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Comb Polymer Architecture, Ionic Strength, and Particle Size Effects on the $BaTiO_3$ Suspension Stability

Jun Yoshikawa*,†† and Jennifer A. Lewis**,†

Materials Science and Engineering Department, and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, Champaign, Illinois 61801

Byong-Wa Chun

W. R. Grace & Co., Cambridge, Massachusetts 02140

We investigate the stability of aqueous barium titanate suspensions as a function of dispersant architecture, ionic strength, counterion valency, and particle size. Both pure polyelectrolytes, poly(acrylic acid) and poly(methacrylic acid) (PMAA), and comb polymer dispersants composed of a PMAA backbone with methoxy-poly(ethylene oxide) (mPEO) teeth of varying molecular weights are studied. While each dispersant imparts stability to barium titanate suspensions at low ionic strength ($<\sim 0.01M$), only the PMAA–mPEO comb polymer with the longest teeth provides stability at higher ionic strengths independent of particle size and counterion valency. Our findings provide new insight into the design of comb polymer dispersants for stabilizing aqueous ceramic suspensions over a broad range of processing conditions.

I. Introduction

In ceramic fabrication methods, such as tape casting[1,2] and direct ink writing,[3–5] stable colloidal suspensions are desired in order to achieve high solids loading and minimize drying-induced shrinkage. Polyelectrolyte dispersants, such as poly (acrylic acid) (PAA) or poly(methacrylic acid) (PMAA), are typically used to impart the desired stability to aqueous formulations.[6,7] Unfortunately, pure polyelectrolytes are subject to dramatic conformational changes[8–10] and ion-bridging effects[11–13] that limit their effectiveness under certain pH, ionic strength, or ion valency conditions. Hence, there is growing interest in the use of comb polymer dispersants because of their ability to provide enhanced suspension stability.[14–23] These novel dispersants consist of a polyelectrolyte backbone, like PAA[15–18] or PMAA,[19] and charge neutral teeth, such as poly(ethylene oxide) (PEO)[14–20] or methoxy-poly(ethylene oxide) (mPEO).[21–23] In most cases, the polyelectrolyte backbones strongly adsorb onto the ceramic particles, while the neutral teeth extend away from the particle surface in solution.[21–23]

Comb polymers were first investigated as novel dispersants for cement-based formulations nearly a decade ago.[16,18,24] Yoshioka *et al.*[24] calculated the interparticle potential for cement–comb polymer systems and showed that the extent of steric stabilization increased with increasing teeth density and length. In a complementary effort, Kirby and Lewis[18] carried out systematic experiments to probe the effects of comb polymer architecture on cement stability. Specifically, they studied PAA–PEO comb polymers, whose PEO teeth molecular weight ranged from 100 to 3000 g/mol. Interestingly, they found that even PAA–PEO comb polymers composed of the shortest PEO teeth significantly enhanced system stability, relative to pure polyelectrolyte dispersants, like PAA. Based on this remarkable observation, they hypothesized that the primary contribution of the PEO teeth in those systems was to shield the underlying PAA backbone from ion-bridging effects that drive flocculation.

Kirby *et al.*[17] then extended this research to probe the effects of a single PAA–PEO comb polymer composed of $\sim$2000 g/mol PEO teeth on the stability of aqueous $BaTiO_3$ suspensions. They found that this comb polymer imparted stability over a wide range of pH, ionic strength, and ion valency conditions, where pure PAA failed. Their results further supported the notion that the PEO teeth shield the underlying PAA backbone from ion-bridging effects. Additionally, they observed that compared with pure polyelectrolytes, this comb polymer dispersant exhibited little conformational change under high ionic strength conditions. Yet despite these important findings, the effects of comb polymer architecture and ceramic particle size on suspension stability have yet to be systematically explored.

Here, we investigate the effects of PMAA–mPEO comb polymer architecture on the stability of aqueous $BaTiO_3$ suspensions as a function of teeth length, ionic strength, and particle size. Specifically, comb polymers with three different mPEO teeth molecular weights are synthesized, and their behavior is compared with both pure PAA and PMAA. First, we characterize the polymer solutions by titration and capillary viscometry to determine the hydrodynamic radii of each dispersant as a function of architecture and ionic strength. Second, we investigate the stability of colloidal suspensions produced using two $BaTiO_3$ powders of different sizes coated with PAA, PMAA, or PMAA–mPEO dispersants through rheological measurements. From these observations, we identify a critical teeth length required for the PMAA–mPEO species to serve as high-performance dispersants for aqueous $BaTiO_3$ suspensions over a broad range of processing conditions.

II. Experimental Procedure

(1) Materials System

$BaTiO_3$ powders (BT-03B and BT-005, Sakai Chemical Industry Co. Ltd., Sakai, Japan) composed of two different particle size distributions are used in this study. The particle size, specific surface area, and density of each powder are determined by dynamic light scattering, nitrogen gas adsorption isotherm, and helium pycnometry, respectively. BT-03B powder has an average particle size of 350 nm, a specific surface area of 4.23 m^2/g, and a density of 5.84 g/cm^3, whereas BT-005 powder has an

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*Member, The American Ceramics Society.

**Fellow, The American Ceramics Society.

[†]Author to whom correspondence should be addressed. e-mail: jalewis@illinois.edu

[††]Permanent affiliation: Materials Research Laboratory, NGK Insulators Ltd., Nagoya 467-8530, Japan.

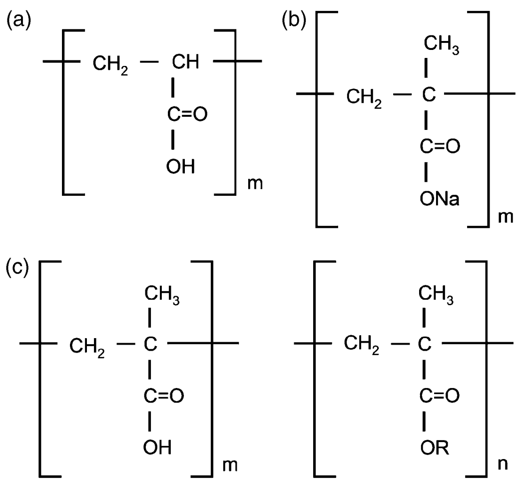

Fig. 1. Chemical structure of (a) poly(acrylic acid), (b) poly(methacrylic acid) (PMAA)–sodium salt, and (c) PMAA–methoxy-poly(ethylene oxide) (mPEO). (Note: $R = (CH_2CH_2O)_x - CH_3$, mPEO.)

average particle size of 50 nm, a specific surface area of 26.3 m^2/g, and a density of 5.57 g/cm^3.

