Rheological Properties of Alumina–Polyacrylate Gel Dispersions

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ABSTRACT: Rheological properties of aqueous alumina–polyacrylate gel dispersions have been investigated with a controlled stress rheometer as functions of both cross-linked polyacrylate and alumina concentrations at pH 13. These studies were conducted to understand the role of alumina–polyacrylate interactions in building the rheology of complex liquids that contain surfactants, sodium hypochlorite, alkali, and inorganic salts. Viscosity and viscoelasticity of polyacrylate gel dispersions can be enhanced by the addition of colloidal alumina. The trends in viscosity and viscoelasticity are explained on the basis of changes in the conformation of polyacrylate and repulsive interactions of negatively charged polyacrylate and alumina particles.

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KEY WORDS: Alumina, gel, loss modulus, polyacrylic acid, sodium hypochlorite, storage modulus, thickened bleach, viscoelasticity, viscosity, yield stress, zeta potential.

The macromolecular chemistry and technology of high-molecular weight polymeric (sodium) polyacrylate gels and alumina suspensions are described frequently in the scientific and patent literature. Such systems are used as thickening and structuring agents in water-based systems (1–6). Alumina suspensions, which are rheologically similar to clay suspensions, have been studied extensively in the presence of surfactants (alcohol ethoxylates, sodium dodecyl sulfate, and sodium linear alkylbenzene sulfonate) (7,8), and polymers, such as low-molecular weight polyacrylic acids (MW = 88,000–90,000), and a hydrophobically modified anionic polymer (a maleic anhydride α-olefin copolymer) (9,10). Although much can be learned about such properties as surface-charge effects, molecular configuration of adsorbed polymer, dispersion stability, and viscosity enhancement or reduction from the existing literature on alumina, alumina–surfactant and alumina–polyacrylate dispersions, relatively few attempts have been made to study the dynamic mechanical properties of alumina–polyacrylate–water systems.

This work describes systematic investigations of the rheological properties of colloidal alumina in aqueous cross-linked polyacrylate gel dispersions. The effects of electrolyte, sodium hypochlorite and a detergent matrix on the rheology of alumina–polyacrylate dispersions were also examined.

EXPERIMENTAL PROCEDURES

General details. The materials employed in this study, polyacrylic acid (trade name Carbopol-614, believed to be highly cross-linked polymers with molecular weights of about 1×10^6–4×10^6; BFGoodrich Company, Cleveland, OH) and Dispal T-23 alumina (Vista Chemical Company, Austin, TX) were used as received from the companies. Deionized water was used as a solvent for all experiments. The NaOCl used was a commercially prepared material containing NaCl equivalent to NaOCl. Hypochlorite concentration of the commercial sample was determined iodometrically (11). The weight percentage of hypochlorite in solutions containing alumina, polyacrylate, or alumina–polyacrylate was determined with a Brinkmann (Westbury, NY) 686-Titroprocessor. A Brookfield (Stoughton, MA) Digital Viscometer (RVTD) was used for viscosity measurements at 21–22°C with spindle #6 (unless otherwise mentioned) at 20 rpm. Measurements were taken after 90 s of equilibration time. Rheological measurements were performed on a Carri-Med CSL Controlled Stress Rheometer (Mitech Corp., Twinsburg, OH) at room temperature with parallel plate geometry (plate diameter, 4 cm), with the Oscillation Package. Test dispersions were prepared a few days before the viscosity and rheological measurements by the procedure explained below. The age of different test dispersions was not necessarily the same at the time of measurement.

Electrokinetic measurements. Electrokinetic measurements were made with the Matec System ESA-8050 (Matec Applied Sciences, Hopkinton, MA). This system consists of a measuring cell with a pH electrode system, a conductivity and a temperature probe, a high-speed stirrer, and automatic burettes for addition of acid or base. The Matec electroacoustic detector was placed approximately 2.5 cm deep into the mixtures of testing dispersions. To ensure a maximum electroacoustic signal, the frequency of the electrical field was optimized for alumina or polyacrylic acid by using the Matec phase calibrating program. The average particle radius for an aqueous dispersion of alumina was 0.02 μm and that for a cross-linked polyacrylic acid gel dispersion was 0.5 μm. The size information was provided by the manufacturers of alumina and cross-linked polyacrylic acid. For alumina and polyacrylic acid dispersions, powder densities of 3.9 and 1.41 g/cc were used, respectively. These parameters (particle size and density) are required by the Matec technique to convert the electrokinetic sonic amplitude into zeta potential (ζ). In ζ

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determinations, titrations of alumina and polyacrylic acid dispersions were carried out with 1N NaOH aqueous solutions. Experimental procedures for the Matec System can be found in several references (12–14).

Preparation of alumina dispersions. Typically, 20 g of alumina was slowly dispersed into 980 g stirring water (2% solution) at room temperature. Upon mechanical stirring for at least 10 min, a homogenously dispersed mixture was obtained.

Preparation of 4% dispersion of polyacrylic acid. A 4% (weight %) aqueous solution of polyacrylic acid was prepared by slowly dispersing the polymer powder (80 g) into the stirring water (1500 g). The powder container was thoroughly rinsed with 420 g water, and the washings were combined with the stirring mixture. Upon stirring for at least 30 min with a conventional impeller, a thin, cloudy, lump-free dispersion was obtained. Additional batches were similarly prepared. These stock solutions were stored in one gallon capped jars at room temperature in the dark.

Preparation of alumina–polyacrylate gel dispersions. Generally, an aqueous dispersion of alumina was added into a neutralized polyacrylic acid gel (2% polyacrylic acid/2% NaOH) with stirring at room temperature. A stock solution of polyacrylate gel was prepared at least two days in advance. Additional amounts of water and NaOH (~1M) solution (only a couple of drops, to adjust the pH of the system to ~13) were added to the stirring gel to prepare samples of varying concentrations of polyacrylate and alumina–polyacrylate. The resulting gel dispersions were either transluscent or milky.

As an example, a gel dispersion containing 0.75% polyacrylic acid + 1% alumina + 1.17% NaCl was prepared by the following procedure. Water (206.65 g) was added into the stirring neutralized polyacrylic acid gel (187.50 g; 2% polyacrylic acid/2% NaOH) at room temperature. The gel was stirred thoroughly for a few minutes, and an aqueous dispersion of alumina, 100 g (5% by weight), was added into the diluted gel. After 10 to 15 min of stirring, solid NaCl (5.85 g) was added into the alumina–polyacrylate gel. The contents were mixed thoroughly for at least 10 min.

Incorporation of NaOCl solution into the alumina dispersions. Water (110.83 g) was added into 30.0 g of 25% alumina dispersion. The mixture was stirred with a conventional impeller for 5 min. Aqueous solution (5.0 g) of 50% NaOH was added, and the dispersion was mixed for another 5 min. Finally, 104.17 g of 12% NaOCl solution was added slowly into the alkaline alumina, and the mixture was stirred for 10 min. The resultant gel showed a pH of 13.6 and a viscosity of 1.08 × 10^3 mPa.s (spindle #4, 20 rpm) after one day.

