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Dispersion Mechanisms of Comb-Type Superplasticizers Containing Grafted Poly(ethylene oxide) Chains

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SUMMARY: This paper discusses the influence of graft chain length and dosage of comb-type superplasticizers on adsorption and dispersion mechanisms, and their subsequent effect on the fluidity of concentrated limestone suspensions. Contrary to the results obtained from interparticle potential calculations, the fluidity of concentrated suspension is improved by the use of comb-type polymers having shorter grafted chain length. The dispersion mechanism of comb-type polymers in a concentrated suspension is evaluated from the perspective of molecular structure, the amount of adsorbed polymer, and the amount of entrapped water in the clusters of $CaCO_3$ particles. Furthermore, the addition of certain soluble salts, which can effect the concentration of Ca^{2+} in liquid phase of $CaCO_3$ suspensions, has been observed to decrease the adsorption of comb-type polymers on $CaCO_3$. Thus, the polymer adsorption process on solid surfaces can be selectively influenced by certain types of ions.

Introduction

In recent years, comb-type polymers with polyethylene oxide grafted pendant groups are attracting increasing attention in construction industry. When added to concrete, these polymers, referred to as superplasticizers, improve flowability or fluidity. In addition, comb-type superplasticizers maintain the fluidity of concrete much longer than normally observed with the naphthalene and melamine sulfonates type polymers without the occurrence of excessive retardation. In Japan, the worsening situation with aggregate resources has tend to increase the water demand of concrete, development of comb-type superplasticizer is indispensable for securing concrete durability. Comb-type superplasticizers are also especially useful for producing self-compacting concrete and high strength concrete mixtures as well as improving concrete durability 1).

Recently, several researchers have reported compatibility problems between certain cements and comb-type superplasticizers, which can adversely effect concrete workability. For example, the fluidity of concrete with this type superplasticizer can decrease if sulfate ion concentration is high2-3). In order to determine how comb polymers control the fluidity of

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such concrete mixtures, there is need to clarify their adsorption and dispersion mechanisms, especially in the presence or absence of certain ions found in the pore solution. In previous reports the dispersion mechanism for inorganic particles treated with comb-type superplasticizers has been discussed in terms of interparticle potential calculations[4]. With regard to the dispersion mechanism of comb-type superplasticizers, the authors have already reported that it is difficult to explain particle repulsion using the DLVO theory, which is based on electrostatic forces, but rather using the steric hindrance effect. This observation is based on the finding that particles to which comb-type superplasticizers have adsorbed do not exhibit a large negative charge[4]. Based on the interparticle potential calculated from the adsorption model of comb-type superplasticizers, the authors have also reported that dispersibility of inorganic particles is improved as a function of graft chain length [5]. Using a particular comb polymer structure, the influence of the amount and thickness of adsorbed polymer on the interparticle potential has been investigated [6]. However, very few studies exist concerning the relation between calculated interparticle potential, adsorption mechanisms, and the resulting fluidity of concentrated suspensions.

Therefore, this paper discusses the influence of chain length and dosage of dispersing agents such as comb-type superplasticizers on the fluidity of concentrated suspension. Furthermore, the effect of Ca^{2+} in liquid phase on the adsorption mechanism of comb-type superplasticizers was also investigated. Limestone powder, which has a Hamaker constant characteristic of inorganic particles, was selected for this study because of its increasing importance as a mineral admixture for new concrete technology such as self-compacting concrete.

Comb-type superplasticizer

The polymers used in this study are α-allyl-ω-methoxypolyethylene-maleic anhydride copolymers with graft chains of polyethylene oxide (PEO), where the PEO has following degrees (n) of polymerization: 10, 34, 70 and 80 [The expression P-XX refers to the degree of polymerization of the PEO graft chain (Fig.1)].

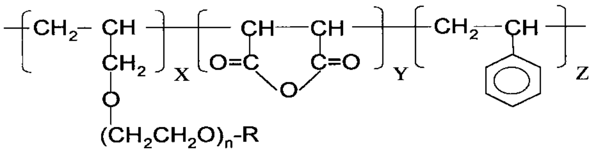

Figure 1. Molecular structure of comb-type superplasticizer; x=1.0, Y=1.01, Z=0.003~0.03 (mole).

