

Comb Polymer Architecture Effects on the Rheological Property Evolution of Concentrated Cement Suspensions

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We have studied the rheological behavior of concentrated cement suspensions in the absence and presence of comb polymers comprised of a polyacrylic acid (PAA) backbone and charge-neutral, poly(ethylene oxide) (PEO) teeth. These species possessed a uniform backbone molecular weight and graft density, with varying teeth molecular weight. Both PAA, a linear polyelectrolyte, and PAA/PEO comb polymers imparted initial stability to concentrated cement suspensions above a critical weight fraction, w^* of 4 mg/(g of cement). Cement–PAA suspensions, however, set prematurely. Their rapid, irreversible stiffening stemmed from deleterious interactions between PAA and multivalent counterions in solution. Interestingly, the presence of PEO teeth comprised of only a few monomer units in length mitigated such interactions. The rheological property evolution of concentrated cement–PAA/PEO suspensions exhibited complex behavior ranging from the reversible gel-like response observed at short teeth lengths to a remarkable gel-to-fluid transition observed during the deceleratory period for systems comprised of longer PEO teeth. At longer hydration times, all cement–PAA/PEO suspensions exhibited initial elastic modulus values, $G'_i \sim \exp(t/\tau_c)$ before the onset of the acceleratory period, followed by initial set. Their characteristic hydration time, τ_c , and set time depended strongly on the concentration of “free” carboxylic acid groups $[\text{COO}^-]$ arising from non-adsorbed polyelectrolyte species in solution.

I. Introduction

THE rheological property evolution of concentrated cement suspensions is poorly understood, despite its importance on concrete mixing and placement. Cement pastes consist of multiphase particles with a broad size distribution ($\sim 1\text{--}100\ \mu\text{m}$) suspended in an aqueous medium. Particle interactions are dominated by long-range, attractive van der Waals interactions that must be overcome by electrostatic, steric, or other repulsive forces to induce the desired degree of suspension stability.¹ Polyelectrolyte-based additives, referred to as superplasticizers by the cement industry, are widely used to control the stability of concentrated cement suspensions. The first generation of these additives are linear polyelectrolytes, e.g., sulfonated naphthalene formaldehyde (SNF) and poly(acrylic acid) (PAA), that have one ionizable sulfonate and carboxylic acid group, respectively, per

monomer unit. Second-generation superplasticizers are copolymers possessing a comb structure with PAA backbone and charge-neutral poly(ethylene oxide) (PEO)-based “teeth” grafted onto the PAA backbone at frequent intervals. Lewis *et al.*² have recently shown that cement pastes exhibit strong shear-thinning flow behavior in the absence of these additives. However, on the addition of a critical concentration of these species (i.e., both first- and second-generation superplasticizers), cement suspensions exhibited nearly Newtonian flow behavior indicative of improved stability. Such observations are in good agreement with interparticle force calculations,^{2,3} which predict that cement particles (mean diameter $\sim 10\ \mu\text{m}$) would flocculate into a strong, primary minimum in the absence of polyelectrolyte additions, whereas they would flocculate into a shallow, secondary minimum in their presence.

The impact of superplasticizer molecular architecture on the rheological property evolution in concentrated cement suspensions has been a subject of recent interest.^{4–6} The use of PAA/PEO comb polymers leads to important processing advantages over linear polyelectrolytes, as comb polymers provide stability over much longer time scales than linear polyelectrolytes. However, the exact mechanism(s) by which they impart stability remains a subject of debate. Nawa *et al.*⁷ hypothesized that the thick steric barrier stemming from the comb polymer architecture facilitates long-term stability, as hydration products “bury” the adsorbed layers over time. Kinoshita *et al.*,⁸ however, have observed the opposite trend; i.e., cement–PAA/PEO suspensions with short PEO teeth (1000 g/mol) retain their stability over longer hydration times than cement–PAA/PEO suspensions with long PEO teeth (3000 g/mol). Yamada *et al.*⁹ and Kreppelt *et al.*¹⁰ hypothesize that such variations stem from differences in the concentration of “free” $[\text{COO}^-]$ groups in solution, which suppress the nucleation and growth of hydration products.

Fundamental knowledge regarding the mechanisms by which PAA/PEO comb polymers impart stability to cement systems is required to optimize the comb polymer architecture and provide guidelines to develop the next generation of superplasticizers. This is a challenging problem to address, because cement particles undergo hydration reactions in aqueous media that yield concurrent changes in both solution and cement surface chemistry, and the formation of hydration products. Kirby and Lewis³ have developed an oscillatory shear technique to probe the elastic modulus evolution (G') of concentrated cement suspensions. In their approach, the “reversibility” of a cement particle network after a given hydration time is assessed by disrupting its structure under high shear, then measuring the rise of $G'(t)$ under quiescent conditions. The dynamic probe of suspension structure offered by this approach, coupled with the analysis of dilute polymer solutions under analogous pH and ionic strength conditions and with analysis of the hydration behavior of concentrated cement suspensions (i.e., calorimetry and conductivity measurements), can help to elucidate the mechanisms by which the rheological property evolution occurs in a given cement system.

Here, we study the elastic modulus evolution of concentrated cement suspensions in the absence and presence of PAA and

M. Grutzeck—contributing editor

Manuscript No. 10523. Received September 19, 2003; approved May 6, 2004.

This work was financially supported by W. R. Grace Construction Products.

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Table I. Chemical and Phase Compositions of Type I Ordinary Portland Cement

Component	OPC composition (%)
Chemical Composition	
SiO ₂	21.09
Al ₂ O ₃	4.75
Fe ₂ O ₃	3.4
CaO	65.1
MgO	1.2
K ₂ O	0.69
Na ₂ O	0.18
SO ₃	2.94
LOI	0.83
Phase Composition	
C ₃ S	59.6
C ₂ S	15.5
C ₃ A	6.8
C ₄ AF	10.4
CSH ₂	6.3

PAA/PEO comb polymers of varying PEO teeth molecular weight. Cement–PAA suspensions undergo rapid irreversible stiffening within a few minutes of hydration due to ion bridging interactions between the adsorbed PAA species and multivalent counterions that dissolve from the cement particles. In sharp contrast, the presence of PEO teeth comprised of only a few monomer units mitigate deleterious ion bridging interactions, thereby promoting cement suspension stability under conditions where pure PAA fails. With larger PEO teeth (i.e., 700–3000 g/mol), cement–PAA/PEO suspensions exhibit a remarkable gel-to-fluid transition during the deceleratory period. At longer times, all cement–PAA/PEO suspensions exhibit $G'_i \sim \exp(t/\tau_c)$ before the onset of the acceleratory period and a sharp rise in G'_i after the onset of the acceleratory period. These findings are attributed to the hydration of C₃A/gypsum and C₃S, respectively, to form solid hydration products. The nonadsorbed PAA/PEO species interact with dissolved ions and solid nuclei to suppress the formation of solid hydration products, but, ultimately, the cement–PAA/PEO suspensions undergo initial set (i.e., C–S–H solid bridges form at the solid contacts of a gelled network).

II. Experimental Procedure

(I) Materials System

An ASTM type I ordinary portland cement (W. R. Grace & Co., Cambridge, MA) was used in this study. The cement composition, shown in Table I, was determined by X-ray fluorescence and Bogue analysis.¹¹ This ordinary portland cement powder had a specific surface area of 1.0 m²/g, mean diameter of 10.7 μm, and particle size distribution ranging from 0.3 to 30 μm as determined by BET (Model ASAP 2400, Micrometric, Norcross, GA) and particle size analysis (Model CAPA-700, Horiba, Ltd., Tokyo, Japan), respectively. PAA and PAA/PEO comb polymers^{12,13}

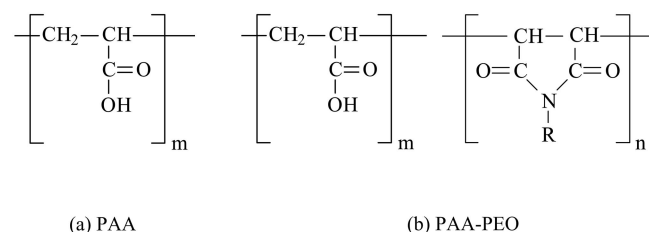


Fig. 1. Chemical structure of (a) PAA and (b) PAA/PEO comb polymers. (Note: The PEO teeth, R = (CH₂CH₂O)_x-CH₃, are grafted onto the PAA backbone through imide linkages.)

served as dispersants in this study. Their chemical structures and molecular weights (M_N and M_w) are described in Fig. 1 and Table II, respectively.