PMAA–mPEO comb polymers with three different teeth molecular weights, 475, 1100, and 2000 g/mol, are synthesized from mPEO methacrylate and methacrylic acid using the method developed by Kinoshita *et al.*[25] and used as dispersants. We denote these species as PMAA–mPEO(475), PMAA–mPEO(1100), and PMAA–mPEO(2000), respectively. Before characterization, each dispersant solution is purified using ultrafiltration to remove any unreacted monomer. The molecular weight cut-off (MWCO) of the ultrafiltration membranes is 5000 Da for PMAA–mPEO(475), and 10 000 Da for PMAA–mPEO(1100) and PMAA–mPEO(2000). The pure polyelectrolytes, PAA (Polyscience Inc., Warrington, PA) and PMAA-sodium salt (Sigma-Aldrich Co., St. Louis, MO), are used as-received. The chemical structures and schematic representations of each dispersant are shown in Figs. 1 and 2, respectively. The acid/teeth ratios associated with the backbone of the comb polymers are also shown in Fig. 2.

(2) Polymer Solution Characterization

The molecular weight distribution of each dispersant is determined by gel permeation chromatography (GPC) using a PEO standard and 1 wt% KNO_3 aqueous solution as the eluent.

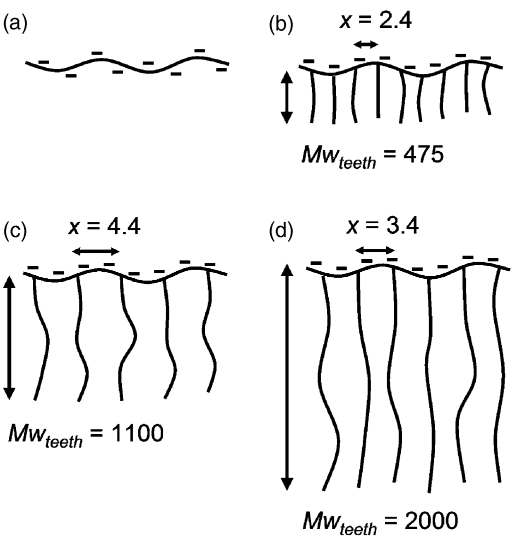

Fig. 2. Schematic representations of polymer dispersant architecture. (a) poly(acrylic acid) or poly(methacrylic acid) (PMAA), (b) PMAA–methoxy-poly(ethylene oxide) (mPEO) (475), (c) PMAA–mPEO(1100), (d) PMAA–mPEO(2000), where x denotes the acid/teeth ratio.

Titrations are carried out on dilute polymer solutions (~2 wt%) to determine the dissociation behavior of the ionizable carboxylic acid groups present along the backbone of each dispersant at pH values ranging from 2 to 11. Each solution is prepared by adding an appropriate amount of dispersant to deionized water. The titrant is a 1*M* NaOH (Fisher Scientific, Fair Lawn, NJ) solution, which is added in small aliquots to each sample, while it is magnetically stirred. The pH response is measured as a function of titrant amount and data analysis is performed, as described previously.[7]

The hydrodynamic radii, R_h, of each dispersant is determined as a function of ionic strength, [I], by capillary viscometry carried out on the dilute polymer solutions. These measurements, along with the suspension viscometry and zeta potential (ζ), measurements described below, are conducted at pH 9.0±0.1, because Ba^{2+} ion leaching from $BaTiO_3$ particle surfaces becomes significant at lower pH.[26–29] The pH of each polymer solution is adjusted using either a 1M HNO_3 (Fisher Scientific) or 25 wt% tetramethylammonium hydroxide (Fisher Scientific) solution. The ionic strength of each polymer solution is adjusted by adding KCl (Fisher Scientific). A Ubbelohde type viscometer (Model 9722-M53, Cannon Instrument Company, State College, PA) is used for the viscosity measurements. Flow-time measurements are carried out in a constant temperature bath at 30.0°±0.1°C. Relative viscosities, η_r, are determined at five different polymer concentrations in a dilute regime for these polymers (4×10^{-3}–2×10^{-2} g/mL), and then the intrinsic viscosities, $[\eta]$ (mL/g), are determined by extrapolation of the plots of η_{sp}/c to $c = 0$,[30] where η_{sp} is the specific viscosity, η_r–1, and c the concentration of the polymer solution (g/mL). The hydrodynamic radius, R_h, is estimated by[31]

$$R_h = \left(\frac{3M[\eta]}{10\pi N_A}\right)^{\frac{1}{3}} \qquad (1)$$

where M is the polymer molecular weight and N_A is Avogadro's number. In this study, the weight average molecular weight is used for M.

Turbidity measurements are conducted on dilute polymer solutions (5×10^{-3} g/mL) of varying salt concentration and counterion valency at pH 9.0±0.1 to determine the stability of polymeric species in the presence of ions. Stock solutions of 0.2 and 2*M* KCl or 0.05 and 0.5*M* $BaCl_2$, prepared by dissolving KCl (Fisher Scientific) or $BaCl_2 \cdot 2H_2O$ (Fisher Scientific) in deionized water, are added to the polymer solutions to vary their monovalent and divalent cation concentrations, respectively. The solution turbidity is determined by measuring the light transmittance ($\lambda = 560$ nm) using a UV–Vis spectrophotometer (Model UV-2401, Shimadzu Corporation, Kyoto, Japan).

(3) Suspension Characterization

Colloidal suspensions are prepared by adding an appropriate amount of the $BaTiO_3$ powder to aqueous solutions that have the desired dispersant concentration and whose pH is adjusted to 9.0±0.1. After the powder is added to each solution, the suspension is ultrasonicated on ice for 5 min using a 1-s on/off pulse sequence. All suspensions are then stirred for a 24-h equilibration time at room temperature. The suspension pH is readjusted to the desired value, if necessary.

