

RAFT polymerization of poly (acrylic acid-co-maleic anhydride) as dispersant for raw ceramic suspension

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In this study, an effective dispersant for raw ceramic suspension, poly (acrylic acid-co-maleic anhydride) (P(AA-MA)) has been synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. The static viscosity, zeta potential, rheological behavior and sedimentation measurements of P(AA-MA) modified ceramic suspension were carried out, respectively. The measurements suggested that the amount of dispersant affected the suspensions stability significantly. When 0.3 wt.% dispersant was used, the resulting suspension provided the lowest static viscosity and the highest stability. Moreover, the area of the thixotropy loop was small, when dispersant amount was 0.25 wt.% based on solid content and it turned flat as the dispersant amount increased to 0.3 wt.%.

Key words: Poly (acrylic acid-co-maleic anhydride), Raw ceramic suspension, Dispersant amount, Stability, Thixotropy.

Introduction

With large amount of products offered by the ceramic industry, the processing of ceramic suspension has attracted much more attention. It is important to control colloidal properties and stability at high solid volume ceramic suspensions [1, 2], which eliminate the structural defects and stress center in the sintered product [3, 4]. However, the difficulty in ceramic suspension processing rises with high the solid volume fraction, due to the aggregation and sedimentation of the particles. An effective solution to this problem is to add dispersant into ceramic suspension, which enable to keep the stability and the rheological behavior of the suspension [5].

Polyelectrolytes are extensively studied and employed as dispersant during the processing of ceramic suspensions. The suspension can be stabilized through electrostatic and steric repulsive forces by absorbing polyelectrolytes on the particle surface [6–8]. Polyacrylic acids are a class of commonly used dispersant for the oxide particles [9–11] and barium titanate [12–14] in ceramic industry. More importantly, the newly developed P(AA-MA) was a more efficient dispersant for ceramic suspension [6, 15, 16].

The quantity of negatively charged carboxylic groups in polymer controls the effective charge density of the particle surface, and forms the electrostatic repulsive force between particles, which determines the particles dispersion [17, 18]. The appropriate molecular weight

with higher charge density could disperse ceramic suspension adequately [15, 19]. The average molecular weight and the polydispersity index (PDI) strongly influence the suspension stability, and the viscosity decreases with the decrease in PDI [20]. To this end, reversible addition-fragmentation chain transfer (RAFT) polymerization was a powerful tool to prepare near-monodisperse polymers [21, 22] and to control molecular weight.

In the present study, P(AA-MA) was prepared by RAFT polymerization, and then applied for raw ceramic suspension. The as-prepared suspensions dispersed well in the presence of the P(AA-MA), and the suspension stability was improved significantly with the increase in dispersant amount.

Experimental

The main chemical compositions of raw ceramic particles (foshan, China) are SiO₂ 89.03 wt.%, Al₂O₃ 4.80 wt.%, Fe₂O₃ 0.62 wt.%, CaO 0.45 wt.%, K₂O 0.54 wt.%, MgO 0.34 wt.%, Na₂O 0.19 wt.%, TiO₂ 0.09 wt.%. The mean particle size was 13.068 μm by using laser diffraction (Mastersizer 2000, Malvern Instruments INC, UK). The specific surface area of the raw porcelain particles was 8.0339 m² · g⁻¹, measured by the Brunauer-Emmet-Teller (BET) method at 77 K on a FlowSorb III 2310, Micromeritics Instrument Corporation, USA. The isoelectric point (IEP) of these raw materials was at pH 9.0, determined by acid-base titration.

S,S'-Bis(α,α'-dimethyl-α"-acetic acid)-trithiocarbonate was synthesized as chain transfer reagent (CTA) according to literature [23]. P(AA-MA) was prepared by RAFT polymerization. The solution of AA, MA and CTA

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were degassed in a 250 mL flask equipped with a cold water condenser. The flask was brought to 50 °C under argon to homogenize the solution, and then heated to 70 °C and 4,4'-azobis (4-cyanopentanoic acid) was added. The polymerization was kept for 3 hrs and neutralized to pH = 8, with an aqueous solution of 10 M NaOH. The products were put into ethyl acetate to precipitate, filtered, and then thoroughly dried in a vacuum oven. The number average molecular weight of the P(AA-MA) was 14348, with PDI = 1.19.

The FT-IR analysis was carried out using a spectrometer (Perkin-Elmer). The suspensions prepared by adding 200 g fine ceramic particles into 86 g deionized water for static viscosity, which was measured by a digital rotational viscometer (NDJ-8S, China). A diluted suspension was prepared by dispersing 0.1 g of ceramic particles in 100 mL deionized water for zeta potential measurement, which was done by electrophoresis (Malvern Nano-ZS90 particle size analyzer, United Kingdom). Rheological measurement was carried out in a coaxial cylinder rotational rheometer (AR-G2, T.A. Instruments Ltd, USA) with 70 wt.% solid content. Sedimentation measurement was conducted according to the literature [24, 25].

