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Effects of dispersant concentration and pH on properties of lead zirconate titanate aqueous suspension

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Abstract

Lead zirconate titanate (PZT) aqueous suspensions were prepared at 60 wt.% solids loading using a commercial ammonium polyacrylate (APA) dispersant. Effects of the dispersant concentration on rheological behavior, dispersion and stability of PZT aqueous suspensions were investigated by means of zeta potential, viscosity and sedimentation height measurements. The results showed that, under suitable conditions, APA dispersant promoted particle dispersion and stabilization in PZT aqueous suspensions. For 60 wt.% solids loading suspensions, the dispersant concentration yielding the lowest viscosity was 0.5 wt.% based on PZT powder dried weight basis. Effects of pH on particle dispersion in the suspensions prepared with APA were studied by laser light scattering technique and scanning electron microscopy. The results showed an improvement in particle dispersion for the alkaline condition, which led to relatively low viscosity and highly stable suspension. Possible particle stabilization mechanisms at various pHs were discussed based on dissociation of the dispersant in water, polymer conformation and adsorption behavior of the dispersant on the particle surface.

Keywords: A. Suspensions; D. PZT; Ammonium polyacrylate; Particle dispersion

1. Introduction

Piezoelectric ceramics based on PZT are widely used in multilayered electronic devices such as actuators, transducers and transformers [1–3]. The common shape forming technique to produce thin and flat sheets of ceramic for the applications is tape casting, in which suspension is passed under blades and coated on a carrier surface. In order to produce a uniform and defect-free green tape, a well-dispersed and highly stable system of high solids loading is necessary.

Traditionally, organic solvents such as toluene, *n*-hexane, ethanol and acetone have been used as media to prepare well-stabilized tape casting suspensions [4,5]. Low latent heat of evaporation and low surface tension of the organic solvents result in quickly dried green tapes with high density and smooth surface. However, organic solvents are toxic, flammable and costly. Therefore, aqueous suspension has been considered recently due to environmental, safety and economic considerations. Preparation of aqueous tape casting suspensions has been extensively studied on systems such as alumina [6–8], barium titanate [9,10] and PLZT [11,12]. Although several advantages, some difficulties of aqueous-based system have been reported including flocculation of particles due to strong agglomeration effects, low evaporation rate and high binder concentration requirement [13]. The suitable dispersant at optimum concentration and strictly controlled processing conditions are essential to achieve a dense and homogeneous powder compact upon tape casting.

In an aqueous suspension, particles can be dispersed and stabilized by electrostatic, steric or electrosteric mechanisms [14]. Particles with a sufficient surface charge repel each others and disperse in a suspension by electrostatic stabilization. In most cases, a polymer is introduced in the system as a dispersant. The repulsion between the adsorbed polymer chains at the particle surfaces provides steric stabilization. When both mechanisms concurrently present, the mechanism is referred as electrosteric, which is considered a better stabilization mechanism [15]. The electrostatic component may originate

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from a net surface charge of particle and/or charges from dissociation of polyelectrolyte used as dispersant.

The objective of this research is to study the effects of dispersant concentration and pH conditions on particle dispersion and stability of PZT aqueous suspensions using an anionic polyelectrolyte dispersant. While most research works on aqueous colloidal processing [16–19] investigated particle dispersion via viscosity measurement, the present work included the results on particle size distribution and SEM micrographs. With the information, straightforward indications of particle dispersion in the suspensions can be presented. Zeta potential and sedimentation height measurements were conducted to study suspension stability. The role of APA dispersant in particle dispersion and suspension stability were discussed with regard to the polyelectrolyte concentration and pH of the suspensions.

2. Experimental procedure

2.1. Materials

Powder used in this study was spray-dried, soft composition PZT (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. The dispersant was APA (Dispex A40, Ciba Specialty Chemicals, Inc.) with 40% active content, pH of 8.0 and average molecular weight of 4000 according to the supplier. The structure of APA and its dissociation in water to produce negatively charged polyions and ammonium counter ions were illustrated in Fig. 1. The degree of dissociation increases gradually from the acid to alkaline ranges.

2.2. Preparation of PZT aqueous suspensions

PZT aqueous suspensions were prepared at 60 wt.% solids content by ball milling PZT powder, double-distilled water and Dispex A40 in high density polyethylene (HDPE) bottles using zirconia grinding media. Particles with a median diameter of 0.97 μm (Mastersizer 2000, Malvern Instruments, Ltd.) were achieved after ball milling for 24 h without dispersant.