The optimum dispersant concentrations are determined by measuring the viscosity of $BaTiO_3$ suspensions (volume fraction, $\phi = 0.2$). In each case, the dispersant concentration is increased in increments of 0.1 mg/m^2 of $BaTiO_3$ surface area, and the optimum concentration of a given dispersant is defined by the value that yields the lowest suspension viscosity.

For the remainder of the viscometry tests, the suspensions are subjected to an additional processing step to remove large agglomerates from the as-received powder. First, a series of suspensions ($\phi = 0.1$) are prepared, each with the optimum dispersant concentration, and then allowed to undergo sedimentation for several hours. The supernatants are then decanted and

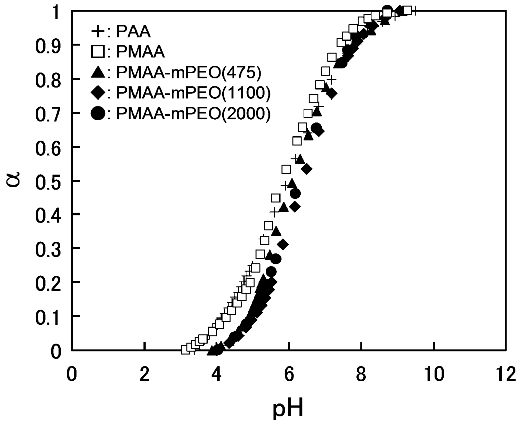

Fig. 3. Fraction of ionized carboxylic acid groups, α, versus pH for dilute polymer solutions.

centrifuged (Avanti J-25I, Beckman Coulter Inc., Fullerton, CA) in order to concentrate the remaining particles in suspension to $\phi \sim 0.52$–0.55 and $\phi \sim 0.35$–0.38 for BT-03B and BT-005, respectively. The concentrated suspensions are diluted using deionized water to a desired concentration. This process is effective at removing large agglomerates, those above ~1 μm for BT-03B and above ~350 nm for BT-005, such that the final particle size distributions in suspension are nearly identical regardless of the dispersant used. The aforementioned KCl and $BaCl_2$ stock solutions are used to vary the counterion concentrations of the suspensions.

Viscosity measurements are carried out using a controlled-stress rheometer (Model Bohlin CS-50, Malvern Instruments Ltd., UK) fitted with concentric cylinder geometry. A specially designed solvent trap is used to minimize water evaporation. To ensure reproducibility of the data, suspensions are presheared at a shear rate of 200 s^{-1} for 30 s and then allowed to equilibrate for 300 s before each measurement. All rheological measurements are carried out at 25°C.

The ζ of the $BaTiO_3$ particles is measured at pH 9 in both the absence and presence of optimum concentration of each dispersant. The electrokinetic sonic amplitude (ESA) method (Model ESA-8000, Matec Applied Sciences, Hopkinton, MA) is used for this measurement, using the suspension volume fraction $\phi = 0.03$. This method is utilized to minimize the effects of Ba^{2+} ion leaching, which alters the particle surface chemistry, as observed in suspensions of low solids loading ($\phi \sim 10^{-4}$) used in laser microelectrophoresis.[32]

III. Results and Discussion

(1) Polymer Solution Behavior

The ionization behavior of each dispersant is shown in Fig. 3, where the fraction of ionized groups is denoted by $\alpha = [COO^-]/([COO^-] + [COOH])$. The value of α exhibits a nearly identical pH dependence for all dispersants studied. At pH 3–4, there are almost no ionized groups ($\alpha = 0$) along the polyelectrolyte backbone of each dispersant. As pH increases, there is a concomitant rise until all ionizable groups are fully charged at ~ pH 9.

The molecular weight of each dispersant is provided in Table I. The pure polyelectrolytes, PAA and PMAA, have an M_w (weight average) of roughly 1.0×10^4 g/mol, whereas the PMAA–mPEO comb polymers each have a similar M_w of approximately 2.5×10^4 g/mol.

Using the above results, the acid/teeth ratio and backbone molecular weight of the comb polymers are estimated as follows. First, the number of carboxylic acid groups per molecule, N_{acid}, is obtained from titration results. Next, the number of teeth per macromolecule, N_{teeth}, is calculated by

$$N_{teeth} = (MW_{whole} - N_{acid} \times MW_{acid})/MW_{teeth} \quad (2)$$

where MW_{whole} is the molecular weight of the entire polymeric dispersant (backbone + teeth) (g/mol), MW_{acid} is the molecular weight of methacrylic acid (86.1 g/mol), and MW_{teeth} is the mPEO teeth molecular weight. The acid/teeth ratio is given by N_{acid}/N_{teeth}. The backbone molecular weight (g/mol), $MW_{backbone}$, is determined by replacing the mPEO teeth with methacrylic acid groups as follows:

$$MW_{backbone} = MW_{acid} \times (N_{acid} + N_{teeth}) \quad (3)$$

The acid/teeth ratios and $MW_{backbone}$ obtained using number- and weight-average MW_{whole} are reported in Table I. The acid/teeth ratios vary over a relatively narrow range from 2.4 to 4.4 for the three comb polymer dispersants studied. A smaller acid/teeth ratio means that there is a higher mPEO teeth density along a given PMAA backbone. The weight-average $MW_{backbone}$ ranged from 4.2×10^3 to 1.0×10^4 g/mol. The effects of these parameters on the polymer conformation in solution are highlighted below.

