The Dynamics of Polymer Bridge Formation and Disruption and Its Effect on the Bulk Rheology of Suspensions

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ABSTRACT: Bridge-flocculated colloidal gels are used in many important processes and products such as gel casting for advanced ceramics, precursor inks for 3D printing, and waste treatment strategies. An important aspect of polymer bridged gels that makes them excellent candidates for these applications is the precise control it affords for control of rheological properties. Recent studies have shown that adhesion between bridged surfaces increases with time as the number of polymer bridges formed grows. However, the consequences of the dynamics of these processes toward bulk rheological properties have not been studied. Here we investigate the link between the dynamics of polymer bridging and disruption and bulk rheology in dense colloidal silica particle suspensions flocculated by polyethylene oxide (PEO). Microscale pull-off force measurements using atomic force microscope (AFM) show that upon repeated disruption and establishment of bridged contact, the adhesion between the surfaces is reduced. During contact disruption, the polymer chains bridging the two surfaces are stretched leading to chain scission. On the re-establishment of contact, these fragmented polymer chains are unable to fully re-establish the adhesion. Macroscale measurements using oscillatory rheology show that this reduced adhesion results in reduction of both the storage modulus and the yield stress. If the slurry is subjected to high shear for long periods, polymer chain scission is amplified, and the fragmented polymer chains are unable to bridge the particles again, resulting in free-flowing slurries.

■ INTRODUCTION

In a dense particulate suspension, envisioned as weakly aggregated or percolated particulate structures, the interparticle forces determine the details of the microstructure, i.e., aggregate compactness, structure, and strength, which define the overall rheological performance of the system.[1−4] The interparticle forces and microstructure are dynamic in nature.[5−9] Both evolve over time and during flow (aging interparticle bonds and changing aggregate structures), which leads to time/frequency and flow (shear history) dependent rheological behavior.[6,7] The first step toward controlling the rheological performance of particulate suspensions is to fundamentally understand interparticle forces, which can be challenging in industrially relevant complex dispersions. Often these suspensions contain polymeric rheology modifiers and surfactants.

A number of previous reports have investigated bare particle adhesion dynamics and shown that the dynamics of particle adhesion play a central role in slurry rheology.[7,9−13] AFM measurements by Vakarelski et al.[9] showed increased adhesion between SiO_2 and mica surfaces with contact time. Optical tweezer studies by Meng et al.[7] also showed increased adhesion between polystyrene particles with time. Diffusing wave spectroscopy and bulk rheological measurements have shown that this increased particle adhesion leads to a higher elastic modulus of the suspension.[12] However, very few studies[8,14,15] have investigated particle adhesion dynamics in the presence of polymers or surfactants, motivating the characterization of particle adhesion/contact dynamics with and without polymeric

rheology modifiers. The consequences of this adhesion dynamics for bulk rheological performance are also unexplored.

The addition of polymeric modifiers can induce attractive forces between colloidal particles by bridging and depletion flocculation.[16] Both adhesion mechanisms are dynamic in nature. While theoretical studies of polymer adsorption and desorption are focused primarily on equilibrium, such conditions may not prevail in most cases of practical interest.[17] Recently, Sprakel et al.[8] addressed this issue by measuring the kinetics of polymer bridging and disruption experimentally using atomic force microscopy (AFM) for the case of polyethylene oxide MW $14−20 \times 10^3$ g/mol adsorbed on SiO_2 surfaces. It was shown that the adhesion force increased with contact time as the number of polymer bridges increased. In this study surface micelles of alkyl tail modified low molecular weight polyethylene oxide (PEO) chains (MW $14−20 \times 10^3$ g/mol) were preadsorbed on the surface and the colloidal probe particle before they were brought into contact.

The above study left unanswered a number of questions, e.g.: (1) If the polymer bridge is broken, does the polymer desorb from the surface or is the polymer backbone broken? (2) When contact is re-established, what is the strength of the reformed bridge? (3) If polymer chains scission is possible, how many times can such contact be re-established? (4) What are the

consequences of repeated contact and disruption on bulk rheology? To address these questions we have investigated the dynamics of polymer bridge formation and disruption at the microscale using AFM pull-off force measurements for a spherical silica colloidal probe against a flat silica surface in the presence of an aqueous solution of high molecular weight PEO MW 10^5 g/mol. We have focused on repeated disruption and establishment of polymer bridges under conditions believed to be relevant to practical flow situations. Macroscopic oscillatory rheology measurements were then conducted on dense aqueous silica slurries in the presence of the same polymer. The slurries were subjected to various levels of repeated mixing and rest time to investigate the correlation, if any, between the macroscopic behavior and microscopic dynamics of bridge formation and disruption.

