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Interaction Forces between Silica Surfaces in Aqueous Solutions of Cationic Polymeric Flocculants: Effect of Polymer Charge

Ying Zhou,[†] Yang Gan,[‡] Erica J. Wanless,[§] Graeme J. Jameson,[†] and George V. Franks^{*,||}

Chemical Engineering and the Centre for Multiphase Process, University of Newcastle, Callaghan, NSW 2308, Australia, Department of Applied Chemistry, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China, School of Environmental and Life Science, University of Newcastle, Callaghan, NSW 2308, Australia, and Department of Chemical and Biomolecular Engineering, University of Melbourne, VIC 3010, Australia

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Three cationic polymers with molecular weights and charge density of 3.0×10^5 g/mol and 10% (D 6010), 1.1×10^5 g/mol and 40% (D6040), and 1.2×10^5 g/mol and 100% (D6099) were investigated in aqueous NaCl solutions in the presence of silica. The atomic force microscope (AFM) colloidal probe technique was used to determine silica interparticle interaction forces, which were compared to macroscopic information on the strength of interactions such as compressive yield stress measurements. It was found that in 30 mM NaCl solution the 10% charged polymer produced steric repulsion upon approach and long-range adhesion with multiple pull off events upon retraction at the optimum flocculation concentration. This suggests that the polymer was adsorbed in a conformation where segments extend from the surface, resulting in bridging flocculation. The 40 and 100% charged polymers produced attraction upon approach and strong adhesion with snap out from contact upon separation at optimum polymer dosages. This suggests that these polymers are adsorbed with flat conformations and is typical of charge neutralization or patch attraction. The attractions for 40 and 100% charged polymers measured with the AFM are significantly larger than for the 10% charged polymer. The polymer dose that produced the optimum flocculation and the maximum compressive yield stress typically corresponded to the polymer concentration that produced the maximum adhesion for each polymer. It was found that the magnitude of the adhesive force was more significant in determining the compressive yield stresses of the silica particle sediments than the aggregate size and structure.

1. Introduction

Polyelectrolytes are important in a variety of fields, such as papermaking,¹ food manufacturing,² medicine,^{3,4} pharmaceuticals,⁵ ceramic processing,^{6–9} mineral processing,^{10–12} and water¹³ and wastewater treatment processes.^{14,15} Polyelectrolytes may adsorb onto the surfaces of particles and thus change the interaction forces between the particles. These forces are the primary factor influencing suspension behavior.¹⁶ For example, the adsorption of polyelectrolytes onto solid surfaces influences the rheology of suspensions, so that they may be used as

dispersants in ceramic processing to reduce the viscosity of concentrated suspensions by creating electrosteric repulsion between particles.^{6–9} The use of polyelectrolytes that is most relevant to the present paper is their role as flocculants. Polymeric flocculants create attraction between fine particles in order that they may be aggregated and separated from a liquid by gravity sedimentation. The attraction may be created by one or a combination of mechanisms such as bridging flocculation, electrical double layer attraction, charge neutralization, and charged patch attraction. The compressive yield stress of the flocculated sediment controls the consolidation behavior of the sediment bed as well as its behavior during filtration.^{10–13,17} Hence, it is of great interest to study the interaction forces between surfaces with adsorbed polyelectrolytes to help us better understand and control suspension behavior (particularly de-watering and compressibility of sediments).

Polyelectrolytes adsorb onto a surface as a result of competition between various short-range and long-range forces including electrostatic forces, van der Waals forces,^{18,19} and specific interactions such as hydrogen bonding. The electrostatic force is attractive between polyelectrolyte segments and oppositely charged surfaces; this force is extremely important in facilitating

* Corresponding author. E-mail: gvfranks@unimelb.edu.au.

[†] Chemical Engineering and the Centre for Multiphase Process, University of Newcastle.

[‡] Harbin Institute of Technology.

[§] School of Environmental and Life Science, University of Newcastle.

^{||} University of Melbourne.

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adsorption of polyelectrolytes. Mean-field models^{18,20–26} and molecular simulations^{25,27–29} have advanced our understanding of polyelectrolyte adsorption and the resulting surface interactions. The structure and conformation of adsorbed polyelectrolytes and the interactions between surfaces are strongly affected by the charge density of polyelectrolytes, surface charge density, nonelectrostatic polymer–surface interactions, salt concentration, and quality of solvent. Depending upon these factors, as well as the adsorbed amount of polymer, either steric repulsion (typically at higher polymer concentrations) or attraction (bridging, charge neutralization, or charge patch, typically at lower polymer concentrations) may exist.^{13,17,30–32}

There have been limited systematic experimental investigations evaluating the influence of these factors on surface interactions.^{27,33–44} Additionally, there have been some reports of the role of polymer type, solvency, and molecular weight on surface forces using SFA⁴⁵ and AFM.^{35,41–44,46–49} The influence of polymer charge density has also received attention.^{27,40} Osterberg et al.⁴⁰ found that xylans, despite having 0.5–9% negative charge, adsorbed onto negatively charged mica surfaces. Other carboxylate-containing polymers are known to adsorb via specific interactions onto negatively charged surfaces.^{41,50–53} In Osterberg et al.'s work, the xylan with 9% charge density induces a slightly more long-ranged repulsion than the xylan with 0.5% charge density. Abraham et al.⁵⁴ studied the effects of copolymers of acrylamide and acrylic acid with three different charge densities

(15, 40, 70%) on interactions between two silica surfaces. They found that the 15% charged polymer caused a purely repulsive force profile, regardless of the polymer concentration. In both the 40 and 70% charge density polymers, bridging attraction was observed at low polymer concentrations, whereas a purely repulsive interaction was observed at higher polymer concentrations. The range of repulsion was significantly smaller than in the case of the 15% charge density copolymer. Dahlgren et al.²⁷ investigated interactions between mica surfaces in the presence of random copolyelectrolytes of neutral acrylamide (AM) and positively charged (2-acryloxy ethyl) trimethylammonium chloride. Polymers with 10 and 30% charge were investigated. The positively charged segments were electrostatically attracted to the negatively charged mica surface, while the AM segments attach by hydrogen bonding. At 10% charge, repulsive interactions dominate, whereas at 30% charge, an attractive force was observed at separations below 10 nm.