Incorporation of NaOCl solution into the polyacrylate gels. Water (13.3 g) was added into the stirring dispersion of polyacrylic acid (4% solution, 125.0 g). The resultant mixture was stirred for 5 min to ensure proper mixing. A solution of 50% NaOH (7.5 g) was added to the above mixture. Upon addition of NaOH, the system was immediately thickened, and this produced a stiff, clear gel. After 5 min of stirring, 104.17 g of 12% NaOCl solution was added, and the mixture was stirred for an additional 10 min. The resultant dispersion showed a pH of 13.5 and a one-day viscosity of 3.5 × 10^2 mPa.s (spindle #4, 20 rpm).

Incorporation of NaOCl solution into the alumina–polyacrylate gels. A typical example is the preparation of a sample containing 2.0% polyacrylic acid, 1.0% alumina, and 5.0% NaOCl. Water (3.3 g) was added into the stirring dispersion of Carbopol-614 (4% solution, 125.0 g). The resultant mixture was stirred for 5 min to ensure proper mixing. Aqueous solution (7.5 g) of 50% NaOH was added to the above mixture. Upon addition of NaOH, the system was immediately thickened, and this produced a stiff, clear gel. Alumina dispersion (10.0 g of 25% dispersion) was mixed into the stirring clear gel. This resulted in a thick, opaque gel. The gel was thoroughly mixed and diluted with 104.17 g of 12% NaOCl solution. The measured pH of the opaque gel dispersion was 13.5, and a viscosity (spindle #4, 20 rpm) of 1.32 × 10^3 mPa.s was observed at room temperature for a one-day-old sample.

RESULTS AND DISCUSSION

Viscosity dependence on the concentration of alumina in polyacrylate gel dispersions. Alumina–polyacrylate gel dispersions were prepared by the addition of aqueous dispersions of alumina into the preformed cross-linked polyacrylate gels at pH ~13 and room temperature. The pH of these gel dispersions was adjusted to 13 by the addition of a few drops of aqueous NaOH (where required). The effect of the weight percentage of colloidal alumina on the Brookfield viscosity of the dispersions of polyacrylate gel particles at a fixed shear rate (20 rpm) is depicted in Figure 1.

The curves, corresponding to dispersions with 0.50, 0.75, and 1.00% polyacrylate, clearly show an increase in viscosity with an increase in the concentration of alumina. The figure also shows that the increase in viscosity depends upon the polymer concentration. Mixtures, comprising 0.25% poly-

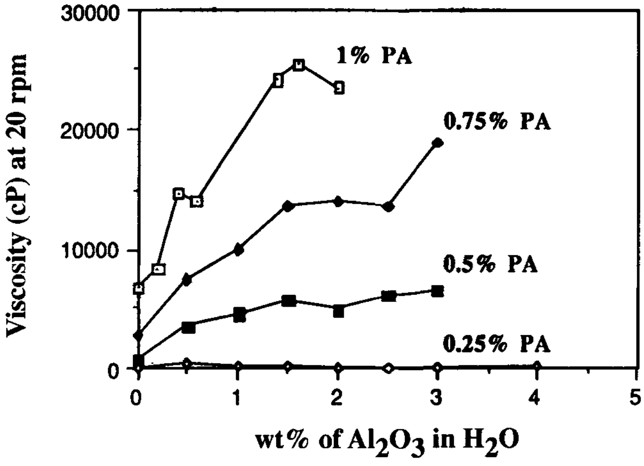

FIG. 1. Effect of concentration of Al_2O_3 on the Brookfield viscosity of polyacrylate (PA) gel dispersions at pH 13.

acrylate and varying amounts of alumina, result in relatively low viscosities. Such mixtures have an alumina concentration of >0.5% flocculate. This behavior may be attributed to the high levels of alumina, which, under alkaline conditions, flocculate, and to the low levels of polymer concentration.

It is important to point out that aqueous alumina mixtures (0–2% by weight) at pH 13 exhibit viscosities of less than 100 mPa.s. At this pH, alumina is probably highly negatively charged by adsorption of OH^- ions (7). So, an increase in viscosity with the addition of alumina is considered to be due to alumina–polyacrylate interactions.

Dynamic mechanical properties of alumina–polyacrylate gel dispersions. The oscillatory measurements at room temperature within the linear viscoelastic region were carried out to probe the "at rest" structure of dispersions (15). In general, within the linear viscoelastic region, both G′ (storage modulus) and G″ (viscous or loss modulus) are independent of strain γ, and the moduli are only functions of temperature and frequency. G′ is a measure of the energy stored and retrieved when a strain is applied to the composition, while G″ is a measure of the amount of energy dissipated as heat when strain is applied. In other words, the storage moduli are measures of the elasticity of the systems; the loss moduli are representative of the viscous behavior of the compositions.

To observe the strain sensitivity and to locate the linear viscoelastic region, strain sweep experiments were conducted at 10 $rads^{-1}$ frequency over the torque range of 0–150 μNm (Figs. 2–4). For alumina–polyacrylate gel dispersions (3:0.5, 1.5:0.75, and 2:1 wt% ratios), the storage moduli (G′) show solid-like behavior. The storage moduli are almost independent of strain and higher than the loss moduli (G″) over the entire region of applied strain (Figs. 2–4). In contrast, the storage moduli are highly dependent upon strain for the polyacrylate gel dispersions. In the 0.5% polyacrylate gel dispersion (Fig. 2), the magnitude of the storage moduli drops below that of the loss moduli G″, indicating the disruption of the network structure by strain. These results strongly suggest that the polymeric network structures in alumina–crosslinked polyacrylate gel dispersions are much more stable than the corresponding polyacrylate gel dispersions. This finding is important in preparing long-lived stable suspensions or dispersions.

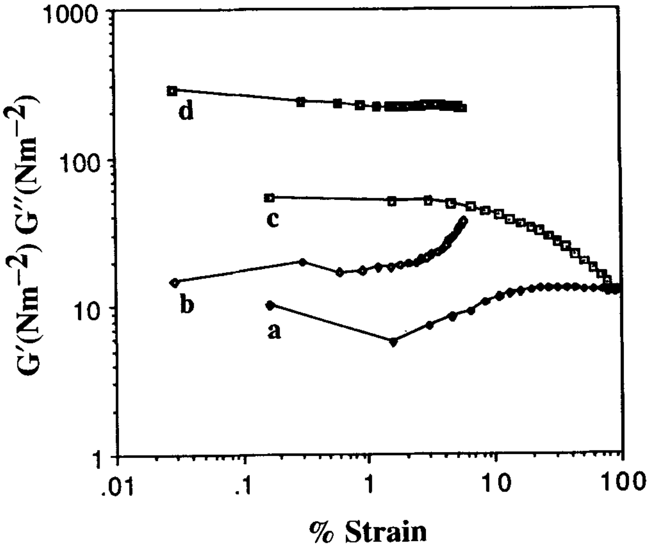

FIG. 3. Plots of G′ and G″ against % strain for a (G″, 0.75% polyacrylate), b (G″, alumina–polyacrylate, 1.5:0.75%), c (G′, 0.75% polyacrylate), and d (G′, alumina–polyacrylate, 1.5:0.75%).

