Extensional rheology and stability behavior of alumina suspensions in the presence of AMPS-modified poly(carboxylate ether)-based copolymers

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Abstract

A series of polycarboxylate ether-based copolymers that include acrylic acid, 2-acrylamido-2-methylpropane sulfonic acid, and polyethylene glycol-1000 was synthesized and the performance of these copolymers as rheology modifiers in aqueous alumina suspensions was characterized. We discussed the effect of monomer feed ratio and molecular weight on dispersing ability of these copolymers and on extensional behavior of alumina suspensions. Results of zeta potential analysis determined that using the copolymers even at 0.5 wt% results in all-negative zeta potentials for the entire pH range (2–12). These copolymers immensely affect the extensional rheological behavior of alumina suspensions— while 20 vol% pure alumina suspension showed severe strain hardening behavior, suspensions with 1 wt% copolymers and 35 vol% alumina particles displayed no strain hardening. In this series, the copolymer with lowest molecular weight decreased the extensional viscosity of suspensions at the rupture of thread with 3 orders of magnitude as well.

Introduction

Water is the solvent of choice during ceramic powder processing since it is environmentally benign and cost-effective [1,2]. Dispersion of colloidal ceramic particles in aqueous media is, therefore, critical for industrial processing such as frequently used casting, ink-jet printing [3], and spray drying [4]. Stable suspensions with high solid loadings (>40 vol%) are desirable since obtaining sinterable and crack-free ceramic compact can hardly be achieved using suspensions with low solids contents [5]. However, concentrated colloidal systems often show complex rheological behavior because of particle aggregation [6]. Dispersing of particles is necessary to obtain stable systems and it usually relies on prevailing of repulsive electrostatic force over Van der Waals force [7]. To impart charge on ceramic suspensions with high solid content, dispersants are used. Dispersants decrease the viscosity and agglomeration, homogenize the microstructure thus improve mechanical properties of final product. The dispersant amount should be optimized since excess amounts can cause bridging flocculation whereas inadequate amounts lead to a reduction in absolute value of zeta potential [8-11].

Polyacrylic acid (PAA) is widely used in many systems [10-12] such as dispersion of Ti, Al_2O_3, and yttria-stabilized zirconia in aqueous media; but, performance of PAA is limited due to its simple structure. On the other hand, linear copolymers of

PAA, depending on the types of synergistic functional groups, can provide various properties such as wider pH range for high absolute zeta potential value, lower optimum dosage of dispersant, and less sensitivity to flocculation in the presence of excess amount of dispersant [12-14]. The stabilizing effect of linear polymers can be improved by addition of side chains in order to harness steric hindrance effect as well. These amphipathic structures are usually composed of long hydrophilic side chains grafted to a backbone. The backbone bears ionizable groups such that they can anchor to the surface of particles while side chains protrude into the medium and produce steric hindrance effect [1,2,7]. Bouhamed *et al*. [1] confirmed the stabilizing effect of 2-acrylamido-2-methylpropane sulfonic acid-polyethyleneglycol methacrylate copolymers at 30 vol% alumina suspension. Ran *et al*. [15] reported poly (styrene-co-maleic anhydride)-methoxy polyethylene glycol copolymer as an effective dispersant to reduce viscosity of suspension with ~30 vol% alumina particles. The performance of dispersants in these systems is usually evaluated by rotational rheometry. However, many applications of ceramic suspensions such as ink-jet printing [3], ink-jet deposition in microchannels [16], and spray drying [4] necessitate visco-elasto-capillary characterization of these suspensions. The elongational behavior of the drop of suspension can be studied by capillary breakup extensional rheometer (CaBER) since it can determine the extensional properties of the drop before the pinch-off point [17].

Here, we report the preparation and characterization of a new comb-type copolymer that includes acrylic acid (AA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and polyethylene glycol-1000 (PEG-1000). Copolymers with different chemical formulations and molecular weights were synthesized by changing the reaction conditions and feed ratio. CaBER was used to investigate the effect of addition of copolymers on the extensional flow behavior of alumina suspensions. Results of zeta potential analysis indicated that addition of copolymers to alumina suspensions shifts the isoelectric point (IEP) to lower pH and also leads to negative zeta potentials for entire pH range even at 0.5 wt% of alumina particles. Rheological measurements revealed that addition of 1 wt% of the copolymer with lowest molecular weight increases the maximum fraction of alumina particles in the system to 44 vol% compared to 20 vol% in pure alumina suspensions.

