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Roles of polymeric dispersant charge density on lead zirconate titanate aqueous processing

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Abstract

Poly(acrylic acid) (PAA) and poly(acrylic acid-*co*-maleic acid) (PACM) were used as dispersants in preparation of lead zirconate titanate (PZT) aqueous suspensions. The effects of dispersant structure on particle stabilization were investigated through properties of the suspensions. Viscosity and sedimentation height measurements showed that addition of the dispersants improved particle stabilization. The dispersant concentrations to obtain the lowest viscosity were 0.4 wt% for PAA and 0.2 wt% for PACM based on powder dried weight basis. Furthermore, effects of pH were studied on the suspensions prepared with 0.2 wt% dispersants. Viscosity and sedimentation behaviors indicated the improvements of particle dispersion and suspension stability with an increasing pH. Particle dispersion revealed by laser light scattering and scanning electron microscopy supported an improvement of particle dispersion at alkaline pHs. Detailed analysis of these data indicated that the PACM exhibited higher dispersant efficiency for PZT aqueous suspension in all conditions. The results were discussed based on the concentrations of anionic –COO$^-$ groups at various pHs and charge density along polymeric backbone of the dispersants.

Keywords: A. Suspensions; A. Mixing; B. Surfaces; D. PZT

1. Introduction

Colloidal processing is very important in ceramic technology. High quality ceramic products can be obtained by controlling rheological properties, particle packing and maximum solids loading of a suspension [1]. To produce a well-dispersed suspension, the net interparticle potential energy must be repulsive. Particles can be stabilized through electrostatic and/or steric mechanisms. The electrostatic stabilization separates particles by like-charge repulsion while the steric stabilization increases distance between particles through the extension of the adsorbed macromolecules into the solution. A combination of both mechanisms is termed electrosteric stabilization, which has been reported to be more effective [2].

Polyelectrolytes are widely used as dispersants in aqueous processing of PZT family [3–6]. The polymers dissociate in the media and adsorb onto the particle surface shielding particles from each others. As a result, the particles are separated and stabilized in the suspension via the electrosteric mechanism. From a number of factors [7,8], efficiency of a polyelectrolyte as a dispersant is mainly dictated by its molecular structure [9] and pH of the suspension [10,11]. Both parameters strongly influence dissociation degree of the polyelectrolytes, polymer chain conformation and adsorption behavior of the polymeric chains on particle surface. Although many research groups have extensively investigated aqueous ceramic processing in the past decade, there were a few profound studies on the effects of pH and dispersant structure which compared various dispersants in a systematic way [9,10,12–14]. Effects of pH on stabilization of barium titanate aqueous suspension using anionic and cationic polyelectrolytes were studied by Blanco López et al. The ammonium salt of poly(acrylic acid) (PAA) dispersant was reported to be very effective in the alkaline pH range due to ionization of carboxylic group, which gradually increased from the acid range to pH 10. Hidber et al. studied series of small molecule dispersants based on benzene ring substituted with carboxylic (COOH) groups in alumina aqueous suspension.

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Adsorption was found to increase with numbers of COOH groups/molecule and in low pH regions. Palmqvist et al. compared PAA, lignosulphonate and a comb polymer as dispersants for alumina aqueous suspension at processing condition around pH 10. PAA was found to be the most effective dispersant, providing both electrostatic and steric stabilizations. However, the effectiveness of PAA is limited to high pH region. Studies by Vamvakaki et al. [15] and Kirby et al. [16] demonstrated that structural modification of PAA or poly(methacrylic acid) (PMA) by attaching poly(ethylene oxide) (PEO) as side chains resulted in the increase of dispersion efficiency over a wider range of pH. At low pH, the PAA or PMA segments became less effective due to the protonation of carboxylic group but the PEO segments still provided steric barrier for the stabilization of particles. It is clear that the understanding of structure–property relationship of polyelectrolyte is very important for advancing research area of aqueous ceramic processing. In this current research, we addressed the effects of charge density of polyelectrolytes on dispersion efficiency for PZT aqueous suspension. This molecular parameter of polymeric dispersant was not investigated in any previous studies. Two polymers, PAA and poly(acrylic acid-*co*-maleic acid) (PACM), constituting of different mole ratios of ionisable carboxylic groups were used as model dispersants. In addition, the pH of suspensions was varied from 2 to 11 to systematically control the amount of negative charge groups ($-COO^-$) along the polymeric backbone.