(2) PAA and PAA/PEO Solution Behavior

Dilute polymer solutions (5 mg/mL) were prepared by adding an appropriate amount of a given dispersant to deionized water. Note, this concentration was about an order of magnitude below the dilute-to-semidilute transition that occurs at ~50 mg/mL at pH 9. Stock solutions of KCl (1 M), CaCl₂ (1 M), BaCl₂ (1 M), and LaCl₃ (0.2 M) were prepared by dissolving various salts (KCl, CaCl₂·2H₂O, BaCl₂·2H₂O, or LaCl₃·7H₂O, Fisher Chemicals, Fair Lawn, NJ) in deionized water, which were added to the polymer solutions to adjust their ionic strength. The following ratio, $[I]/[\text{COO}^-]$, was used to facilitate direct comparison between samples. $[I] = \frac{1}{2} \sum_i n_i z_i^2$ is the ionic strength, where n_i and z_i are the molar concentration and valency, respectively, of ions “ i ” dissolved from the added salt species and $[\text{COO}^-]$ is the molar concentration of ionized carboxylic acid groups along the PAA backbone. Note, $[\text{COO}^-]$ was 0.069, 0.052, 0.023, 0.017, 0.012, and 0.008 M for dilute solutions of PAA, PAA/PEO100, PAA/PEO700, PAA/PEO1000, PAA/PEO2000, and PAA/PEO3000, respectively. The solution pH was adjusted using either a 0.1 M HNO₃ or 0.1 M NaOH solution. Dilute polymer solutions with mono- and divalent salt additions were prepared under conditions where PAA is fully ionized (pH 9),^{14,15} whereas those with trivalent salt additions had to be prepared at pH 7.8 to avoid precipitation of lanthanum hydroxide, which would increase solution turbidity. After adjusting the ionic strength and pH, the solutions were magnetically stirred for 0.5 h for equilibration.

Dynamic light scattering measurements (Zetasizer 3000HS, Malvern Instruments, Ltd., United Kingdom) were conducted on dilute polymer solutions (pH 9) of varying salt concentration to determine their hydrodynamic radius (R_H) as a function of counterion concentration. A refractive index, n , of 1.53, 1.51, and 1.47 was used in the scattering experiments for PAA, PAA/PEO100, and PAA/PEO2000, respectively. Data analysis was conducted using the CONTIN algorithm by Provencher,¹⁶ which provided a reasonable fit (i.e., less than 1% error). Turbidity measurements were conducted on dilute PAA and PAA/PEO solutions of varying salt concentration and counterion valency. The solution turbidity was determined by measuring the intensity of transmitted light ($\lambda = 560$ nm) through samples contained in glass cells. The raw data were normalized by the maximum and minimum transmitted intensities to determine the percent light transmittance.

(3) PAA and PAA/PEO Adsorption Behavior

The adsorption of PAA and PAA/PEO comb polymers on ordinary portland cement in aqueous suspension was determined by total organic carbon (TOC) analysis (Model DC80, Dohrmann), which provided a quantitative measure of the nonadsorbed fraction of such species in solution. Cement suspensions with a water-to-cement ratio (w/c) of 0.35 (47 vol% cement) were prepared by adding an appropriate amount of cement powder to an aqueous stock solution of varying PAA or PAA/PEO weight fraction. After mixing for 5 min, suspensions were centrifuged at 2000 rpm for 10 min. The supernatant was immediately decanted and diluted with deionized water for TOC analysis. Several aliquots of each sample were measured, and an average value was reported on the basis of standard calibration curves (the correlation coefficient, R , was 0.998) obtained for polymer solutions of known composition.

(4) Hydration Behavior

Calorimetry and conductivity measurements were conducted to determine the hydration behavior of cement pastes and suspensions. Concentrated suspensions ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) were prepared for calorimetry by adding the appropriate amount of cement to an aqueous stock solution of varying PAA/PEO weight fraction. The suspensions were hand-mixed for 30 s, capped, and placed in the calorimeter (Thermometric TAM AIR). The heat

Table II. PAA/PEO Comb Polymer Architectures

PAA/PEO architecture	PAA M_w (g/mol)	PEO M_w (g/mol)	acid:imide	No. of COO ⁻ groups per molecule	GPC M_N (g/mol)	GPC M_w (g/mol)	Theoretical M_w (g/mol)
Pure PAA	5000	—	—	69	†	†	5 000
PAA/PEO100	5000	100	7:1	61	†	†	5 870
PAA/PEO700	5000	700	7:1	61	8 135	13 200	11 100
PAA/PEO1000	5000	1000	7:1	61	7 626	18 040	13 700
PAA/PEO2000	5000	2000	7:1	61	8 380	25 800	22 400
PAA/PEO3000	5000	3000	7:1	61	12 944	36 510	31 100

†GPC molecular weight not available.

profile was recorded over a span of 48 h. The pore solution composition of cement pastes was determined by inductively coupled plasma (ICP). Their solution conductivity could not be measured directly due to their solidlike nature. Such measurements, however, were conducted as a function of hydration time for cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) prepared at their critical PAA/PEO weight fraction (w^*) of 4 mg of PAA/PEO/(g of cement) and continuously stirred.

(5) Rheological Property Evolution

Oscillatory shear measurements were conducted on concentrated cement suspensions ($w/c = 0.35$, $\phi_{\text{cement}} = 0.474$) using a controlled-stress rheometer (Model CS-50, Bohlin Rheologi AB, Lund, Sweden) equipped with a vane tool geometry (cup diameter, 27.5 mm; vane diameter, 25 mm; vane height, 20 mm).¹⁷ The suspensions were prepared by adding an appropriate amount of cement powder to aqueous stock solutions of varying PAA or PAA/PEO weight fraction. The samples were mixed under low-shear conditions for 60 s followed by high-shear mixing for 60 s to ensure homogeneity. After mixing, the suspensions were immediately transferred into the sample cup. The samples were presheared at a constant shear rate of 200 s^{-1} applied for $\sim 60 \text{ s}$, which was initiated 5 min after cement contact with water. A thin layer of 1000-cP silicone oil was then placed on top of the suspension to prevent water evaporation. Modulus data were acquired as a function of time at a constant strain of roughly 0.02%. This value was selected to ensure that the samples remained in the linear viscoelastic region throughout the measurement. These data were acquired after 10 1-Hz oscillatory stress cycles (for a total time of 10 s between measurements). These measurements were repeated on cement suspensions that were first allowed to hydrate for varying times before subjecting them to an additional preshear at a shear rate of 200 s^{-1} for 60 s. Their modulus data were then collected following the same procedure outlined above for the fresh pastes. By monitoring the elastic property evolution in this manner, we could separate the observed G' evolution into both reversible and irreversible components, thereby allowing us to assess the influence of hydration phenomena on colloidal interactions and initial setting behavior.

III. Results

(I) PAA and PAA/PEO Solution Behavior

The R_H of PAA and PAA/PEO comb polymers as a function of increasing salt addition is shown in Fig. 2. On adding either mono- or divalent salt species to pure PAA solutions, R_H decreased rapidly from 4.7 nm to roughly 1.8 nm. This dramatic size decrease reflects a change in conformation from highly extended chains at low ionic strength to collapsed coils at high ionic strength. This collapse, driven by counterion interactions,^{18,19} reflects the reduced intersegment repulsion between screened COO⁻ groups along the polyelectrolyte backbone. In sharp contrast to PAA, the PAA/PEO2000 species exhibited only a slight decrease in R_H with decreasing pH or increasing ionic strength. The relative insensitivity of PAA/PEO2000 conformation on these conditions likely arises due to the presence of neutral PEO teeth attached at frequent intervals along the PAA backbone. These teeth prevent large conformational changes in response to counterion screening due to

steric hindrance effects arising from PEO–PEO teeth interactions. Even the short PEO teeth (PAA/PEO100) were sufficient to suppress conformational changes in solutions of high ionic strength, although they were not as effective as the larger PEO teeth (PAA/PEO2000). It is important to note, however, that in both cases the extent to which internal rearrangements of the PAA backbone are suppressed is not fully known as some conformational changes could occur that do not induce dramatic changes in R_H .

A plot of transmitted light as a function of the ratio $[I]/[\text{COO}^-]$ is shown in Fig. 3 for dilute PAA and PAA/PEO solutions with varying salt concentration and counterion valency. Stable solutions, in which the polymeric species remain well-solvated, are transparent (i.e., 100% light transmission). Their turbidity increases as the solution stability decreases, as reflected by a decrease in the percent of transmitted light. In the presence of monovalent counterions, each polymer solution remained transparent (stable) over a broad range of $[I]/[\text{COO}^-]$ values, i.e., $[\text{KCl}] = 0\text{--}2.8 \text{ M}$. In the presence of divalent counterions, marked differences were observed between PAA and PAA/PEO solutions. PAA solutions were only stable over a narrow range of $[I]/[\text{COO}^-]$ values, i.e., $0\text{--}0.023 \text{ M CaCl}_2$. These solutions became turbid at higher salt additions, as PAA chains were condensed by divalent counterions (Ca^{2+}) in solution.²⁰ In the presence of trivalent salt additions, similar behavior was observed for PAA solutions (pH 7.8), which only remained stable over a narrow range of $[I]/[\text{COO}^-]$ values, i.e., $0\text{--}0.012 \text{ M LaCl}_3$. Unlike PAA solutions, PAA/PEO700–3000 solutions remained transparent (stable) over a

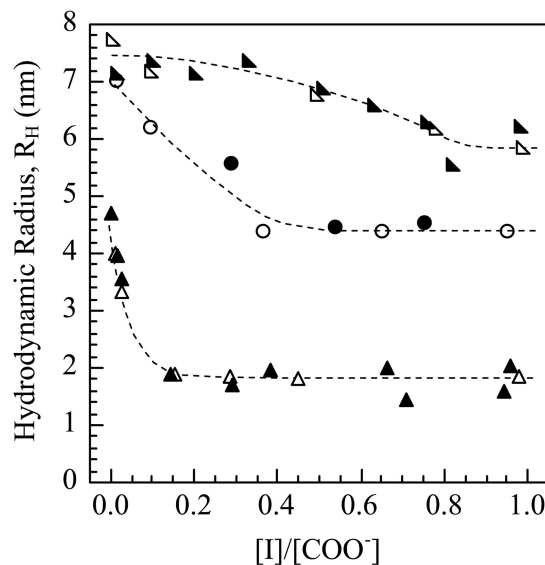


Fig. 2. Plot of the hydrodynamic radius as a function of salt addition for dilute (Δ , \blacktriangle) PAA, (\circ , \bullet) PAA/PEO100, and (\square , \blacktriangleright) PAA/PEO2000 solutions. Open and closed symbols correspond to mono- (KCl) and divalent (CaCl_2 or BaCl_2) salt additions, respectively. Note, $[I] = \frac{1}{2} \sum n_i z_i^2$ due to added salt only and $[\text{COO}^-] = 0.07, 0.049, \text{ and } 0.011 \text{ M}$ for PAA, PAA/PEO100, and PAA/PEO2000, respectively. The dashed lines merely guide the eye.