The aim of this paper is to understand how the forces between surfaces in polyelectrolyte solutions influence solid/liquid separation of mineral suspensions, particularly the compressibility of sediments.⁵⁵ Polyelectrolyte flocculants cause attraction between suspended particles, resulting in aggregation. Aggregates with sufficient mass can be separated from the liquid by gravity sedimentation; the larger the mass, the faster the sedimentation. Aggregate mass depends upon the size and density (structure) of the aggregate, which are related to the magnitude of the attraction between particles.^{30,56} The individual aggregates that settle to the bottom of the container form a three-dimensional interconnected attractive particle network. The strength of the particle network, which determines the shear yield stress, elastic modulus, and compressive yield stress, is directly related to the strength of individual bonds between particles, the structure of the particle network, and particle size.^{57–62} The strength of the attractive bond between individual particles is controlled by the interparticle attractive forces, which is the focus of the present work. Several investigations^{57–59} have qualitatively established the relationship between the strength of the attractive bond and the shear and compressive yield stresses of the particle networks, while others have derived models for the relationship.^{60–62} The compressive yield stress is the key factor in determining the liquid content of dewatered product under equilibrium conditions. Thus, an understanding of how polymeric flocculant charge influences interparticle interactions and thus compressibility of suspensions is important in improving solid/liquid separations in the multibillion dollar per year mineral processing industry.

In our previous work,³⁰ we measured ζ -potentials, polymer adsorption, and flocculation as a function of polymer dosage for the same polymers and silica particles used in the current study. The conclusions of that work are summarized here. For the 10% charged polymer, 30 mM of NaCl is needed to produce good flocculation, as judged by supernatant clarity. Without the added salt, some particles remain suspended in the supernatant. The added salt alone produced neither aggregation nor sedimentation. Polymer bridging was found to be the dominant flocculation

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Table 1. Charge Densities and Molecular Weights of the Three Cationic Polymers Used in This Study

polymer	charge density (%)	molecular weight (g/mol)
D6010	10	3.0×10^5
D6040	40	1.1×10^5
D6099	100	1.2×10^5

mechanism for the 10% charged polymer. The bridging attraction is stronger as polymer dose increases to 12 mg of polymer/g of silica (the maximum concentration investigated) because more polymer loops and tails protrude from the particles' surfaces beyond the electrical double layer. For the 40% charged polymer, at the maximum dose investigated (12 mg/g), bridging is also the dominant flocculation mechanism, because the polymer molecules adopt extended conformations (loops and tails protrude from the surface). At dosages of 4–8 mg/g, the surface coverage of polymer molecules is lower and flocculation is caused by both charge neutralization and bridging. The contribution due to bridging is more significant as the concentration increases. For the 100% charged polymer, at dosages of 1 and 2 mg/g, the polymer molecules are adsorbed with flat conformations on the surface and electrostatic patch attraction is the dominant flocculation mechanism. At dosages of 8 and 12 mg/g, the polymer molecules adopt extended conformations by forming loops and tails, and bridging flocculation results. The optimum dose for each polymer was found to be 12 mg/g silica for the 10% charged polymer at 30 mM NaCl, 12 mg/g for the 40% polymer, and 2 mg/g for the 100% polymer.

In the current study, the forces between silica surfaces in solutions of the same three cationic polymers were studied using the dosages reported above as a guideline. One aim of this study is to characterize the influence of polymer properties (particularly charge density) on the interparticle forces. Also, the measured force profiles along with adsorption isotherms and ζ -potentials previously measured³⁰ are used to better understand how polymer properties affect the polymer conformation on the surface and surface interactions. Finally, by providing an understanding of the link between the interparticle forces and the measured compressive yield stresses of particle sediments,⁵⁵ the results of this paper can facilitate the design of improved solid–liquid separation processes.

2. Experimental Section

2.1. Materials. Three polymeric flocculants were provided by SNF Floerger. Two were cationic random copolymers of acrylamide/diallyldimethylammonium chloride with 10% charge (D6010) and 40% charge (D6040), and the other one was the cationic homopolymer of diallyldimethylammonium chloride (D6099, 100% charged). The polymers were used without further purification. The molecular weight of these polymers was determined by static light scattering in 0.01 M NaCl solution at pH 5.5 and 25 °C with a Zetasizer Nano ZS (Malvern Instruments, UK).³⁰ The charge density and molecular weight of each polymer is listed in Table 1. Sodium chloride, sodium hydroxide, and hydrogen chloride were of analytical grade and were not purified further. Silica spheres (nominal diameter 5 μm) were obtained from Bangs Laboratories (Fishers, IN) for use as colloid probes. For studies of compressive yield stresses of sediments, nearly monodisperse and spherical silica particles (M 1040) were purchased from Nissan Chemical America Corp., with a BET surface area of 30 m² g^{−1}, a mean particle diameter of 90 nm, and a density of 2.2 g cm^{−3}. All experiments were performed at pH 5.5 (the measured stable pH value of solutions in air). Silicon wafer substrates (purchased from Silicon Valley Microelectronics, CA, with a well-defined 115 nm oxide layer) were prepared by ultraviolet irradiation (BioForce Nanosciences, Inc., IA) for 10 min and then soaked in 10 wt % NaOH for 20 min, followed by rinsing with copious amounts of

Milli-Q water, and then dried under a clean, dry, dust-free nitrogen stream.

2.2. Methods. **2.2.1. Force Measurements.** A Nanoscope III atomic force microscope (Digital Instruments, Santa Barbara, CA) with a liquid cell was used. The long wide cantilever of standard silicon nitride probes (Nanoprobe, Veeco) was used for AFM force measurements. The spring constant was determined by the added mass method.⁶³ The average spring constant of five cantilevers from the wafer area of the cantilever actually used was found to be 0.14 N/m. The errors in determining the spring constant can be as high as 20% due to the limitations of calibration method. An S-shaped thin wall O-ring was used to create a sealed liquid volume for colloidal probe force measurements in solutions. Hydrophilic silica spheres of 5.0 μm in diameter were glued to the tip of the cantilever with epoxy resin, as described by Gan.⁶⁴ Before force measurements, the attached sphere was inspected by scanning over a grating of ultrasharp silica spikes with nominal tip radius less than 10 nm and tip angle less than 20° (Model TGT01, ND-MDT Co.) to ensure that the surface of the sphere was free of any debris. The rms roughness of the spherical surface was 1.5 nm over an area of 1 μm^2 . The probe was then put into a UV cleaner (BioForce Nanosciences, Inc.) for 10 min to remove any remaining adsorbed organics immediately before force measurements. The peak intensities of the UV lamp were at wavelengths of 185 and 254 nm. The UV light intensity is slightly below 20 mW/cm² at the 254 nm wavelength. The distance between the lamp and upper surface of the sample was around 2 mm.

The polymers were supplied as aqueous solutions and were further diluted with Milli-Q water to the desired concentration. The prepared solutions were gently stirred for 1 h. The salt solutions were prepared at least 1 day before the experiments. All force measurements were conducted after incubating for 20 min at room temperature (25 \pm 1 °C). No significant changes were found in the AFM force profiles even after 1 h incubation. Therefore, our system can be considered to have reached equilibrium after 20 min incubation. During force measurements, the silica sphere and the silica plate were brought into contact and separation at a rate of 0.5–1 Hz. Multiple force curves were collected at various locations across the surface of the planar silica. For a specific polymer charge, the solution concentration was increased stepwise. For each measurement, multiple force curves were collected at several locations with one colloid probe on one planar substrate for each concentration. The colloidal probe used was selected after confirming system cleanliness by collecting force curves on a clean silica substrate in water before proceeding to the polymer solution.

