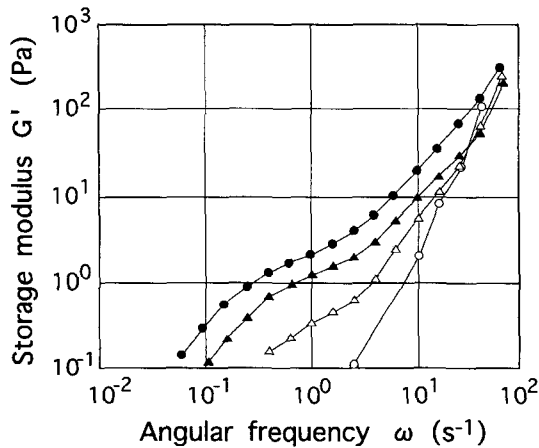

Fig. 2. Frequency dependence of storage modulus for suspensions at different polymer concentrations: 0.1 (○); 0.3 (△); 0.5 (▲); 1.5 wt% (●).
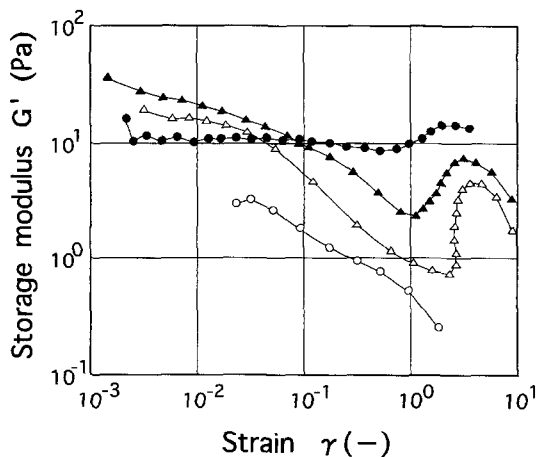

Fig. 3. Strain dependence of storage modulus at an angular frequency of 6.28 s^{-1} for suspensions at different polymer concentratins: 0.1 (○); 0.3 (△); 0.5 (▲); 1.0 wt% (●).
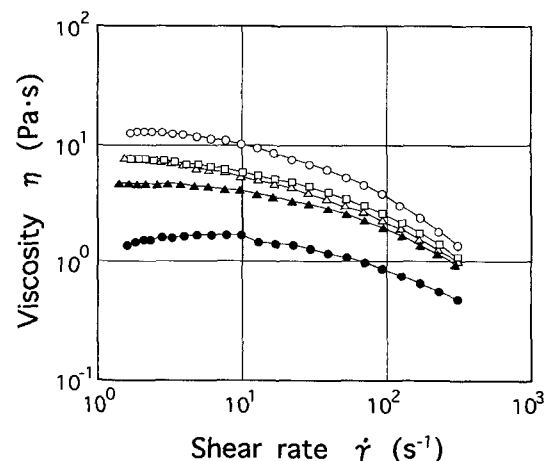

Fig. 4. Shear rate dependence of viscosity for suspensions in 0.5 wt% polymer solutions containing surfactant at different concentrations: 0 (○); 0.3 (△); 0.5 (□); 1.0 wt% (▲); 1.5 wt% (●).
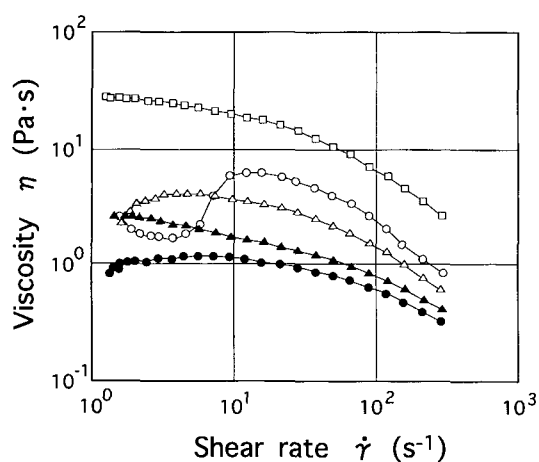
Fig. 5. Shear rate dependence of viscosity for suspensions in 0.3 wt% polymer solutions containing surfactant at different concentrations: 0 (○); 0.3 (△); 0.5 (□); 0.7 wt% (▲); 1.0 wt% (●).