The objective of this research was to investigate the effects of dispersant molecular structure and pH of the suspension on the properties of PZT aqueous suspension. PAA and PACM were used as dispersants based on the difference of their charge density. PAA is commonly used in aqueous processing of several ceramics [17–20] including PZT [21]. PACM, although very few reports, was found to be a potential dispersant for an aqueous-based system [22]. Here, the efficiency of PAA and PACM as dispersants was systematically compared through the investigation of viscosity, sedimentation behaviors and particle dispersion at various pH ranges. The effects of the molecular structure on the particle stabilizing efficiency were discussed in terms of dissociation degrees, polymer chain conformation and adsorption behaviors on particle surface.

2. Experimental procedures

2.1. Materials

PZT powder (APC International, Ltd.) with an average agglomerate size of 49.97 μm (Mastersizer 2000, Malvern Instruments, Ltd.) and a specific surface area (BET) of 1.248 m^2/g was used as received. PAA and PACM were obtained from Aldrich to use as dispersants. The average molecular weights (Mw) of PAA and PACM, according to the supplier, were 1800 and 3000 g/mol, respectively. For PACM, the mole ratio of acrylic acid:maleic acid was 1:1. The structures of PAA and PACM were illustrated in Fig. 1. These two polymers constitute of the same backbone but with different density of carboxylic groups. When the dispersants are dissolved in water, the COOH groups dissociate, providing the $-COO^-$ groups along the backbone and protons (H^+) in the suspension. The degree of dissociation and, therefore, $-COO^-$ concentration depend on the molecular structure of each dispersant and pH of the suspension. The adsorption of $-COO^-$ groups onto the particle surface leads to particle separation and stabilization via electrosteric mechanism. A parallel investigation of these two polymers as dispersants can reveal the effects of charge density of polyelectrolytes on the properties of PZT aqueous suspension.

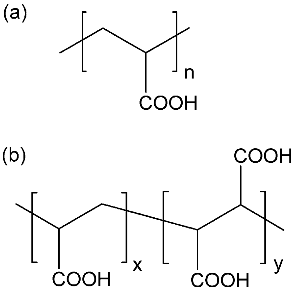

Fig. 1. Molecular structures of (a) poly(acrylic acid) and (b) poly(acrylic acid-*co*-maleic acid).

2.2. Preparation of PZT aqueous suspensions

The PZT powder was mixed with double-distilled water at 60 wt% solids content, then ball milled for 24 h in high density polyethylene (HDPE) bottles using zirconia grinding media. The dispersants were added at various amounts of 0.2–1.4 wt% based on PZT powder dried weight basis. Viscosity and pH of the suspensions were measured after stirring for 15 min. For the study of pH effect, the suspensions with 0.2 wt% dispersants were prepared and divided into batches for pH adjusting. This was to minimize batch-to-batch variations caused by the mixing process. HCl and NH_4OH were used to adjust pH of the suspensions in the range of 2–11. The pH-adjusted suspensions were stirred for 15 min before viscosity and particle size distribution measurements.

2.3. Viscosity measurement

The viscosity of the PZT aqueous suspensions were measured at room temperature using a Brookfield RVDV-E viscometer (Brookfield Engineering Laboratories, Inc.). The measurement was carried out in a small sample size adapter at the shear rate of 18.6 s^{-1}. The results of viscosity versus dispersant concentration, i.e. the deflocculation curves, suggested the optimum concentrations of each dispersant at the point where the viscosity reached the minimum. The viscosity measurement of the pH-adjusted suspensions exhibited the effects of pH on particle stabilization in the suspensions.