The polymer concentrations investigated in the AFM measurements were chosen to correlate with those in measurements of aggregate properties³⁰ and compressive yield stresses⁵⁵ measured for silica suspensions aggregated with the polymers in a minithickener described elsewhere.³⁰ The adsorption isotherms that we measured previously³⁰ describe the equilibrium between the adsorbed amount and the equilibrium concentration of polymer in solution, as shown in Table 2. In order to correlate the AFM measurements at the same adsorbed amount as in the suspension studies, we were careful to have the same equilibrium polymer concentration in solution.

2.2.2. Flocculation Experiments. Details of the minithickener fabricated for the production of aggregates have been presented elsewhere.³⁰ The minithickener was designed so that the aggregates produced settled directly into a Perspex cup with a minimum of shear and disruption to their structure. The Perspex cup was sized so that, after removal from the minithickener, it could be used directly as the container for centrifugal consolidation. This is very important, since pouring the suspension from one container to another might destroy the particle networks formed during aggregation and consolidation. This apparatus enabled us to measure in situ the compressive yield stress of the sediment bed. All flocculation experiments were conducted at room temperature. In the minithick-

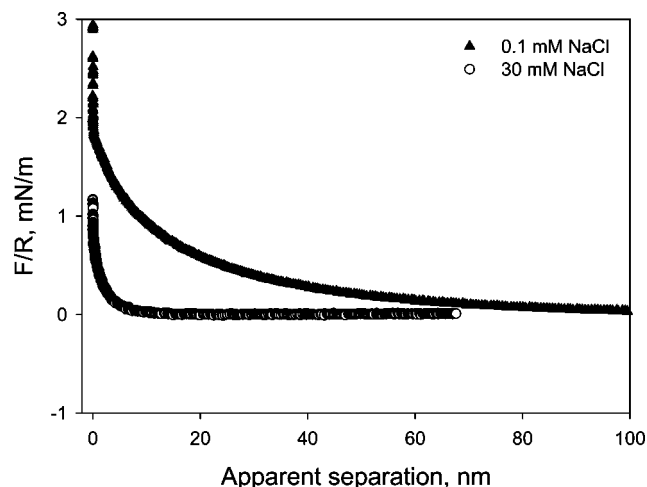
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Table 2. Polymer Concentrations C_{eq} (mg of polymer/L of solution) Used in AFM Experiments and Adsorbed Amounts Γ (mg/m²) That Correspond to the Dosages (mg of polymer/g of silica) Used in Flocculation Studies in Our Previous Work³⁰

polymer	1 mg/g		2 mg/g		4 mg/g		6 mg/g		8 mg/g		12 mg/g	
	C_{eq}	Γ	C_{eq}	Γ	C_{eq}	Γ	C_{eq}	Γ	C_{eq}	Γ	C_{eq}	Γ
D6010 ^a	na	na	na	na	1.2	0.11	1.8	0.16	2.5	0.21	4.0	0.31
D6040	na	na	na	na	1.2	0.08	2.1	0.11	3.1	0.13	4.9	0.18
D6099	0.3	0.02	0.4	0.03	na	na	na	na	3.5	0.09	6.7	0.11

^a At the background salt concentration of 30 mM NaCl. na: not available. Note the plateau adsorption amount Γ_{max} is 1.49 mg/m² for D6010^a, 0.31 mg/m² for D6040, and 0.13 mg/m² for D6099.

**Figure 1.** The measured approach interaction forces for a silica sphere interacting with a silica substrate in 0.1 and 30 mM NaCl.

ener, a 25 L suspension of silica particles was flocculated at pH 5.5 in all experiments. The weight concentration of silica particles was 0.16%. The suspensions of silica particles, while being stirred continuously at 142 rpm, were allowed to flocculate for 90 s after addition of polymer.

2.2.3. Compressive Yield Stress Measurements. Compressive yield stress measurements were performed in the Perspex cup containing the sediment from the minithickener. The sediments were consolidated by either gravity or centrifugal acceleration, as described in detail previously.^{55,65–67} The compressive yield stress was determined using the volume fraction profiling method, one of several available.^{65,66,68–71}

3. Results and Discussion

3.1. AFM Force Measurements between Silica Surfaces in NaCl Solutions. Figure 1 shows the measured interaction forces for a silica sphere interacting with a silica substrate in 0.1 and 30 mM NaCl. Force curves were converted from raw cantilever deflection and piezotube displacement data. In 30 mM NaCl solution, the interaction is purely repulsive and of short-range; the repulsion appears at a separation of about 10 nm. This purely repulsive force curve is consistent with the fact that the addition of 30 mM salt alone is insufficient to coagulate the silica particles. The forces in 0.1 mM NaCl solution are also repulsive and are of longer range; the repulsion appears at a separation of around 120 nm. The F/R vs separation curves can be fitted very well with DVLO theory at the boundary condition

of constant surface charge.^{72,73} The fitted diffuse layer potential is -6.5 mV in 30 mM NaCl, for which the Debye length is 5.2 nm, whereas it is -72.1 mV in 0.1 mM NaCl, for which the Debye length is 30 nm. A Hamaker constant of 8.5×10^{-21} J was used during calculations.⁷⁴

3.2. AFM Force Measurements in 10% Charged Polymer Solutions (D6010). Figure 2 shows the measured interaction forces upon approach of two silica surfaces in 30 mM NaCl containing 10% charged polymer (D6010) solutions at different concentrations as a function of separation distance. Slight variations in subsequent approach/separation cycles were observed, presumably due to conformation variation of polymer chains. However, the difference in the general shape of the force curves and adhesion at any particular polymer concentration is less than the variation found between different polymer concentrations. Therefore, it is possible to distinguish the key features and adhesion of the force curves for the different polymer concentrations investigated. The addition of between 0.2 and 1.8 mg/L polymer leads to a weak attraction, and then the force increases rapidly as hard wall contact occurs. The minimum in attractive energy is about 0.03 mN/m for 1.2 mg/L and 0.04 mN/m for 1.8 mg/L. At concentrations above 2.5 mg/L, the repulsion becomes stronger than when no polymer was added (Figure 1). The repulsion continues to increase as polymer concentration is increased from 4 to 40 mg/L. The absence of attractive forces close to the silica surfaces at higher polymer concentration suggests that a steric repulsion is the dominating force upon approach of surfaces.