Results and Discussion

The FT-IR spectra of P(AA-MA) was shown in Fig. 1. The peak at wavelength of 3430 cm^{-1} was attributed to O-H stretching vibration. The peak at 2958 cm^{-1} was assigned to C-H groups, whose bending vibration appeared at 1406 cm^{-1} . The two peaks at 1649 cm^{-1} and 1552 cm^{-1} are corresponding to the symmetric and asymmetric stretching vibration of C=O groups, respectively. There was no absorption peaks at $1820\text{ cm}^{-1} \sim 1840\text{ cm}^{-1}$ of the anhydride groups, or 665 cm^{-1} to 995 cm^{-1} of the C=C groups in the polymer.

Fig. 2 illustrated the static viscosity of suspensions at different dispersant amount. The static viscosity decreased drastically at the dispersant amount was lower than 0.3 wt.% of dry solid, and then increased slightly at 0.35 wt.% of the dispersant. The polymer with ionized

anionic carboxylic group affected the viscosity of suspension by electrostatic interaction with raw ceramic particles. As the dispersant amount increased, the adsorbed charge density of particles surface increased at the same time, thus stabilized suspension and reduced viscosity were achieved. After saturation of adsorption at dispersant amount was 0.3 wt.% of dry solid, the viscosity of suspension increased slightly with increase in amount of dispersant. The excess dispersant changed the ions environment, affected the thickness of diffusion layer or destroyed the electrical double layer [15].

Zeta potential reflects the influence of dispersant on the particle surface charge and the electrostatic stabilization in the suspension [13]. The Smoluchowski zeta potential of raw ceramic particles was investigated at the dispersant concentration ranging from 0 mg/L to 2000 mg/L. The Smoluchowski zeta potential of the raw porcelain particles surface without dispersant was -27.5 mV, while the value of the zeta potential decreased significantly after dispersant added. The zeta potential reached a plateau value of approximately -65.2 mV at dispersant concentration was 500 mg/L. Sodium of P(AA-MA) was anionic polymer and dissociated in the aqueous suspension. The particles surface adsorbed the dispersant through electrostatic

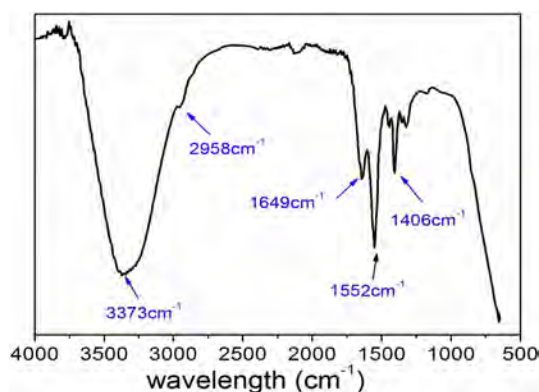


Fig. 1. FT-IR of P(AA-MA).

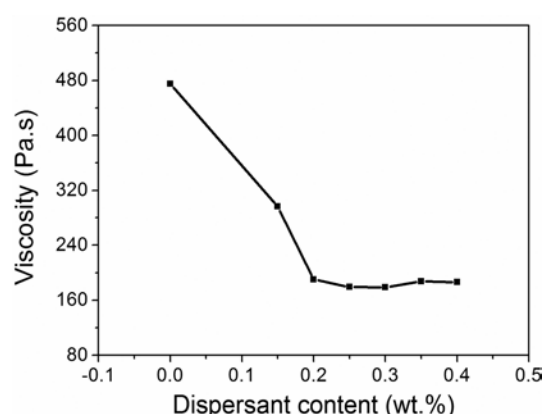


Fig. 2. Effect of polymer concentration on viscosity of raw ceramic suspension.

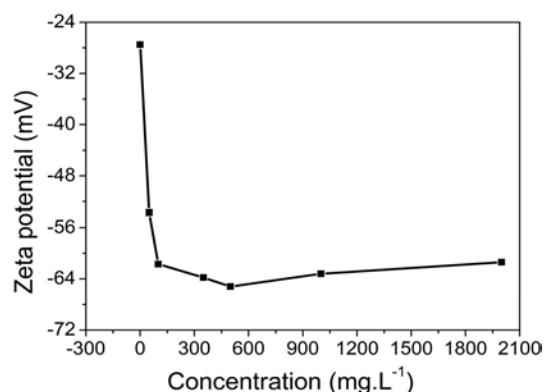


Fig. 3. Effect of polymer concentration on zeta potential of raw ceramic suspension.

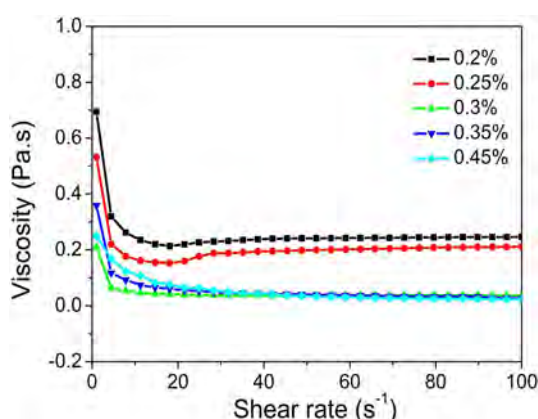


Fig. 4. Viscosity (Pa · s) versus shear rate (s^{-1}) at different polymer weight amount.