2.4. Sedimentation behavior

Particle stabilization in the suspensions was studied by means of sedimentation experiment. The suspensions were filled in sealed graduate test tubes and initial suspension heights

(h_0) were measured. Sedimentation heights (h) and characteristics of the supernatant were investigated after 7 days. The h/h_0 ratios were reported as a function of dispersant concentrations and pH of the suspensions.

2.5. Particle dispersion

Effects of pH on particle dispersion were quantitatively and qualitatively investigated for the suspensions of various pHs. Laser light scattering technique (Mastersizer 2000, Malvern Instruments, Ltd.) provided the median diameter and size distribution of PZT particles in the suspensions. The qualitative results of particle dispersion were acquired by SEM. The SEM samples were prepared by drop-casting the suspensions on heated glass slides. Once completely dried, the samples were gold-coated before the experiment.

3. Results and discussion

3.1. Effects of dispersant concentration

Viscosity of the suspensions prepared with PAA and PACM at various concentrations was shown in Fig. 2. The suspensions prepared with no dispersants exhibited a relatively high viscosity of ~340 cPs and an alkaline pH of 10.1. The viscosity decreased and reached the lowest values at 0.4 wt% PAA and 0.2 wt% PACM, which indicated the optimum concentration of each dispersant. With further addition of the dispersants up to 1.4 wt%, the viscosity slightly increased. This result showed that the optimum concentrations of PAA and PACM was strongly affected by their molecular structures. With additional numbers of the COOH group/monomer unit, PACM dissociated to higher extent compared to the PAA and, thus, produced more –COO$^-$ groups. The increase in charge density along the polymer backbone was expected to promote the adsorption onto the particle via ionic interaction. As a result, the optimum concentration of PACM to produce the suspension with the lowest viscosity was less than that of PAA. Along with the –COO$^-$ group, dissociation of the dispersants also supplied H$^+$ into the suspensions. Therefore, the pH of suspension reflects the concentration of –COO$^-$ group. We observed that the suspensions prepared with PACM exhibited lower pH values compared to those prepared with PAA at the same concentration, indicating higher dissociation of PACM. Further details regarding degree of dissociation, i.e. –COO$^-$ group concentration, will be discussed in the later sections.

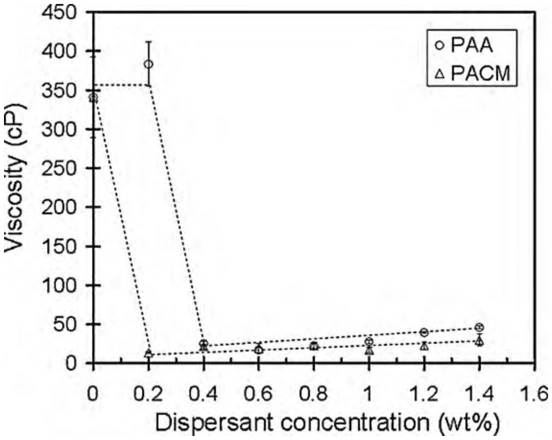

Fig. 2. Viscosity as a function of dispersant concentration for suspensions prepared with poly(acrylic acid) (PAA) and poly(acrylic acid-co-maleic acid) (PACM), measured at 20 rpm.