The retraction force curves when the two silica surfaces are separated in 30 mM NaCl solutions with 10% charged polymer (D6010) at different polymer concentrations are shown in Figure 3. The forces upon separation of the silica surfaces are not the same as upon approach when the polymer concentration is higher than 0.2 mg/L. At a polymer concentration of 1.2 mg/L, there is an adhesive energy of about -0.2 mN/m. The two surfaces begin to separate, but the probe does not jump off the surface until a separation of 13 nm. For 1.8 and 2.5 mg/L, the adhesive energy is larger (about -0.76 to -0.9 mN/m), and the detachment separation is greater, about 25 nm. When the concentration is increased to 4.0 mg/L, the adhesive energy reaches a maximum (-2.9 mN/m) and complete detachment does not occur until 100 nm. The probe first experiences a sudden release from the surface at 20 nm, and then the probe experiences seven or eight weaker pull-off events before it pulls completely free from the surface. This behavior is typical of adhesion observed between surfaces held together with polymer bridges.^{35,41–44} We can see that, as the polymer concentration increases from 1.2 to 4.0 mg/L, the adhesive force is stronger and therefore extends to larger separation (see Figure S1 of the Supporting Information). At very high concentrations of 20–40 mg/L, the adhesive energies

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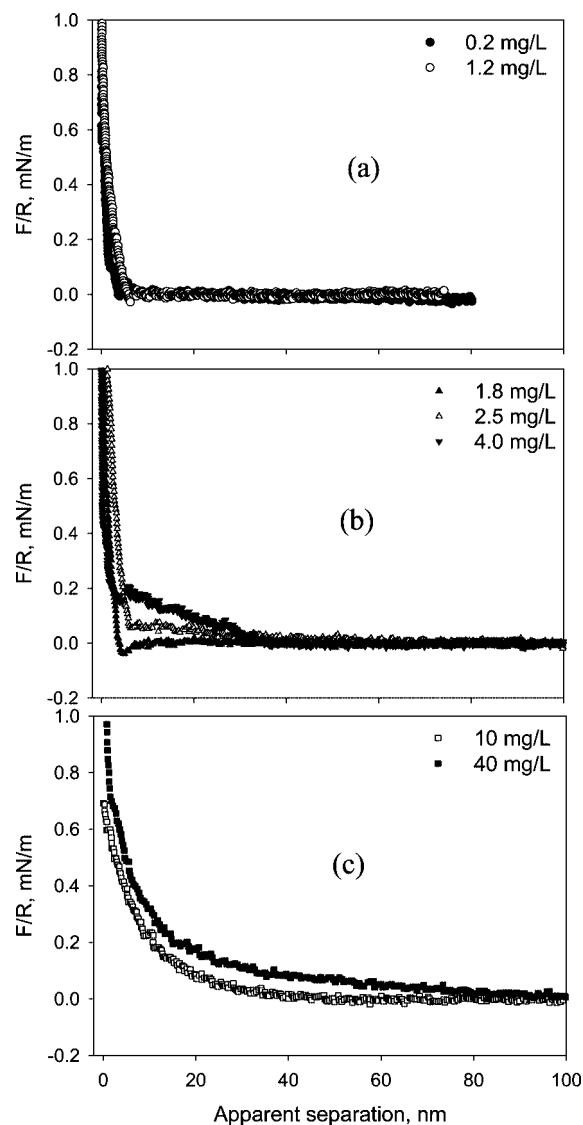


Figure 2. The approach force curves as a function of separation between two silica surfaces in 30 mM NaCl solutions containing 10% charged polymer at different polymer concentrations.

are smaller than at 4.0 mg/L and decrease with increasing polymer concentration. However, the eventual detachment separation for these two highest concentrations is the largest at more than 200 nm, the probe experiencing five or six pull-off events before it is finally freed from the surface.

At polymer concentrations of 1.2 and 1.8 mg/L (Figure 2), the weak attractive minimum on approach arises from the weak bridging attraction caused when a few polyelectrolyte chains cross the gap between two surfaces.^{27,75–77} The attractive bridging between surfaces caused by polymer chains slightly shifts the position of a primary attractive minimum from typically less than 1 nm for a system at its isoelectric point (only van der Waals and double-layer forces) to up to a several nanometers for a bridging flocculated system. From Table 2 of this paper and Figure 5 of our previous paper,³⁰ it can be seen that the adsorbed amounts of polymer at these concentrations (1.2 and 1.8 mg/L) are 0.11² and 0.16 mg/m², respectively. Because Γ_{\max} (the plateau

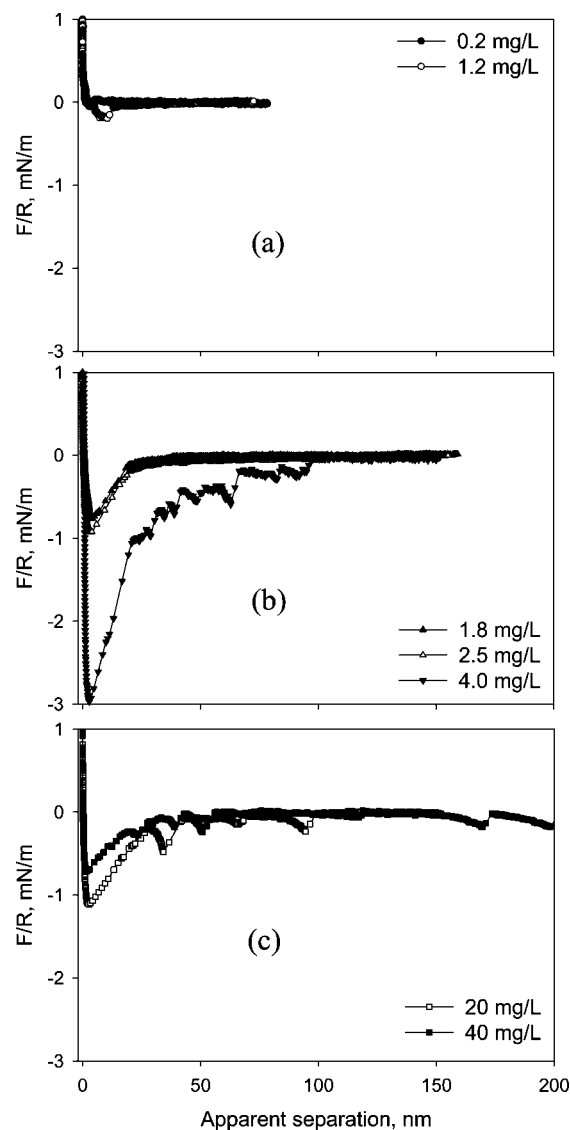


Figure 3. The retraction force curves as a function of separation between two silica surfaces in 30 mM NaCl solutions containing 10% charged polymer at different polymer concentrations.

adsorption amount) is 1.49 mg/m² for D6010 in 30 mM NaCl, Γ/Γ_{\max} is between 7 and 11% of complete coverage. Since there are relatively few polymer molecules adsorbed to the surfaces, the attraction and adhesion between surfaces is weak.