Experimental

Materials

An α-Al$_2$O$_3$ powder (AKP-500, Sumitomo Chemical Company) was used with the mean particle size of 220 nm and specific surface area of 17 m^2/g determined by BET method. AA (99%), AMPS (99%), potassium persulfate (KPS, $\geq$99.0%), and hydrochloric acid (HCl, 37%) were obtained from Sigma Aldrich. PEG-1000, maleic anhydride (MA, 99%), and sodium hydroxide (NaOH, $\geq$97%) were purchased from Merck. All reagents were of analytical grade and used as received without further purification.

Synthesis of copolymer

The esterification of PEG-1000 by MA was carried out via the procedure that was proposed in literature [18]. This product, hereafter referred as PEGMA, was used for polymerization without any purification. Choosing PEG-1000 for esterification was based on the higher dispersing ability of AMPS/PEG-1100 copolymer than AMPS/PEG-2000 [19].

Different polycarboxylate ether-based AA/AMPS/PEGMA copolymers were synthesized based on a method described by Salami and Plank [20]; these copolymers are named from PCE1 to PCE6 in Table 1. To optimize solid content of suspensions and dispersing ability of copolymers, we explored a matrix of

conditions such as changing of reaction pH and molar ratios of monomers to produce copolymers with different formulations. In a typical aqueous free radical polymerization, 15 wt% aqueous solution of reactants was prepared by using different molar ratios in 110 ml water (Table 1). Subsequently, pH of this mixture was adjusted by using aqueous solutions of NaOH and HCl and then the mixture was charged into a three neck flask that is connected to a reflux condenser. Nitrogen was used to remove free oxygen throughout the reaction. After 30 min, the flask was heated up to 50 °C and 10 ml aqueous solution of 0.25 g KPS, the initiator, was added to the reaction chamber. After 50 min, temperature was raised to 60 °C and the 10 ml solution of 0.25 g KPS was added to the medium for the second time. The temperature, then, was increased to 80 °C and the reaction continued for another 4 hours. Finally, the reaction was cooled down to room temperature and copolymers were precipitated in acetone and dried under vacuum at 50 °C until reaching a constant weight. As a reference, we also synthesized AA/AMPS linear copolymer (without PEGMA) referred as PC in Table 1.

Characterization methods

Chemical and structural characterization of copolymers was carried out by nuclear magnetic resonance (NMR, Varian Unity Inova 500MHz spectrometer) and dilute solution viscometry (Cannon glass capillary viscometer 1C) at room temperature (22 °C), respectively.

Dispersing ability of copolymers was determined by measuring particle size distribution and hydrodynamic radius (r_h) of alumina suspensions with and without copolymers (Zetasizer nanoseries, Malvern Instruments, Ltd.). Alumina suspensions were prepared by adding 0.01 wt% alumina particles to a solution containing different amount of copolymers and, then, an ultrasound probe (Vibra Cell 75041, Bioblock Scientific) was used for 5 min in pulse mode to break soft agglomerations. To monitor the effect of time on particle size of suspensions, all specimens remained uninterrupted throughout the testing. Each test was repeated 6 times with 20 cycles and average value was reported.

A zeta potential analyzer (Zetasizer nanoseries, Malvern Instruments) was used to monitor the electrokinetic behavior of alumina particles in the presence of different amounts of copolymers. After addition of 0.001 wt% alumina particles to polymer solutions and 1 hour of stirring, pH of the mixture was adjusted to 2–12. Subsequently, 6 measurements with at least 20 cycles were performed at 25 °C and the average value was reported.