MATERIALS AND METHODS

The interaction forces between a silica particle and a silicon wafer (surface SiO_x) in the presence of polyethylene oxide MW $100 \pm 50 \times 10^3$ g/mol were measured with a diCaliber scanning probe microscope (Veeco Instruments Inc., Plainview, NY). A spherical silica particle (15 μm) was attached to the AFM cantilever spring (Hydra Probes, Nanoscience Instruments Inc., Phoenix, AZ) with 5 min Epoxy (ITW Devcon, Danvers, MA). The spring constant of the cantilever was calculated to be 0.0387 N/m with use of the resonance method suggested by Cleveland et al.[18] The PEO solution (0.02 mg/mL, i.e., 0.4 mg/m^2) in ultrapure water (0.01 M KNO$_3$) was placed in a custom-made glass cell along with the silicon substrate and colloidal probe. Experiments were conducted after 15 min to allow polymer adsorption. The equilibrium adsorption time for PEO on glass surfaces is 6.5 min.[19] Repeated pull-off force measurements were carried out at a probe velocity of 300 nm/s. The velocity was selected to emulate the shear induced disruption of polymer-bridged contact between colloidal particles in a suspension. All the solutions used were prepared in polyethylene bottles which were precleaned with ultrapure water. The glass cell and silicon substrate were first ultrasonicated in ethanol, acetone, methanol, and ultrapure water for 20 min each. The silicon substrate and colloidal probe were then further cleaned by UV light and ozone for 20 min in UV/Ozone ProCleaner Plus (Bioforce Nanoscience Inc. Ames, IA). The spherical silica probe particle was purchased from the Corpuscular Inc. (Cold Spring, NY), and the PEO MW $100 \pm 50 \times 10^3$ g/mol[20] was obtained from Polyscience Corp. (Warrington, PA). Ultrapure water and all other chemicals were purchased from Fisher Scientific (Pittsburgh, PA).

For bulk rheology experiments 62 wt % ($\phi = 0.38$) aqueous slurries of silica particles (1 μm) obtained from Fiber Optic Center Inc. (New Bedfort, MA) were dispersed in 0.01 M KNO$_3$ solution. To obtain consistent slurries, particles were mixed in a high shear mixer, SpeedMixer (FlackTek Inc., Landrum, SC), for 3 min at 3300 rpm. This mixer is a dual asymmetric centrifuge that differs from a conventional centrifuge by providing an additional rotation around the vertical axis of the sample. Conventional centrifugal motion pushes the sample outward while the rotation around the vertical axis pushes the sample inward. This combination of forces results in high shear and fast homogenization without trapping of air in the suspension. The PEO solution (2.5 mg/g of silica) was then added to the dispersion and gently mixed in the SpeedMixer at very low speed (300 rpm) for 30 s to flocculate silica particles. The resulting slurries were studied with use of a Physica MCR 300 rheometer (Anton Paar, Ashland, VA) with a cup-and-bob tool. Samples were gently poured into the rheometer cup and the tests were conducted after 1 h wait time to minimize preshearing and wall slip effects. Oscillatory rheology tests (amplitude sweep) were performed to repeatedly break the colloidal gel structure and study the effect of disruption and establishment of polymer bridges on bulk rheological properties, i.e., the storage (G′) and loss moduli (G″). During the strain sweep the amplitude of the deformation is changed at a constant frequency (1 Hz). Flocculated

silica dispersions were also subjected to high shear in the SpeedMixer at 3300 rpm for 6 min to completely break down the gel network.