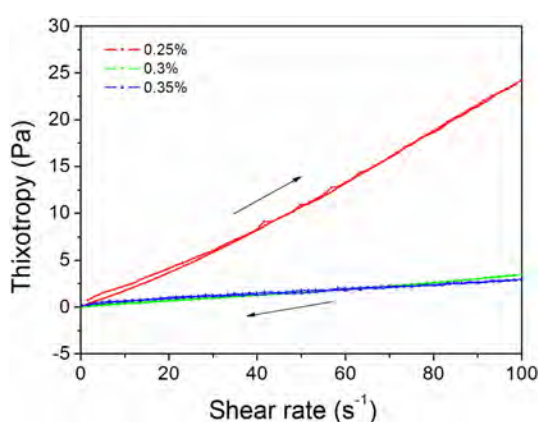


Fig. 5. thixotropy (Pa) versus shear rate (s^{-1}) at different polymer weight amount.

force, which stabilized the raw porcelain suspension, thus lowered the zeta potential. The zeta potential decreased slightly when the concentration of dispersant was over 500 mg/L. The electrical double layer formed by the electrostatic force between particles and dispersant was influenced by the excess free state dispersant [16]. The results indicated that the amount of dispersant controlled the charge density of the particles surface and the electrostatic repulsion effectively.

The rheological behavior of raw ceramic suspension is strongly dependent on the nature of deoculant [19]. The rheological behavior also reflected the surface charge on the particles in suspension [26]. Fig. 4 showed the viscosity of each suspension with 70 wt.% solid content at different shear rate ($0 S^{-1}$ to $100 S^{-1}$). The raw ceramic suspensions displayed a shear-thinning behavior at different dispersant weight amount. The viscosities decreased drastically at the shear rate of $0 S^{-1}$ when the amount of dispersant is lower than 0.3 wt.%. Then the value started to increase slowly with the decrease in dispersant. Similar tendency in static viscosity was also observed. The charge density of the ceramic particles surface is depended on the quantity of adsorbed carboxylic groups. The more adsorbed charge

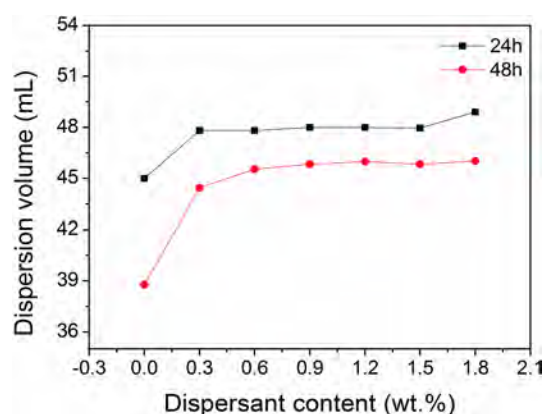


Fig. 6. Effect of polymer concentration on dispersion volume of raw ceramic suspension.

density, the more stable and less viscous the suspension was.

The dispersant weight amount affected the thixotropy of the suspension as well. The thixotropy of the suspension with 70 wt.% raw ceramic content were given in Fig. 5. The area of the thixotropy loop almost changed into a line, when the dispersant amount increased from 0.25 wt.% to 0.35 wt.% of solid content, since the upwards and downwards shear rate curves coincided fairly well at higher dispersant amount. The thixotropy of raw ceramic suspension with P(AA-MA) prepared by RAFT polymerization was much smaller than traditional polymerization [15], indicating that the dispersant prepared by RAFT polymerization kept suspension much more stable. The low PDI of the dispersant formed much more uniformity electrostatic force with ceramic particles, which reduced the aggregation of the charged particles, offering a reduced thixotropy loop.

Fig. 6 showed the dispersion volume curves of raw ceramic suspension at different dispersant concentration. The dispersion volume of the suspension was very low with no dispersant and rose with increasing a dispersant amount. When dispersion volume reached the plateau state, at the dispersant amount of 0.6 wt.% after sedimentation for 48 hrs. There was no further sedimentation with excess dispersant amount, which indicated that P(AA-MA) was an effective dispersant to keep the suspension stable at high solid ceramic content.

Conclusions

P(AA-MA) was an effective dispersant for raw ceramic suspension. The amount of anionic carboxylic group affected the stability of the suspension. The viscosity and zeta potential of the suspension were reduced drastically with P(AA-MA). The suspension showed much stable with the fixed dispersant. And much smaller thixotropy of the suspension containing P(AA-MA) prepared by RAFT polymerization, indicated that RAFT polymerization was a promising way to synthesis effective dispersant for high solid content

ceramic suspension processing.

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