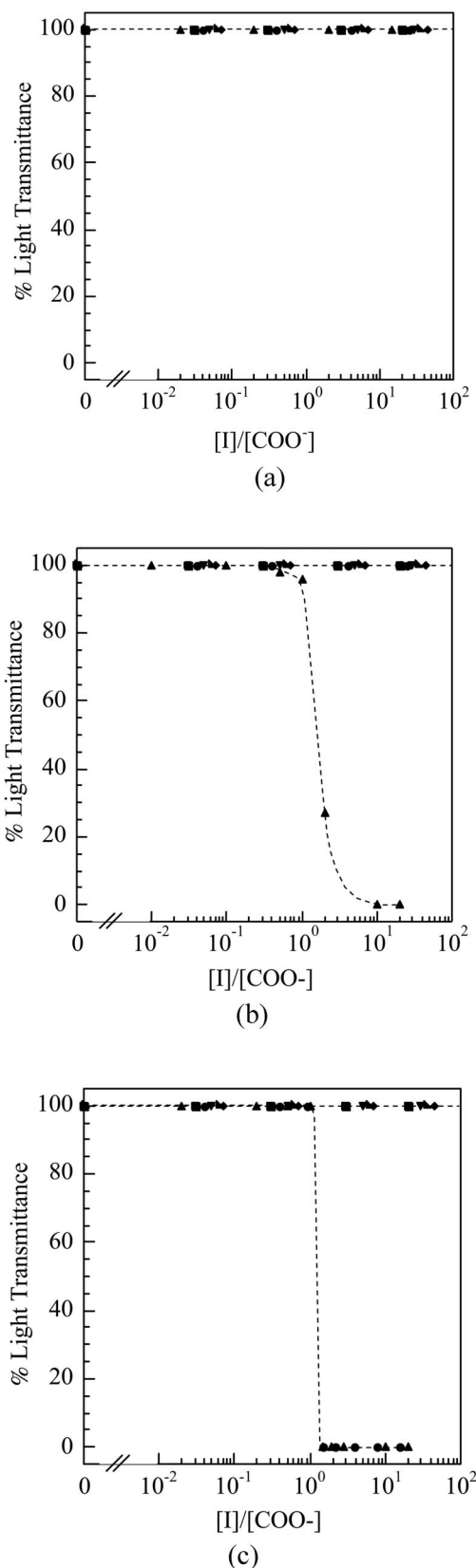


Fig. 3. Plot of the percent light transmittance as a function of (a) KCl, (b) CaCl_2 , and (c) LaCl_3 addition for dilute PAA and PAA/PEO solutions of pH 9, 9, and 7.8, respectively. The PAA species (\blacktriangle) had a molecular weight of 5000 g/mol and the PAA/PEO species had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varied widely in PEO molecular weight: (\bullet) 100, (\blacksquare) 700, (\blacktriangledown) 1000, (\blacktriangleleft) 2000, and (\blacklozenge) 3000 g/mol. Note, $[I] = \frac{1}{2} \sum n_i z_i^2$ due to added salt only and $[\text{COO}^-] = 0.069, 0.052, 0.023, 0.017, 0.012, \text{ and } 0.008 \text{ M}$ for PAA/PEO species with PEO molecular weights of 100, 700, 1000, 2000, and 3000 g/mol, respectively. The dashed lines merely guide the eye.

broad range of mono-, di-, and trivalent salt additions, whereas PAA/PEO100 solutions were only stable in the presence of mono- and divalent salt additions. These solutions became turbid (unstable) on adding 0.008 M LaCl_3 .

(2) PAA and PAA/PEO Adsorption on Ordinary Portland Cement

The adsorption of PAA and PAA/PEO comb polymers on ordinary portland cement from solutions of varying concentration is shown in Fig. 4. PAA exhibited significantly stronger adsorption relative to PAA/PEO comb polymers. An important figure of merit is the w^* at which the cement suspensions are observed to undergo a transition from strong shear thinning behavior to a nearly Newtonian flow response. Interestingly, a uniform adsorbed PAA/PEO amount (Γ) of 1.6 mg/m^2 cement was required to induce stability for comb polymers with PEO teeth molecular weights of 700–3000 g/mol. In each case, this coverage occurred at the same critical polymer concentration of 4 mg/(g of cement) in solution. For these systems, there was a significant amount of excess (or “free”) PAA/PEO in solution after initial mixing, as reflected by differences between the 100% adsorption line and the data shown. PAA and PAA/PEO with the shortest teeth (100 g/mol PEO) possessed an analogous w^* of 4 mg of PAA/PEO/(g of cement); yet, there was a significant increase in the adsorbed amount ($\Gamma_p = 3.5 \text{ mg PAA/PEO}/(\text{m}^2 \text{ of cement})$) at this critical concentration. Moreover, under these conditions, nearly all species were adsorbed onto the cement particle surfaces with little excess in solution.

(3) Hydration Behavior of Cement Pastes and Suspensions

The rate of heat evolution (dq/dt) as a function of hydration time is shown in Fig. 5 for pure cement pastes and cement–PAA/PEO suspensions prepared at the critical PAA/PEO weight fraction. The calorimetry curves are divided into three regions of hydration behavior: (1) deceleratory period, (2) induction period, and (3) acceleratory period.^{21–23} The onset of the acceleratory period is of particular interest, because it reflects nucleation and growth of calcium silicate hydrate (C–S–H). This phase forms as a result of C_3S hydration and generally coincides with the initial set of cement pastes. For the pure cement paste, the onset of the acceleratory period occurred at ~ 2 h hydration. In the presence of PAA/PEO species of increasing teeth length (i.e., 100, 700, 1000, 2000, and 3000 g/mol PEO), the onset of the acceleratory period occurred at $\sim 18, 38, 30, 20, \text{ and } 11.5$ h, respectively. Beyond the onset of the acceleratory period, the area under the $dq(t)/dt$ curves increased at a rate that varied with PEO teeth length (i.e., the respective slopes of the $dq(t)/dt$ curves were 0.25, 1.0, 1.0, 1.0, and 0.22 $\text{mW}/(\text{g}\cdot\text{h})$).

Solution conductivity measurements could not be conducted on pure cement pastes. Their solution chemistry was therefore characterized by ICP analysis, as shown in Table III. On the basis of these data, the ionic strength was calculated to be 0.52 M for ordinary portland cement paste.²⁴ This value largely reflects contributions from its high alkali sulfate content. The conductivity of cement–PAA/PEO suspensions is shown as a function of hydration time in Fig. 6. The results were corrected by subtracting out the background conductivity associated with the nonadsorbed PAA/PEO species in solution. The measured conductivity is directly related to the amount of dissolved ions in solution; thus, an increase or decrease in the solution conductivity with time reflects the dominance of particle dissolution or hydration product formation, respectively. The conductivity was observed to increase rapidly at short hydration times, followed by a gradual rise until a maximum value was obtained. A maximum solution conductivity of 11.7, 17.5, 17.6, 17.4, and 17.9 mS/cm was observed for cement suspensions containing PAA/PEO with varying PEO teeth length (i.e., 100, 700, 1000, 2000, and 3000 g/mol PEO). At the maximum conductivity values, characteristic hydration times of 0.27, 17.2, 19.5, 5.6, and 2.8 h were determined for these respective PAA/PEO species. Beyond these τ_c , the conductivity

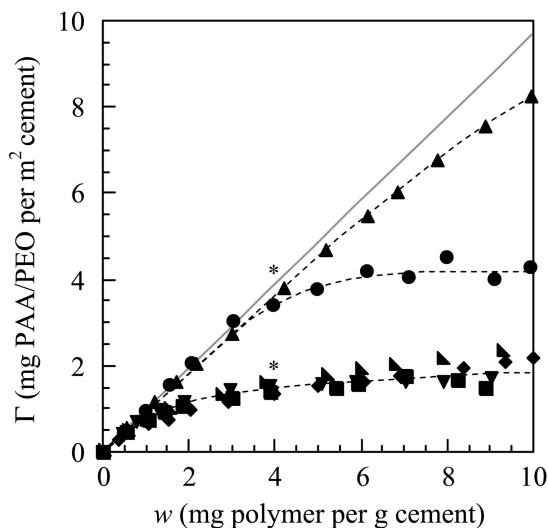


Fig. 4. Adsorption of PAA (▲) and PAA/PEO on cement particles in suspension ($w/c = 0.35$, $\phi = 0.47$). The PAA/PEO species had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varied widely in PEO molecular weight: (●) 100, (■) 700, (▼) 1000, (▲) 2000, and (◆) 3000 g/mol. The gray lines indicate 100% adsorption. (Note, the dashed lines merely guide the eye.)

decreased during the experimental times probed, except for cement-PAA/PEO100 suspensions, in which the conductivity increased once again at the onset of the induction period.