To estimate the hydrodynamic radius, R_h, of each dispersant, the relative viscosities, η_r, of polymer solutions are measured using capillary viscometry as a function of ionic strength. Over the range of values explored, a linear dependence of η_{sp}/c on polymer concentration, c, is observed, from which intrinsic viscosities, $[\eta]$, could be extrapolated (results not shown). The hydrodynamic radius, R_h, is estimated from each $[\eta]$ value using Eq. (1). The values of R_h for each dispersant are plotted as a function of ionic strength in Fig. 4(a). Both PAA and PMAA exhibited lower R_h values relative to the PMAA–mPEO comb polymers at all ionic strengths studied, which is expected given their identical ionization behavior and differences in overall molecular weight and architecture. The R_h of each dispersant decreased with increasing ionic strength, reflecting a change in conformation from that of extended chains at low ionic strength to a more collapsed state at high ionic strength. This collapse is caused by the reduced intersegment repulsion between COO^- groups along the polyelectrolyte backbone driven by the counterion screening. Of the three comb polymers, R_h of PMAA–mPEO(475) is the largest at low ionic strength ($3 \times 10^{-3}M$). We attribute this finding to its large backbone molecular weight and significant electrostatic intersegment repulsion at low ionic strength.

To better understand the conformational changes induced by enhanced counterion screening, we present the normalized R_h,

Table I. Dispersant Architectures

	Whole molecular weight		Backbone molecular weight		
Dispersant	M_n (g/mol)	M_w (g/mol)	M_n (g/mol)	M_w(g/mol)	Acid/teeth ratio
PAA	5.4×10^3	1.1×10^4	–	–	–
PMAA	5.4×10^3	9.5×10^3	–	–	–
PMAA-mPEO(475)	1.3×10^4	2.6×10^4	5.4×10^3	1.0×10^4	2.4
PMAA–mPEO(1100)	1.4×10^4	2.5×10^4	4.4×10^3	8.2×10^3	4.4
PMAA–mPEO(2000)	1.3×10^4	2.4×10^4	2.1×10^3	4.2×10^3	3.4

PAA, poly(acrylic acid); PMAA, poly(methacrylic acid); mPEO, methoxy-poly(ethylene oxide).

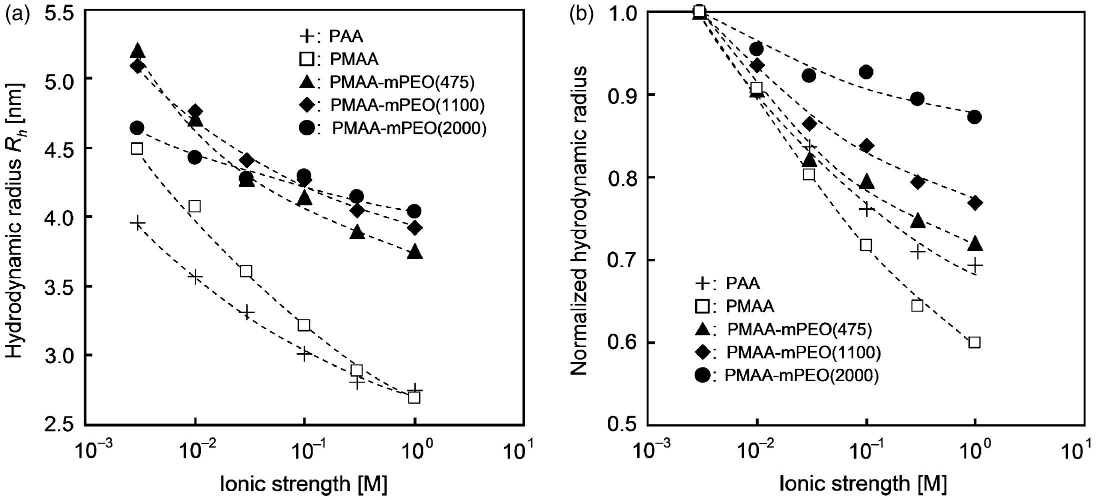

Fig. 4. Plots of (a) hydrodynamic radius and (b) normalized hydrodynamic radius, where $R_h/(R_h$ at $[\mathrm{I}] = 3 \times 10^{-3} M)$, as a function of ionic strength [I],which is varied by KCl addition. (Note: dashed lines merely guide the eye.)

which is defined as R_h at a given ionic strength divided by that observed at the lowest ionic strength probed (R_h at $[\mathrm{I}] = 3 \times 10^{-3} M$), for each dispersant in Fig. 4(b). These data reveal that the conformations of pure polyelectrolyte dispersants, PAA and PMAA, exhibit a much stronger dependence on ionic strength than their comb polymer counterparts. Equally important, our observations show that as the mPEO teeth molecular weight increases, the comb polymers are less susceptible to undergoing counterion-induced, conformational changes. This trend likely stems from the enhanced steric hindrance between bulkier mPEO teeth that arises as the underlying PMAA backbone attempts to adopt a more compact (coil-like) conformation in solutions with increasing ionic strength. The slight variation between the acid/teeth ratios of the three comb polymers appears to have little effect on these observations.

Figure 5 shows the turbidity measurements carried out on polymer solutions as a function of ionic strength of the added salt. The solutions appear clear when the polymeric species are well solvated and become increasingly turbid as the polymer chains undergo aggregation in solution. All polymer solutions remain clear in the presence of the monovalent counterions (Fig. 5(a)), exhibiting nearly 100% light transmittance. By contrast, the pure polyelectrolyte and comb polymer solutions exhibit widely different behavior in the presence of the divalent counterions (Fig. 5(b)). Ion-bridging effects lead to pronounced turbidity that stems from the aggregation of pure polyelectrolyte species in the presence of Ba^{2+} ions when $[\mathrm{I}] = 10^{-2}$–$10^{-1} M$, whereas the comb polymer solutions remain clear, independent of their polymer architecture. These observations reveal that even comb polymers with the shortest teeth studied here are effectively shielded from counterion-induced aggregation, or ion bridging.