Fig. 6. Strain dependence of storage modulus at an angular frequency of 6.28 s^{-1} for suspensions in 0.3 wt% polymer solutions containing surfactant at different concentratins: 0 (○); 0.3 (△); 0.5 (□); 0.7 wt% (▲); 1.0 wt% (●).

factant at different concentrations. From the concentration dependence of viscosity behavior shown in Fig. 1., the flocculation level seems to near the saturation at polymer concentration of 0.5 wt%. The viscosity decreases with increasing surfactant concentration. It looks likely that the additions of surfactant contribute to the decrease in degree of flocculation, when the suspensions are flocculated to a great extent.

Fig. 5 shows the shear rate dependence of viscosity for suspensions in 0.3 wt% polymer solutions containing surfactant at different concentrations. Because of low concentration of polymer, the flocculation still does not reach the saturation. Although the monotonous decrease of viscosity with increasing surfactant concentration can be easily predicted from the results in Fig. 4, the effect of surfactant on the viscosity behavior is very complicated. The addition of 0.3 wt% surfactant causes a viscosity increase at low shear rates and a decrease at high shear rates. As a result, the viscosity behavior changes from shear-thickening to shear-thinning curves. At 0.5 wt%, the suspension shows a higher viscosity than that without surfactant over the entire range of shear rates. The flocculating power of polymer can be enhanced by surfactant. However, when the surfactant concentration is increased above 0.7 wt%, the viscosity is drastically decreased. From Fig. 4 and 5, it is interesting to note that the surfactant influences the viscosity in two opposing ways depending on the flocculation level.

Fig. 6 shows the strain dependence of storage modulus for suspensions in 0.3 wt% polymer solutions containing surfactant at different concentrations. When the surfactant is added, the jump of storage modulus at large strains disappears and this behavior can be related to the conversion of flow curve from shear thickening to shear thinning in
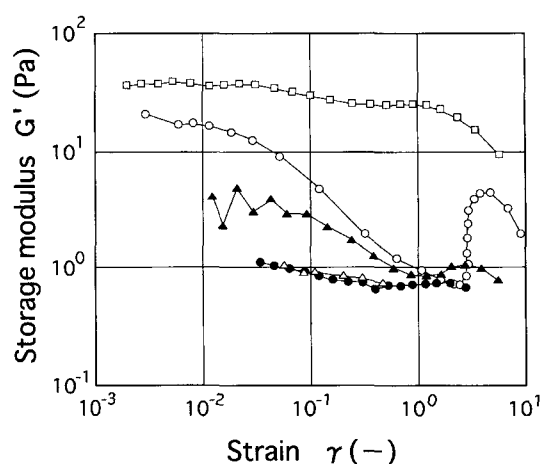
Fig. 5. At low strains the storage modulus decreases at first, increase and then decreases as the surfactant concentration is increased. Presumably we can prepare a suspension containing surfactant, whose storage modulus in linear ranges is comparable to that without surfactant. However, this suspension would show a monotonous decrease of storage modulus with increasing strain. The difference in curve shapes of two suspensions suggests that the dynamic structures at large strains should be quite different.

Through the rheological measurements, the adsorption conformation of associating polymer and particle-particle interactions can be strongly influenced by surfactant. To understand the flocculation mechanism, the sedimentation experiments were carried out.

Fig. 7 shows the polymer concentration dependence of the sedimentation volume and viscosity of supernatant solution for suspensions in the absence of surfactant. At 0.5 wt% and below, the viscosity of supernatant solution is about 0.9 mPas and this value is the same as water viscosity. All polymer chains are considered to adsorb onto the particle surfaces in dilute solutions. The viscosity begins to increase at 0.7 wt%, where the polymer adsorption exceeds the saturation and the small amount of non-adsorbing chains remains in solution phase. When the polymer concentration is increased up to 1.0 wt%, the suspension was not separated by centrifugation. The flocculated structures are fully developed over the system. From Fig. 1 showing that the viscosity level approaches the equilibrium as the polymer concentration is increased, the full coverage of particle surfaces with polymer chain can be achieved at 0.5 wt%. The polymer adsorbance at saturation is estimated to be 0.5 mgm^{-2}.