A small amount of styrene is incorporated within the backbone of the polymer. The comb polymers may also contain impurities such as low molecular weight non-grafted polyethylene oxide oligomers produced during the polymerization process. However, since these impurities do not act as dispersing agents, their concentration, determined from GPC analysis, was used to adjust the total dispersant concentration yielding a net comb polymer dosage when added to the concentrated suspensions.

Adsorption of comb-type superplasticizers on limestone powder

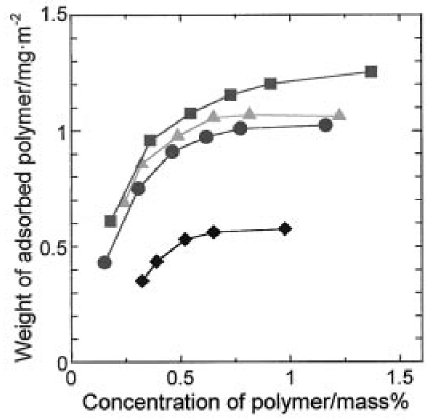

Figure 2. Amounts of polymer adsorbed on $CaCO_3$; ■=P-10, ▲=P-34, ●=P-70, ◆=P-83.

Fig. 2 shows the relationship between the dosage and the amount of adsorbed comb-type superplasticizer with different lengths of grafted chains. These values were calculated from the concentrations of the polymer in the initial solution and the liquid phase (after polymer adsorption), which was obtained by centrifugal separation of the limestone-polymer solution-suspension (water to solid ratio, 1/1vol). The unadsorbed polymer concentration was measured by carbon analysis using a Total Organic Carbon Analyzer (TOC). Based on TOC measurements of the treated limestone suspensions made at 10, 30, and 60 minutes after initial mixing, adsorption equilibrium was achieved within 10 minutes. For this study, a 30 minute adsorption time was adopted to assure equilibrium conditions. Limestone powder (95.2% $CaCO_3$) was used as a dispersed phase, and had a Blaine surface area of 8380cm^2/g, a specific gravity of 2.79, mean particle diameter of 5.13 micrometers, and crystal structure consistent with that of limestone powder as determined by X-ray diffraction (XRD).

The extent of adsorption was found to increase incrementally with polymer dosage, and reach saturation at about the same dosage regardless of graft chain length. The saturated concentration of adsorbed polymer displays a tendency to decrease with increasing graft chain length. Compared with P-70, the saturated amount of adsorbed P-83 is significantly decreased. This may result from a change in the conformation of the comb polymers having relatively long grafted chain lengths, and will be the subject of a future study.

Influence of graft chain length of comb-type superplasticizer on fluidity of suspension

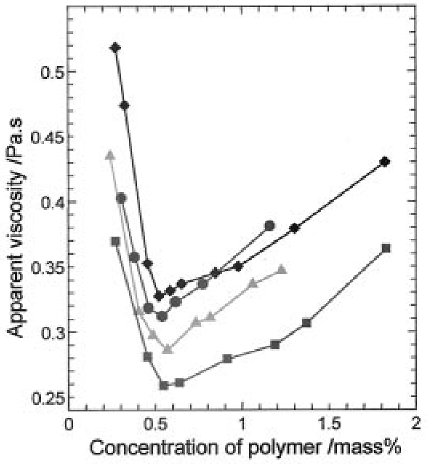

Figure 3. Apparent viscosity of $CaCO_3$ suspension with comb-type superplasticizers; ■=P-10, ▲=P-34, ●=P-70, ◆=P-80.

The relationship of the viscosity of limestone suspensions, treated with comb-type superplasticizers having different grafted chain lengths, is shown in Fig. 3. Using a control stress type rheometer (rotational cylinder viscometer), the viscosity of the suspension at 20 °C, under a 15 minute shear stress cycle of 0 - 200 - 0 Pa, was measured to estimate the apparent viscosity at shear stress of 200 Pa. The apparent viscosity of suspension was found to significantly decrease with the increasing polymer dosage. Furthermore the apparent viscosity decreases as P-XX decreases. The viscosity of suspensions gradually increased when the polymer dosage exceeded the concentration where the adsorbed amounts reached saturation. Investigation of the causes associated with this phenomenon using the concepts of depression effect or cross-linking is highly warranted. The minimum value of apparent viscosity of the suspensions increased as a function of longer graft chain length.