Adsorption behavior of copolymers was investigated via UV-vis spectroscopy (UV-3150 Shimadzu spectrometer) and thermogravimetrical analysis (Netzsch STA 449C Jupiter thermal analyzer). Alumina suspensions with 4 wt% of particles and different amounts of copolymers were prepared. After 3 hours of stirring, suspensions were centrifuged to separate the alumina particles. The amount of

adsorbed polymer was quantified by measuring the difference between UV-adsorption of supernatant and bulk concentration of copolymers before addition of alumina particles. Moreover, these particles were further used for thermogravimetrical analysis (TGA). To eliminate unadsorbed and weakly bonded copolymers on these particles, they were redispersed in water and then centrifuged at 4,500 rcf for 1 hour. This process was repeated for six times following by drying at 70 °C under moderate vacuum for 3 days. Thereafter, TGA was carried out by heating up the dried samples at 10 K/min from room temperature to 600 °C under nitrogen atmosphere.

To observe the effect of different copolymers on stability of suspensions, a gravity-settling based test was designed. Suspensions with 4 wt% alumina particles and 2 wt% copolymers (compared to alumina particles) were prepared in native pH of suspensions and then placed in 100 ml graduated cylinder. We took 1 ml of samples at the depth of 60 ml by using a stainless steel needle connected to a 10 ml syringe. These samples were immediately placed in a moisture analyzer (Shimadzu uniBloc MOC63u) to measure the solid content.

Rheological measurements were carried out by using a capillary breakup extensional rheometer (HAAKE CaBER 1, Thermo Scientific, Germany) with two plates which have a diameter of 6 mm. Plate separation was changed from $L_0 = 2$

mm to $L_f = 7.6$ mm within 50 ms. The extension rate ($\dot{\varepsilon}$), 26.7 s^{-1}, was set according to the relation $L_f = L_0 \exp (\dot{\varepsilon}t)$, where t is time (s). After establishing liquid bridge, the midpoint diameter (D(t)) was monitored as a function of time using the laser micrometer. Suspensions with 20–45 vol% alumina particles and different amounts of copolymers were prepared by using ultrasound probe in pulse mode and stirring for 24 hours in a capped container to prevent evaporation. All samples were tested at ambient temperature immediately after stopping the stirring process.

Results and discussion

Polymer characterization

Chemical structure of copolymers was characterized by using ^{1}H-NMR (Fig. 1). Proton chemical shifts were observed at δ 1.5, 1.7, 2.1, 3.4, and 3.7 ppm that are attributed to $-CH_3$ group of AMPS (5), $-CH_2$ (2) and $-CH$ (1) groups in main chain of polymer, $-CH_2$ group of AMPS (4), and $-CH_2CH_2-O$ group of PEG chain (3), respectively. Dilute solution viscometry was used to confirm the polymerization of copolymers with different molecular weights. Fig. 2 shows reduced viscosity of the copolymers as a function of concentration. Expectedly, AA/AMPS copolymer exhibited the lowest intrinsic viscosity (1.7 dl/g) while PCE1, PCE2, and PCE3

display the 4.3, 3.1 and 5.4 dl/g, respectively. Thus, we concluded that the molecular weight of PCE2 is the lowest among these comb type copolymers.

Adsorption of PCEs on alumina particles

Fig. 3a shows the adsorption isotherms of different copolymers at native pH (7–8) of alumina suspensions. The amount of adsorbed copolymers increases significantly with initial amount and then stabilizes near a plateau value that is typical for a monolayer adsorption isotherm [21]. This plateau is reached at higher amounts when the molecular weight of copolymers increases (PCE2 < PCE1 < PCE3). Fig. 3b is a representative result of TGA on dried alumina suspensions that contain different amounts of PCE2. Increasing amount of initial copolymer in the suspensions raised the amount of weight loss indicating the presence of strongly adsorbed copolymers on the surface of alumina particles.

Given the importance of the electrokinetic behavior of suspensions for interpreting the adsorption behavior and also change of rheological properties in the presence copolymers, the effect of pH on zeta potential of alumina suspensions was given in Fig. 4. Fig. 4a shows the results of zeta potential measurements that were carried out on alumina suspensions with different amounts of PCE2. Isoelectric point (IEP) of pure alumina suspension is ~8 indicating that the surface of alumina particles hold Al–OH bonds and positively charged sites of Al–OH$_2^+$ between pH 7