Figures 5–7 show the storage moduli and loss moduli plotted against the oscillation frequency, ω (a fixed strain γ of 0.02), for polyacrylate and alumina–polyacrylate gel disper-

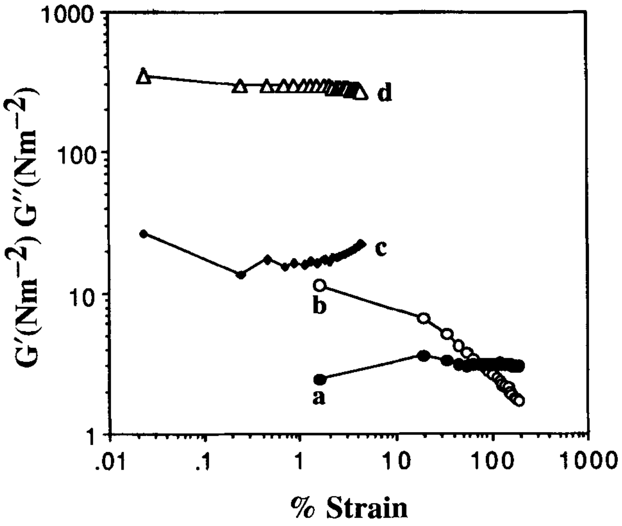

FIG. 2. Plots of G′ and G″ against % strain for a (G″, 0.5% polyacrylate), b (G′, 0.5% polyacrylate), c (G″, alumina–polyacrylate, 3:0.5%), and d (G′, alumina–polyacrylate, 3:0.5%).

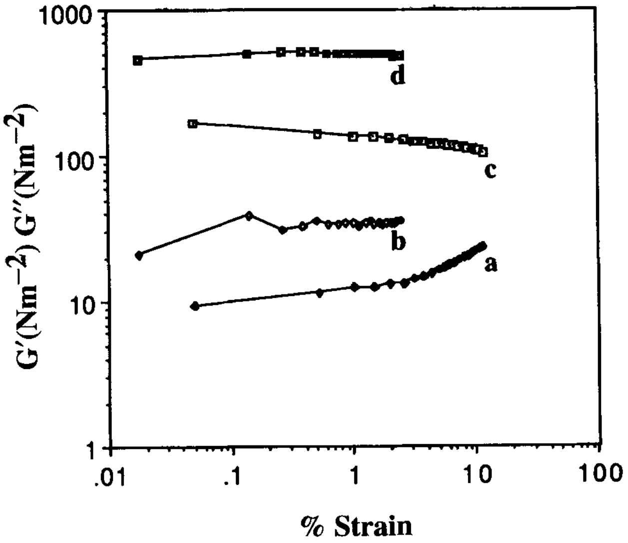

FIG. 4. Plots of G′ and G″ against % strain for a (G″, 1% polyacrylate), b (G″, alumina–polyacrylate, 2:1%), c (G′, 1% polyacrylate), and d (G′, alumina–polyacrylate, 2:1%).

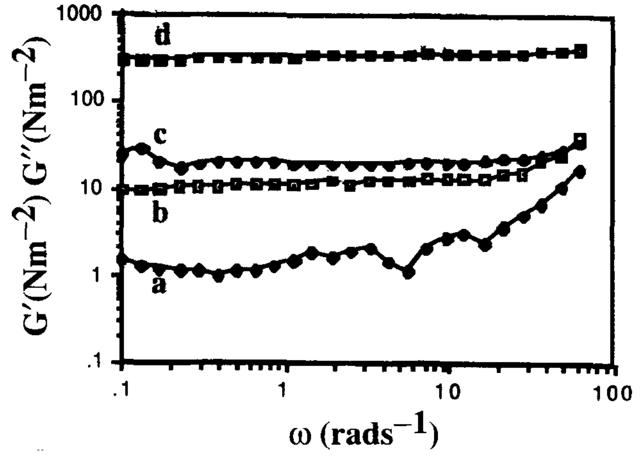

FIG. 5. Dependence of G′ and G″ on ω (rads^{-1}) for a (G″, 0.5% polyacrylate), b (G′, 0.5% polyacrylate), c (G″, alumina–polyacrylate, 3:0.5%), and d (G′, alumina–polyacrylate, 3–0.5%).

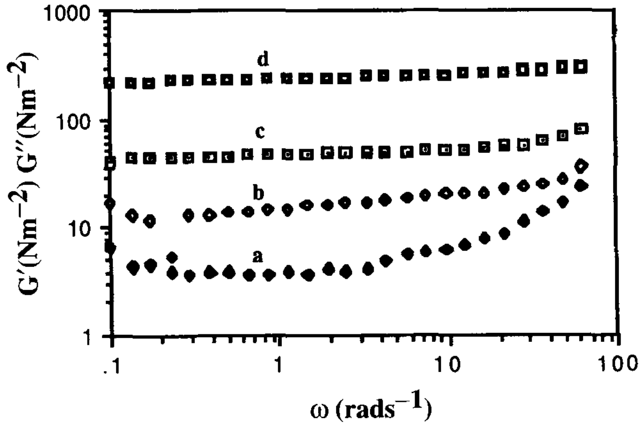

FIG. 6. Dependence of G′ and G″ on ω (rads^{-1}) for a (G″, polyacrylate, 0.75%), b (G″, alumina–polyacrylate, 1.5:0.75%), c (G′, polyacrylate, 0.75%), and d (G′, alumina–polyacrylate, 1.5:0.75%).

sions. Frequency sweep experiment results serve as fingerprints of a sample's structure. In all dispersions, the storage moduli are higher than the loss moduli over the entire frequency range studied, meaning that the dispersions are predominantly elastic. It is evident from the figures that G′ changes slowly with the frequency, corresponding to little stress relaxation, which is also indicative of the nearly perfectly elastic behavior. Comparison of the storage moduli of alumina–polyacrylate (3:0.5% ratio) gel dispersion with polyacrylate gel dispersion (Fig. 5) reveals that the amplitude of G′ for alumina–polyacrylate (at ω = 62.83 rads^{-1}) is ten times greater than that for the corresponding polyacrylate gel dispersion. This is a remarkable result, which means that the viscoelasticity is enhanced ten times by the addition of 3% alumina into the polyacrylate gel (0.5% by weight) dispersion. A similar trend in the enhancement of the amplitude of G′ of polyacrylate gels on addition of alumina is also observed in other combination systems (Figs. 6 and 7).

Figure 8 summarizes the dependence of storage moduli, G′, of polyacrylate gel dispersions on the alumina concentration at 0.02 strain and 62.83 rads^{-1} (frequency sweep experiment). The G′ amplitude increases with the weight percentage of alumina. The results are in agreement to the viscosity data shown in Figure 1. Based on the data of Figure 8, one could estimate the amount of alumina required to achieve the same magnitude of G′ as is exhibited by a polyacrylate gel dispersion at relatively higher loading, by employing low concentrations of polyacrylate. For example, a pure 1% polyacrylate gel dispersion exhibits about the same G′ amplitude (~150 Nm^{-2}) as an alumina–polyacrylate gel dispersion of 0.5:0.75%. In this regard, Figure 8 is of real practical value. The enhanced elasticity (G′) in the alumina–polyacrylate gel dispersions suggests the formation of a three-dimensional network structure where the colloidal alumina particles are trapped in the matrix of cross-linked negatively charged polyacrylate ions.