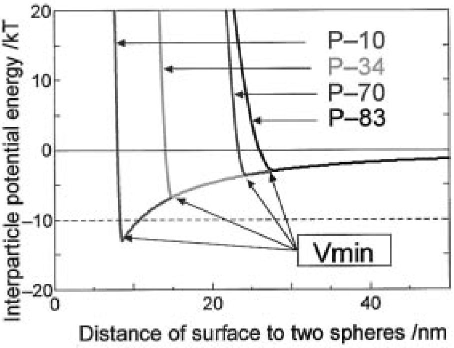

Figure 4. Total potential energy of $CaCO_3$ particles- H_2O system with comb-type polymer.

Fig. 4 illustrates the interparticle potential curves associated with the steric hindrance and van der Waals forces, which are based on previously reported calculations. The van der Waals interaction was calculated using a Hamaker constant of 2.23×10^{-20}J for calcite ($CaCO_3$)7), and a 0.3 micrometer average particle diameter. The steric hindrance effect was calculated from the thickness of adsorbed polymer layer as reported in previous papers, 4) along with the amounts of adsorbed polymer. The stability of the dispersion system resulting from the adsorption of comb polymers is associated with the minimum value of the interparticle potential, Vmin. Furthermore, it is generally known that when Vmin is at least -5kT to -10kT, flocculated particles can easily be redispersed to form a stable dispersion. In Fig. 4, the -10kT potential is displayed by a dashed line and represents a standard Vmin value for the dispersed state. It has been observed that in order to achieve a stable dispersion adsorption of comb polymers having increased grafted chain length is necessary. The result of this calculation indicates that increased grafted chain should improve the dispersibility of fine particles, which is contrary to the results of the above-mentioned viscosity measurements.

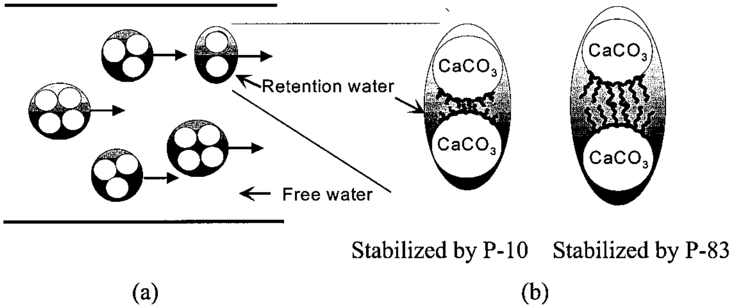

Figure 5. Schematic illustrations of flow model of $CaCO_3$ suspension with P-10 or P-83.

The reason for this discrepancy may be explained as follows. In the flow model for concentrated suspensions, though particles are dispersed by superplasticizer, individual particles may not be completely separated from each other but may form loosely associated clusters. As shown in Fig. 5 (a), the flow model assumes the presence of both free and retained water within the concentrated suspension [8]. The retention water associated with the particle clusters is believed to have a significant effect on the fluidity of concentrated suspension. The calculation of interparticle potential is made without any consideration of retention water in the clusters. Fig. 6 shows the relationship of the amount of free water in the suspensions versus the concentration of admixed P-10 and P-83 polymers.

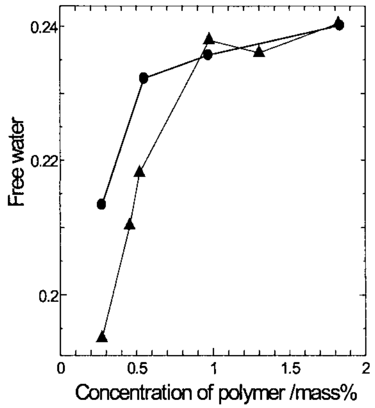

Figure 6. Amounts of free water of $CaCO_3$ suspension with P-10 or P-83; ● = P-10, ▲ = P-83.

After centrifugal separation (3000 rpm, 10 min) was applied to the $CaCO_3$ suspension, the amount of supernatant liquid was measured. The supernatant liquid was considered to be clusters of flocculated powder in suspension and was defined as free water. The free water corresponds to the difference between the total water content and the amounts of retained water in the cluster not contributing to the fluidity of the suspension. When the dosage of polymer is low, the amount of free water tends to decrease with polymers having longer graft chain. An increased apparent viscosity of suspension, produced by polymers having longer graft chain lengths, may be due to the longer interparticle distances in the clusters. As shown in Fig. 5 (b), the addition of P-83, having the longer grafted chains, produce larger inter particle distances, which in turn, appear to use larger volumes of retained water.