(2) Optimum Dispersant Concentrations for BaTiO$_3$ Suspensions

To determine the optimum concentration of each dispersant, the apparent viscosities of the $BaTiO_3$ suspensions ($\phi = 0.2$) are measured as a function of the dispersant concentration (Fig. 6). For all systems, the suspension viscosity first decreases with increasing dispersant concentration before reaching a minimum value at a given dispersant concentration. In each system, we define the optimum concentration to be the value that coincides with the lowest viscosity measured. Figure 7 depicts the apparent viscosity as a function of shear rate for suspensions that contain the optimum concentration of each dispersant. In each case, they exhibit nearly Newtonian behavior, which is indicative of complete stabilization. The optimum dispersant concentrations range from 0.3 to 0.8 mg/m^2 and from 0.2 to 0.5 mg/m^2, for 350 nm $BaTiO_3$ particles and 50 nm $BaTiO_3$ particles, respectively, where the pure polyelectrolytes have the lowest optimum concentration, and these values increase with increasing mPEO teeth length. Interestingly, the optimum dispersant concentrations per unit surface area are lower for the 50 nm $BaTiO_3$ particles than those for the 350 nm $BaTiO_3$ particles. This trend

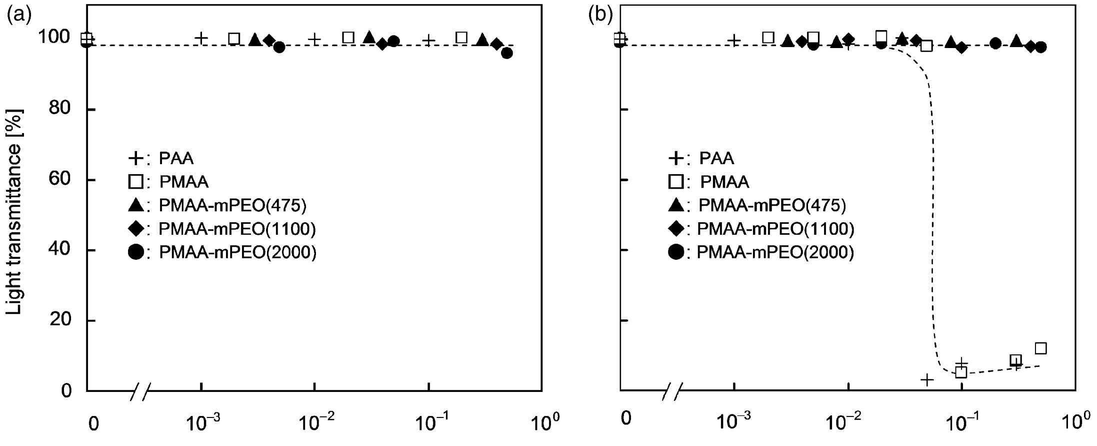

Fig. 5. Plots of light transmittance of dilute polymer solutions as a function of ionic strength [I], which is varied by (a) KCl and (b) $BaCl_2$ addition. (Note: dashed lines merely guide the eye.)

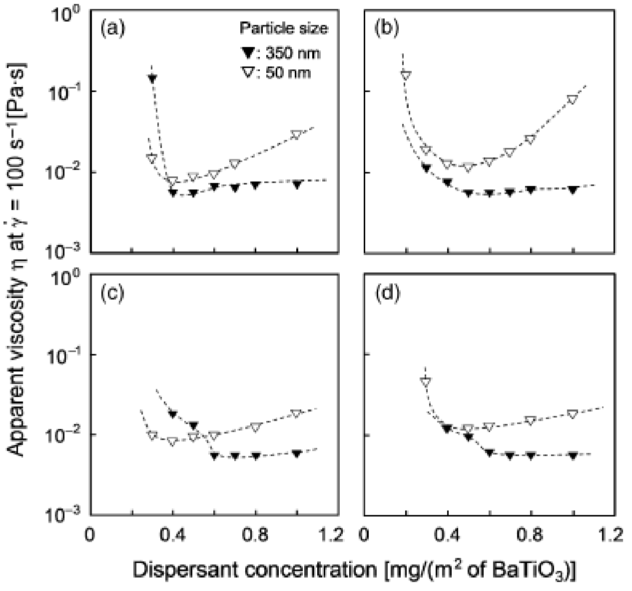

Fig. 6. Apparent viscosity of the $BaTiO_3$ suspensions ($\phi = 0.2$) as a function of the concentration of (a) poly(methacrylic acid) (PMAA), (b) PMAA–methoxy-poly(ethylene oxide) (mPEO) (475), (c) PMAA–mPEO(1100), and (d) PMAA–mPEO(2000). (Note: dashed lines merely guide the eye.)

may arise because of the difference in surface curvature, which is known to alter polymer adsorption.[33]

The ζ of both bare $BaTiO_3$ particles and those particles coated with the optimum concentration of each dispersant are reported in Table II. The bare particles have a minimal ζ at pH 9, while the dispersant-coated particles possess ζ values that range from −11.3 to −39.8 mV. Their negative effective charge reflects the presence of ionized carboxylic acid (COO^-) groups along the polyelectrolyte backbones of each adsorbed dispersant.

Table II. ζ of Bare and Dispersant-Coated $BaTiO_3$ Particles at pH 9

Dispersant	ζ (mV) 350 nm particles (BT-03B)	 50 nm particles (BT-005)
None	+2.1	−1.6
PAA	−22.6	−24.7
PMAA	−39.8	−22.9
PMAA–mPEO(475)	−20.0	−30.3
PMAA–mPEO(1100)	−22.5	−20.6
PMAA–mPEO(2000)	−13.6	−11.3

PAA, poly(acrylic acid); PMAA, poly(methacrylic acid); mPEO, methoxy-poly(ethylene oxide).

(3) Dispersant Adlayer and Particle Size Effects on $BaTiO_3$ Suspension Rheology

We first investigate the effects of polymer adlayer and particle size on suspension behavior under low ionic strength conditions, i.e., in the absence of added salt species. The apparent suspension viscosity is measured as a function of $BaTiO_3$ volume fraction (ϕ) for systems stabilized with an optimum concentration of each dispersant and varying particle size. Representative results for suspensions stabilized by PMAA–mPEO(475) are shown in Figs. 8(a) and (b) for systems that contain 350 and 50 nm of $BaTiO_3$ particles, respectively. From these data, we identify the respective maximum solids loadings of these suspensions to be ϕ_{max} ~0.58 and ϕ_{max} ~0.37, which are defined as those values at which the viscosity diverges to infinity. The pronounced reduction in ϕ_{max} with decreasing $BaTiO_3$ particle size arises from the enhanced contribution of the polymeric adlayer to the effective solids volume fraction, ϕ_{eff}, which is given by[17,34]

$$\phi_{eff} = \phi(1 + \delta A_s \rho_s) \tag{4}$$

where δ is the thickness of the dispersant adlayer, A_s is the specific surface area of the ceramic particles, and ρ_s is the density of the ceramic particles.