At moderate polymer concentrations like 2.5 and 4.0 mg/L, the adsorbed amounts of polymer are 0.21 and 0.31 mg/m², respectively, as shown in Table 2 of this paper.³⁰ These adsorbed amounts correspond to between 14 and 21% of complete coverage. This amount of polymer is sufficient to produce a weak steric repulsion because the polymer chains experience crowding on the surfaces, causing an osmotic interaction between the chains. It is likely that this weak repulsion could be overcome during particle–particle aggregation by Brownian or hydrodynamic forces caused by shear during aggregation. Once the surfaces have been pushed into contact, there are still sufficient surface sites available for adsorption of polymer molecules, so a large fraction of molecules can easily bridge between the two surfaces. This large number of bridges results in the strong adhesion observed in Figure 3b upon separating the two surfaces. Figure 3b also shows that the breakdown of bridging links is a gradual process involving stretching, disentanglement, and detachment of polymer molecules, resulting in seven or eight weaker pull-

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off events instead of a single event. At 4.0 mg/L, the adhesive minimum and range is greater than at 2.5 mg/L, because the polymer molecules are adsorbed with more and larger loops and tails extending away from the surface into solution. These loops become entangled when the surfaces are in contact with a type of “Velcro” effect.). Similar pull-off events have been also observed by other researchers.^{35,41,42,54}

At even higher polymer concentration, the polymer adsorbs strongly onto each surface, most likely filling more than half of all available adsorption sites, as judged by extrapolating the adsorption isotherms in our previous paper³⁰ to higher equilibrium concentrations. As shown in Figure 2c, polymer concentrations ranging from 10 to 40 mg/L produce strong monotonic repulsive interactions on approach of the surfaces. The presence of a high coverage of polymer molecules on the two surfaces and the resulting electrosteric repulsion are the cause of this behavior. The strong repulsion should be sufficient to prevent particles in suspension from aggregating due to shear or Brownian forces. However, the surfaces can be forced into contact by the AFM. Once in contact, there is little opportunity for polymer bridging, because the majority of surface sites are already occupied by polymer. Some few molecules will be able to bridge or become entangled, resulting in the adhesion observed in Figure 3c.

3.3. AFM Force Measurements in 40% Charged Polymer Solutions (D6040). Figure 4 shows the approach force curves as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing 40% (D6040) charged polymer at different polymer concentrations. At a polymer concentration of 0.2 mg/L, there is a weak repulsion. At polymer concentrations of 1.2 and 2.1 mg/L, the repulsion is completely eliminated and attraction dominates. As the polymer concentration is increased to 3.1 mg/L and above, repulsion again dominates and increases as polymer concentration is further increased. The forces decay exponentially with separation. The ζ -potential measurements in our previous work³⁰ indicate that the 40% polymer neutralizes the charge on the surface at about 3–4 mg/L (about 8–10 mg/g silica). This concentration is similar to the concentration where the maximum attractive force on approach occurs (2.1 mg/L).

In Figure 5, the measured retraction forces as a function of separation between two silica surfaces in 0.1 mM NaCl solution containing the 40% (D6040) charged polymer at different concentrations are presented. With all concentrations ranging from 0.2 to 40 mg/L, there is a primary adhesion and the silica probe jumps off the surface sharply. For concentrations from 0.2 to 20 mg/L, the adhesive force increases as the concentration increases; however, at the highest concentration (40 mg/L), the adhesive force is reduced to less than that for 3.1 mg/L (see Figure S1 in the Supporting Information).

The force curves for 40% charged polymers in 0.1 mM NaCl solution are, in general, quite different from those for 10% charged polymers in 30 mM NaCl solution. It is evident that the attraction upon approach is more long-ranged for the 40% charged polymer than for the 10% charged polymer. Since the plateau adsorbed amount for the 40% charged polymer is 0.31 mg/m²,³⁰ which is significantly less than for the 10% charged polymer, it is reasonable to assume that the 40% charged polymer is adsorbed as a thinner, flatter layer on the silica surface, consistent with our previous findings on polymer adsorption experiments.³⁰ The stronger attraction in the approach interaction of the 40% charged polymer (1.2 and 2.1 mg/L) compared to the 10% charged polymer is because the 40% charged polymer is adsorbed in a flatter conformation. Thus, steric repulsions are not observed at short-range on the approach force curves. Instead, the van der Waals attraction seems to dominate at small separation distances upon

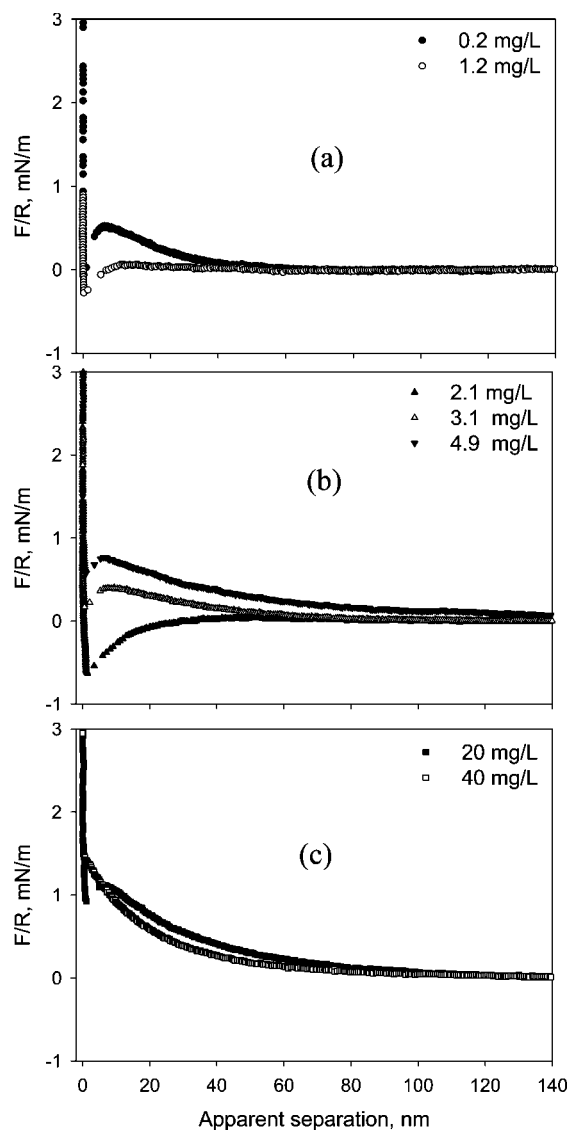


Figure 4. The approach force curves as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing 40% charged polymer at different polymer concentrations.