(4) Rheological Property Evolution of Concentrated Cement Systems

The G' evolution of pure cement pastes as a function of hydration time are shown in Fig. 7. The four curves plotted correspond to cement pastes that were hydrated for ~ 5 min, 0.5 h, 1 h, and 1.75 h, respectively, before disrupting the evolving particle network under high shear. G'_i values of $\sim 10^4$ Pa were observed for ordinary portland cement pastes at 6.5-min hydration. Interestingly, ordinary portland cement pastes experienced a two-fold decrease in their G'_i value with increasing hydration time

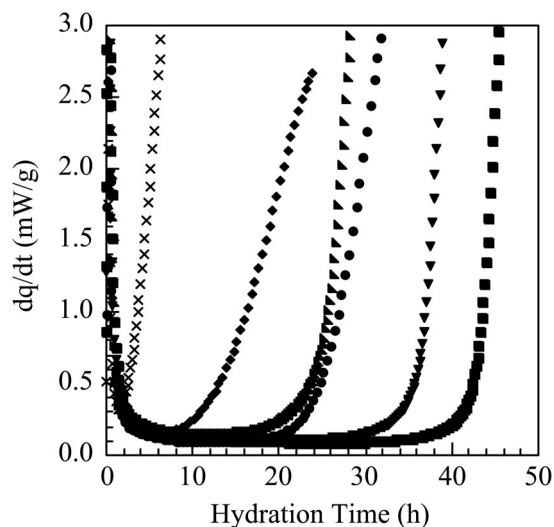


Fig. 5. Rate of heat evolution, dq/dt , as a function of hydration time for (×) cement pastes and cement-PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$, $w = w^*$). The PAA/PEO species had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varied widely in PEO molecular weight: (●) 100, (■) 700, (▼) 1000, (▲) 2000, and (◆) 3000 g/mol.

Table III. Pore Solution Composition and Calculated Ionic Strength of Type I Ordinary Portland Cement Paste

Dissolved ion content	In OPC (M)	Contribution to $[I]_{\text{OPC}}$ (%)
SO_4^{2-}	0.147	56.5
K^+	0.258	24.7
Ca^{2+}	0.022	8.4
Na^+	0.076	7.3
OH^-	0.032	3.1
$\text{Al}(\text{OH})_4^-$	2.3×10^{-4}	0.022
$\text{Fe}(\text{OH})_4^-$	5.8×10^{-5}	0.006

before the onset of the acceleratory period (~ 2 h). The high initial G'_i values and their reversible $G'(t)$ behavior (< 2 h of hydration) are indicative of particle flocculation in a deep primary attractive minima, which is in good agreement with interparticle potential calculations (see Ref. 25). At the onset of the acceleratory period (~ 2 h), the paste could no longer be disrupted under high shear. Instrument limitations hindered our ability to make accurate measurements beyond these hydration times.²⁶

The G'_i evolution of cement-PAA suspensions is shown in Fig. 8. An initial G'_i value of 10 Pa was approximately 3 orders of magnitude lower than observed for the pure cement pastes, indicating that PAA additions dramatically improve the initial stability of such systems. However, unlike our observations for the pastes or the cement-PAA/PEO suspensions described below, only a single $G'(t)$ curve was developed in this system corresponding to a rapid, irreversible rise in G' . On applying high shear to disrupt the particle network in cement-PAA suspensions that were hydrated for 3–6 min, the measured G'_i values fell along this master curve. After only 6 min of hydration, these suspensions stiffened irreversibly and there was no longer any recovery in G'_i as compared with the plateau modulus value of $\sim 10^5$ Pa.

The $G'(t)$ evolution of cement-PAA/PEO100, cement-PAA/PEO700, and cement-PAA/PEO3000 suspensions ($w = w^*$) are shown in Figs. 9(a)–(c). Several curves are presented in each plot, corresponding to suspensions that were hydrated for varying times before disrupting the evolving particle network under high shear. The initial G'_i values, which depended weakly on PEO molecular

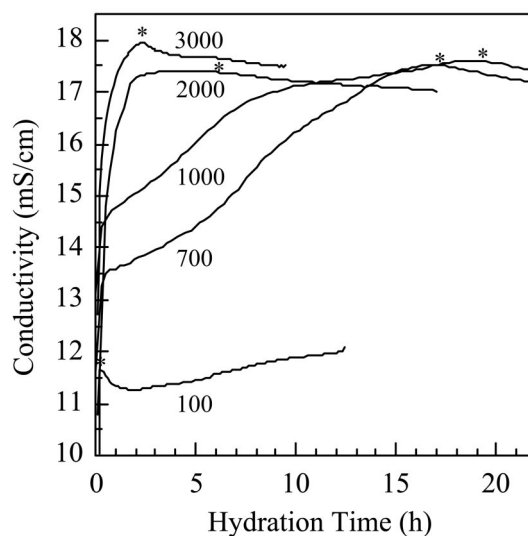


Fig. 6. Plot of the conductivity of cement-PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$) as a function of hydration time. The PAA/PEO comb polymers had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varying PEO molecular weight of 100, 700, 1000, 2000, and 3000 g/mol as labeled. The asterisks denote characteristic hydration times, τ_c , of 0.27, 17.2, 19.5, 5.6, and 2.8 h for PAA/PEO species with PEO molecular weights of 100, 700, 1000, 2000, and 3000 g/mol, respectively.

weight, ranged from ~ 6 to 50 Pa for PEO molecular weights of 100 to 3000 g/mol ($t = 6.5$ min). These values were several orders of magnitude below those observed for pure cement pastes (10^4 Pa) and reflect the dramatic improvement in stability imparted by PAA/PEO species. In their initial quiescent state, these systems experienced a rapid buildup in G' as a function of hydration time (see first curve in each plot). However, on disrupting the particle network at short hydration times (< 1 h), remarkable differences were observed between the $G'_i(t)$ evolution of cement–PAA/PEO700–3000 and cement–PAA/PEO100 systems. The cement–PAA/PEO700–3000 suspensions exhibited an order of magnitude or higher decrease in G'_i when the hydration time increased from 6.5 min to 1 h. Even more striking, these suspensions experienced a gel-to-fluid transition that resulted in cessation of the G' evolution under quiescent conditions until the onset of the acceleratory period. At the onset of the acceleratory period, the particle network re-formed within the cement suspensions leading to the reappearance of a gel-like response. In sharp contrast, cement–PAA/PEO100 suspensions exhibited a gel-like response over all hydration times. Beyond these initial differences, G'_i increased exponentially for all cement–PAA/PEO systems studied. For cement–PAA/PEO100 suspensions, the rise in G'_i was sharp and approached a maximum of ~ 100 Pa at 2 h, after which G'_i remained constant throughout the remainder of the induction period. For cement–PAA/PEO700–3000 suspensions, the exponential rise in G'_i was more gradual and increased with increasing PEO molecular weight. Beyond the onset of the acceleratory period, it became increasingly difficult to break down the particle networks under high shear and G'_i increased rapidly. Initial set was defined when there was no longer any recovery in G'_i as compared with the plateau modulus of $\sim 10^5$ Pa.

IV. Discussion

Our observations reveal that the rheological property evolution of concentrated cement suspensions depends strongly on PAA/PEO comb polymer architecture. The remarkable differences observed between the G' evolution for pure cement pastes, cement–PAA suspensions, and cement–PAA/PEO suspensions highlight the important role of PEO teeth. For example, even comb polymers with the shortest PEO teeth (i.e., a few monomer units in length) yielded dramatic improvements in stability relative to pure

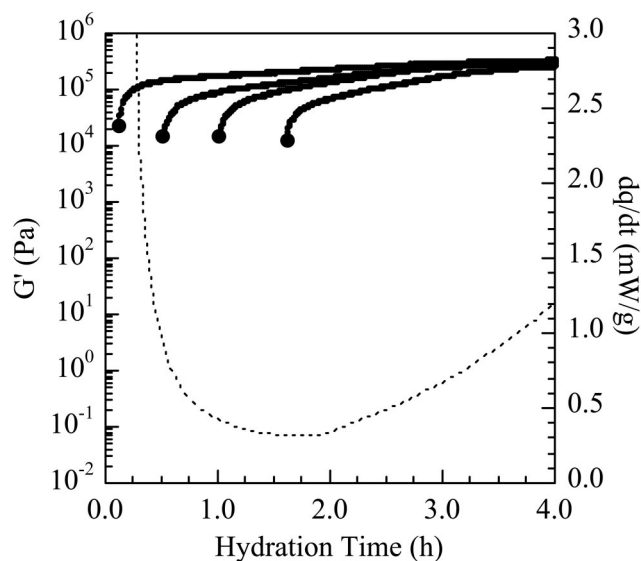


Fig. 7. Elastic shear modulus as a function of time for cement pastes ($w/c = 0.35$, $\phi = 0.47$) presheared at varying hydration times. The large symbols (●) indicate the initial elastic modulus values measured immediately after preshear. The calorimetry data (dashed curve) are replotted on the secondary y-axis for comparison.