Fig. 8 shows the effect of surfactant concentration on the sedimentation volume and viscosity of supernatant solution
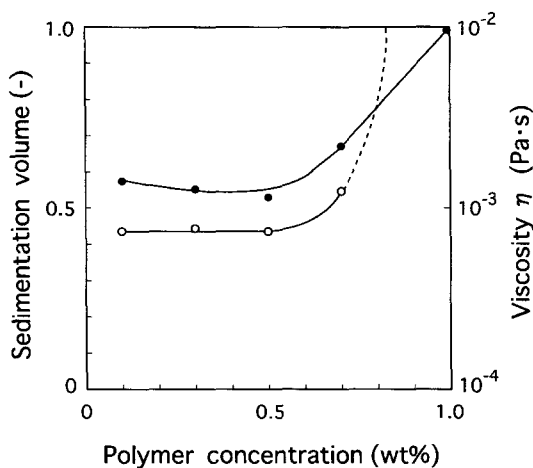
Fig. 7. Sedimentation volume (●) and viscosity of supernatant solution (○) plotted against the polymer concentration for suspensions without surfactant.
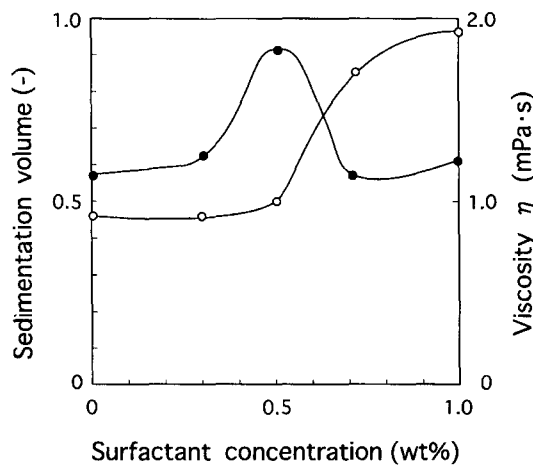

Fig. 8. Sedimentation volume (●) and viscosity of supernatant solution (○) plotted against the surfactant concentration for suspensions containing associating polymer at 0.3 wt%.

for suspensions containing associating polymer at 0.3 wt%. The viscosity of supernatant solution is 0.9~1.0 mPas at surfactant concentrations below 0.5 wt%. The solution phase may contain no residual chains. At 0.7 wt%, the viscosity begins to increase and hence the surfactant contributes to the desorption of polymer chains. On the other hand, the sedimentation volume shows a maximum at a surfactant concentration of 0.5 wt%. In flocculated suspensions, the formation of flocs traps part of the continuous medium and leads to a larger effective volume of dispersed phase than that of the primary particles. The increase in sedimentation volume implies the development of highly flocculated structures. Although the reduction of degree of flocculation can be induced above 0.7 wt%, it must be stressed that the flocculation is enhanced by the additions of small amount of surfactant.

4. Discussion

Assuming that the particles are arranged in random sphere packing in the sediment, the surface separation is determined from the mean distance between particle surfaces. For suspensions prepared with 0.3 wt% polymer solution, the values determined are 16.3 nm and 60 nm at surfactant concentrations of 0 and 0.5 wt%, respectively. For suspensions flocculated by bridging of associating polymer, we have previously reported (Horigome and Otsubo, 2002) that the bridging distance is about 16 nm when one polymer chain is directly adsorbed onto two particles. The surface separation without surfactant is comparable to the bridging distance of direct connection. Although the addition of small amount of surfactant gives rise to a drastic increase in surface separation, the system is still regarded as flocculated by bridging mechanism. The bridging conformation of associating polymer must be strongly influenced by surfactant.

When the particles are partially covered with surfactant, the sites available for polymer adsorption decrease and the polymer segments are forced to desorb from the particle surfaces. The surfactant molecule serves as a displacer. Therefore, the chains may adopt a stretched conformation with only one hydrophobe attached to the surface. The hydrophobes extending into the solution can form micelles which can influence the particle-particle interactions or bridging conformation. The multichain bridging due to micellar formation might account for the large value of surface separation.