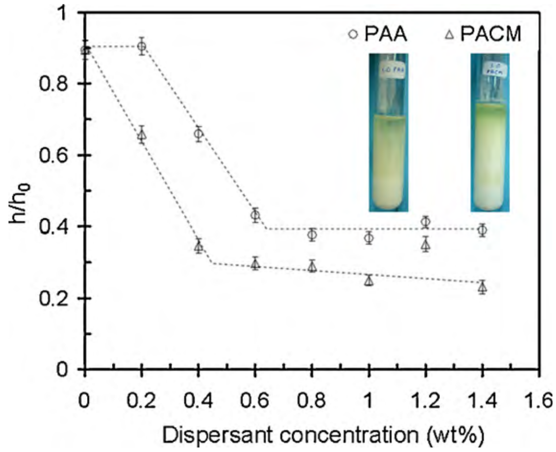

Fig. 3. The ratios of sedimentation height (h) to the initial suspension height (h_0) of the suspensions prepared with PAA and PACM. The height was measured at 7 days after ball milling. The inset illustrated the characteristics of the suspensions prepared with 1 wt% dispersants.

The sedimentation heights of the suspensions prepared with various dispersant concentrations were measured after a settling time of 7 days. The ratios of sedimentation height (h) to the initial suspension height (h_0) were evaluated and shown in Fig. 3. Initially, for both suspensions prepared with PAA and PACM, the h/h_0 ratios decreased with increasing dispersant concentration and became steady with concentrations of PAA and PACM higher than 0.6 and 0.4 wt%, respectively. Since the low h/h_0 ratios indicated a well-dispersed and highly stable suspension, the results illustrated that both dispersants promoted dispersion and stability of the suspensions. Moreover, at 7 days after ball milling, supernatants of the suspensions prepared with 1 wt% PAA and PACM appeared cloudy as shown in the inset. This characteristic of the supernatant verified well-dispersed and highly stable suspensions. When compared at the same dispersant concentrations, the suspensions prepared with PACM exhibited lower h/h_0 ratios. This observation indicated that PACM was a more efficient dispersant compared to the PAA, which was consistent with the viscosity measurements. The higher efficiency of PACM as a dispersant is attributed to the higher density of –COO$^-$ groups as discussed earlier.

3.2. Effects of suspension pH

As one of the important parameters in aqueous processing, the effects of pH must be considered. The pH affects the net particle surface charges, the degrees of dissociation of carboxylic group and polymer chain conformation, causing the variation in the adsorption behaviors of the polymer on particle. As a result, particle stabilization and suspension

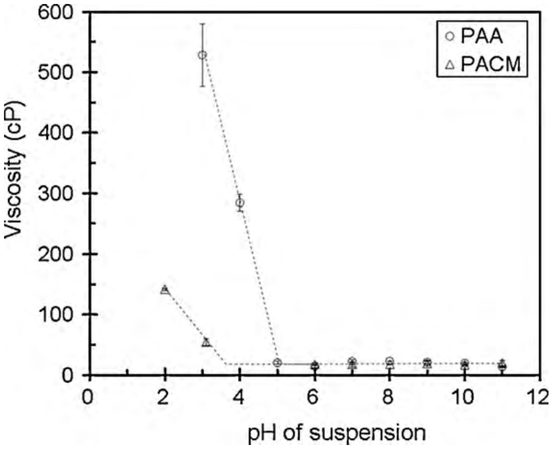

Fig. 4. Viscosity as a function of pH for the suspensions prepared with 0.2 wt% dispersants.

properties are altered with pH of the suspension. In this section, the effects of pH on the properties of PZT aqueous suspension were studied. The suspensions under investigation were prepared with 0.2 wt% PAA and PACM dispersants.

3.2.1. Viscosity and sedimentation measurements

The change of viscosity as a function of suspension pH was illustrated in Fig. 4. The viscosity of both suspensions decreased with increasing pH, then, reached the lowest values and became steady when pH > 5. Interestingly, the viscosity of PACM system appeared to reach the lowest value at lower pH. This discrepancy was attributed to the differences in degree of dissociation of carboxylic group in each dispersant at various pH values. Dissociation behavior of PAA and PACM in water can be expressed as