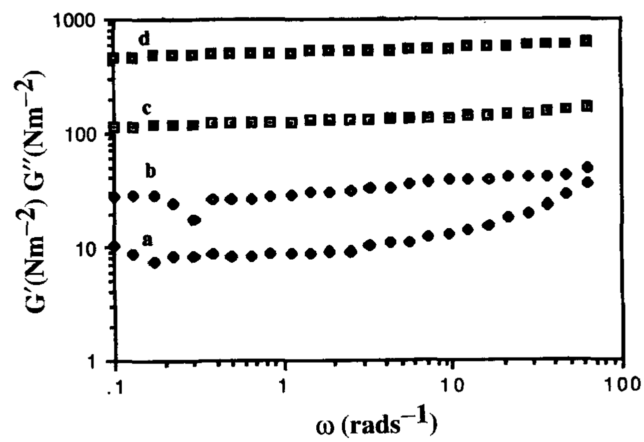

FIG. 7. Dependence of G′ and G″ on ω (rads^{-1}) for a (G″, polyacrylate, 1%), b (G″, alumina–polyacrylate, 2:1%), c (G′, polyacrylate, 1%), and d (G′, alumina–polyacrylate, 2:1%).

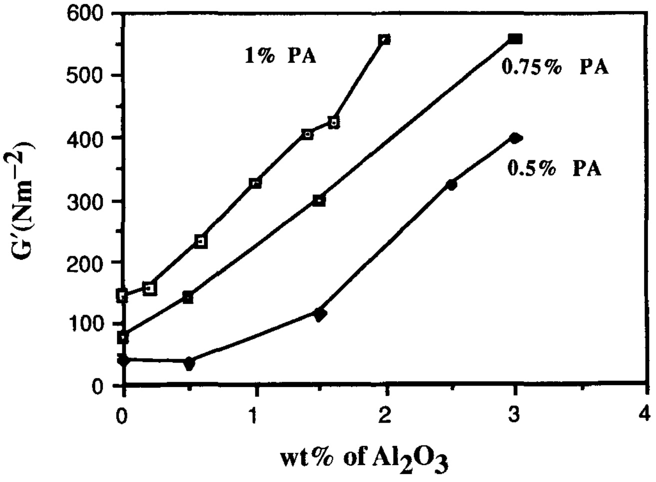

FIG. 8. The dependence of storage moduli, G′, of polyacrylate (PA), gel dispersions on alumina.

The rheological experiments suggest that alumina–polyacrylate gel dispersions are stable to high temperature (60°C) and have good structural recovery if the structure is broken apart by applying a high strain.

To test the effect of temperature on the integrity of an alumina–polyacrylate gel dispersion, an experiment was conducted in which an alumina/polyacrylate gel dispersion (1:1%) was divided into two parts. One sample was kept at room temperature, and the other sample was heated at 60°C for three days and then cooled to room temperature. Both samples were then subjected to dynamic rheological measurements. The gel dispersion subjected to high temperature shows no degradation at all in its structure.

Figure 9 shows the time sweep experiments at fixed frequency and strain (or torque) for 0.5% polyacrylate and alumina–polyacrylate (3:0.5%) gel dispersions. The variation of G′ (and G″; not shown in Fig. 9) was monitored with time, with and without preshearing the samples. For the 0.5% polyacrylate gel dispersion, the preshear torque used was only 200 μNm, as compared to 500 μNm for alumina–polyacrylate gel dispersion. A lower preshear value was used for polyacrylate gel dispersion because of the strain sensitivity of the 0.5% polyacrylate system (Fig. 3). Both types of gel dispersions showed good recovery of the structures within a short period of time.

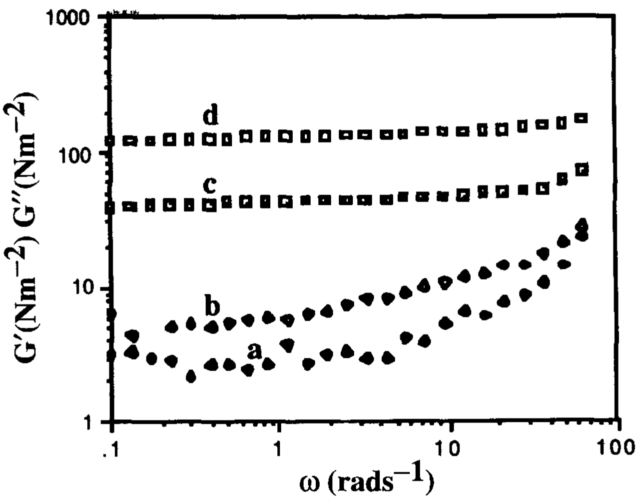

FIG. 10. Variation of G′ and G″ with oscillation frequency ω (rads^{-1}) for 1% polyacrylate (with 0.6% NaCl) [curves a (G″), and c (G′)], and alumina–polyacrylate (1:1%) gel dispersion containing 0.6% NaCl [curves b (G″), and d (G′)] at a strain of 0.02.

The dynamic mechanical properties of some polyacrylate and alumina–polyacrylate gel dispersions in the presence of NaCl were also measured (Figs. 10 and 11). These figures clearly show that the structure of alumina–polyacrylate gel dispersion, (1:1 + 0.6% NaCl) is stronger than the corresponding 1% polyacrylate gel dispersion containing 0.6% NaCl. In the alumina–polyacrylate gel dispersion, the structure is predominantly elastic and survives the imposed deformation well (Fig. 11). In contrast, the structure of polyacrylate gel dispersion containing NaCl breaks at torque values >70 μNm. The observed relative Brookfield viscosities were 9750 mPa.s for alumina–polyacrylate (1:1 + 0.6% NaCl) and 2650 mPa.s for polyacrylate (1 + 0.6% NaCl) gel dispersions.

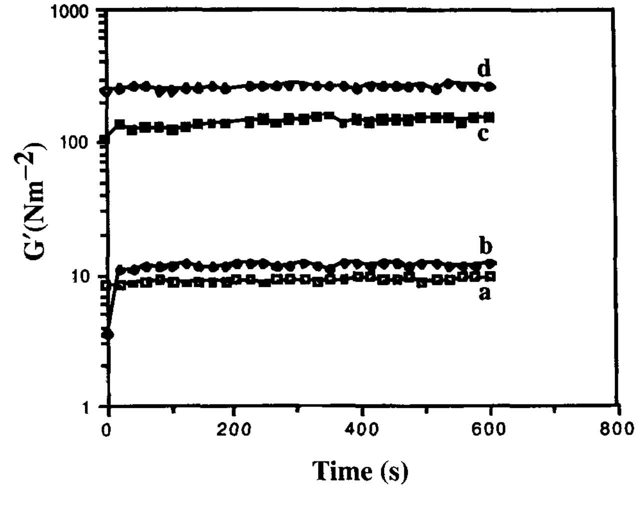

FIG. 9. Variation of G′ with time for 0.5% polyacrylate [a (preshear torque = 0), and b (preshear torque = 200 μNm)], and for alumina–polyacrylate (3:0.5%) [c (preshear torque = 500 μNm), and d (preshear torque = 0 μNm)], at 2 and 5 μNm, respectively, and at 6.283 rads^{-1}.