approach. This is consistent with the two different flocculation mechanisms hypothesized for the 40% charged polymer (mainly charge neutralization at low polymer dosage) and the 10% charged polymer (mainly bridging).³⁰ On separating the surfaces, the cantilever snaps back sharply to the undeflected position, so that there is no series of multiple pull-off events as are observed for 10% charged polymers in 30 mM NaCl solution. Therefore, for 40% charged polymers, it is likely that the adhesion is caused by a “charge neutralization” or “electrostatic patch” mechanism.³⁰

3.4. AFM Force Measurements in 100% Charged Polymer Solutions (D6099). The interactions upon approach as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing the 100% (D6099) charged polymer at different polymer concentrations are shown in Figure 6. It can be seen that, with the polymer concentration at 0.2 and 0.4 mg/L, short-range attractive interactions are observed at separation less than about 20 nm, and the attractive minima are between 0.4 and 0.6 mN/m. Also, weak, long-range attractions, between separations of 110 and 20 nm, are observed. At polymer concentrations of 3.5, 6.9, and 10 mg/L long-range repulsive interaction and short-range attractions are observed. The repulsion increases with polymer concentration. These results are consistent with the

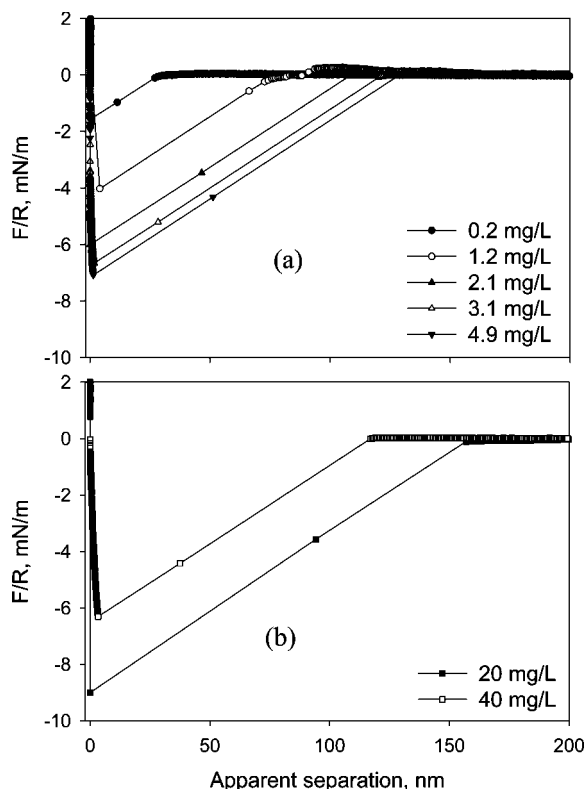


Figure 5. The retraction force curves as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing 40% charged polymer at different polymer concentrations.

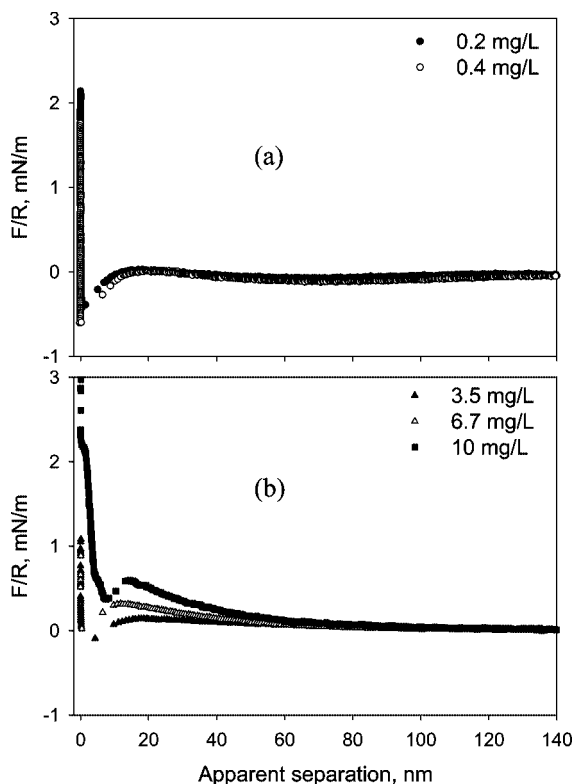


Figure 6. The approach force curves as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing 100% charged polymer at different polymer concentrations.

ζ -potential measurements published previously,³⁰ which indicate that the increased amount of adsorbed polymer overcompensates the negative charge on surfaces, resulting in charge reversal. The

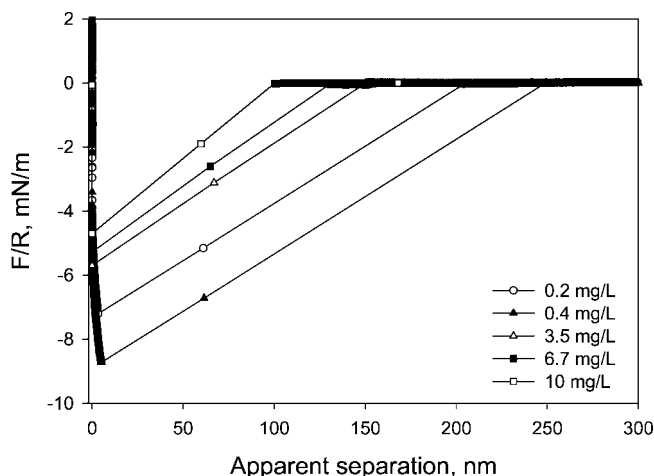


Figure 7. The retraction force curves as a function of separation between two silica surfaces in 0.1 mM NaCl solutions containing 100% charged polymer at different polymer concentrations.

charge reversal occurs somewhere between about 3 and 5 mg/g silica dosage, which corresponds to about 0.4–3.5 mg/L polymer concentration. This corresponds to the polymer concentration where maximum attraction upon approach occurs.

The measured interaction forces upon separation as a function of apparent distance between two silica surfaces in 100% (D6099) charged polymer solutions containing 0.1 mM NaCl at different polymer concentrations are shown in Figure 7. The measured retraction interaction force profiles have a primary adhesive minimum, followed by a rapid and sharp pull-off as the surfaces separate with the polymer concentration ranging from 0.2 to 10 mg/L. The positions of the energy minima occur close to the apparent contact. The maximum adhesive force occurs at 0.4 mg/L, where the adhesive minimum has a magnitude of 8.7 mN/m. Over the polymer concentration ranging from 3.5 to 10 mg/L, the adhesive minimum decreases as the polymer concentration increases further.