$$\mathrm{RCOOH} \rightleftharpoons \mathrm{RCOO^-} + \mathrm{H^+} \tag{1}$$

where R is the polymeric backbone of the dispersants. In acidic condition, high concentration of H^+ caused the equilibrium to shift to the left-handed side in Eq. (1). In other words, it favored the formation of COOH functional groups. The low-charged polymeric chains were less hydrophilic and, thus, expected to shrink in a polar aqueous medium. Instead of promoting dispersion, the coiled polymer on the particle surface hindered electrostatic force between charged particles, leading to a decrease in the interparticle distance. As a result, the suspensions with lower pH exhibited higher viscosity. When pH was increased, the equilibrium in Eq. (1) shifted to the right-handed side, resulting in the higher concentration of $–COO^-$ groups. The favorable interactions between the negatively charged polymers and aqueous medium caused an extension and/or swelling of the chains adsorbed on the particle surface. The particles were separated and stabilized by electrosteric mechanism, resulting in the suspensions with low viscosity.

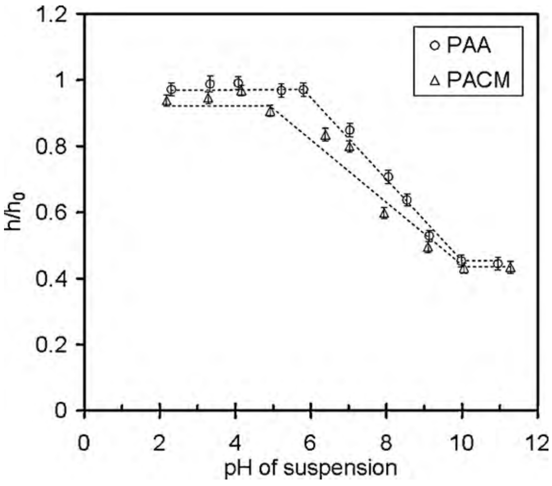

Fig. 5. The sedimentation behaviors as a function of pH for the suspensions prepared with 0.2 wt% dispersants.

Sedimentation results were in agreement with the viscosity. As shown in Fig. 5, the h/h_0 ratios were very high in low pH values. The ratios gradually decreased upon increasing of the pH above ~5 and ~6 for the systems of PAA and PACM, respectively. The lowest h/h_0 ratios were obtained when the pH values reached ~10. The results suggested the improvement of particle dispersion and suspension stability at high pH ranges. Similar to the viscosity, the effects of pH on sedimentation behavior of the suspensions can be explained based on degree of dissociation of the dispersants. We also observed that the suspensions containing PACM always exhibited lower h/h_0 ratios compared to those of PAA system prepared under the same conditions. This further confirmed that PACM was a more efficient dispersant.

3.2.2. Determination of $–COO^-$ group concentration

To further explain the pH effects on suspension behaviors, the concentration of $–COO^-$ group in the suspensions were evaluated at various pHs. First, K_a values of PAA and PACM were determined experimentally. For each dispersant, a known concentration was dissolved in water and pH was measured. The H^+ concentration, which was equal to $RCOO^-$ concentration at this state, was calculated from pH of the solution. Then, K_a of each dispersant can be determined from

$$K_a = \frac{[\mathrm{RCOO^-}][\mathrm{H^+}]}{[\mathrm{RCOOH}]} \tag{2}$$

The K_a values were 9.58×10^{-7} for PAA and 5.06×10^{-6} for PACM. We noted that the molar concentration of the polymers was calculated based on molecular weight (MW) of a repeating unit, constituting of two methylene groups. Therefore, a repeating unit of PAA (MW = 72 g/mol) constituted of one carboxylic group while there were 1.5 carboxylic groups in that of PACM (MW = 94 g/mol). Next, the K_a values of each dispersant were used to determine $[\mathrm{RCOO^-}]$ in PZT aqueous suspensions. At the pH of interest, $[\mathrm{RCOO^-}]$ in the suspension can be evaluated using Eq. (2). K_a and $[\mathrm{H^+}]$ were known variables, and [RCOOH] was the difference in concentration of the initial dispersant and $RCOO^-$ group.