and 8. Carboxylate and sulfonate groups are reported to be adsorbed on the surface of alumina particles by making bonds with $Al–OH_2^+$ ions [2,10]. The inclusion of the copolymer leads to bonding between ionized functional groups (COO^- and SO_3^-) in the backbone of the copolymer and $Al–OH_2^+$ sites on the particles. Consequently, positively charged alumina particles are covered with negatively charged copolymers as shown by IEP shifting to lower pH values. At higher than 0.3 wt% copolymer loadings, the number of negative charges introduced by the copolymer surpasses the number of positively charged sites and changing the sign of zeta potential values takes place as a result of this overcompensation phenomenon [22]. Fig. 4b illustrates the zeta potential values in the presence of 0.5 wt% and 2 wt% of different copolymers. PCE1 and PCE2 display almost identical electrokinetic behavior while maximum absolute value of zeta potential was detected in the suspension containing PCE3. The latter observation can be attributed to the higher number of ionized groups in the backbone of PCE3 due to its higher molecular weight.

Analysis of electrokinetic behavior of suspensions in the presence of PCE1 and PCE2 is helpful to understand the conformation of adsorbed copolymers. Affinity of both copolymers to the surface of alumina particles is close to each other since the curves that they generate in zeta potential vs pH graph are superimposable (Fig. 4b). However, according to adsorption isotherm test, more PCE1 is adsorbed on

the surfaces of alumina particles; hence, we speculate that not all parts of the main chain of copolymers are adsorbed and copolymers adopt a loop structure on the surface of particles [23]. Furthermore, this loop conformation explains the difference among the amounts of adsorbed copolymer in plateau region in adsorption isotherm test (Fig. 3a). A fraction of backbone of a copolymer with no bonding to the surface increases the amount of adsorbed copolymer. When molecular weight of copolymers increases, a rise in the length of copolymers with no bonding is inevitable. Given the certain number of sites on the surface of the particles available for adsorption, higher amount of adsorbed copolymer in plateau region with increasing molecular weight of copolymer (PCE3 > PCE1 > PCE2) is expected.

Stability

Fig. 5a shows change in hydrodynamic radius (r_h) of alumina particles with time in 4 wt% alumina suspensions with 2 wt% of different copolymers compared to alumina particles at pH 7.5. Choosing 2 wt% copolymers was based on the fact that all copolymers reach saturation that is indicated by steady zeta potential values for entire pH range at this amount of loading (Fig. 4b). Pure alumina suspension displayed r_h of 350 nm initially and 390 nm after 10 min due to the formation of aggregated colonies. Since zeta potential of pure alumina suspension at this pH is around 5 mV (Fig. 4), repulsive interactions among particles are not sufficient to

prevent agglomeration. On the other hand, in the presence of 2 wt% copolymers, initial r_h of 117, 116, and 121 nm were observed in suspensions containing PCE1, PCE2, and PCE3, respectively (Fig. 5a).

We based stability measurements on a procedure proposed by Cynthia *et al.* [24] Since no discrete layer was observable during gravity settling, we used the time needed for 25% mass removal of alumina particles at a certain sampling height (height of 60 ml in 100 ml graduated cylinder). In the absence of copolymers, alumina suspension reached 75% of initial concentration at sampling height in 25 min while suspensions that contain 2 wt% PCE1, PCE2, and PCE3 necessitated 90, 110, and 35 min, respectively. This observation indicates the higher stability of suspensions in the presence of copolymers and is also consistent with the results of r_h measurements (Fig. 5a). In the absence of sufficient repulsive forces in pure alumina suspensions that is evidenced by low zeta potential values (Fig. 4), attractive van der Waals force prevails over interparticle interactions [25] and aggregated colonies with particle size of ~400 nm are formed (Fig. 5a). Hence, formation of these clusters decreased the time of sedimentation and caused higher mass removal of particles compared to well-dispersed particles in the presence of copolymers.

To determine the lowest amount of copolymer that is needed for further rheological measurements, we worked with PCE2 since it displayed highest

stability among all copolymers based on gravity settling. We measured particle size distribution of suspensions containing different amounts of PCE2 15 minutes after sonication (Fig. 5b). Sample with 0.3 wt% PCE2 displayed a low intensity peak at particle size of 1 μm in addition to the main peak centered at 110 nm. Appearance of this small peak can be described by incomplete surface coverage of 0.3 wt% PCE2. Addition of 0.5 wt% PCE2 led to disappearance of this small peak and observation of a single population curve centered at ~120 nm; hence, we concluded that 0.5 wt% is the minimum amount of PCE2 needed to stabilize alumina suspensions for further rheological tests.