The multichain bridges may be weak to external forces and constantly forming and breaking by thermal energy in a quiescent state. The reversible bridging is supported by a fact that the Newtonian flow is observed in the limit of zero shear rate even for highly flocculated suspensions. The reasonably accepted effect of surfactant adsorption would be the reduction of strength of individual bridges. The polymer bridges are broken down at high surfactant concentrations. However, the viscosity as a macroscopic response of suspensions is increased by the addition of small amounts of surfactant. Although the particle-particle interactions are the most important factor, the geometrical structures of flocs are also closely connected with suspension rheology. In general, the rheological properties of suspensions are drastically changed when the flocs cease to be discrete and a network structure is formed above some critical particle concentration. The distribution of particles in the flocs and the network formation process are described through percolation concept (Mall and Russel, 1987; Otsubo and Nakane, 1991). Percolation theory deals with the distribution of cluster sizes for particles distributed in an infinite lattice composed of sites linked together by bonds. In suspensions flocculated by polymer bridging, the flocs are considered to consist of sites (particles) connected

by bonds (bridges). The effect of polymer bridging on the floc structure can be analyzed as the bond percolation process and the network of unbounded floc is constructed when the bridging density exceeds a critical probability p_c^B. According to the empirical equation (Ziman,1968) for the bond problem, the percolation threshold for various three-dimensional lattices is $zp_c^B \sim 3/2$, where z is the coordination number. If the particles build up a floc structure whose coordination number z is 6, the critical bond probability would be 0.25. Since the full bridging ($p_c^B=1$) is established at polymer concentration of 0.5 wt% from Fig. 1 and 7, the suspension containing 0.3 wt% polymer is regarded as a percolating system.

The surfactant adsorption causes the forced desorption of associating polymer and the reduction of number of polymer chains forming one bridge. Unless the degree of bridging reaches the saturation in the absence of surfactant, the desorbed chains have the chances for adsorption to another bare particles. The bridging density can be increased by the additions of small amount of surfactant. For percolating systems, the scaling arguments predict that the rheological quantity show a power law dependence on the difference of bridging density from the critical value. Therefore, the increase in the bridging density can lead to a drastic effect on the suspension rheology. The viscosity increase induced by surfactant can be explained through percolation and scaling concepts, although the strength of individual bridges is reduced.

The suspensions in which the degree of bridging is low under the saturation adsorption show shear-thickening flow. From Fig. 3, the storage modulus of shear-thickening suspensions shows a sharp increase, as the strain amplitude is increased up to 1~3. Based on the statistical mechanical model (Vrahopoulou and McHugh, 1987), the shear-thickening flow can be explained by the decrease in entropy of polymer chains in the network during extension under shear field. In the suspensions, the extension of bridges may be responsible for the increase in resistance to flow. In a previous paper (Otsubo, 1992; 1999), the shear-thickening flow of suspensions flocculated by reversible bridging of nonassociating polymers is discussed in connection with the elastic properties under large strains. To quantitatively describe the shear-thickening behavior, a nonlinear elastic model is derived. In a similar manner, the shear-thickening flow of suspensions flocculated by associating polymer can be primarily attributed to the elastic effect of extended bridges, because the elastic and deformable flocs are built up by multichain bridges in suspensions. When the bridges are subjected to rapid extension at shear rates where the time scale of extension is much shorter than that of desorption of polymer chains, the extended bridges can generate the high resistance to flow due to the restoring forces. The restoring forces produced by rapid extension of flexible bridges are responsible for the shear thickening.

5. Conclusions

At low concentrations of associating polymer, the flow of suspensions is shear-thickening. Since the deformable flocs are built up by multichain bridges in suspensions, the extended bridges can lead to high resistance to flow due to the restoring forces. The elastic effects of flexible bridges are responsible for shear- thickening flow.

The surfactant influences the viscosity of suspensions flocculated by associating polymers in two opposing ways depending on the degree of bridging. The surfactant molecule behaves as a displacer and the polymer chains are forced to desorb from the particle surfaces. The overall effect of surfactant is the reduction of viscosity. However, the additions of a small amount of surfactant to suspensions, in which the degree of bridging is low, cause a viscosity increase. This is attributed to the increase in bridging density in the system, because the polymer chains desorbed from one bridge can form another bridge between bare particles.

Acknowledgments

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