At the polymer concentration ranging from 0.2 to 0.4 mg/L, no repulsive interaction forces are observed on approach; just deep short-range and shallow long-range attractive interaction forces are measured. This indicates that attractive forces are significant in the approach interaction of the surfaces for the 100% charged polymer. Compared with the 10% charged polymer in the presence of 30 mM NaCl, 100% charged polymer layers appear to be adsorbed in a flat conformation at the interface, since no steric repulsive barriers and compressive components are observed in the approach interaction force profile at short range at concentrations ranging from 0.2 to 6.7 mg/L. On retraction, the cantilever snaps to an undeflected position very quickly; there are no multiple adhesive events, as is observed in the measurements of the 10% charged polymer. So for the 100% charged polymer, it is also likely that the adhesion is a measure of the force required to detach the polymer from the opposing surface. This can be explained by the “electrostatic patch” model.³⁰

Since the 40 and 100% charged polymers have equivalent molecular weights (1.1×10^5 and 1.2×10^5), we suggest that the difference in charge density of these polymers is primarily responsible for the slight difference in force profiles. Compared to the 40 and 100% charged polymers, the 10% charged polymer possesses lower charge density and higher molecular weight (3.0×10^5) and is also in higher ionic strength solution, each of which can lead to adsorbed molecule conformation with large loops and tails extending away from the surface into the solution phase, thus facilitating bridging flocculation.

3.5. Correspondence of Force Profiles and Flocculation Results.

The AFM studies for the 10% charged polymer in 30 mM NaCl solution are consistent with the bridging mechanism postulated previously.³⁰ Both the AFM and suspension studies indicate that bridging is increased with increased polymer concentrations, and polymer conformational information correlates well with flocculation studies. The maximum adhesion at 4.0 mg/L found in the AFM studies correlates well with the optimum flocculation condition of 12 mg/g silica found in the suspension studies. The weak repulsion observed in the force studies at 4.0 mg/L concentration is not believed to be significant in preventing aggregation under orthokinetic conditions.

The agreement between the AFM force measurements and the results of the suspension studies for the 40 and 100% charged polymers, however, is not quite as good. Information about polymer conformation is only consistent with that from flocculation studies at certain polymer concentrations. The optimum flocculation concentration for the 40% charged polymer (12 mg/g silica) correlates well with the maximum attraction upon approach (4.9 mg/L). Although the maximum adhesion occurs at 20 mg/L, the adhesion at 4.9 mg/L is nearly as strong (see Figure S1 in the Supporting Information). Likewise, the optimum flocculation concentration for the 100% charged polymer (2 mg/g silica) corresponds with the concentration (0.4 mg/L) that has both the maximum attraction and maximum adhesion.

However, the AFM studies showed no sign of bridging mechanism for 40 and 100% charged polymers as postulated in our previous work.³⁰ Our previous suspension results suggested that, for the 40% charged polymer, bridging would occur at the optimum concentration (12 mg/g silica dosage), while charge neutralization should dominate at lower concentration. Also for the 100% charged polymer, we postulated that bridging should occur at concentrations greater than the optimum. Instead, the AFM results indicate that the polymer layers of both 40 and 100% charged polymers are adsorbed in a flat conformation, since no steric repulsion and short-range compressive components are observed on the approach force curves. Additionally, the sharp pull-off observed on retraction curves also implies a flat conformation of adsorbed polymers and no bridging interaction.

This apparent discrepancy can be explained as follows. The time frame of the adsorption is different for the suspensions studies and the AFM measurements. In the suspension studies, the adsorption and aggregation occur nearly simultaneously within a matter of seconds, resulting in aggregation, while polymer is still in an extended conformation on the surface. (It does not have enough time to flatten out.) In the AFM studies, the polymer has more time (several minutes) to adopt a flatter conformation before the force is measured. Also, it is known that different techniques are not equally sensitive to the quantities of loops and tails of adsorbed polymers. For example, light scattering is very sensitive to loops and tails, whereas ellipsometry is unable to detect them.⁷⁸ It is expected that AFM offer sensitivity between these two techniques.⁴³ Therefore, the conformations of polymer molecules at the surfaces are different in the flocculation and AFM studies.

3.6. Relating AFM Adhesive Forces with Compressive Yield Stresses of Sediment Beds. The compressive yield stress versus volume fraction results for several polymer dosages measured for the sediments of the 10% charged polymer in 0.03 M NaCl solution, the 40% charged polymer, and the 100% charged polymer are presented in Figure 8.⁵⁵ For the 10% charged polymer in 0.03 M NaCl solution (Figure 8a), the compressive yield stress

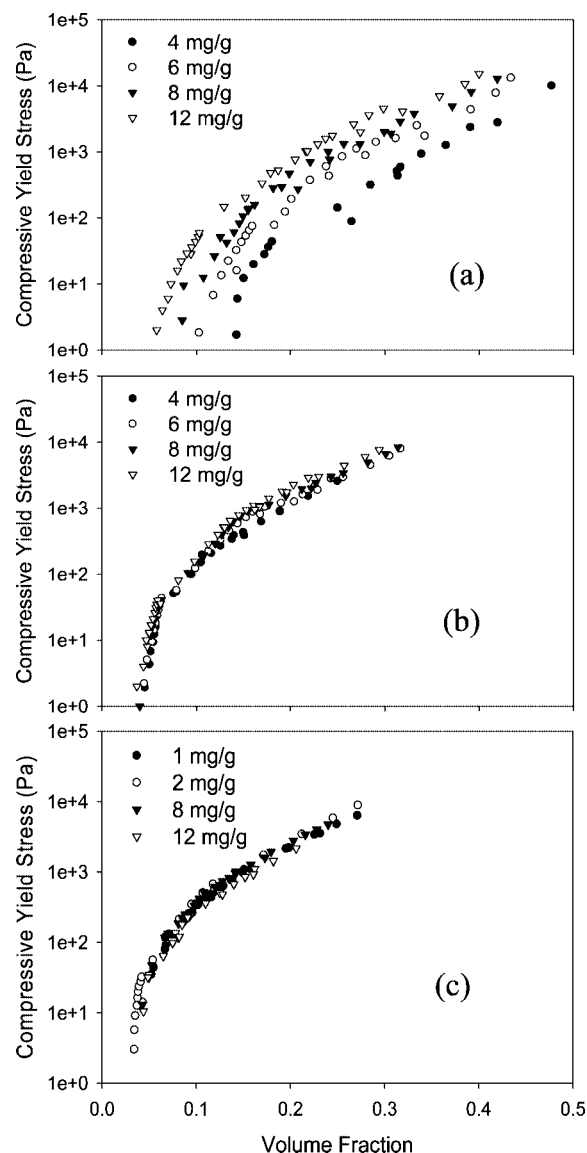


Figure 8. Effect of polymer dose on the compressive yield stresses of silica sediments from the flocs induced by (a) 10% charged polymer in 30 mM NaCl solution, (b) 40% charged polymer, and (c) 100% charged polymer, respectively.