Fig. 6 illustrates the concentration of carboxylate group $[–COO^-]$ as a function of pH in PZT aqueous suspensions prepared with PAA and PACM. In the low pH ranges of 2–4, both suspensions contained extremely low concentration of the –COO$^-$ group, corresponding to low degree of dissociation for both dispersants. When pHs of the suspension were in the intermediate ranges of 5–7, the [–COO$^-$] increased rapidly. Then, the [–COO$^-$] reached the plateau around pH 8 corresponding to complete dissociation (100%). At this condition, the actual concentrations of carboxylate group in the suspension with 0.2 wt% of the dispersants are 0.017 and 0.019 mol/l for systems of PAA and PACM, respectively. The result was in agreement with the previous reports [16,23] that PAA was fully ionized above pH 8. With high density of charged groups, the dispersant provided strong electrostatic repulsion. Highly charged polymer also formed stretched configuration which adsorbed in trains and loops and contributed to steric stabilization. Therefore, electrosteric stabilization of particles by –COO$^-$ groups was expected to increase with the suspension pH and reached the maximum extents around pH 8. The variation of [–COO$^-$] with pH explained the viscosity and sedimentation behaviors of the suspensions in Figs. 4 and 5. For pH < 5, the concentration of –COO$^-$ group was extremely low and insufficient to stabilize particles in the suspensions. The results were poorly dispersed and unstable suspensions that exhibited high viscosity and h/h_0 ratios. With increasing pHs, the additional [–COO$^-$] resulted in well-dispersed and highly stable suspensions presented by low viscosity and h/h_0 ratios. In addition, dissociation degrees of PAA and PACM at various pH ranges were different. Fig. 6 shows that the dissociation of PACM completed at lower pH. At the same pH, the PACM also constituted of higher fraction of –COO$^-$ group along its polymeric backbone.

3.2.3. Particle dispersion

To further verify the dispersion of particles in the suspensions, the particle size distribution was explored. The results obtained from the suspensions with pH ranging from about 2 to 11 are shown in Figs. 7 and 8. When comparing the particle size distribution of the suspensions prepared with PAA and PACM at the same pH, the dispersant efficiency can be determined. Fig. 8 clearly shows that the suspensions prepared with PACM always exhibited smaller median particle size in all pH ranges. In addition, the size distribution of particles was narrower in the system of PACM (Fig. 7). These results were consistent with the measurements of viscosity and sedimentation height (Figs. 4 and 5), indicating higher efficiency of PACM as a dispersant for PZT aqueous suspension. Increasing of the suspension pH resulted in the decrease in median size of particles. We also noted that the suspensions with pH of ~7.5 appeared to exhibit the smallest median particle size. At this pH value, a complete dissociation of COOH group occurred in the suspensions (Fig. 6). Further increasing in the suspension pH did not affect the concentration of –COO$^-$ group. However, the increase in Na$^+$ and OH$^-$ ions in higher pH ranges (i.e. pH > 8)

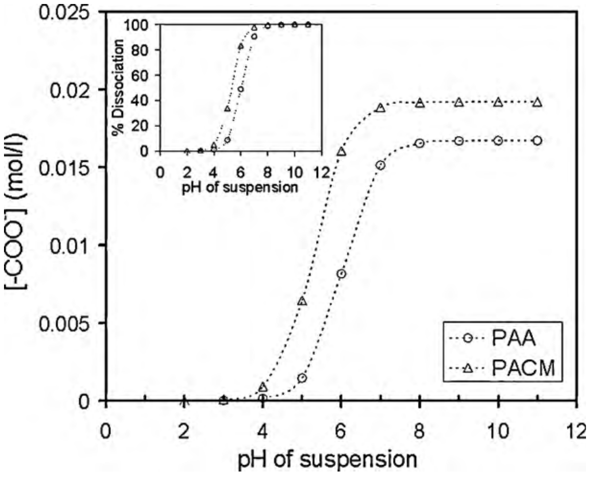

Fig. 6. The –COO$^-$ concentration as a function of pH in PZT aqueous suspensions prepared with 0.2 wt% dispersants. The corresponding %dissociation was shown in the inset.

