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Effect of Shear Flow on Polymer Desorption and Latex Dispersion Stability in the Presence of Adsorbed Polymer

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ABSTRACT: Poly(ethylene oxide) (PEO) and poly(vinyl alcohol) (PVA) molecules were adsorbed on polystyrene (PS) latex as stabilizing agents for the latex dispersion. The effect of shear flow on the desorption of the adsorbed polymer and the flocculation of the latex were investigated by measuring the hydrodynamic layer thickness of the adsorbed polymer and the average particle diameter of the latex with photon correlation spectroscopy (PCS), respectively. For PEO molecules with molecular weights of 100 000 and 900 000, shear flow caused the layer thickness of the adsorbed polymer to decrease rapidly in the early stage and then approach a steady-state value. The average particle diameter showed little change for a short period followed by a rapid increase during the flocculation. The shear rate and molecular weight affected negligibly the layer thickness but considerably the average particle diameter. On the other hand, the layer thickness of the adsorbed polymer showed a small reduction only at a higher shear rate for PVA of molecular weight 15 000. The flocculation behavior was similar to the case of PEO molecules. For PVA with molecular weight 49 000, there was no change of the layer thickness but a slight increase of the average particle diameter after a long shearing time. It was assumed that PVA molecules had a higher resistance to the shear-induced desorption than PEO molecules because of the strong hydrophobic interaction of residual acetate groups in PVA with the surface of PS latex. The shear-induced desorption influenced strongly the flocculation of the latex stabilized with adsorbed polymer.

Introduction

Polymer adsorption has attracted considerable attention in recent years for the control of dispersion stability. Most works have been devoted to the effect of adsorbed polymer on the stability in the quiescent state and few studies have been done for the flowing system.[1-5] However, most practical applications involve a flow field, e.g., waste water purification, mineral processing, and pigment dispersion. Adsorbed polymer in the flow can affect the dispersion stability in two ways. First, polymer preadsorbed on the surface of a particle may be deformed or desorbed under the flow.[6-8] Such changes could influence the dispersion stability. Second, the flocculation rate may increase with the collision frequency of particles in the flowing system.

Conformational changes of adsorbed polymer could be induced by shear flow[6,7] or by elongational flow.[8] This was investigaged for the PS/cyclohexane/chrome plate system by using ellipsometry. In the shear flow,[6,7] the desorption was initially rapid, becoming negligible after a long period, and increased with the shear rate and molecular weight. The shear-induced desorption did not influence greatly the layer thickness, except for the very high molecular weight polymer. This means that there was little effect of flow on the conformational change in the adsorbed layer. In the elongational flow[8] generated by a jet flow, a "bull's-eye" pattern was observed, showing the region of adsorption of polymer at the center by the elongational flow, a region of shear-induced desorption, and the outer region of polymer adsorbed under equilibrium condition.

Although it has been well established that charge-stabilized dispersions[9-12] and ones with adsorbed surfactant molecules[1-4] could be aggregated under shear flow, there are few studies on the effect of shear flow on the stability of the dispersion stabilized with adsorbed polymer. To understand the shear flocculation of the dispersion in the presence of adsorbed polymer, the flow-induced desorption as well as the hydrodynamic force must be considered. In addition, the desorption may be determined by the interaction force of the polymer with the surface of the adsorbing substrate and by the hydrodynamic force of the solvent exerted on the adsorbed layer. This leads to the consideration of the polymer–surface interaction in the flow-induced desorption and flow stability as well.

The objective of this work is to study the shear-induced desorption of adsorbed polymer from the latex surface and its effect on the shear stability. In addition, we will investigate the influence of the polymer–surface interaction on the shear-induced desorption and on the shear flocculation.

Experimental Section

Materials. PS latex was prepared by an emulsifier-free dispersion polymerization using potassium persulfate as the initiator following the method of Goodwin et al.[13] The styrene monomer was vacuum-distilled prior to use. The latex was dialyzed against distilled water for ca. 3 weeks. It was monodisperse with an average diameter of 263 ± 5 nm from transmission electron microscopy and 265 ± 4 nm from PCS. The solids content determined by evaporation was 3.57 wt %.

PEO and PVA with 12 wt % acetate content were used. Samples of PEO and PVA were purchased from Aldrich Chemical Co. and Fluka Chemie, A.G., respectively. Their nominal molecular weights are listed in Table I.

All of the water used was distilled twice, and the electrolyte, NaCl, was analytical grade.

Latex samples of 1.40 g were accurately weighed into stoppered tubes, and 100 cm^3 of the 1000 ppm polymer solution was added. This amount of polymer was large enough to obtain saturated surface coverage according to our preliminary work. The solution was left to equilibrate for 24 h.