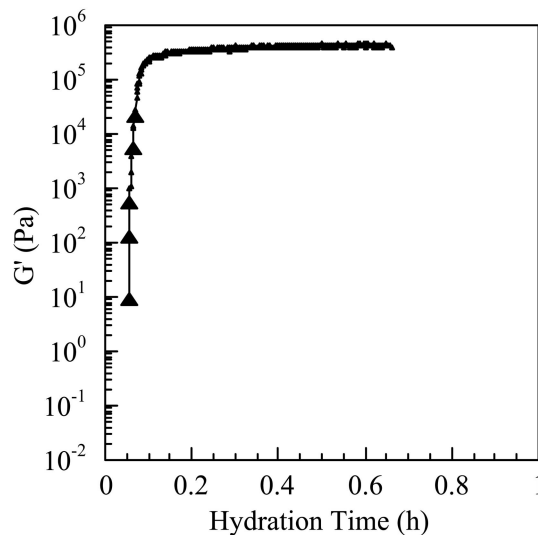


Fig. 8. Elastic shear modulus as a function of time for cement–PAA suspensions ($w/c = 0.35$, $\phi = 0.47$) presheared at varying hydration times. The large symbols (▲) indicate the initial elastic modulus values measured immediately after preshear.

PAA during initial hydration (< 1 h) where the cement particle surface and solution chemistry are evolving rapidly. At longer hydration times (> 1 h), the evolution of G'_i , measured on disrupting the cement–PAA/PEO suspensions under high shear, followed an exponential dependence. Here, we discuss the origins of the $G'_i(t)$ behavior for these systems with an emphasis on how PEO teeth enable comb polymers to impart stability to cement suspensions under conditions where pure PAA fails.

(1) Pure Cement Pastes

Ordinary portland cement pastes exhibited $G'_i(t)$ behavior that was fully reversible until the onset of the acceleratory period at ~ 2 h. Beyond this hydration time, the pastes stiffened irreversibly; i.e., their particle network could no longer be disrupted under high shear. This transition is of interest, because it generally coincides with initial setting due to the nucleation and growth of calcium silicate hydrate (C–S–H) resulting from C_3S hydration.¹¹ The observed stiffening strongly suggests that there is a fundamental change in the type of bonding between cement particles beyond this critical transition time. We attribute this to solid bridge formation at the contact points between particles within the flocculated network, as initially proposed by Lei and Struble.²⁷

(2) Cement–PAA Suspensions

PAA additions yielded enhanced initial stability for cement suspensions, as indicated by the 3 orders of magnitude decrease in their initial G'_i values relative to pure cement pastes. However, cement–PAA suspensions exhibited a dramatic rise in G' with increasing hydration time in the quiescent state indicative of particle network formation. Surprisingly, this rapid, irreversible rise in G' did not occur near the onset of the acceleratory period, as it would for pure cement pastes or cement–PAA/PEO suspensions, but rather took place only minutes after the initial contact between cement particles and water. At such short hydration times, particle dissolution results in a rapid rise of solution ionic strength (conductivity), but not significant formation of solid products. This remarkable network formation (or setting) must therefore differ in origin from the formation of solid bridges at the contact points between particles within the network, as commonly accepted.

To explain our findings, we must explore why initial hydration leads to such rapid setting in the cement–PAA system. This behavior can be understood by examining the behavior of PAA molecules in dilute solution under analogous pH and ionic strength conditions.^{18,28,29} We show that multivalent ions have a dramatic

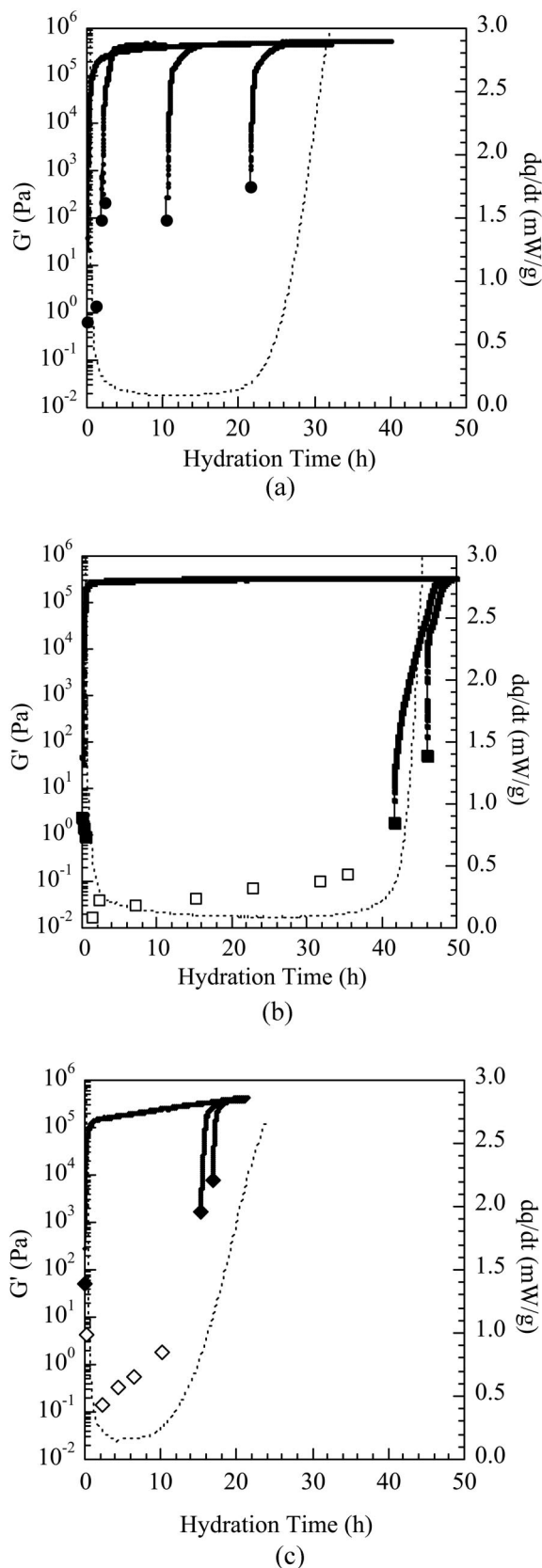


Fig. 9. Elastic modulus as a function of time for cement-PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$) presheared after varying hydration times. The PAA/PEO comb polymers had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varying PEO molecular weight of (●) 100, (■, □) 700, and (◆, ◇) 3000 g/mol. The large symbols indicate the initial elastic modulus values measured immediately after preshear. Open and filled symbols indicate fluid- and gel-like behavior, respectively. The calorimetry data (dashed curve) are replotted on the secondary y-axis for comparison.

impact on solution stability at high pH values, where PAA is highly ionized. Such species promote aggregation of PAA via ion-bridging interactions, when the ratio $[I]/[COO^-]$ exceeds unity. Analogous to the solution behavior, multivalent ion bridging also promotes the aggregation of PAA-coated particles in suspension;^{20,30–34} i.e., divalent Ca^{2+} ions dissolved into solution during initial cement hydration are likely responsible for the observed, rapid setting behavior. We estimate the calcium ion concentration and $[I]/[COO^-]$ ratio to be 0.022 M and 3.25, respectively. Therefore, we propose that the rapid setting of cement-PAA suspensions stems from ion-bridging effects, in which “bonds” comprised of polymeric bridges cross linked by multivalent ions form at the contact points between particles in a gelled network, as illustrated schematically in Fig. 10.

(3) Cement-PAA/PEO Suspensions

The $G'(t)$ evolution observed for cement-PAA/PEO suspensions at short hydration times ($t < 1$ h) was far different from that observed for pure cement pastes or cement-PAA suspensions. The addition of PAA/PEO species yielded dramatic improvements in stability to these suspensions over the entire range of PEO teeth lengths investigated. Their enhanced stability led to a significant decrease in the initial G'_i values, i.e., roughly four orders of magnitude lower relative to initial values measured for the pure cement pastes, which was comparable to the initial values measured for the cement-PAA suspensions. Because PAA/PEO species impart a nearly identical degree of initial stability to cement suspensions as PAA, the primary contribution of the PEO teeth cannot simply be enhanced steric stabilization, as is commonly reported in the literature.^{8,9,35–42}

In the quiescent state, cement-PAA/PEO suspensions exhibited a dramatic rise in G' with increasing hydration time indicative of particle network formation. Unlike cement-PAA suspensions, however, this particle network was easily disrupted under high shear. Both the network reversibility and phase behavior depended strongly on PEO teeth length. For example, cement-PAA/PEO suspensions prepared with the shortest PEO teeth length (100 g/mol PEO) exhibited a substantial rise in the initial G' values during the first hour of hydration and remained in a gelled state throughout the hydration process. In contrast, cement-PAA/PEO suspensions comprised of longer PEO teeth (700–3000 g/mol PEO) became more stable when their particle network was disrupted during initial hydration (< 1 h). After shearing, their G'_i values were about 2 orders of magnitude lower after 1 h of hydration than those observed initially. Moreover, these systems became fully stabilized, as evidenced by a gel-to-fluid transition. Without dynamically probing their rheological property evolution, these remarkable observations would not have been uncovered.