Rheological measurements

We present the change of midpoint diameter in 20 vol% (~50 wt%) alumina suspension thread as a function of time in Fig. 6a. In the absence of any additives, this 20 vol% solid content was found to be the highest amount of alumina for preparation of a suspension. As seen in Fig. 6a, pure alumina suspension exhibits Newtonian behavior in low deformation times, characterized by linear necking rate in time that is followed by exponential decrease of midpoint diameter until the break up point. The deformation imposed on the fluid can be described by Hencky strain, $\varepsilon = 2\ln D_0/D(t)$, where D_0 is the plate diameter (mm). Fig. 6b shows extensional viscosity of pure alumina suspension as a function of Hencky strain.

The apparent transient extensional viscosity (η_E) of stretching fluid can be calculated as:

$$\eta_E = \frac{\Delta\tau(t)}{\dot{\epsilon}(t)} = -\frac{\sigma}{D(t)/dt} \qquad (1)$$

where $\Delta\tau(t)$ is the total extensional stress difference in elongating flow (Pa), $\dot{\epsilon}(t)$ is instantaneous strain rate (s^{-1}), and σ is the fluid surface tension (N/m) [26]. Without inclusion of additives, pure alumina suspension displays a severe strain-hardening behavior and extensional viscosity diverges to maximum value of approximately 2,000 Pa.s. Since, alumina particles hold low surface charge in the native pH of alumina suspension, dominance of Van der Waals attraction among particles results in particle flocculation. Thus, we postulated that the non-Newtonian stress contribution, generated by flocculation of particles, to total stress evolution retarded the necking rate of the thread. This behavior resembles the creation of a connected 3D network of aggregates beyond the percolation threshold [23], which similarly increases the viscosity asymptotical to infinity.

Effect of AA/AMPS ratio on the rheological behavior

After inclusion of different copolymers even at 0.3 wt%, 20 vol% alumina suspensions showed high necking rates—the viscosity has decreased significantly such that change of midpoint diameter was not traceable by the laser micrometer. Consequently, we increased the solid content of suspensions to 35 vol% (~68

wt%). In the samples containing 0.5 wt% of different copolymers, Fig. 7a and Fig. 7b show the change of midpoint diameter in time and extensional viscosity as a function of Hencky strain, respectively. Presence of copolymers with different AA/AMPS ratio changed the extensional flow behavior of alumina suspensions, that is, Newtonian behavior in low deformation time followed by elastocapillary thinning region before the break up point (Fig. 7a). As seen in Fig. 7b, all samples except the one with PCE2 display a modest strain hardening before break up point. Increase of AA/AMPS ratio from 0.25 in PCE4 to 1 in PCE2 resulted in disappearance of strain hardening while further increase of AA/AMPS ratio to 1.5 (PCE6) led to observation of strain hardening in these samples.

For a model viscoelastic fluid, elastocapillary thinning region—the region before the break up point, can be described by an exponential decay of the midpoint diameter in time for $t > t_1$ as shown in eq. 2 [27]:

$$\frac{D(t)}{D_0} = \left(\frac{G_1 D_0}{4\sigma}\right)^{1/3} \exp\left(-\frac{t - t_1}{3\lambda_e}\right) \tag{2}$$

where G_1 is related to elastic modulus, t_1 (s) is the onset of elastocapillary region, and λ_e is the longest fluid relaxation time (s^{-1}). Fitting experimental points in elastocapillary thinning region in Fig. 7a with eq. 2 indicated that the increase of AA/AMPS ratio from 0.25 in PCE4 to 1 in PCE2 reduces the relaxation time (λ_e) of suspension from 1.9 ms to 1.2 ms. Further increase of AA/AMPS ratio to 1.5 in

PCE6 raised the λ_e to 3.1 ms. In addition to the deflocculating effect of copolymers, change in extensional flow behavior can be attributed to the increase in the fast motion of alumina particles as a result of the lower attraction between particles. We, therefore, concluded that using AA/AMPS ratio of 1 leads to the highest synergistic effect of functional groups as indicated by the smallest relaxation time.