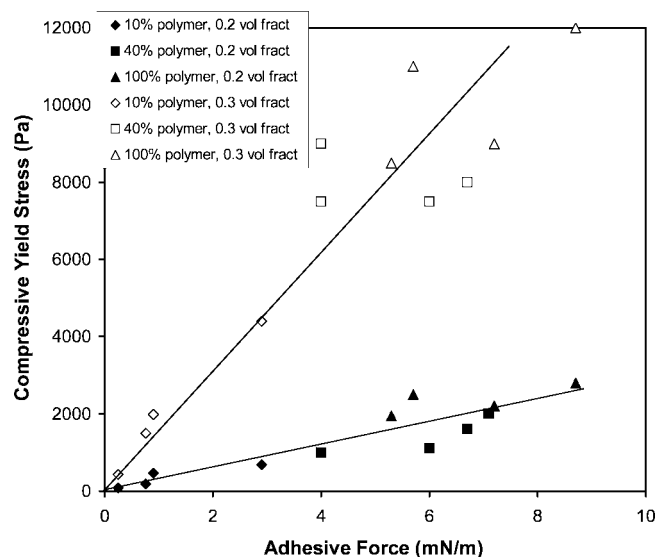
at a given volume fraction of solids increases as polymer concentration increases. For the 40% charged polymer (Figure 8b), the flocs are slightly less compressible (greater pressure has to be applied to achieve a particular volume fraction) as polymer dose increases. In the case of the 100% charged polymer (Figure 8c), the compressibility is nearly independent of polymer concentration. At 2 mg/g, the suspension is slightly less compressible than at other polymer concentrations.

The compressive yield stress of sediments is directly related to the adhesive force between the particles that make up the network.^{57–62} The adhesive force must be overcome to separate particles to allow them to rearrange into more densely packed structures. During consolidation by gravity or centrifugation, the applied pressure reduces the volume of sediments by squeezing out water. The particle network must rearrange in order to densify. A large adhesive force means that a large pressure must be applied to the particle network to cause the particles to rearrange. The densification of the particle network also depends to some extent upon the structure of the particle network (number of bonds that needs to be broken) and particle size (which is constant in the

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Table 3. Adhesive Force (mN/m) at the Polymer Concentration Which Corresponds with the Polymer Dosage (mg/g) in Flocculation Studies

polymer	1 mg/g	2 mg/g	4 mg/g	6 mg/g	8 mg/g	12 mg/g
D6010 ^a	na	na	−0.2	−0.76	−0.9	−2.9
D6040	na	na	−4.0	−6.0	−6.7	−7.1
D6099	−7.2	−8.7	na	na	−5.7	−5.3

^a At the background salt concentration of 30 mM NaCl.**Figure 9.** Compressive yield stresses at 0.2 and 0.3 volume fraction as a function of adhesive force for each combination of polymer type and concentration presented in Figure 8.

present work). In Figure 8a there is a clear trend that the compressive yield stress of the sediments formed from the aggregates induced by the 10% charged polymer in 0.03 M NaCl solution increases as the polymer dose increases from 4 to 6 to 8 to 12 mg/g silica. This corresponds well with the increase in adhesive minima upon retraction (see Table 3), which increases from −0.2 to −0.76 to −0.9 to −2.9 mN/m as polymer concentration increases from 1.2 to 1.8 to 2.5 to 4.0 mg/L. In Figure 8b, the slight increase in compressive yield stress of sediments aggregated with 40% charged polymer, as polymer dose is increased from 4 to 12 mg/g silica, also corresponds well with the increase in adhesion as adhesion increases from about −4 to −7 mN/m. Although for the 100% charged polymer the adhesive minima for the retraction force curves vary between −5 and −9 mN/m as the polymer concentration varies from 0.2 to 6.7 mg/L, as shown in Figure 8c, the compressive yield stresses of sediments vary very little. It appears that the influence of adhesive force on sediment compressive yield stress is a function that decreases in sensitivity as the adhesive force increases. Figure 9 shows the compressive yield stress at 0.2 and 0.3 volume fraction plotted as a function of the magnitude of the interparticle attraction for each of the conditions presented in Figure 8. As expected from theory,^{60–62} an approximately linear increase in compressive yield stress as a function of adhesive force is observed at both volume fractions.

Figure S2 in the Supporting Information is a comparison of the compressive yield stress versus volume fraction of the sediments from the flocs induced by three charged polymers both at the optimum dose and at a low dose. Table S1 in the Supporting Information presents the adhesion forces from AFM studies that

correspond with the polymer dosages in flocculation studies under both low and optimal dosages for three charged polymers. The compressive yield stresses follow the same trend as the adhesive forces upon separation obtained from AFM studies. Therefore, compressive yield stress results correlate with the adhesive forces.

4. Conclusions

The effects of charge density (10, 40, and 100%) of three charged polymers on interaction forces between silica surfaces were investigated using an atomic force microscope. The forces upon approach between silica surfaces in 10% charged polymer solutions in 30 mM NaCl initially produce a weak attraction then increasing steric repulsion as the polymer concentration was increased. Upon separating the surfaces, the adhesion tends to increase with polymer concentration until a maximum occurs at the concentration that corresponds with the optimum polymer dose for flocculation. At even higher doses, the retraction adhesion decreases. The retraction curves show a number of “release and hold” events, indicating the disentanglement and detachment of polymer chains upon separation. These results are consistent with polymer adsorption in an extended conformation and a bridging flocculation mechanism.

The 40 and 100% charged polymers have attractive minima and adhesive forces that are significantly larger than those measured for 10% charged polymer. The 40 and 100% charged polymers exhibit similar behaviors in controlling the surface force at most polymer concentrations, although the forces are different in magnitude. Both the 40 and 100% charged polymers cause long-range attractive forces at certain polymer concentrations. The adhesion upon retraction shows a distinct snap-off rather than a series of release and hold events. These results are consistent with polymer that is adsorbed in thinner layers and adopts flatter conformations than 10% charged polymers in 30 mM NaCl solution. The force profiles of the 40 and 100% charged polymers indicate that the likely mechanisms for attraction and adhesion are either charge neutralization or patch attraction.

A good correspondence between the optimum polymer dose for flocculation and the polymer concentration that produced the strongest adhesion for each polymer was observed. The force curves were also compared to compressive yield stress measurements of sediments. A linear relationship was found between the compressive yield stresses and adhesive forces obtained from AFM studies. The overall conclusion is that the larger the magnitude of the adhesive force, the higher the compressive yield stress of sediments, although other factors such as aggregate size and structure may also play a minor role.

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Supporting Information Available: A plot of the adhesive force as a function of polymer concentration for each polymer, 10, 40, and 100% charged (Figure S1); additional compressive yield stress measurements (Figure S2) and Table S1, with the corresponding adhesive forces. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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