The critical flocculation concentration (CFC) of electrolyte was determined by measuring the average particle diameter of the latex as a function of electrolyte concentration. The average particle diameter was measured 1 h after the electrolyte and latex solutions were mixed.

The shear experiments were performed in a Haake-Rotovisco Model PK 100 cone-and-plate viscometer, where the cone's radius

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Table I
Nominal Molecular Weight (M_w) and Hydrodynamic Layer Thickness (δ_H) for Polymers Used in This Work

polymer	M_w	δ_H, nm
PEO-100000	100 000	28
PEO-900000	900 000	72
PVA-15000	15 000	12
PVA-49000	49 000	38

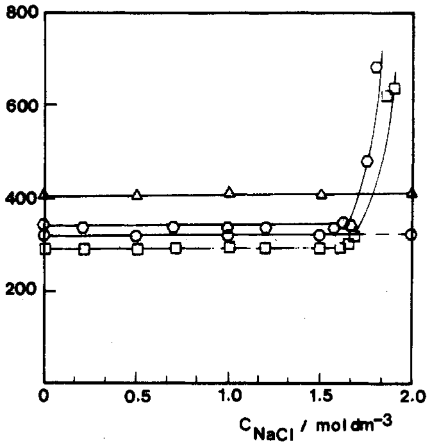

Figure 1. Variation of average diameter with NaCl concentration in the presence of adsorbed polymer: (○) PEO-100000; (△) PEO-900000; (□) PVA-15000; (<ex) PVA-49000.

is 36.0 mm and its angle is 52.4 mrad. In the shear-induced desorption, the latex without electrolyte was tested. However, the latex with various concentrations of electrolyte was used in order to see the effect of an electrostatic repulsive force on the shear flocculation. After the desired solution was made, it was immediately placed onto the plate of the viscometer, and the shearing was started. After exposure to the shear for the desired time, the flow was stopped. The sheared sample was immediately diluted to prevent further change, and the average particle diameter was measured as soon as possible. Experiments, however, showed little change in the average particle diameter during 2–4 h of storage. All shear experiments were performed at a fixed latex concentration of 2.5 × 10^{-4} w/w, 20 °C, and three different shear rates. The average particle diameter was measured by using PCS. The shear-induced desorption and shear flocculation were determined from the reduction of the hydrodynamic layer thickness and from the increase of the average particle diameter, respectively. The PCS equipment consists of a He–Ne laser operating at 633 nm, a Malvern Instruments spectrometer, and a multichannel correlator. The light scattered at 90° is detected by a photomultiplier.

Results and Discussion

Critical Flocculation Concentration. Figure 1 shows the average diameter variation of the latex with adsorbed polymer for various NaCl concentrations. The average diameter remains virtually constant up to the CFC but increases sharply beyond the CFC. The CFC was found to be 1.50 mol dm^{-3} for PVA-15000 and 1.55 mol dm^{-3} for PVA-49000. In the case of PEO molecules, however, no such break point corresponding to the CFC was observed up to 2.5 mol dm^{-3}. The NaCl concentration could not be extended because of its limited solubility. The latex dispersions stabilized with PEO molecules are more stable toward the addition of NaCl than those stabilized with PVA molecules. Tadros and Vincent[14] also observed a similar trend for various electrolytes.

Shear-Induced Desorption. The hydrodynamic layer thicknesses of adsorbed polymer in the quiescent condition are given in Table I. The effects of shear flow on the layer thickness are shown in Figures 2–4. The layer thicknesses in Table I and Figures 2–4 were measured in the absence of added electrolytes, respectively. The variation of layer thickness is plotted as a function of time and shear rate. Figure 2 shows that the layer thickness decreases abruptly in the early stage after the inception of shear flow and then approaches a steady state. Figure 3 shows a similar variation of the layer thickness for PEO-900000 to that for PEO-100000. It is seen from Figures 2 and 3 that the effect of shear rate is negligible. As the molecular weight increases, polymer chains make multiple points of contact with the latex surface. This may make the simultaneous disengagement of these contacts difficult. In addition, entanglement of polymers at the latex surface prevents the diffusion of detached polymer chains to the bulk phase. Therefore, the results in Figures 2 and 3 are not consistent with the overall trend that higher molecular weight polymer chains are more difficult to be desorbed. This