RESULTS AND DISCUSSION

Figure 1 shows the approach and pull-off force distance curves obtained by an AFM with a spherical silica probe particle
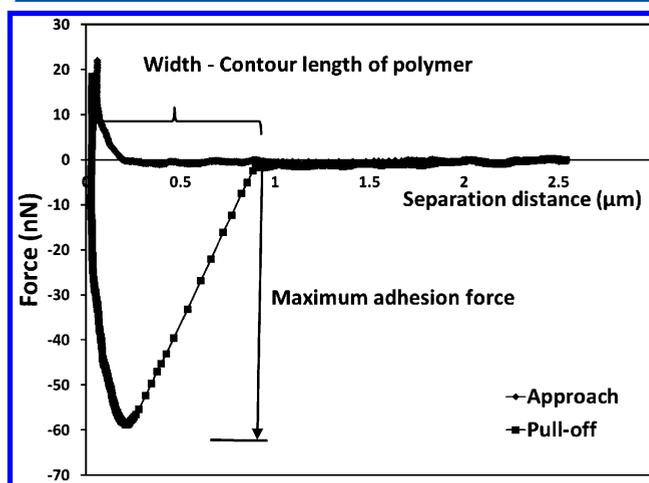

Figure 1. AFM approach and pull-off force vs distance curves obtained for a spherical silica colloidal probe against SiO$_2$ substrate in a 0.02 g/L solution of PEO MW 10^5 g/mol in water (0.01 M KNO$_3$).

against a SiO$_2$ substrate in 0.02 g/L solution of PEO MW 10^5 g/mol in DI water (0.01 M KNO$_3$). On approach toward the substrate, the silica probe experienced a steric repulsion, whereas upon pull-off, a strong adhesion force was measured as the PEO chains bridged the two surfaces. The parabolic nature of the pull-off force distance curve is very similar to previously reported results;[8] however, both the width and depth of the curve are much greater due to the higher molecular weight (10^5 g/mol) of PEO used. A gradual decrease in adhesion force shows a consecutive breaking of polymer bridges. As the two surfaces are separated, the polymer backbone is stretched, and bridges are broken at different separation distances. The full width of the pull-off curve should represent the contour length of the adsorbed polymer. The calculated contour length of PEO MW 10^5 g/mol is 900 nm, assuming a Kuhn length 0.9 nm[8] and 1000 segments. This is comparable to the width of the pull-off curve, 883 nm. The maximum adhesion force can be correlated to the number of bridges formed between the two surfaces if the molecular weight and number of polymer segments adsorbed on the surface are known.[8] Figure 2 shows the pull-off force vs distance curves measured at varying surface delay times, i.e., the amount of time the colloidal probe was in contact with the surface before pull-off was initiated. Similar to the previously reported results (PEO MW $14-20 \times 10^3$ g/mol) for the higher molecular weight PEO used (MW 10^5 g/mol), the maximum adhesion force increased as the surface delay time increased from zero to ten seconds due to an increase in the number bridges formed. The 0 s surface delay time represents instrumentally the lowest possible contact time in the system studied. The width of the pull-off curve also increased with increasing contact time. This was likely due to the high polydispersity of the PEO used. The increase in contact time leads to adsorption of longer polymer chains and thus the greater width of the pull-off curves.[17]
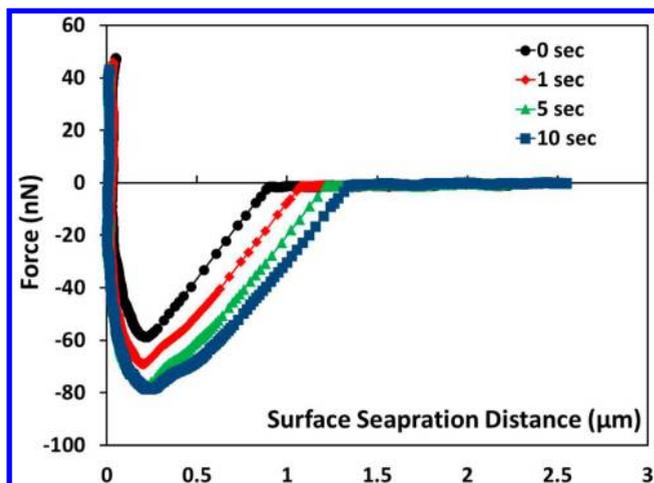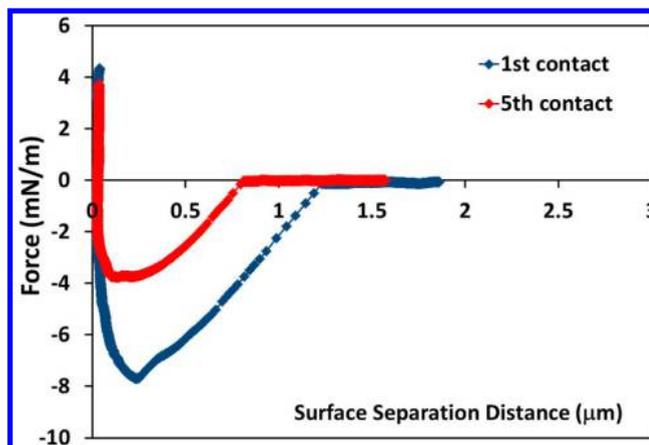
Figure 2. AFM pull-off force vs distance curves at varying surface delay time. The silica colloidal probe was moved at 300 nm/s in a 0.02 g/L solution of PEO MW 10^5 g/mol in water (0.01 M KNO_3).