Proposed thickening mechanism of polyacrylate gels with alumina. We propose a three-stage thickening mechanism (Fig. 12) of polyacrylic acid resin with alumina, considering the results of previous sections and known literature of polyacrylic acid (Carbopol) (1,10). The first step involves the dispersion of cross-linked polyacrylic acid in water. In the dry state, the polymer is tightly coiled. The polymer chains begin to hydrate and partially uncoil upon addition of water, due to the build-up of some negative charges along the polymer

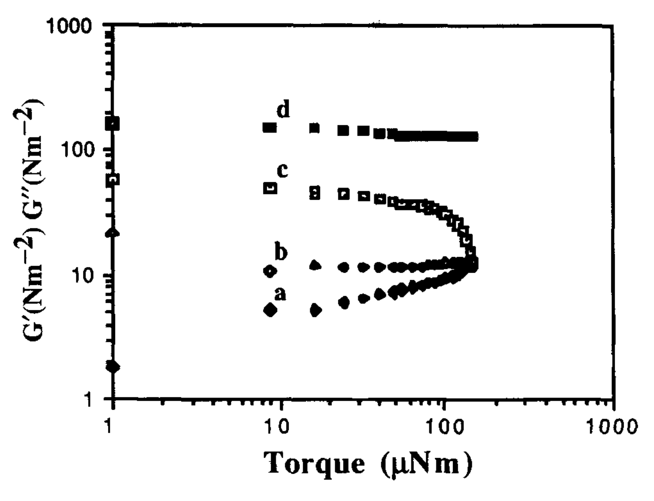

FIG. 11. Plots of G′ and G″ against torque (μNm) for 1% polyacrylate (with 0.6% NaCl) [curves a (G″), and c (G′)], and alumina–polyacrylate (1:1%) gel dispersion containing 0.6% NaCl [curves b (G″), and d (G′)] at an oscillation frequency of 10 rads^{-1}.

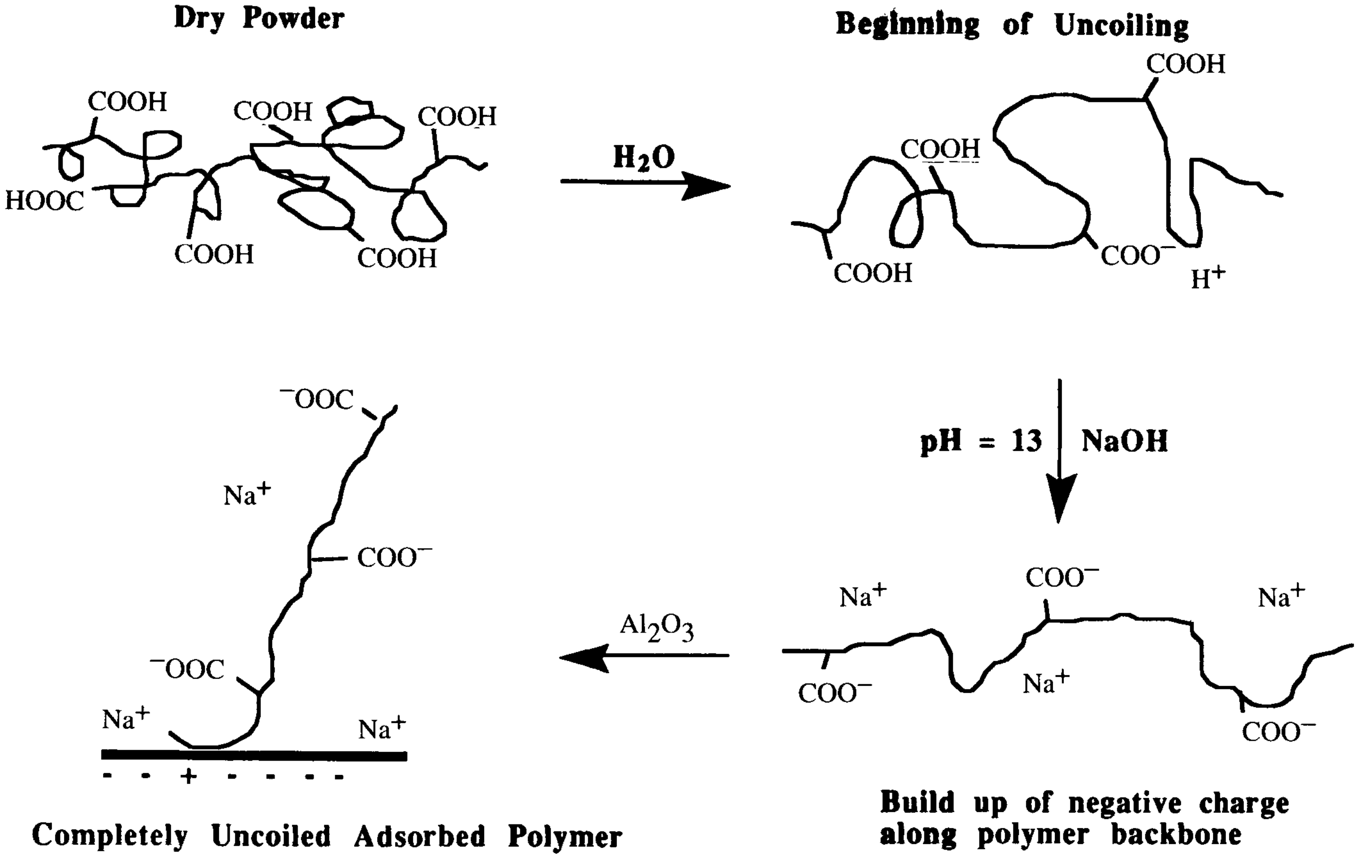

FIG. 12. Three-stage thickening mechanism of polyacrylate resin with alumina.

backbone. Partial coil expansion certainly increases the polymer's hydrodynamic volume, which in turn slightly increases the viscosity of the system. Upon addition of excess NaOH (pH = 13), the carboxylic groups are neutralized, and a negative charge is built up along the polymer backbone. This step results in further coil expansion because of electrostatic repulsion of the carboxyl–anion charge centers in close proximity to one another.