The relative viscosity in high shear limit, $\eta_{r\infty}$, for suspensions composed of 350 nm $BaTiO_3$ particles as a function of volume fraction is shown in Fig. 9. The high shear apparent viscosity is obtained by fitting the shear rate–viscosity curve using the relationship[35]

$$\eta = \frac{\eta_0 - \eta_\infty}{1 + (b\dot{\gamma})^q} + \eta_\infty \tag{5}$$

which is known to provide a good description of the observed shear thinning behavior, where η_0 is low shear viscosity, $\dot{\gamma}$ is shear rate, and b and q are constants. The behavior predicted by the Krieger–Dougherty relationship[36]

$$\eta_r = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-k\phi_{max}} \tag{6}$$

where $\phi_{max} = 0.63$ for random close packing and $k = 2.5$ for spheres, is also shown in Fig. 9 for comparison. At the same solids volume fraction, the high shear viscosities are larger for

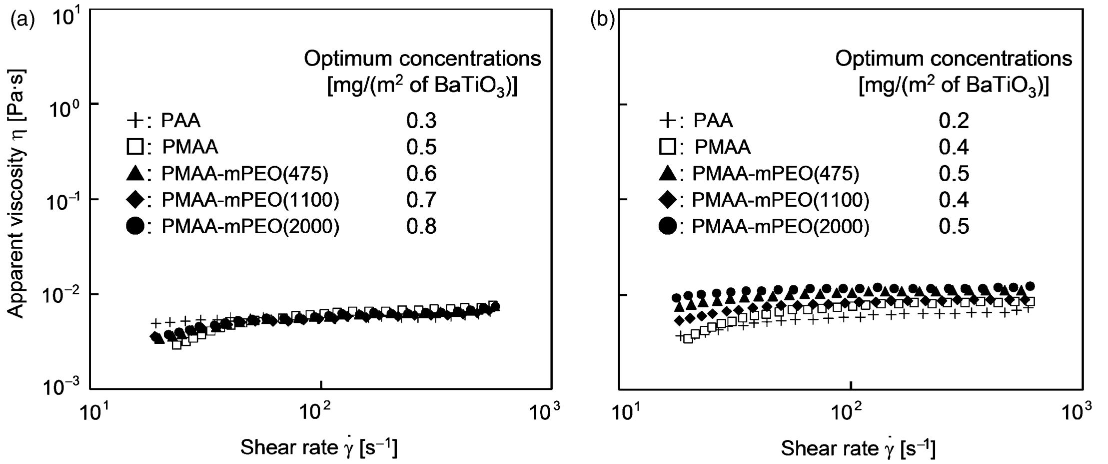

Fig. 7. Apparent viscosity of the $BaTiO_3$ suspensions ($\phi = 0.2$) composed of (a) 350 nm particles and (b) 50 nm particles that are stabilized by optimum concentrations of each dispersant as a function of shear rate.

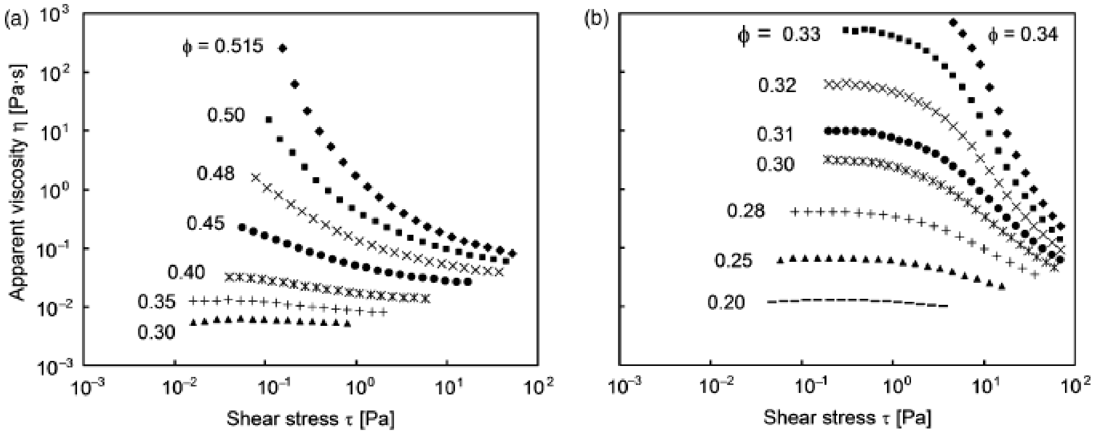

Fig. 8. Apparent viscosity of $BaTiO_3$ suspensions of varying solids volume fraction (ϕ) composed of (a) 350 nm particles and (b) 50 nm particles that are stabilized by poly(methacrylic acid)–methoxy-poly(ethylene oxide)(475) as a function of shear stress.

systems stabilized by the comb polymers as compared with those stabilized by pure polyelectrolytes. Moreover, the values observed for comb polymer-based systems increase with increasing teeth molecular weight. Such observations imply that the adlayer thickness is larger for comb polymers than for pure polyelectrolytes and increases with increasing teeth molecular weight, leading to a greater enhancement in ϕ_{eff}.

Based on the rheological data, we estimate the adlayer thickness, δ, of each dispersant using the ϕ–η_r relationship.[37] The adlayer thickness is defined by the value that gives the best fit of the ϕ_{eff}–$\eta_{r\infty}$ curve to the Krieger–Dougherty model using Eqs. (4) and (6). The estimated adlayer thicknesses are reported in Table III. The adlayer thicknesses range from 4.6 to 7.6 nm, with the lowest values observed for the pure polyelectrolyte dispersants, PAA and PMAA. For the comb polymers, δ increases with increasing mPEO teeth molecular weight. We note that the estimated values of δ are in good agreement with their respective hydrodynamic radii determined for the dilute dispersant solutions.