The charge-neutral PEO teeth provide two important functions to improve the stability of concentrated cement suspensions. First, they shield the underlying polyelectrolyte (PAA) backbone from ion-bridging interactions with multivalent counterions in solution, as illustrated schematically in Fig. 10.^{18,28,29} We have shown that only a few monomeric ethylene oxide (EO) units (i.e., 100 g/mol PEO) are needed to protect PAA/PEO species from aggregating in solution in the presence of divalent ions. Mitigating these ion-bridging interactions clearly prevents the rapid, premature stiffening observed for cement-PAA suspensions. Second, PAA/PEO comb polymers do not experience large size changes in response to variations in pH or ionic strength.⁴³ As a result, it is expected that the steric barrier they provide when adsorbed on cement particle surfaces is relatively insensitive to ionic strength changes stemming from cement hydration. Prieve and Russel have recently demonstrated that van der Waals (vdW) forces between colloidal particles are actually weakened as ionic strength increases.⁴⁴ Since ionic strength increases are substantial during ordinary portland cement hydration, we believe that the sudden drop in G'_i and concurrent gel-to-fluid transition observed for the cement-PAA/PEO700–3000 suspensions likely reflect a weakening of the net attractive vdW interactions in this system.

PAA/PEO comb polymers provide stability to concentrated cement suspensions well beyond the first few minutes of hydration where pure PAA fails. At longer times (>1 h), the cement–PAA/PEO suspensions exhibited a rise in G'_i proportional to $\exp(t/\tau_c)$ (see Fig. 11). Characteristic hydration times of 0.27, 17.2, 19.5, 5.6, and 2.8 h were determined for cement–PAA/PEO100, –PAA/PEO700, –PAA/PEO1000, –PAA/PEO2000, and –PAA/PEO3000 suspensions, respectively, from the solution conductivity measurements. This dependence is significant, because it establishes a link between the rheological and hydration behavior of cement–PAA/PEO suspensions through τ_c as well as the generality of this relationship for cements containing comb polymers of varying architecture.

In the fluid state, the observed G'_i evolution cannot be related to microstructural changes (e.g., bond strength increase) stemming

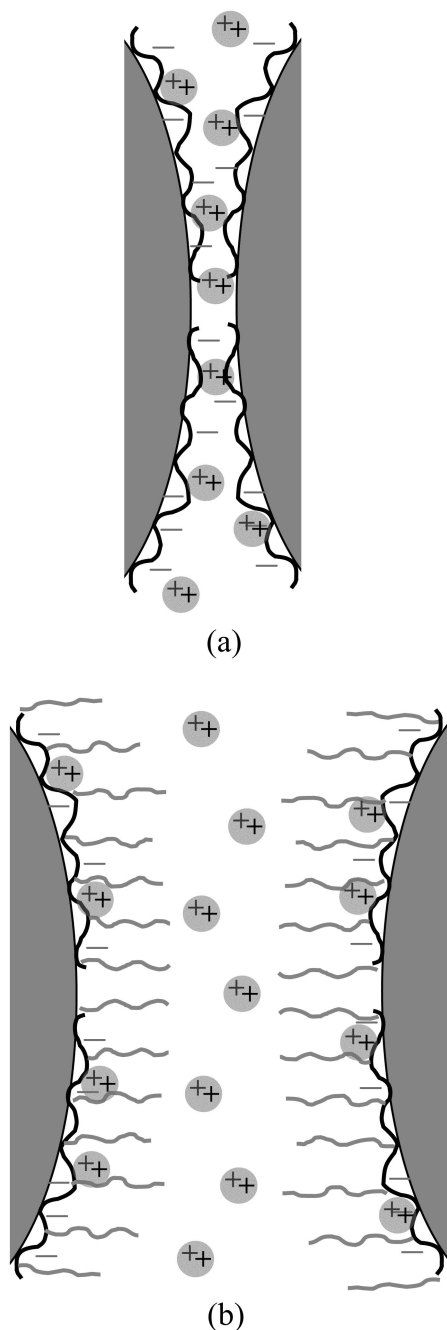


Fig. 10. Schematic illustrations of (a) flocculation between two PAA-coated ceramic particles due to multivalent ion bridging and (b) “shielding” from ion-bridging interactions provided by the PEO teeth. [Not drawn to scale.]

from formation of a particle network, as the net interparticle interaction is repulsive in nature. Thus, one must view their observed elastic response in an alternate context by examining the behavior expected for concentrated colloidal fluids.⁴⁵ Lionberger and Russel⁴⁶ have studied model systems comprised of colloidal microspheres in index-matched solvents and have shown that their elastic modulus increases with increasing solids volume fraction. This dependence is relevant for cement systems, in which solid hydration products (e.g., ettringite and calcium–aluminate–sulfate monohydrate) form in solution as hydration proceeds. These products are known to have deleterious effects on the flow behavior of cement–polyelectrolyte suspensions, especially when the C_3A /gypsum content is high.¹¹ Because these species grow in preferred, crystallographic directions that result in rodlike morphology,^{10,47} they can occupy large excluded volumes (even at low actual volume fractions), giving rise to significant increases in the shear elastic modulus. We therefore propose that the primary mechanism responsible for the evolution of G'_i observed beyond the deceleratory period is the creation of new solids. This finding is significant, because it contradicts our earlier hypothesis that such changes mainly reflect an increase in bond strength within the particle network.³ This new interpretation is also better aligned with our observations that PAA/PEO comb polymers are highly robust additives that are insensitive to pH and ionic strength changes.⁴⁸

Nonadsorbed (or “free”) PAA/PEO species in solution play an important role in inhibiting the nucleation and growth of solid hydration products, and thus, the irreversible changes in G' at long hydration times in cement–PAA/PEO suspensions. PEO teeth length has a direct influence on their adsorption behavior and, thus, the amount of such species that remain free in solution (see Fig. 4). In the absence of nonadsorbed species in solution, hydration products grow uninhibited in preferred, crystallographic directions.^{10,47,49–56} For example, C_3A /gypsum hydration products preferentially form with long, rodlike morphology that can occupy large excluded volumes and result in a strong, exponential rise in the elastic shear modulus of concentrated cement suspensions.^{10,47} In the presence of nonadsorbed species in solution, however,

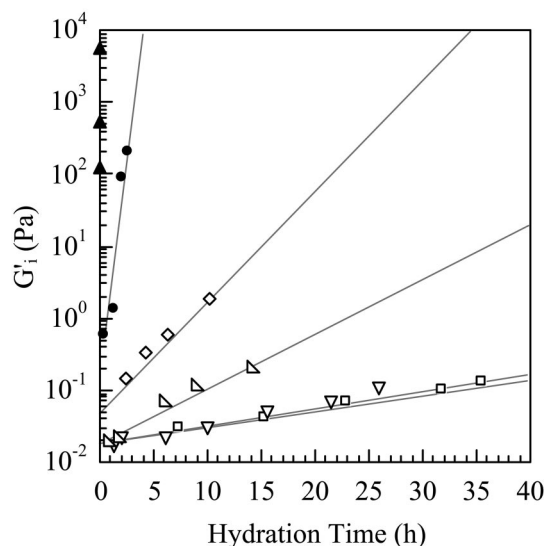


Fig. 11. Semilog plot of the initial elastic moduli (measured after preshearing the suspensions at intermittent hydration times) plotted as a function of hydration time for (▲) cement–PAA suspensions and cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$, $w = w^*$). The PAA/PEO species had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varied widely in PEO molecular weight: (●) 100, (□) 700, (▽) 1000, (◻) 2000, and (◇) 3000 g/mol. Open and closed symbols indicate liquid- and gel-like behavior, respectively. The lines were determined using $\frac{1}{2} \sum n_i z_i^2(t) \sim \exp(t/\tau_c)$, where τ_c was 0.27, 17.2, 19.5, 5.6, and 2.8 h for PAA/PEO comb polymers with PEO teeth lengths of 100, 700, 1000, 2000, and 3000 g/mol, respectively.

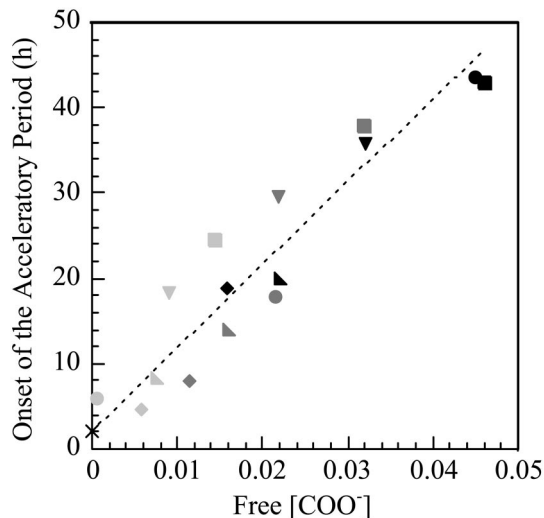


Fig. 12. Onset of the acceleratory period in concentrated, cement–PAA/PEO suspensions ($w/c = 0.35$, $\phi = 0.47$) plotted as a function of the molar concentration of free carboxylic acid groups (due to nonadsorbed PAA/PEO). The PAA/PEO species had constant PAA molecular weight (5000 g/mol) and acid:imide ratio (7:1), but varied widely in PEO molecular weight: (●) 100, (■) 700, (▼) 1000, (▲) 2000, (◆) 3000 g/mol. Normalized PAA/PEO weight fractions (w/w^*) of 0.6, 1.0, and 1.3 are indicated by light gray, dark gray, and black symbols, respectively. The dashed line is the best-fit to the data (correlation coefficient, R , is 0.94) intersecting the y -axis at 2 h (i.e., the set time for (×) pure cement pastes).

preferential growth along certain crystallographic directions is inhibited, leading to a slower, more uniform growth in all directions.^{49–54,57} In cement–PAA/PEO suspensions with PEO teeth lengths between 700 and 3000 g/mol, there is a significant fraction of free species in solution that may suppress crystallographic growth of solid hydration products. As a result, cement–PAA/PEO700–3000 suspensions have an exponential rise in G'_i , where τ_c ranges from 2.7 to 19.5 h. In sharp contrast, cement–PAA/PEO suspensions with the shortest PEO teeth (100 g/mol PEO) exhibited an exponential rise in G'_i during the deceleratory period with a τ_c value of 0.27 h. In this system, the PAA/PEO100 species are strongly adsorbed onto the cement particles, leaving few free species in solution to suppress rodlike growth. This sharp rise in G'_i ceased at the end of the deceleratory period because C_3A /gypsum hydration product formation (e.g., ettringite and monosulfate) proceeded so rapidly that, likely, the limiting reactant species (i.e., $Al(OH)_4^-$) was completely consumed.