The effect of molecular weight of copolymers on the rheological behavior

We also investigated the effect of molecular weight of the copolymers on extensional flow of suspensions. Among the polymers with AA/AMPS ratio of 1 (PCE1, PCE2, and PCE3), we first plotted extensional viscosity of 35 vol% alumina suspensions in Fig. 8a as a function of Hencky strain for samples containing increasing amounts of PCE2. Pure alumina suspension with 20 vol% solid content was also used the reference sample for comparison. Addition of 0.3 wt% PCE2 decreases the strain hardening behavior while thinning is observed in the presence 0.4 and 0.5 wt% copolymer (Fig. 8a). These observations are indicative of the presence of interparticle interactions in the system [28]. In addition, deviation from Newtonian behavior is minimal in the suspension with 1 wt% copolymer due to the significant decrease of interparticle attraction that is in agreement with zeta potential measurements.

We, then, studied the extensional viscosity of alumina suspensions as a function of Hencky strain in the presence of copolymers with different molecular weights. Alumina suspension that contains the copolymer with the highest molecular weight (PCE3) displayed the highest extensional viscosity and modest strain hardening effect. Decrease of molecular weight led to reduction of extensional viscosity and disappearance of the strain hardening region. These results can be explained by the effect of adlayer thickness on the effective volume fraction (ϕ_{eff}) and effective particle distance (2Λ) in suspensions. The effective volume fraction of solids in suspension ($\phi_{eff} = \phi \left[1 + \frac{\delta}{a} \right]^3$) consists of the real volume fraction (ϕ) of particles with radius of (a) and the excluded volume formed by the stabilizing adlayer with thickness of (δ). This adlayer should be sufficiently thick in order to prevent agglomeration and also thin enough to minimize the excluded volume [29]. Presence of this excluded volume reduces the interparticle distance, which can be estimated by ($\frac{\Lambda}{r} = [\frac{\phi_m}{\phi_{eff}}]^{\frac{1}{3}} - 1$), where ϕ_m is the maximum packing fraction of monodisperse spherical particles (0.638 for random packing) [30]. Using the difference between the hydrodynamic radius of the coated and bare alumina particle as the polymer adlayer thickness [31], effective volume fraction and effective interparticle distance were calculated (Table 2).

As seen in Table 2, presence of PCE3 reduces the interparticle distance to 24 nm, which is in the range of adlayer thickness ($\delta \sim \Lambda$). Therefore, the strain hardening behavior observed in this suspension potentially results from the interaction of copolymers. On the other hand, decrease of molecular weight (PCE1 and PCE2) led to lower δ and higher Λ such that the system can incorporate higher volume fraction of alumina particles.

Maximum volume fraction of alumina in suspensions

Fig. 9a shows the change of midpoint diameter in time for samples with 1 wt% PCE2 and increasing amount of alumina particles to find the maximum volume fraction (ϕ_{max}) of the dispersed phase. We chose 1 wt% PCE2 since in extensional viscosity measurements, deviation from Newtonian behavior was minimal in the suspension with 1 wt% copolymer (Fig. 8). To describe the time evolution of the neck diameter, we used the power-law fluid expression, that is, the midpoint diameter changes as:

$$\frac{D(t)}{D_0} = \phi(n)\left(\frac{\sigma}{K}\right)(t_c - t)^n \qquad (3)$$

where n is the power-law exponent, K is the consistency index and $\phi(n)$ is a numerically determined factor [26]. The suspension with 30 vol% alumina particles ruptured in less than 0.02 s while increasing amount of particles retarded

the onset of elastocapillary region (t_1). The onset is found by intersection point of the lines that are fitted to linearly decaying regime and exponentially decaying regime of elastocapillary region [27]. By fitting experimental points to the power-law fluid expression in eq. 3 and elastocapillary region to eq. 2, the fitting parameters were calculated as shown in Table 3.

Fig. 9b demonstrates extensional viscosity of suspensions with 1 wt% PCE2 as a function of Weissenberg number ($\lambda_e.\dot{\varepsilon}$), which is used to horizontally collapse the results. Increasing solid volume fraction shifted the extensional viscosity curve to higher values and led to observation of thinning behavior above 35 vol%. Change of flow behavior from well-dispersed system in 30 vol% to flocculated system in 40 vol% is also evidenced by reduction of n from 1, which is the characteristic value for Newtonian fluid, to n=0.85.