(4) Ionic Strength and Counterion Valency Effects on $BaTiO_3$ Suspension Stability

We now investigate the effects of ionic strength and counterion valency on suspension behavior for systems stabilized by either pure polyelectrolyte or comb polymer dispersants. The apparent viscosities of $BaTiO_3$ suspensions ($\phi = 0.1$) are measured at a constant shear rate of 5 s^{-1}, while their ionic strength is varied by the addition of either monovalent (KCl) or divalent ($BaCl_2$) salt species (Fig. 10). The viscosity at a given ionic strength is compared with the baseline value of 10^{-3} Pa · s observed in the absence of salt additions for each system. Upon adding salt, suspensions are deemed stable if their viscosity remains nearly equivalent to this baseline value. By contrast, a sharp rise in suspension viscosity denotes the onset of particle flocculation.

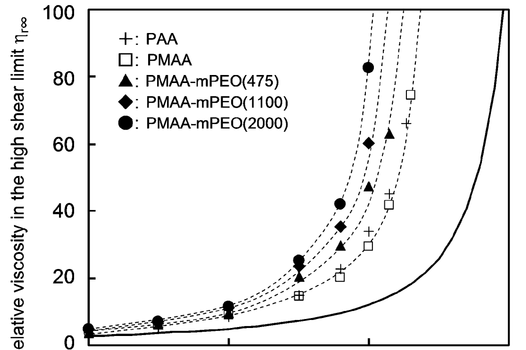

Fig. 9. Relative viscosity in the high shear limit for $BaTiO_3$ suspensions of varying solids volume fraction composed of 350 nm particles that are stabilized by optimum concentrations of each dispersant. The solid line shows the behavior predicted by the Krieger–Dougherty relationship ($\phi_{max} = 0.63$ and $k = 2.5$). (Note: dashed lines merely guide the eye.)

At low ionic strength ($< \sim 0.01M$), all dispersants are effective at promoting suspension stability irrespective of the $BaTiO_3$ particle size. Under these conditions, each dispersant is able to stabilize the ceramic particles due to an electrosteric mechanism, as reported previously for $BaTiO_3$–PMAA-NH_4 and PAA systems.[6,38] However, at higher ionic strengths, only the comb polymer dispersant composed of the longest teeth, PMAA–mPEO(2000), is effective at promoting suspension stability over the entire range of solution conditions explored. Interestingly, there appears to be a difference in stability for $BaTiO_3$ suspensions containing comb polymer dispersants with intermediate teeth lengths (i.e., PMAA–mPEO(475) and PMAA–mPEO(1000)). Neither of those dispersants is able to fully stabilize these suspensions at high ionic strengths ($> 0.03M$) and there is a more pronounced rise in suspension viscosity at the onset of flocculation in systems containing smaller $BaTiO_3$ particles ($d = 50$ nm).

The apparent viscosities of $BaTiO_3$ suspensions ($\phi = 0.1$) composed of 350 nm particles with $0.1M$ $BaCl_2$ addition are shown in Fig. 11, as representative data. The suspensions containing pure polyelectrolyte or comb polymer dispersant with intermediate teeth lengths display shear thinning behavior, indicative of flocculation. By contrast, the suspension containing PMAA–mPEO(2000) remains nearly Newtonian over the entire range of ionic strengths explored. At high ionic strengths, the steric mechanism is expected to dominate because the electrostatic repulsion between coated particles is diminished by counterion-screening effects.[39] In fact, the PMAA–mPEO(2000) dispersant is least susceptible to undergoing conformational changes in solution as the ionic strength increases, as shown in Fig. 4(b). Hence, this dispersant is able to maintain a nearly

Table III. Adlayer Thicknesses Estimated from the ϕ–η_r Relationship for the $BaTiO_3$ Suspensions Composed of 350 nm Particles

Dispersant	Adlayer thickness (nm)
PAA	4.7
PMAA	4.6
PMAA–mPEO(475)	5.7
PMAA–mPEO(1100)	6.9
PMAA–mPEO(2000)	7.6

PAA, poly(acrylic acid); PMAA, poly(methacrylic acid); mPEO, methoxy-poly(ethylene oxide).

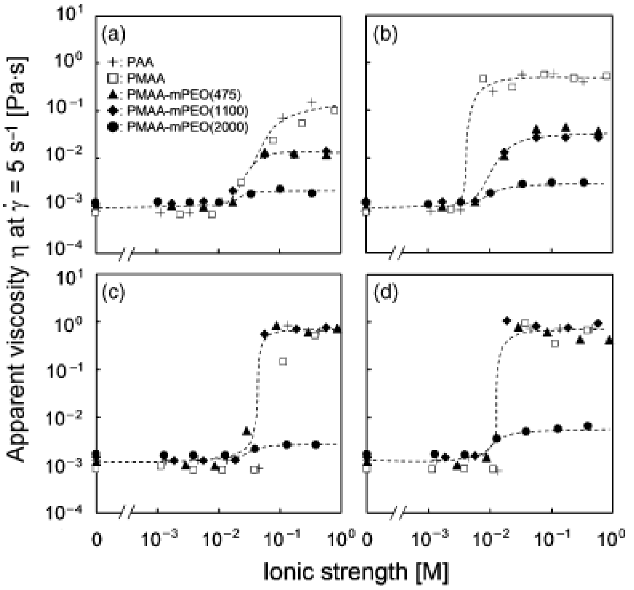

Fig. 10. Apparent viscosity of $BaTiO_3$ suspensions ($\phi = 0.1$) composed of 350 nm particles (top row) and 50 nm particles (bottom row) that are coated with the optimum amount of each dispersant as a function of ionic strength, which is varied by either KCl (left column) or $BaCl_2$ (right column) addition. (Note: dashed lines merely guide the eye.)