Nonadsorbed PAA/PEO species also have a marked effect on the nucleation of C–S–H and, thus, strongly influence the initial setting behavior of cement–PAA/PEO suspensions.⁹ Such species bind Ca^{2+} cations due to electrostatic interactions with the negatively charged PAA backbone. Thus, more cement dissolution must occur before the pore solution reaches the Ca^{2+} , OH^- , and silicate ion concentration needed for C–S–H nucleation.⁵⁸ We found that the onset of the acceleratory period depends linearly on free $[COO^-]$ in solution, as shown in Fig. 12, which is in good agreement with the previous observations reported by Yamada *et al.*⁹ At the onset of the acceleratory period, the formation of calcium silicate hydrate (C–S–H) promotes the sharp rise in G'_i . Cement–PAA/PEO700–3000 systems undergo gelation that coincides with this onset, yielding a particle network that can still be partially disrupted under high shear well into the acceleratory period of hydration. Ultimately, these systems stiffen irreversibly (i.e., initial set), which we attribute to the formation of C–S–H solid bridges at the contact points between cement particles in the network.

V. Conclusions

We have studied the rheological property evolution of concentrated cement suspensions in the absence and presence of PAA and PAA/PEO comb polymers of varying PEO teeth molecular weight. Cement–PAA suspensions undergo rapid irreversible stiffening after only minutes of hydration due to ion-bridging interactions between adsorbed PAA species and divalent counterions that dissolve from the cement particles. In sharp contrast, the presence of PEO teeth comprised of only a few monomer units mitigate deleterious ion-bridging interactions, thereby promoting cement suspension stability under conditions where pure PAA fails. With larger PEO teeth (i.e., 700–3000 g/mol), cement–PAA/PEO suspensions exhibit a remarkable gel-to-fluid transition during the deceleratory period. At longer times, all cement–PAA/PEO suspensions exhibited $G'_i \sim \exp(t/\tau_c)$ before the onset of the acceleratory period and a sharp rise in G'_i after the onset of the acceleratory period. These findings were attributed to the hydration of C_3A /gypsum and C_3S , respectively, to form solid hydration products. The nonadsorbed PAA/PEO species interact with dissolved ions and solid nuclei to suppress the formation of solid hydration products, but, ultimately, the cement–PAA/PEO suspensions undergo initial set (i.e., C–S–H solid bridges form at the solid contacts of a gelled network).

Acknowledgments

The authors acknowledge fruitful discussions with J. F. Young, J. Cheung, and A. Jecknavorjian.

References

- 1V. Tohver, J. E. Smay, A. Braem, P. V. Braun, and J. A. Lewis, "Nanoparticle Halos: A New Colloid Stabilization Mechanism," *PNAS*, **98** [16] 8950–54 (2001).
- 2J. A. Lewis, H. Matsuyama, G. Kirby, S. Morissette, and J. F. Young, "Polyelectrolyte Effects on the Rheological Properties of Concentrated Cement Suspensions," *J. Am. Ceram. Soc.*, **83** [8] 1905–13 (2000).
- 3G. H. Kirby, and J. A. Lewis, "Rheological Property Evolution In Concentrated Cement–Polyelectrolyte Suspensions," *J. Am. Ceram. Soc.*, **85** [12] 2989–94 (2002).
- 4M. Collepari, L. Coppola, T. Cerulli, G. Ferrari, C. Pistolesi, P. Zaffaroni, and F. Quek, "Zero Slump Loss Superplasticizer Concrete"; pp. 73–80 in *Proceedings of the Congress of Our World in Concrete and Structures*. Edited by C. T. Tam. Singapore, 1993.
- 5K. Kodama and S. Okazawa, "Development of Superplasticizers for High-Strength Concrete," *Semento Konkurito*, **546**, 24–32 (1992).
- 6T. Andoh, S. Kase, and S. Tanaka, "Cement Dispersion Effect by Polycarboxylic Acid Type Mixture," *Jpn. Cem. Assoc. Proc. Cem. Concr.*, **47**, 184–89 (1993).
- 7T. Nawa, H. Ichiboji, and M. Kinoshita, "Influence of Temperature on Fluidity of Cement Paste Containing Superplasticizer with Polyethylene Oxide Graft Chains"; pp. 195–210 in *Superplasticizers and Other Chemical Admixtures in Concrete* (Ottawa, Ontario, Canada). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 2000.
- 8M. Kinoshita, T. Nawa, M. Lida, and H. Ichiboji, "Effect of Chemical Structure on Fluidizing Mechanism of Concrete Superplasticizer Containing Polyethylene Oxide Graft Chains"; pp. 163–79 in *Superplasticizers and Other Chemical Admixtures in Concrete* (Ottawa, Ontario, Canada). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 2000.
- 9K. Yamada, T. Takahashi, S. Hanehara, and M. Matsuhisa, "Effects of the Chemical Structure on the Properties of Polycarboxylate-Type Superplasticizer," *Cem. Concr. Res.*, **30**, 197–207 (2000).
- 10F. Kreppelt, M. Weibel, D. Zampini, and M. Romer, "Influence of Solution Chemistry on the Hydration of Polished Clinker Surfaces: A Study of Different Types of Polycarboxylic Acid-Based Admixtures," *Cem. Concr. Res.*, **32**, 187–98 (2002).
- 11H. F. W. Taylor, *Cement Chemistry*, 2nd ed. Thomas Telford Publishing, London, 1997.
- 12D. C. Darwin and E. M. Gartner, "Cement Admixture Product," U.S. Pat. No. 5 665 158, 1997.
- 13A. Arfaei and N. H. Milford, "Hydraulic Cement Additives and Hydraulic Cement Compositions Containing Same," U.S. Pat. No. 4 960 465, 1990.
- 14J. Cesarano III, I. A. Aksay, and A. Bleier, "Stability of Aqueous α - Al_2O_3 Suspensions with Poly(methacrylic acid) Polyelectrolyte," *J. Am. Ceram. Soc.*, **71** [4] 250–55 (1988).
- 15J. Cesarano III and I. A. Aksay, "Processing of Highly Concentrated Aqueous α -Alumina Suspensions Stabilized with Polyelectrolyte," *J. Am. Ceram. Soc.*, **71** [12] 1062–67 (1988).
- 16S. Provencher, "A General Purpose Constrained Regularization Program for Inverting Noisy Linear Algebraic and Integral Equations," *Comput. Phys. Commun.*, **27** [3] 229–42 (1982).
- 17N. Q. Dzuy and D. V. Boger, "Yield Stress Measurement for Concentrated Suspensions," *J. Rheol. (N.Y.)*, **27** [4] 321–49 (1983).