To study the effect of repeated disruption and establishment of bridges, the pull-off force measurements were carried out repeatedly with a constant probe velocity (300 nm/s), a constant approach time (6.6 s) to the surface, and a constant surface delay time before disruption. Figure 3 shows the
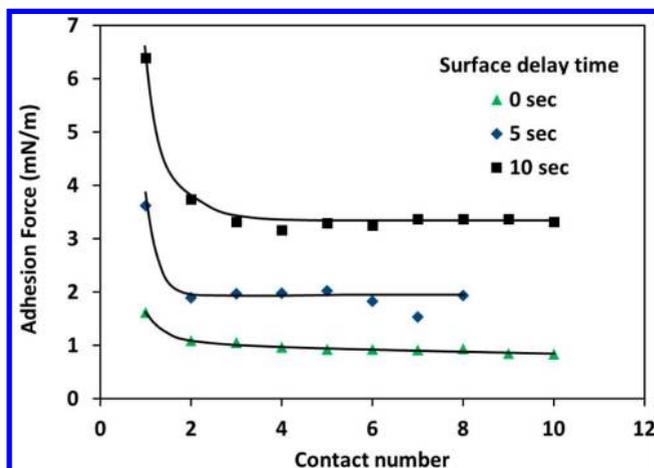
Figure 3. Maximum pull-off force measured on repeated contact with varying surface delay times (probe velocity 300 nm/s). The lines drawn are a guide to the eye.

maximum adhesion force plotted against the number of repeated contacts at varying surface delay times. The measured adhesion force F/R (mN/m) is normalized in the usual way by dividing by the particle radius (15 μm) in the plot. After disruption of the first contact, a significant decrease in maximum adhesion force was observed, followed by very small decreases in adhesion after the third contact. The net decrease in adhesion after the first contact was higher for higher contact times. This decrease in adhesion was probably caused by chain scission during contact disruption. Figure 4 shows pull-off force vs distance curves for the first and fifth contacts at surface delay times of 5 s. A decrease in the width of the pull-off curve suggests lower contour lengths of the polymer fragments on the surface. During contact disruption, the polymer chains are stretched and subjected to elongation stresses which cause chain scission. This chain scission is similar to the mastication

Figure 4. Pull-off force vs distance curves at the first and fifth contacts for PEO 10^5 g/mol adsorbed on silica surfaces (probe velocity of 300 nm/s and 5 s surface delay time).

of polymer chains in elongation and shear flows which was first report by Staudinger in early 1930s.[21−23] In dilute polymer solutions above a critical flow velocity gradient the polymer becomes partially uncoiled and ruptures.[24] Midsection cleavage theory showed that the central bond in the polymer coil experiences the highest mechanical stress and has the highest probability to break.[25−28] When two surfaces are pushed together the polymer chain adsorbs in the spaces between the polymers. After the chain scission, the smaller polymer fragments left on the surface increase the polymer segment density. These fragmented polymer chains form weaker contacts upon second and third repeats. The scission is dominant with long polymer chains.[24] After the third contact, further decreases in adhesion were minimal, suggesting that the polymer scission was limited after the first disruption.