However, at this stage (pH 13), the polymer chain does not completely uncoil or stretch because of partial screening of the electrostatic repulsions by sodium ions. The last step is the adsorption of a segment of the polymer on colloidal alumina. Because the alumina surface is negatively charged at high pH ($\text{Al-OH} + \text{OH}^- \Rightarrow \text{Al-O}^- + \text{HOH}$), this probably imparts strong repulsive interactions between the free segments of the adsorbed polyacrylate and the negatively charged alumina particles. These repulsive forces probably further uncoil the polymer chain into a relatively more extended structure. This uncoiling would result in an increase in the polymer's hydrodynamic volume, which in turn increases intermolecular entanglement and resistance to flow.

The alumina surface at pH 13 is negatively charged. The ζ of Dispal T-23 alumina particles (2%) under changing pH conditions is shown in Figure 13.

The point of zero charge (zpc) for Dispal T-23 alumina particles is approximately pH 9.4. The values of zpc of different kinds of aluminas vary between 6.5–9.4 (16). The measured zpc is in accordance with the literature. Below zpc, the alumina surface is positive, and above zpc, the surface becomes negative. All of our work on alumina–polyacrylate gel dispersions was conducted above the zpc of alumina at pH 13. Yopps and Fuerstenau (16) point out that the mechanism

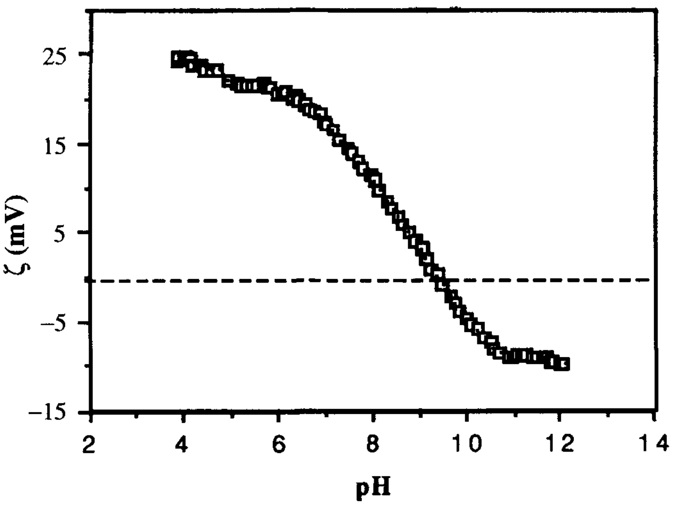

FIG. 13. Zeta potential, ζ (mV), of alumina dispersion (2% by wt) as a function of pH.

by which the alumina surface charge is established generally involves a two-step process: surface hydration followed by dissociation of the surface hydroxide. Dissociation of the hydrated surface to give rise to a charged surface is shown schematically:

$$\mathrm{Al{-}\underset{H}{\overset{+}{O}}H_{(surf)} \rightleftharpoons Al{-}OH_{(surf)} + H^{+}_{(aq)} \rightleftharpoons Al{-}O^{-}_{(surf)} + 2H^{+}_{(aq)}} \qquad [1]$$

positive surface zero point of charge negative charge

The polyacrylic acid polymer is completely ionized at pH 13. The ζ of an aqueous dispersion of polyacrylic acid (0.25%) as a function of pH is shown in Figure 14. Initially, the amplitude of ζ increases with pH, then it levels off above pH 9. The initial increase in the amplitude of ζ is attributed to the build-up of negative surface due to the neutralization of the acidic carboxylic groups.

Adsorption of polyacrylic acids on the alumina surface is a function of pH (9,10). As pH increases, the adsorption decreases. For a hydrophobically modified anionic polymer, Daparal (Akzo Chemicals, Inc., Chicago, IL) (a maleic anhydride ∝-olefin copolymer, Fig. 15) at pH 11, no measurable polymer adsorption on alumina was seen by Li and co-workers (9). Daparal has an average molecular weight of 20,000. It is known from the work of Vedula and Spencer (17) that adsorption of polyacrylic acids on metal oxide surfaces is highly dependent upon the molecular weight. They showed that adsorption of negatively charged polyacrylic acid on surfaces of like charge, such as titania and zirconia, at pH greater than their isoelectric point (pH >6.5) could occur if the molecular weight of the polymer is high enough. Considering the work of Vedula and Spencer (17), we believe that even though the alumina–polyacrylate system is electrostatically repulsive at pH of 13, a weak attractive interaction plays a role on the initial adsorption of the polymer on the alumina surface.

Thickening and structuring of complex liquids. The rheological additive system based on alumina and polyacrylic acid works well in thickening and structuring complex liquids, such as liquid automatic dishwashing detergents (aqueous dispersions) with typical compositions comprising (by weight) polyphosphates (20–30%), silicates (5–25%), carbonate (0–15%), NaOCl (0.5–2%), surfactant (0–2%), structurant (0–1.5%), and fragrance and color (0.001–0.05%).

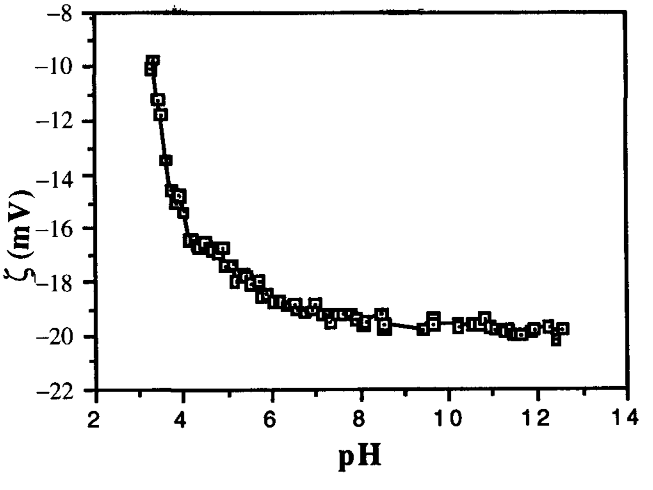

FIG. 14. Zeta potential, ζ (mV), of polyacrylic acid resin (0.25% by wt) as a function of pH.

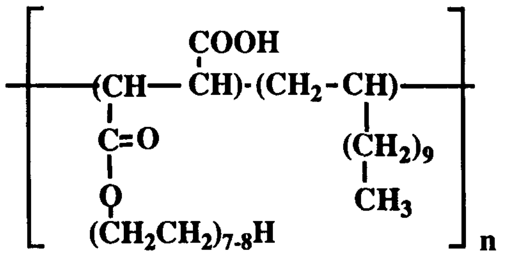

FIG. 15. Molecular structure of Daparal GE 202 (Akzo Chemicals, Inc., Chicago, IL) (Ref. 9).

The role of a structurant in a liquid automatic dishwashing detergent is to keep the product physically stable during storage and to provide a thixotropic rheological behavior, so that the product is sufficiently mobile under moderate shear to be readily dispensed from the bottle but sufficiently viscous at low shear to remain in the machine dispenser. We employed the alumina–polyacrylate system as a thickening and structuring agent in liquid automatic dishwashing detergent formulations, and compared the rheological properties of detergents made with only polyacrylate instead of alumina–polyacrylate. In these compositions, polyacrylic acid was neutralized with NaOH and the pH was ~13. In contrast to the control, containing only 0.75% polyacrylate (**I**) and having a viscosity of 5990 cP, composition **II**, containing 0.75% polyacrylate and 0.5% alumina, exhibited a viscosity of 7300 cP. The viscosity data are for samples aged for two weeks at room temperature. The densities of compositions **I** and **II** were 1.39 and 1.40 g/mL, respectively.