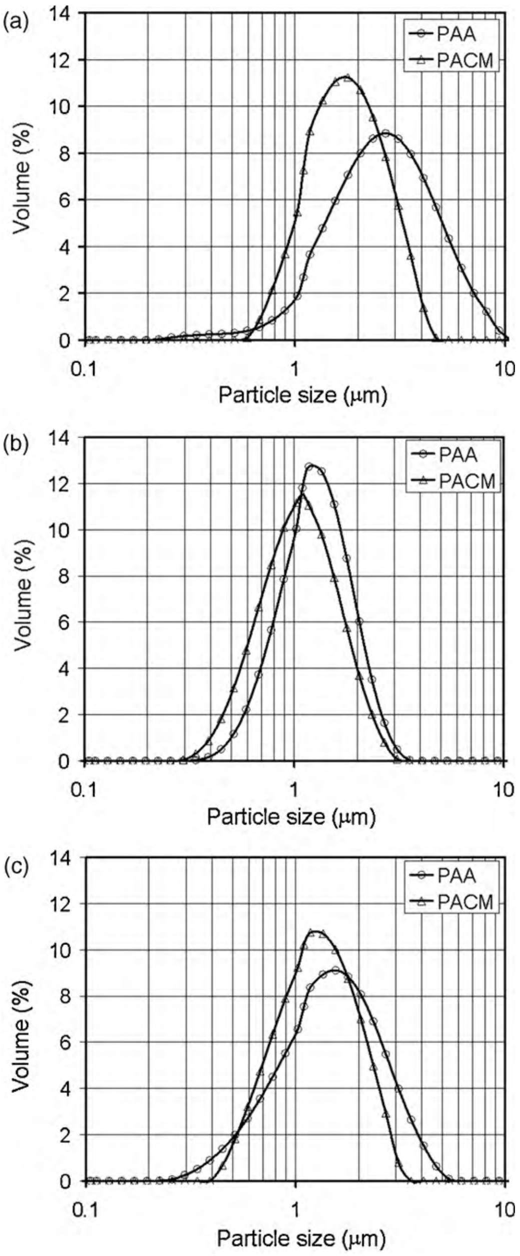

Fig. 7. Particle size distribution of suspensions prepared with 0.2 wt% dispersants. The pHs of suspensions were (a) 4, (b) 7 and (c) 10.

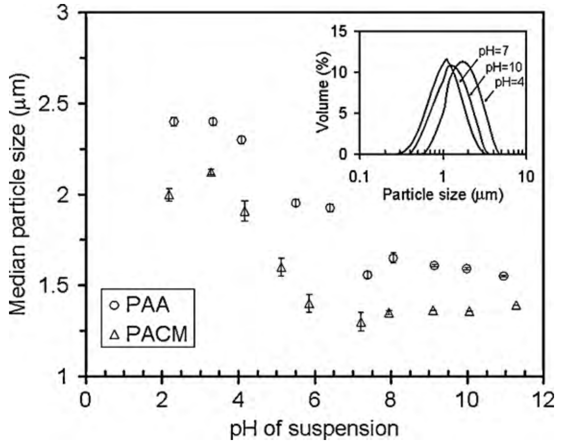

Fig. 8. Plots of median particle size in suspension as a function of pH. The inset compared particle size distribution of suspensions with PACM measured at different pHs.