The consequences of the adhesion dynamics on the bulk properties of flocculated silica particle suspensions was studied with oscillatory rheometry. Figure 5 shows (a) frequency and (b) amplitude sweeps for 62 wt % silica particle (1 μm) suspension with PEO MW 4×10^6 g/mol in DI water (0.01 KNO_3). The frequency sweep (0.01% strain) showed a linear viscoelastic response up to 100 Hz, and the amplitude sweep showed a yield stress at 100 Pa. The yield stress point can be recognized as the stress at which the loss modulus, which represents viscous properties, surpasses the storage modulus, which represents the elastic properties of the suspension. At the yield stress, interparticle bonds are broken leading to a viscoplastic flow.[29] The storage modulus measured below the yield stress can be correlated directly to interparticle bond strength.[30] To study the effect of repeated disruption and re-establishment of particle contact on the bulk rheological properties, repeated amplitude sweep tests were performed. In each test the applied shear was increased above the yield stress to break down the particle network. Figure 6 shows the change in storage modulus with repeated amplitude sweeps. Both the storage modulus and the yield stress of the suspension decreased with each repeat, suggesting weaker adhesion between the particles. In Figure 7, the change in the plateau storage modulus is plotted vs repeat test number. Similar to the colloidal probe AFM measurements (Figure 3), on repeated breakdown of the flocculated suspension, a large drop followed by a gradual decrease in the storage modulus was observed. The same trend was observed for the case of a 1000 s delay time
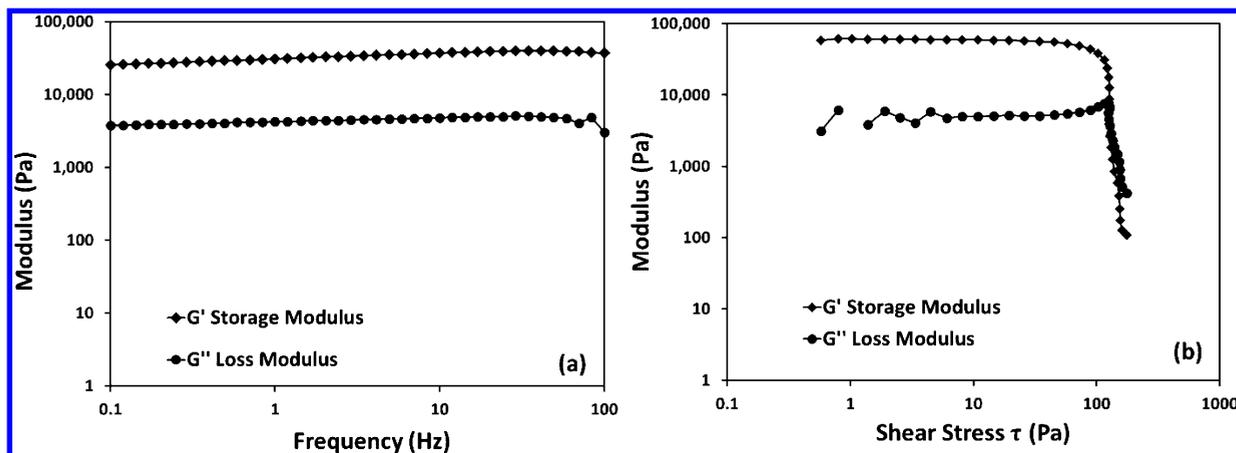
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Figure 5. Frequency (a) and amplitude (b) sweeps for 62 wt % silica particle (1 μm) dispersion bridge flocculated with 2.5 mg/g of PEO MW 4 × 10^6 g/mol in water (0.01 M KNO$_3$).

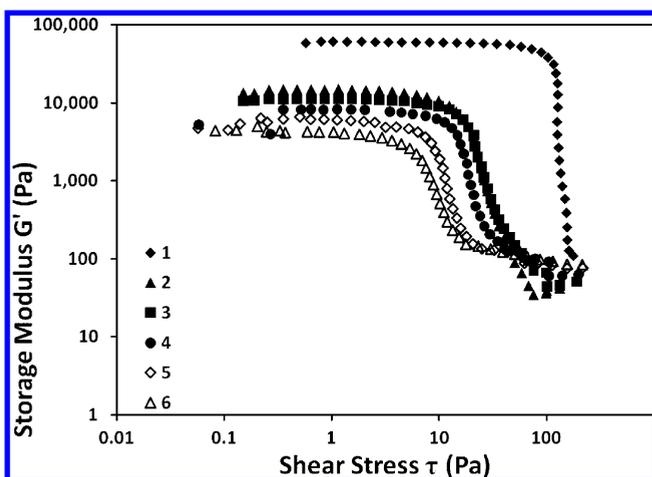**Figure 6.** Change in storage modulus with repeated amplitude sweep for 62 wt % silica particle (1 μm) dispersion bridge flocculated with 2.5 mg/g PEO MW 4 × 10^6 g/mol in DI water (10^{-2} M KNO$_3$).