- ¹⁸M. Olvera de la Cruz, L. Belloni, M. Delsanti, J. P. Dalbiez, O. Spalla, and M. Drifford, "Precipitation of Highly Charged Polyelectrolyte Solutions in the Presence of Multivalent Salts," *J. Chem. Phys.*, **103**, 5781–91 (1995).
- ¹⁹G. S. Manning, "The Molecular Theory of Polyelectrolyte Solutions with Applications to the Electrostatic Properties of Polynucleotides," *Q. Rev. Biophys.*, **2** [2] 179–246 (1978).
- ²⁰C.-C. Li and J.-J. Jean, "Interaction between Dissolved Ba²⁺ and PAA-NH₄ Dispersant in Aqueous Barium Titanate Suspensions," *J. Am. Ceram. Soc.*, **85** [6] 1449–55 (2002).
- ²¹E. J. Gartner, J. F. Young, D. A. Damidot, and I. Jawed, "Hydration of Portland Cement"; pp. 57–108 in *Structure and Performance of Portland Cements*. Edited by J. Bensted and P. Barnes. E&FN Spon, New York, 2002.
- ²²R. Kondo and M. J. Daimon, "Early Hydration of Tricalcium Silicate: A Solid Reaction with Induction and Acceleration Periods," *J. Am. Ceram. Soc.*, **52** [9] 503–508 (1969).
- ²³R. Kondo and S. Ueda, "Kinetics of Hydration of Cements"; pp. 203–55 in *Proceedings of the 5th International Symposium on the Chemistry of Cement Paste and Concrete*, Vol. 2. Japan Cement Association, Tokyo, 1969.
- ²⁴J. N. Israelachvili, *Intermolecular and Surface Forces*. Academic Press: New York, 1992.
- ²⁵G. H. Kirby, "PAA/PEO Comb Polymer Effects on the Rheological Property Evolution in Concentrated Cement Suspensions"; Ph.D. dissertation. University of Illinois, Urbana, IL, 2003.
- ²⁶L. Nachbaur, J. C. Mutin, A. Nonat, and L. Choplin, "Dynamic Mode Rheology of Cement and Tricalcium Silicate Pastes From Mixing to Setting," *Cem. Concr. Res.*, **31**, 183–92 (2001).
- ²⁷W.-G. Lei and L. J. Struble, "Microstructure and Flow Behavior of Fresh Cement Paste," *J. Am. Ceram. Soc.*, **80** [8] 2021–28 (1997).
- ²⁸E. Raspaud, M. Olvera de la Cruz, J.-L. Sikorav, and F. Livolant, "Precipitation of DNA by Polyamines: A Polyelectrolyte Behavior," *Biophys. J.*, **74**, 381–93 (1998).
- ²⁹J. Widom and R. L. Baldwin, "Monomolecular Condensation of λ -DNA Induced by Combust Hexamine," *Biopolymers*, **22** 1595–620 (1983).
- ³⁰J. M. Berg, P. M. Claesson, and R. D. Neuman, "Interactions between Mica Surfaces in Na-PAA Solutions Containing Ca²⁺ Ions," *J. Colloid Interface Sci.*, **161** [182–89] (1993).
- ³¹N. S. Bell, J. Sindel, F. Aldinger, and W. M. Sigmund, "Cation-Induced Collapse of Low-Molecular-Weight Polyacrylic Acid in the Dispersion of Barium Titanate," *J. Colloid Interface Sci.*, **254**, 296–305 (2002).
- ³²M. A. G. Dahlgren, "Effect of Counterion Valency and Ionic Strength on Polyelectrolyte Adsorption," *Langmuir*, **10** 1580–83 (1994).
- ³³S. Biggs and T. W. Healy, "Electrosteric Stabilization of Colloidal Zirconia with Low Molecular Weight Polyacrylic Acid," *J. Chem. Soc., Faraday Trans.*, **90** [22] 3415–21 (1994).
- ³⁴D. J. Rojas, P. M. Claesson, P. M. Muller, and R. D. Neuman, "The Effect of Salt Concentration on Adsorption of Low-Charge-Density Polyelectrolytes and Interactions between Polyelectrolyte-Coated Surfaces," *J. Colloid Interface Sci.*, **205** [77–88] (1998).
- ³⁵E. Sakai and M. Daimon, "Mechanisms of Superplasticity"; pp. 91–111 in *Materials Science of Concrete*. Edited by S. Mindess. The American Ceramic Society, Westerville, OH, 1995.
- ³⁶E. Sakai, A. Kawakami, and M. Daimon, "Dispersion Mechanisms of Comb-Type Superplasticizers Containing Grafted Poly(ethylene oxide) Chains," *Macromol. Symp.*, **175**, 367–76 (2001).
- ³⁷H. Uchikawa, S. Hanehara, and D. Sawaki, "The Role of Steric Repulsive Force in the Dispersion of Cement Particles in Fresh Paste Prepared with Organic Admixture," *Cem. Concr. Res.*, **27** [1] 37–50 (1997).
- ³⁸G. Ferrari, T. Cerulli, P. Clemente, M. Dragoni, M. Gamba, and F. Surico, "Influence of Carboxylic Acid-Carboxylic Ester Ratio of Carboxylic Acid Ester Superplasticizer on Characteristics of Cement Mixtures"; *Superplasticizers and Other Chemical Admixtures in Concrete* (Ottawa, Ontario, Canada). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 2000.
- ³⁹E. Sakai, J. K. Kang, and M. Daimon, "Action Mechanisms of Comb-Type Superplasticizers Containing Grafted Polyethylene Oxide Chains"; pp. 75–89 in *Superplasticizers and Other Chemical Admixtures in Concrete* (Ottawa, Ontario, Canada). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 2000.
- ⁴⁰E. Sakai and M. Daimon, "Dispersion Mechanisms of Alite Stabilized by Superplasticizers Containing Polyethylene Oxide Graft Chains"; *Superplasticizers and Other Chemical Admixtures in Concrete* (Rome, Italy). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 1997.
- ⁴¹A. Ohta, T. Sugiyama, and S. Tanaka, "Fluidizing Mechanism and Application of Polycarboxylate-Based Superplasticizers"; pp. 359–78 in *Superplasticizers and Other Chemical Admixtures in Concrete* (Rome, Italy). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 1997.
- ⁴²M. Shonaka, K. Kitagawa, H. Satoh, T. Izumi, and T. Mizunuma, "Chemical Structures and Performance of New High-Range Water-Reducing and Air-Entraining Agents"; pp. 599–614 in *Superplasticizers and Other Chemical Admixtures in Concrete* (Rome, Italy). Edited by V. Malhotra. American Concrete Institute, Farmington Hills, MI, 1997.
- ⁴³J. Sindel, N. S. Bell, and W. M. Sigmund, "Electrolyte Effects on Nonionic Steric Layers: Bis-hydrophilic PMAA-PEO Diblock Copolymers Adsorbed on Barium Titanate," *J. Am. Ceram. Soc.*, **82** [11] 2953–57 (1999).
- ⁴⁴D. C. Prieve and W. B. Russel, "Simplified Predictions of Hamaker Constants from Lifshitz Theory," *J. Colloid Interface Sci.*, **125** [1] 1–13 (1988).
- ⁴⁵R. L. Larson, *The Structure and Rheology of Complex Fluids*. Oxford University Press, Inc., New York, 1999.
- ⁴⁶R. A. Lionberger and W. B. Russel, "High Frequency Modulus of Hard Sphere Colloids," *J. Rheol.* (N.Y.), **38** [6] 1885–908 (1994).
- ⁴⁷E. E. Hekal and E. A. Kishar, "Effect of Sodium Salt of Naphthalene-Formaldehyde Polycondensate on Ettringite Formation," *Cem. Concr. Res.*, **29** 1535–40 (1999).
- ⁴⁸G. H. Kirby, D. J. Harris, Q. Li, and J. A. Lewis, "PAA-PEO Comb Polymer Effects on the Stability of BaTiO₃ Nanoparticle Suspensions," *J. Am. Ceram. Soc.* **87** [2] 181–86 (2004).
- ⁴⁹H. Furedi-Milhofer, M. Sikiric, L. Tunik, N. Filipovic-Vincekovic, and N. Garti, "Interactions of Organic Additives with Ionic Crystal Hydrates: The Importance of the Hydrated Layer," *Int. J. Mod. Phys. B*, **16**, 359–66 (2002).
- ⁵⁰A. Tsortos and G. Nancollas, "The Role of Polycarboxylic Acids in Calcium Phosphate Mineralization," *J. Colloid Interface Sci.*, **250** 159–67 (2002).
- ⁵¹A. Bigi, E. Boanini, R. Botter, S. Panzavolta, and K. Rubini, " α -Tricalcium Phosphate Hydrolysis to Octacalcium Phosphate: Effect of Sodium Polyacrylate," *Biomaterials*, **23**, 1849–54 (2002).
- ⁵²A. Bigi, E. Boanini, G. Falini, S. Panzavolta, and N. Roveri, "Effect of Sodium Polyacrylate on the Hydrolysis of Octacalcium Phosphate," *J. Inorg. Biochem.*, **78**, 227–33 (2000).
- ⁵³A. Bigi, E. Boanini, M. Borghi, G. Cojazzi, S. Panzavolta, and N. Roveri, "Synthesis and Hydrolysis of Octacalcium Phosphate: Effect of Sodium Polyacrylate," *J. Inorg. Biochem.*, **75**, 145–51 (1999).
- ⁵⁴A. Bigi, E. Boanini, G. Cojazzi, G. Falini, and S. Panzavolta, "Morphological and Structural Investigation of Octacalcium Phosphate Hydrolysis in the Presence of Polyacrylic Acids: Effect of Relative Molecular Weights," *Cryst. Growth Des.*, **1** [3] 239–44 (2001).
- ⁵⁵W. Prince, M. Espagne, and P.-C. Aitcin, "Ettringite Formation: A Crucial Step in Cement-Superplasticizer Compatibility," *Cem. Concr. Res.*, [33] 635–41 (2003).
- ⁵⁶W. Prince, M. Edwards-Lajnef, and P.-C. Aitcin, "Interaction between Ettringite and a Polynaphthalene Sulfonate Superplasticizer in a Cementitious Paste," *Cem. Concr. Res.*, **32**, 79–85 (2002).
- ⁵⁷J. F. Young, "A Review of the Mechanisms of Set-Retardation in Portland Cement Pastes Containing Organic Admixtures," *Cem. Concr. Res.*, **2**, 415–33 (1972).
- ⁵⁸P. C. Hewlett, "Physico-Chemical Interactions between Chemical Admixtures and Portland Cement," *J. Mater. Educ.*, **9** [4] 395–435 (1983). □