The suspension with 40 vol% alumina particles initially showed decrease of strain rate towards the maximum extensional viscosity (η_{max}) and subsequently, decrease of extensional viscosity was observed with increasing strain rate, as shown in the Fig. 9b with arrows. On the other hand, the suspension with 45 vol% alumina particles only displayed the region of decreasing strain rate towards η_{max} (Fig. 10). Similar CaBER response was reported by White *et al.* [32] for 35 vol% cornstarch-water suspensions. They suggested that possibly the compressive flow in the radial

direction is increasing the packing of particles locally and facilitating the jamming of particles or clusters.

In Fig. 11, we present the change in extensional viscosity and relaxation time of alumina suspensions as a function of particle volume fraction. All suspensions contained 1 wt% PCE2 and extensional viscosity was obtained at $\lambda_e\dot{\varepsilon}=0.08$. As particle fraction increases above 30 vol%, viscosity and relaxation times of suspensions gradually increases up to 37.5 vol% and grow significantly beyond this point. Rapid increase of λ_e and η_E towards maximum volume fraction of dispersed phase is an indication of pronounced elasticity and formation of network of aggregates. Dependency of the extensional viscosity on volume fraction of alumina particles is analogous to that of the shear viscosity on volume fraction of dispersed phase [23,33]. This dependency could be fitted by Kreiger-Dougherty equation as:

$$\eta = \eta_0(1 - \frac{\phi}{\phi_{max}})^{-[\eta]\phi_{max}} \tag{4}$$

where η_0 is the viscosity of liquid medium (Pa.s) and $[\eta]$ is the intrinsic viscosity [34]. However, the presence of copolymer adlayer increases the volume fraction of dispersed phase. In order to take into account the effect of higher ϕ_{eff} compared to ϕ on viscosity, we used modified Kreiger-Dougherty model ($\eta = \eta_0(1 -$

$\frac{\phi_{eff}}{\phi_{max}})^{-[\eta]\phi_{max}}$). By satisfactory fitting of the experimental points with modified

Kreiger-Dougherty equation, ϕ_{max} of 44% and [η] of 5.6 were obtained, which are

consistent with reported values in literature [23]. Moreover, ϕ_{max} of 44% is in

agreement with the 45% that we found experimentally (Fig. 10).

4. Conclusion

We investigated the stability and extensional flow behavior of alumina suspensions

in the presence of copolymers composed of acrylic acid, 2-acrylamido-2-

methylpropane sulfonic acid, and polyethylene glycol. Particle size analysis and

rheological measurements confirmed the stabilizing effect of copolymers and we

showed that the maximum amount of alumina that can be fed into the suspension is

~45 vol% at 1 wt% copolymer (PCE2) addition. The effect of copolymers in

reducing extensional viscosity and elimination of strain hardening behavior in

alumina suspensions suggests a strong potential for these copolymers to be used in

tuning of rheological behavior of ceramic suspensions.

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Table 1. Molar compositions of starting materials for polymerization

Polymer no.	Molar ratio AA/AMPS/ PEGMA	pH
PCE1	25/25/1	6
PCE2	25/25/1	8
PCE3	25/25/1	13
PCE4	10/40/1	8
PCE5	20/30/1	8
PCE6	30/20/1	8
PC	25/25/0	6

Table 2. Effective volume fraction and effective interparticle distance of alumina particles in the presence of 1 wt% copolymers with different molecular weight

copolymer	δ (nm)	ϕ_{eff}	2Λ (nm)
PCE1	7	0.42	33
PCE2	6	0.41	35
PCE3	11	0.47	24

Table 3. Onset of elastocapillary region (t_1), relaxation time (λ_e), and power-law exponent of suspensions (n) with 1 wt% PCE2 at increasing amounts of solid volume fraction (ϕ)

ϕ	t_1 (ms)	λ_e (ms)	n
0.30	12	0.8	1.00
0.35	17	1.1	0.99
0.375	35	1.5	0.95
0.40	180	4.1	0.85