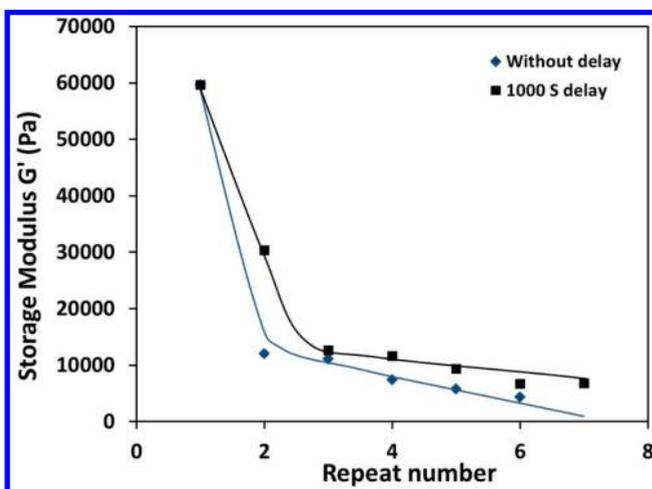**Figure 7.** Change in plateau storage modulus at low shear stress (0.1–1 Pa) with repeated amplitude sweep for 62 wt % silica particle (1 μm) dispersion with 2.5 mg/g PEO MW 4 × 10^6 g/mol in DI water (0.01 M KNO$_3$). Lines are to guide the eye and not actual fit to the data.

between repeat tests, but the net storage modulus was higher, corresponding to stronger adhesion between particles. The

delay time between tests allows the interparticle bond to strengthen, as the number of bridges formed between particles increases with time. After the third repeat the net decrease in modulus was higher compared to the decrease in adhesion force measured by AFM. The high molecular weight PEO (4 × 10^6 g/mol) used in the bulk rheology measurements can undergo chain scission multiple times compared to the PEO MW 10^5 g/mol used in AFM measurements. This additional chain scission gradually reduces particle adhesion after the third repeat.

To further study the hypothesis of chain scission during polymer bridge disruption, we subjected the flocculated silica particle suspensions to very high shear rates for long periods (6 min at 3300 rpm), in the SpeedMixer. When subjected to such high shear conditions, particles go through multiple cycles of contact and disruption during which chain scission should be amplified. Figure 8 shows a flocculated silica particle dispersion

Figure 8. Silica particle (1 μm) suspension bridge flocculated by PEO MW 4 × 10^6 g/mol before and after the mixing in SpeedMixer for 6 min at 3300 rpm.

before (left) and after (right) shear mixing. The flocculated particle network broke down irreversibly, and free-flowing slurry was obtained. Amplified chain scission results in fragmented polymer chains that are unable to bridge flocculate the particles, further corroborating the microscale indications of chain scission obtained by AFM measurements.

CONCLUSIONS

We have measured the dynamics of polymer bridge formation and disruption using colloidal probe microscopy for the case of polyethylene oxide adsorbed on silica surfaces. Adhesion between bridge-flocculated particles increases with contact time as the number of polymer bridges formed increases with time. Upon disruption and re-establishment of the contact, a significant decrease in maximum adhesion was observed. This was attributed to chain scission during pull-off, leaving fragments of lower molecular weight polymer on the surfaces. These smaller fragments then form weaker adhesion on the second and third contacts. After the third contact, very small further decreases in adhesion were observed, indicating chain scission was reduced significantly after the first few contacts. The net decrease in adhesion was higher for higher contact times.

The consequences of the microscale dynamics for the macroscale properties, i.e., the storage and loss moduli of the bridge-flocculated silica suspension, was studied with use of oscillatory rheometry. Similar to the colloidal probe AFM measurements, on repeated breakdown of a flocculated silica particle suspension, a large drop followed by gradual decrease in the storage modulus was observed. When the flocculated suspension was subjected to the high shear for long periods (3−6 min), the gel network broke down irreversibly, and free-flowing slurry was obtained, further supporting the hypothesis of chain scission of the polymer as the bridged contacts are disrupted.

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Notes

The authors declare no competing financial interest.

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