As mentioned above, the influence of graft chain length and the dosage of comb superplasticizer upon the fluidity of concentrated suspensions can be attributed to an increase in free water. By introducing the concept of volume fraction (ϕ) of the dispersed phase, the rheology of the dispersed system can be expressed as a function of relative viscosity (η_r) and ϕ. Equation (1) represents the Brinkman's viscosity expression[9)]. It is possible that as clusters are formed, solvent (water) is contained within the clusters that comprise the concentrated suspension, thus increasing the effective volume fraction of solid phase as shown in Fig. 5. Equation (1) can be rewritten as Equation (2), where $[1-(\phi/\phi_c)]$ is a function of the free water. When the relation between $\log\eta_r$, and $\log[(1-(\phi/\phi_c)]$ is plotted, a straight line with slope, -K, is obtained and the line passes through the origin, indicating that a change in suspension viscosity may be expressed as a function of the amount of free water.

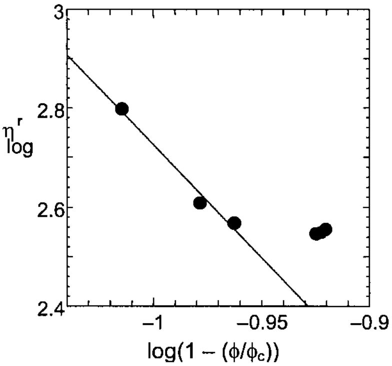

Figure 7. Relationship between $\log\cdot\eta_r$ and $\log[1-(\phi/\phi_c)]$

$$\eta_r = \eta/\eta_o = (1-\phi)^{-K} \quad \text{---} \ (1)$$

$$\eta_r = [1-(\phi/\phi_c)]^{-K} \quad \text{---} \ (2)$$

where: K = a constant corresponding to particle shape(K=2.5 for spherical particle), η_r = :relative viscosity, η = apparent viscosity of suspension, η_o = viscosity of superplasticizer, ϕ = volume fraction of dispersed phase, ϕ_c = ratio of real volume of dispersed phase to effective volume.

The relationship between $\log\eta_r$ and $\log[(1-(\phi/\phi_c)]$ of the suspension admixed with polymer P-83 is shown in Fig. 7. A linear relationship is evident over the dosage of 0.27, 0.46, and

0.52 mass%. Therefore, it appears the that change in viscosity corresponding to the apparent viscosity, which decreases with increasing dosage of polymer, can be expressed by a function of free water volume up to a polymer dosage of 0.52 mass%. At the two polymer dosages which do not fall on the straight line, 0.98 and 1.30 mass%, respectively, the apparent viscosity of the suspension increases with polymer dosage. Withstanding a change of free water volume, this deviation may be primarily due to the depression effect and interparticle cross-linking, and will be the subject for future study.

Adsorption mechanisms of comb-type superplasticizer

The influence of K_2CO_3 on the apparent viscosity of $CaCO_3$ suspension and Ca^{2+} concentration in the liquid phase of suspension are illustrated in Fig. 8. Dilute polymer solutions, with or without K_2CO_3 and limestone powder were mixed at a 1.0:1.0(V_w/V_p) volume ratio, which was maintained at constant temperature (20°C). The Ca^{2+} concentration in a filtered portion of solution was measured with Atomic Absorption Spectrometer. The P-34 polymer was used at a concentration of 0.7 mass% (0.26 mass% to $CaCO_3$). Based on the findings shown in Fig. 8, when the K_2CO_3 dosage increased, the viscosity of $CaCO_3$ suspension rapidly rose, which was accompanied by a rapid decrease in the Ca^{2+} concentration. The decrease of the Ca^{2+} concentration was related to the formation of $CaCO_3$. The effect of K_2CO_3 addition on the absorbed amount of polymer and the free water of suspension are shown in Fig. 9. When K_2CO_3 dosage increases, the absorbed amount of polymer rapidly decreases as well as free water content. With the decrease of the Ca^{2+} concentration from 360ppm to 10ppm, polymer adsorption appears inhibited. Furthermore, the reduced dispersion of calcium carbonate particles is accompanied by a decrease in the amount of free water.