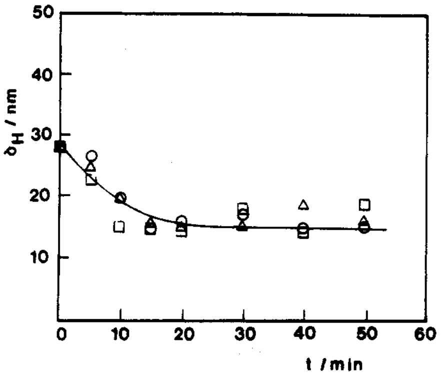

Figure 2. Layer thickness behavior with time at different shear rates for the latex with adsorbed PEO-100000 without NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

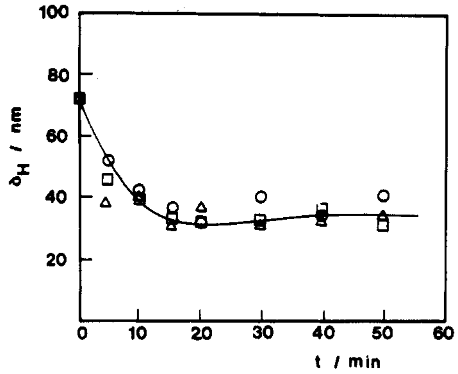

Figure 3. Layer thickness behavior with time at different shear rates for the latex with adsorbed PEO-900000 without NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

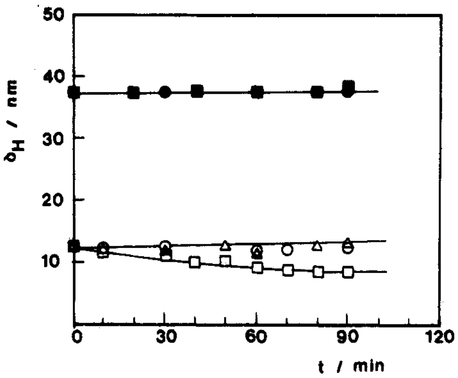

Figure 4. Layer thickness behavior with time at different shear rates for the latex with adsorbed PVA molecules without NaCl: (○, ●) 8000 s^{-1}; (△, ▲) 12 000 s^{-1}; (□, ■) 16 000 s^{-1}. Unfilled and filled symbols refer to PVA-15000 and PVA-49000, respectively.

may be due to the relatively high shear rates for weakly attached PEO molecules on the latex surface.

Figure 4 shows that a reduction in layer thickness is observed only at the highest shear rate of 16 000 s^{-1} for PVA-15000 but that no reduction is detected at all shear rates for PVA-49000. A mechanism of flow-induced desorption has been proposed[7] that would be compatible with the results shown in Figures 2–4. Polymer chains attached weakly to the surface are first desorbed, leaving strongly attached molecules behind. This results in an initially rapid decrease of the layer thickness followed by the obtainment of a steady-state value.

PVA molecules are more stable against the shear-induced desorption although PVA molecules have much lower molecular weights when compared with PEO molecules. PVA is known to be irreversibly adsorbed[15] even at this low molecular weight because of the strong hydrophobic interaction of the preferentially adsorbed residual acetate groups with the surface of the PS latex. No similar interaction occurs between PEO and PS latex in an aqueous solution, and it is likely that PEO is more easily desorbed from the latex surface under shear flow. This indicates that the polymer–surface interaction is a very important factor in the shear-induced desorption.

It is of interest to compare our results with those reported by Lee and Fuller.[7] They used three high molecular weight PS polymers at the θ condition and observed that the reduction in layer thickness increased with increasing molecular weight. We have used lower molecular weight polymers, and the results in Figure 4 are not consistent with those of Lee and Fuller. As predicted by Scheutjens and Fleer,[16] the conformation of a high molecular weight homopolymer will consist of very long dangling ends connected by relatively short loops and trains. On the other hand, the copolymer, which has preferentially adsorbable groups, will not have the weakly attached dangling ends. Such ends can be desorbed easily and play a major role in determining the hydrodynamic layer thickness.[17] Therefore, generally one would observe a larger reduction in layer thickness for the higher molecular weight homopolymer such as the PS used by Lee and Fuller and the PEO studied here. However, in the case of a copolymer such as partially hydrolyzed PVA, we must consider the conformation of the adsorbed polymer, the interaction of the adsorbing polymer with the adsorbent, and the degree of copolymerization as well as molecular weight. As the molecular weight of PVA increases, the adsorption force of the preferentially adsorbed acetate groups is likely to be increased, and, therefore, the reduction of the layer thickness will be decreased under shear flow. Lee and Fuller also showed that normalized steady-state adsorbance could be scaled with the shear rate and molecular weight. Unfortunately, we could not measure the desorption amount. Since the layer thickness is determined by the conformation, the surface coverage and adsorption amount of the adsorbed polymer, and the solvency of the solvent, it is very difficult to compare our results with those of Lee and Fuller.