These samples also were analyzed by dynamic rheological experiments. Figure 16 shows the dependence of storage and loss moduli on % strain for **I** and **II**.

Figure 16 clearly shows that the liquid automatic dishwashing detergent composition **II** consisting of alumina–polyacrylate is stronger than the composition comprising only polyacrylate, **I**.

A stable thickening and structuring system for hypochlorite is a desirable formulation in many applications, such as sanitizers and hard-surface cleaners (4). We prepared thickened hypochlorite bleach formulations with alumina, polyacrylic acid, and a combination of alumina and polyacrylic acid at pH ~13 (Table 1).

The suspension capability and the pourable nature of the composition containing 1% alumina, 2% polyacrylate, and 5% NaOCl are evident from the flow curve shown in Figure 17. The system has a sufficiently high yield value (7.5 $\mathrm{Nm^{-2}}$), indicative of the ability of the composition to suspend solid particles. A yield value of only 1.4 $\mathrm{Nm^{-2}}$ was observed for a 5% hypochlorite solution thickened with only 2% poly-

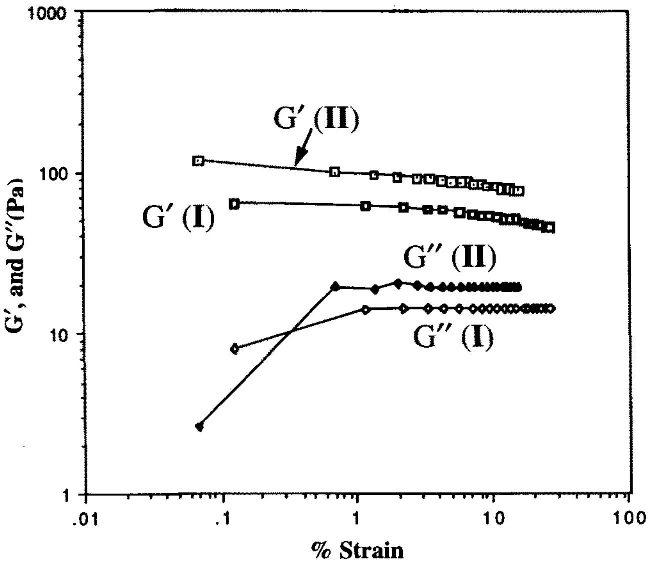

FIG. 16. Dependence of G' and G" (Pa = Nm^{-2}) on % strain for liquid automatic dishwashing detergents (**I** and **II**) at an angular frequency of 6.283 rads^{-1}.

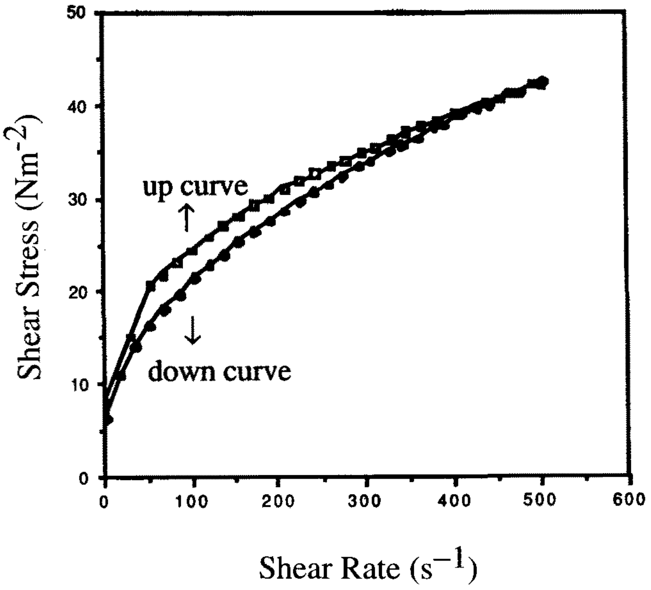

FIG. 17. Flow curve for a 5% hypochlorite solution thickened with alumina–polyacrylate system (1% alumina + 2% polyacrylate, Table 1).

acrylate rather than alumina–polyacrylate (Table 1). Yield value (or yield stress) refers to the minimum stress required to cause a substance to flow. Below this stress, the material behaves like an elastic solid. Yield stress also represents the force that acts against gravity and consequently against sedimentation. The shape of the upward and downward curves, and the slope of the curves (Fig. 17) suggest that the thickened hypochlorite composition is viscoelastic and has uniform flow characteristics because as the shear rate increases, the shear stress increases in a generally proportional manner.

In contrast to the composition of the alumina–polyacrylate structuring system (Table 1, Fig. 17), the 5% hypochlorite solution thickened with 3% alumina shows a false body (yield stress of 6.8 Nm^{-2}, Fig. 18) because, as the shear rate increased, the shear stress remained generally constant. The behavior is indicative of a continued thinning of the system in response to the application of the stress, and it points out that the composition does not exhibit smooth flowability.

The dynamic mechanical properties (G' and G") under torque (strain) sweep conditions for the compositions shown in Table 1 were also measured to further probe the structures of these dispersions (Fig. 19). The torque sweep experiments were conducted at a frequency of 6.282 rads^{-1} over the torque range of 1–150 μNm (Fig. 19). Comparison of the rheograms of the compositions (Table 1) reveals the importance of using alumina in combination with the polyacrylate polymer. For the composition of 1% alumina, 2% polyacrylate, and 5% NaOCl, the storage moduli (G') are higher than the loss moduli (G") and independent of torque up to ~100 μNm. The ratio of G'/G" is maintained at a value of >1 for this composition over the applied torque range of 1–150 μNm (corresponding to 0.1 to 200% strain). In contrast to this composition, the storage and loss moduli are highly dependent upon torque for 5% NaOCl solutions that contain either 2% polyacrylate or

TABLE 1
Brookfield Viscosities of 5% NaOCl Solutions at pH ~13 Containing Various Rheology-Modifying Agents at Room Temperature (RT)

Structuring system	Viscosity, mPa.s (20 rpm, RT)
3% Alumina	1.08×10^3
2% Polyacrylate	3.50×10^2
2% Polyacrylate + 1% alumina	1.30×10^3

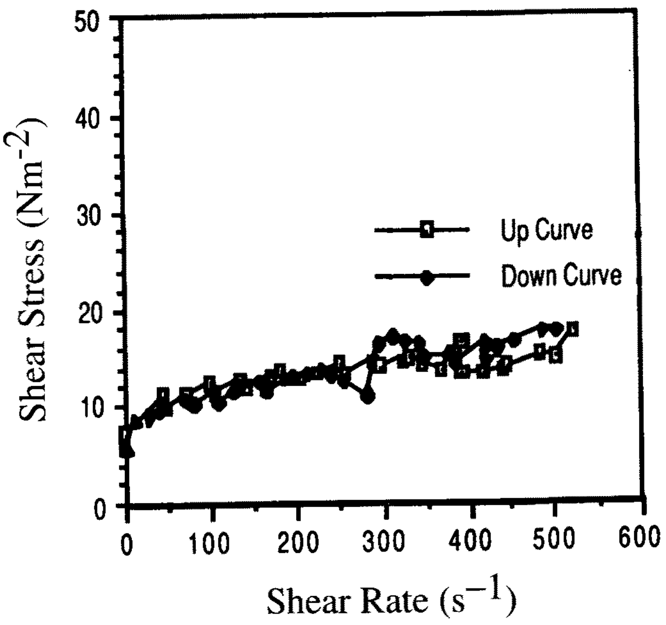

FIG. 18. Flow curve for a 5% hypochlorite solution thickened with 3% alumina (Table 1).