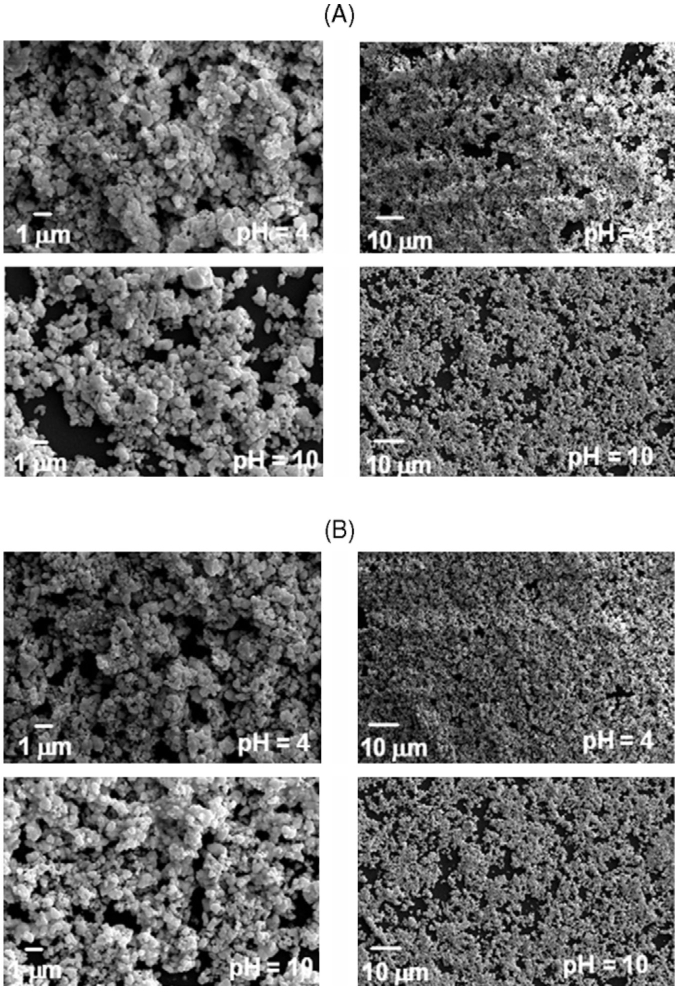

Fig. 9. SEM micrographs of particle dispersion in pH-adjusted suspensions prepared with (a) 0.2 wt% PAA and (b) 0.2 wt% PACM.

interfered the electrostatic interactions between particles, leading to the slight increase in particle size. SEM micrographs of drop cast PZT samples were shown in Fig. 9. The size of particles was in agreement with the results measured by laser light scattering illustrated in Fig. 7. The SEM results also showed the improvement of particle dispersion in the alkaline suspensions compared to the acidic suspensions. However, the efficiency of PAA and PACM dispersants cannot be directly compared.

4. Conclusions

PZT aqueous suspensions were prepared by using PAA and PACM as dispersants. It was found that both PAA and PACM enhanced dispersion and stability of the suspensions. The measurements of suspension viscosity and sedimentation height as a function of dispersant concentration indicated that the PACM was a more efficient dispersant compared to the PAA. In other words, a well-dispersed and highly stable suspension can be achieved with lower PACM concentration than that of PAA. The effects of pH on properties of the suspensions prepared with 0.2 wt% dispersants were also investigated. For both dispersants, the acidic suspensions exhibited high viscosity and h/h_0 ratios, indicating poorly dispersion and instability. On the other hand, the alkaline suspensions were well-dispersed and highly stable with low viscosity and h/h_0 ratios. Particle size distribution data accompanied with SEM micrographs revealed an improvement of particle dispersion in the alkaline suspensions. When comparing the dispersant efficiency, PACM system provided smaller median particle size with narrower size distribution in all pH ranges. This further confirmed that the PACM was a more efficient dispersant for PZT aqueous suspension. Our results demonstrated that increasing in the density of $-COO^-$ group along polymeric backbone resulted in the increase of dispersant efficiency for PZT aqueous suspension.

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