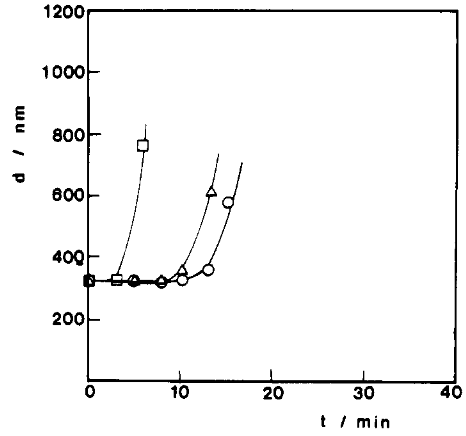

Figure 5. Average diameter behavior with time at different shear rates for the latex with adsorbed PEO-100000 in 0.50 mol dm^{-3} NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

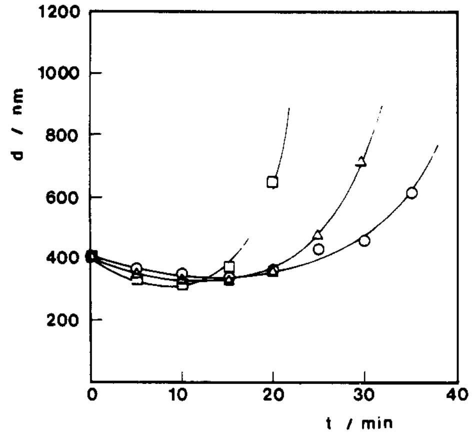

Figure 6. Average diameter behavior with time at different shear rates for the latex with adsorbed PEO-900000 in 0.50 mol dm^{-3} NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

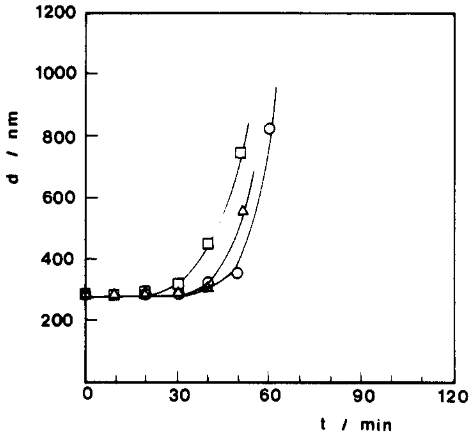

Figure 7. Average diameter behavior with time at different shear rates for the latex with adsorbed PVA-15000 in 0.50 mol dm^{-3} NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

Shear Flocculation. All experiments were conducted at a NaCl concentration of 0.50 mol dm^{-3}, which is high enough to suppress any remaining electrostatic repulsions between the particles but is much lower than the CFC for the latex with the adsorbed polymer. The variations of the average diameter during the shear flocculation are shown in Figures 5–8. Figures 5 and 6 show the effects of shear flow on the flocculation of the latex with adsorbed PEO molecules. Figures 7 and 8 present the results for PVA molecules. The rapid increase of the average diameter means a high rate of flocculation. Figure 5 shows the variation of the average diameter with time for PEO-100000. Behavior of the average diameter is characterized by little change for the short time followed by a rapid increase. The flocculation occurs within a shorter time as the shear rate is increased, whereas the layer thickness in the shear-induced desorption was nearly independent of shear rate as shown in Figure 1. The change of the average diameter for PEO-900000 follows a similar trend to that for PEO-100000. However, close examination of Figure 6 clearly indicates that the initial decrease of the average

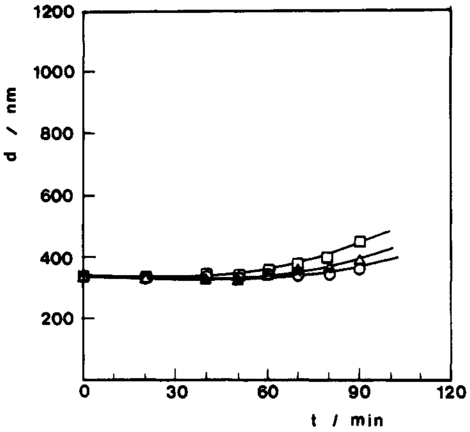

Figure 8. Average diameter behavior with time at different shear rates for the latex with adsorbed PVA-49000 in 0.50 mol dm^{-3} NaCl: (○) 8000 s^{-1}; (△) 12 000 s^{-1}; (□) 16 000 s^{-1}.

diameter results from the reduction in the layer thickness of the adsorbed polymer. Such an observation was impossible for other polymers because of the small change of the layer thickness or the relatively rapid flocculation. When the molecular weight of PEO is increased, the flocculation occurs slowly with time.