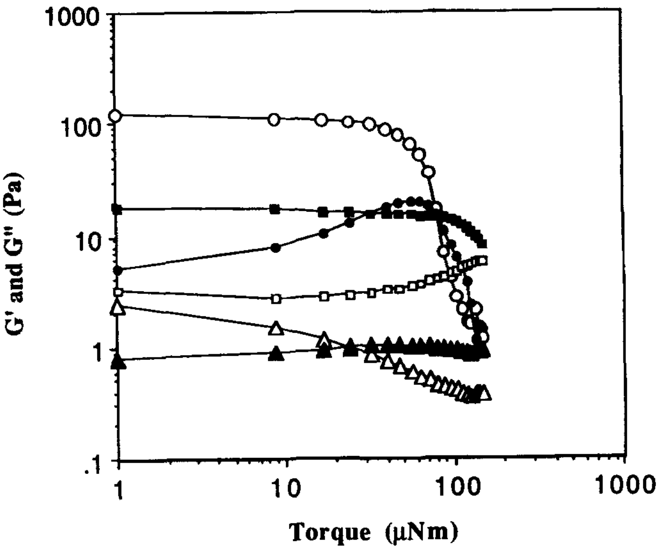

FIG. 19. Plots of G′ and G″ (Pa = Nm^{-2}) against torque (μNm) for 5% hypochlorite solution thickened with 3% alumina (○ = G′; ● = G″), 2% polyacrylate (△ = G′; ▲ = G″), and alumina–polyacrylate, 1:2% (■ = G′; □ = G″).

3% alumina (Fig. 20), and the ratio of G′/G″ becomes less than one over the applied range of the torque. The ratio of G′/G″ of less than one implies a structure break-down or flow of the gel matrix, which may also lead to sedimentation. Physical instability indeed was observed for the composition of hypochlorite that contained only 3% alumina (Table 2). Based on the rheological experiment, we may rule out the sole use of either alumina or polyacrylic acid for thickening and structuring of the aqueous solution of sodium hypochlorite at a level of 5 wt%.

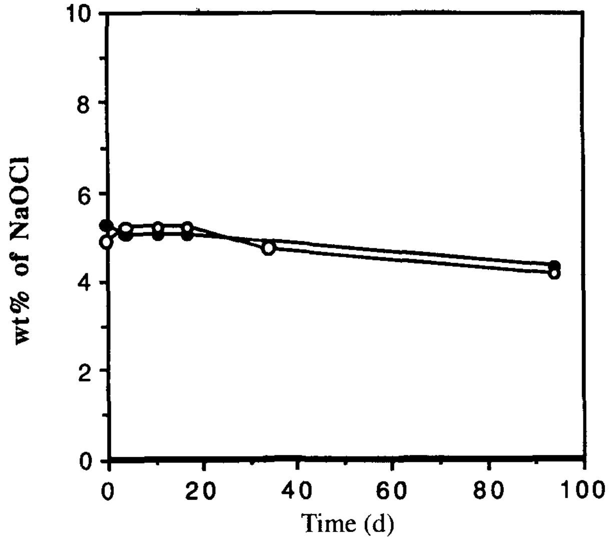

FIG. 20. Sodium hypochlorite stability of a 5% hypochlorite solution thickened with 2% polyacrylate (○) and alumina–polyacrylate (1:2%) (●) at 22–26°C.

TABLE 2
Stability of a 5% Hypochlorite Solution Thickened with 3% Alumina at 22–26°C

Storage time (d)	Viscosity, mPa.s (20 rpm, spindle #4)	pH	wt% of NaOCl	Comments
0	1.08×10^3	13.6	5.02	Stable
4	1.12×10^3	13.6	5.01	Stable
11	1.13×10^3	13.7	4.96	Stable
17	1.12×10^3	13.7	5.01	Stable
31	—	—	—	Separation within sample

The pH, viscosity, and NaOCl stability of compositions (Table 1) are shown in Tables 2 and 3 and Figure 20. The hypochlorite solutions containing 2% polyacrylate or 1% alumina–2% polyacrylate exhibited good pH and hypochlorite stability over a period of two and a half months (Table 3). A hypochlorite composition containing only 3% alumina, as we have already pointed out above, was not phase-stable (Table 2).

The observed decomposition (about 14–15%) of sodium hypochlorite over a period of three months (Fig. 20) is probably due mainly to the auto decomposition of NaOCl solution, although we cannot rule out some reaction of NaOCl with the cross-linking moieties (probably polyallyl sucrose or polyallyl pentaerythritol) of the polyacrylate.

A 14% decomposition was observed over a period of three months for an aqueous 10% sodium hypochlorite solution in the absence of alumina and polyacrylate at room temperature. The auto decomposition of ClO^- could occur by the following reactions (11):

$$2ClO^- \xrightarrow{k_1} Cl^- + ClO_2^- \qquad [2]$$

$$ClO_2^- + ClO^- \xrightarrow{fast} Cl_3^- + Cl^- \qquad [3]$$

$$2ClO^- \xrightarrow{k_0} O_2 + 2Cl^- \qquad [4]$$

According to Church (11), the first two equations account for approximately 95% of the consumption of ClO^- when metallic catalysts are absent. The rates of the decomposition reactions of NaOCl are highly dependent upon pH, concentration, temperature, added salts, and photolysis (11,18).

In summary, alumina–polyacrylate systems may be used to build rheology of complex liquids.

TABLE 3
Viscosity (20 rpm, spindle #4) and pH Stability of a 5% Hypochlorite Solution Thickened with 2% Polyacrylate and with Alumina–Polyacrylate (1:2%), at 22–26°C

Storage time (d)	Viscosity, mPa.s and pH[a] (2% polyacrylate)	Viscosity, mPa.s and pH (alumina–polyacrylate, 1:2%)	Comments
1	3.5×10^2 (13.6)	1.30×10^3 (13.5)	Stable
4	3.3×10^2 (13.6)	1.40×10^3 (13.4)	Stable
11	3.3×10^2 (13.7)	1.45×10^3 (13.6)	Stable
17	— (13.7)	— (13.6)	Stable
70	4.1×10^2 (13.5)	2.28×10^3 (13.5)	Stable

[a] The pH is indicated in the parentheses.

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