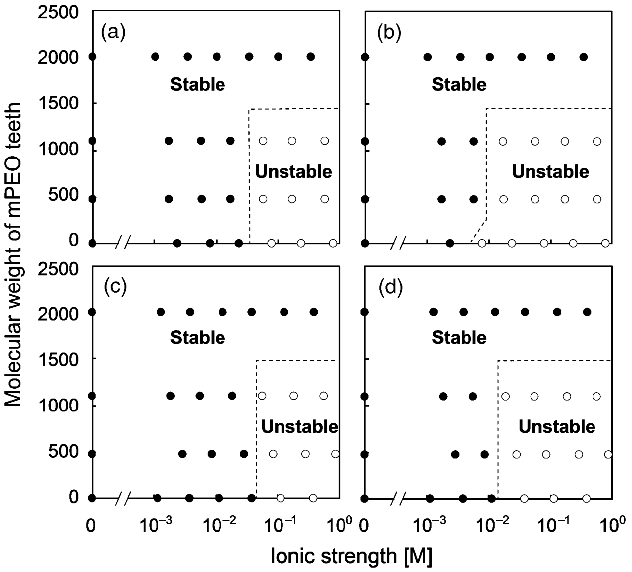

Fig. 12. Stability maps for $BaTiO_3$ suspensions composed of 350 nm particles (top row) and 50 nm particles (bottom row), in which methoxy-poly(ethylene oxide) (mPEO) teeth molecular weight ($M_w = 0$ corresponds to pure poly(methacrylic acid)) is plotted as a function of ionic strength, which is varied by KCl (left column) or $BaCl_2$ (right column) addition. Closed (●) and open (○) symbols reflect stable and unstable suspensions, respectively.

constant adlayer thickness over a broad range of solution conditions.

Based on the above observations, we construct stability maps for the polyelectrolyte-based dispersants of varying mPEO teeth lengths as a function of ionic strength and counterion valency (Fig. 12). The behavior observed for the pure polyelectrolyte, PMAA, is plotted on the x-axis, corresponding to a teeth molecular weight of zero because this dispersant does not contain mPEO teeth. From these maps, we find that there is little difference in system behavior for PMAA and the comb polymers of intermediate teeth molecular weights of 475 and 1100 g/mol. We also see that the region of stability narrows slightly with increasing counterion valency. Paik *et al.*[27] reported that Ba^{2+} ions in solutions adsorb onto $BaTiO_3$ particle surfaces when the pH > 7, thereby lowering the surface charge of the particles. Hence, divalent Ba^{2+} counterions are more effective at reducing the electrostatic repulsion between particles than their monovalent counterparts at a given ionic strength. Interestingly, similar trends are observed for suspensions composed of $BaTiO_3$ particles of 50 and 350 nm, respectively. This is surprising considering the Van der Waals forces that drive the particle aggregation scale linearly with particle size. Further experiments are, therefore, needed to fully resolve the role of particle size on optimal dispersant design. Importantly, we find that only PMAA–mPEO(2000) acts as an effective dispersant over a wide range of ionic strength, counterion valency, and $BaTiO_3$ particle sizes.

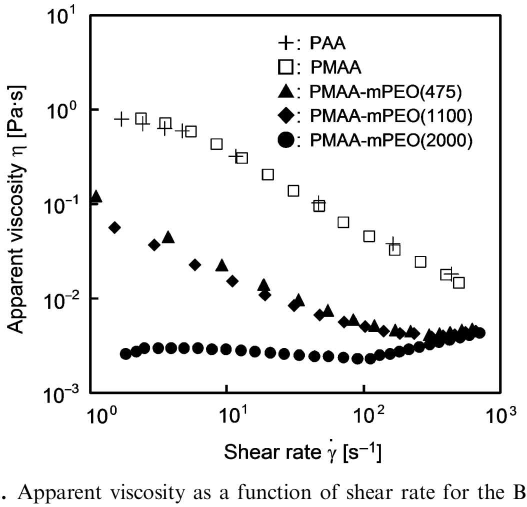

Fig. 11. Apparent viscosity as a function of shear rate for the $BaTiO_3$ suspensions ($\phi = 0.1$ and $0.1M$ $BaCl_2$ added) composed of 350 nm particles with the optimum concentrations of each dispersant.

While prior work by Kirby and Lewis[18] on cement-based suspensions stabilized by PAA–PEO comb polymers revealed that even those with a teeth molecular weight as low as ~100 g/mol could impart stability at high ionic strength, we find that a teeth molecular weight of ~2000 g/mol is required for the $BaTiO_3$ suspensions studied here. We attribute the dramatic variation in critical teeth length between these two systems to the significant difference in their Hamaker constants, because this parameter defines, in part, the magnitude of the Van der Waals attraction between particles. The $BaTiO_3$ particles have a Hamaker constant, $A_{BaTiO_3} \sim 8 \times 10^{-20}$ J,[40] that is nearly 20 times higher than cement particles studied previously.[41] In systems that possess an inherently weak driving force for flocculation, such as cementitious systems, the thickness of the dispersant adlayer is less critical than its ability to shield the underlying polyelectrolyte backbone from ion-bridging effects. Thus, even comb polymers with very short, charge-neutral teeth can impart stability to such systems under high ionic strength. However, when the attractions between ceramic particles intensify, as in the present system, the adlayer thickness plays an essential role by defining the range over which steric forces act to provide stability. In the $BaTiO_3$ suspensions, it is no longer sufficient to merely shield the underlying backbone from ion-bridging effects, but rather the neutral PEO teeth must extend far enough away from the particle surface to prevent flocculation, because the electrostatic repulsion is diminished at high ionic strengths. Based on these collective observations, we believe that comb polymer dispersants must possess a critical mPEO teeth molecular weight (MW_{crit}) to impart suspension stability over a broad range of processing conditions; however, the magnitude of this key parameter depends on the specific materials system of interest.

IV. Conclusions

We have studied the effects of PMAA–mPEO comb polymers on the stability of aqueous $BaTiO_3$ suspensions under various ionic strengths and counterion valency conditions. Two different $BaTiO_3$ particle sizes and three different mPEO teeth molecular weights were investigated, with PAA and PMAA serving as controls. At high ionic strength, the PMAA–mPEO comb polymer with the highest teeth molecular weight provided outstanding suspension stability for both particle sizes compared with the other polymeric dispersants. The presence of the long mPEO teeth provided an appreciable adlayer, whose thickness was nearly insensitive to ionic strength. This comb polymer dispersant provides enhanced stabilization to aqueous ceramic suspensions over a broad range of processing conditions.

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