It is interesting to compare the present results with those reported for the charge-stabilized latex. Van De Ven and Mason[11] and Zeichner and Schowalter[12] have recently developed a trajectory analysis to examine the shear stability which incorporates the hydrodynamic force as well as the London–van der Waals attractive force and electrostatic repulsive force. In order to confirm the predictions of the trajectory analysis, experiments of shear coagulation were carried out with the charge-stabilized latex by Curtis and Hocking,[10] Zeichner and Schowalter,[9] and Van De Ven and Mason.[18,19] Zeichner and Schowalter showed that the coagulation occurs from the initial time of shearing. They also observed that the coagulation rate at higher shear rate increased less rapidly with extent of coagulation. Such observations for the charge-stabilized latex are not clearly consistent with the results of Figures 5 and 6 for the latex stabilized with adsorbed polymer. The charge-stabilized latex without any repulsive forces between the particles can be easily coagulated from the initial time. On the other hand, as seen in Figures 5 and 6, the negligible change of the average diameter for the short time may result from the maintenance of stability by the adsorbed polymer. Desorption of the adsorbed polymer may no longer keep the dispersion stability against the shear flow. Even after a long period of shearing, however, complete desorption did not occur. It is well-known that the incompletely covered latex can be flocculated by polymer bridging.[20]

Polymer-bridging flocculation under shear flow has been considered by Takamura et al.[5] and Van De Ven.[21] Takamura et al.[5] have observed the stability of the latex in the presence of Cat-Floc [poly(3,5-methylenepyridinium chloride)]. They found that the stability was reduced with small amounts of Cat-Floc because of a reduction in the magnitude of the ζ potential caused by the neutralization between the positive charges of the Cat-Floc and the negative surface charges on the latex particles. At a concentration sufficient to cause a charge reversal on the particles they predicted polymer bridging by Cat-Floc or possible steric effects.

Van De Ven[21] suggested that in the absence of polymer bridging the rate of homocoagulation between equal-sized particles is larger at all shear rates than that of heterocoagulation between unequal particles. When polymer bridging is involved, the difference in capture efficiency between homo- and heterocoagulation becomes smaller at a low shear rate as molecular weight increases, whereas the rate of heterocoagulation will be larger than that of homocoagulation at high shear rate or in dispersions consisting of large particles. When particles with incomplete surface coverage approach each other, they can be flocculated by polymer bridging under the complete suppression of electrostatic repulsive force. Once an aggregate of two particles is formed, it grows larger more easily because of the preference of heterocoagulation over homocoagulation in the presence of polymer bridging. The rapid increase of average diameter in Figures 5 and 6, therefore, can be explained by the shear-induced desorption of adsorbed polymer and subsequent polymer bridging between the particles as suggested by Van De Ven. The rapid increase of average diameter can be interpreted by another mechanism. As the layer thickness is decreased by the desorption of adsorbed polymer, the total interparticle potential curve will have a weak secondary minimum. One would expect that the flocculation into a secondary minimum would proceed rapidly since there is no repulsive barrier to be overcome. The precise mechanism for the rapid increase of the average diameter, however, is not well understood.

To elucidate more clearly the effect of polymer desorption on shear flocculation, similar tests were performed with PVA polymers, and the results are shown in Figures 7 and 8. Behaviors of the average diameter with time for PVA-15000 are similar to those for PEO polymers. However, the flocculation occurs more slowly although the molecular weight of PVA-15000 is much lower than that of the PEO polymers. This is attributed to the difficulty of the shear-induced desorption of adsorbed PVA-15000. Since a change in the layer thickness for PVA-49000 was not observed as seen in Figure 4, the latex with adsorbed PVA-49000 will have a strong stability against the shear flocculation even at a high shear rate. Figure 8 shows that, as expected, the change of the average diameter is very small over a long period.

Summary

The preadsorbed polymer on the surface of PS latex was desorbed under high shear flow. The interaction of polymer with the surface of PS latex was more important in the shear-induced desorption than the molecular weight of the adsorbed polymer.

The latex dispersion in the presence of adsorbed polymer was flocculated at the high shear rate, which is otherwise stable in the quiescent state. The shear flocculation could be explained by the phenomena of the shear-induced desorption. Therefore, the shear-induced desorption must be considered to interpret the behavior of the shear flocculation of the dispersion stabilized with adsorbed polymer.

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Registry No. PS, 9003-53-6; PEO, 25322-68-3; PVA, 9002-89-5; NaCl, 7647-14-5.