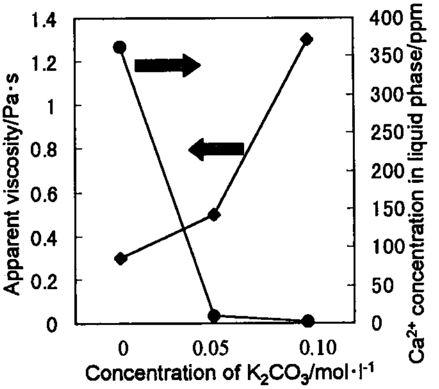

Figure 8. Influence of K_2CO_3 on the fluidity of suspension and the Ca^{2+} concentration in liquid phase.

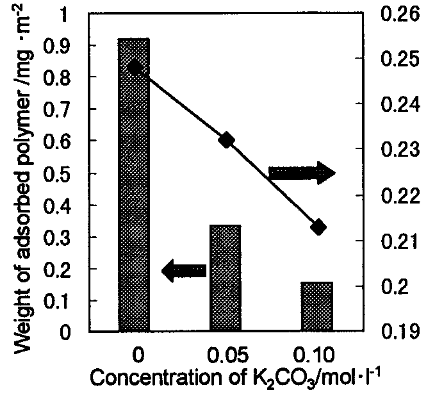

Figure 9. Influence of K_2CO_3 on the adsorbed amounts of polymer and free water in suspension.

As a result of examining the effect of various inorganic electrolyte on the fluidity of $CaCO_3$ suspension dosed with comb-type polymers, we have observed that the addition of inorganic electrolytes, containing the anion which forms relatively insoluble calcium salts, can significantly decrease the fluidity of $CaCO_3$ suspension10)11). The order between solubility of the calcium salt consist with the effect in which the fluidity of suspension lowers. One may suspect that the Ca^{2+} is adsorbed in the solid surface and interferes with polymer adsorption; however, this process has not been verified based on the uncertainty that the surface of the suspended $CaCO_3$, exhibits Ca^{2+} ions. We have also observed that lowering the Ca^{2+} concentration is accompanied by a lower zeta-potential. At about pH10, a decrease in Ca^{2+} concentration corresponds to a change of -10mV to +10mV. This change of zeta-potential or the reduction of adsorption sites seems to possibly account for decreased polymer adsorption as shown in Fig. 10. Moreover, it has also been found that the effect of various electrolytes differs as a function of changing structure of comb-type polymer dispersants12). Further examination of the relationship between the composition of the liquid phase and polymer structure is necessary to understand the factors which influence the fluidity of concentrated suspensions treated with comb-type superplasticizers.

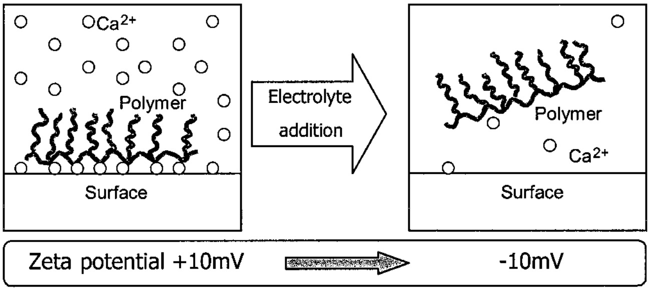

Figure10. Schematic illustration of adsorption mechanisms.

Conclusions

In this study, the influence of comb polymers with different grafted chain lengths has been investigated with regard to the viscosity and fluidity of concentrated $CaCO_3$ suspensions. The adsorption mechanisms associated with comb-type superplasticizers have been also discussed. The viscosity of suspensions has been found to decrease with increasing polymer dosage, which probably results from the increase of free water volume in the suspension produced by deflocculation of particle clusters. Contrary to the predictions of the interparticle potential calculation, the fluidity of concentrated suspensions is found to improve with comb polymers having shorter grafted chain length. This may be due to differences in the amount of retention water in particle clusters, or changes in the amount of free water. With the addition of K_2CO_3, the fluidity of suspensions dosed with comb-type superplasticizers is significantly decreased, which appears to correspond to a decrease in the amount of polymer adsorption. As a result of the decrease of Ca^{2+} in the liquid phase of the suspension due to the formation of $CaCO_3$, the comb polymer dose not significantly adsorbed on $CaCO_3$. Therefor the decrease of Ca^{2+} would appear to modify the solid surface as evidenced by changes in the zeta-potential or the reduction of adsorption sites, and thus effecting the adsorption process of the polymer on to the solid surface.

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