To study the effects of dispersant concentration, Dispex A40 was used at the various amounts of 0–1.5 wt.% based on PZT powder dried weight basis. For investigation of the pH effects, the dispersant concentration was fixed at 1 wt.% based on PZT powder dried weight basis. In order to eliminate the effects of mixing process, a large batch of suspension was prepared, then divided and pH adjusted. The pH of the suspension prior to the alteration was 10.1. Using 1 M HCl and 1 M NaOH, the suspensions were pH adjusted to 3.2 and 11.9, respectively. The pH-adjusted suspensions were stirred for 3 h to reach the equilibrium.

2.3. Zeta potential

PZT suspensions prepared with various APA concentrations were diluted from 60 to 10 wt.% solids content. The pHs of the suspensions were adjusted to 4 and 11 using 1 M HCl and NaOH, respectively. A Zetasizer 4 (Malvern Instruments, Ltd.) was used to measure the zeta potential of the samples by electrophoresis.

2.4. Rheological behavior

The viscosity of PZT aqueous suspensions were measured using a Brookfield RVDV-E viscometer (Brookfield Engineering Laboratories, Inc.) with a small sample size adapter. To study the rheological behavior, the viscosity were measured at the shear rates of 9.3, 18.6, 46.5 and 93 s^{-1}. At each shear rate, the viscosity were measured as a function of the APA concentrations to determine the optimum dispersant level at the point where the viscosity reached the minimum. The viscosity of the pH-adjusted suspensions were also measured to study the suspension behavior under various pH conditions.

2.5. Sedimentation behavior

Dispersion of PZT particles and stability of the aqueous suspensions were studied by means of sedimentation experiment. The suspensions prepared with various APA concentrations and pH conditions were filled in sealed graduate test tubes and initial suspension heights (h_0) were measured. After a settling time of 7 days, the sedimentation heights (h) were

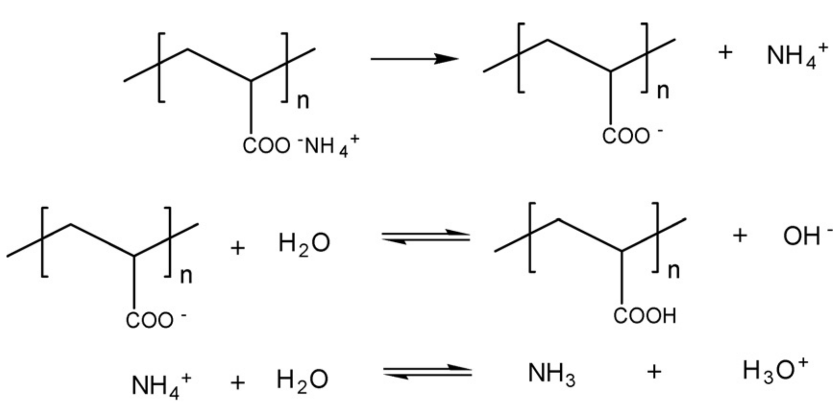

Fig. 1. APA structure and its dissociation in water.

measured. Results were expressed as the h/h_0 ratios and the characteristics of supernatant.

2.6. Particle dispersion

Laser light scattering technique (Mastersizer 2000, Malvern Instruments, Ltd.) was used to measure median diameter and size distribution of PZT particles dispersed in the aqueous suspensions of pH 3.2, 10.1 and 11.9. For SEM micrographs of particles dispersion, the samples were prepared by dropping the suspensions on heated glass slides. The results provided both quantitative and qualitative information of particle dispersion in the suspensions of various pHs.

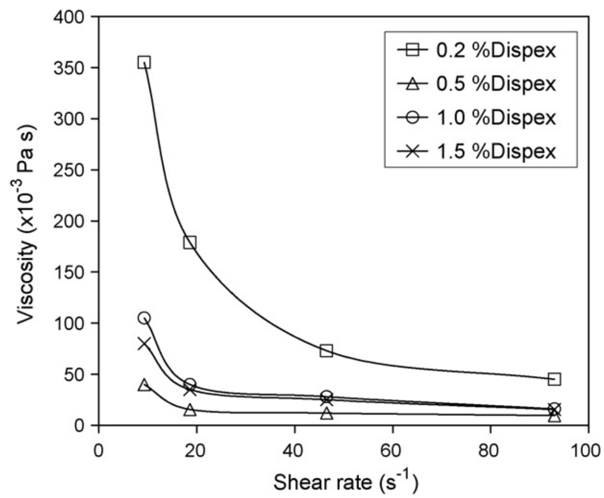

Fig. 3. Shear thinning behavior of PZT aqueous suspensions.

3. Results and discussion

3.1. Effects of dispersant concentration on properties of PZT aqueous suspension

3.1.1. Zeta potential

Fig. 2 shows the zeta potential values of 10 wt.% solids content suspensions at pH 4 and 11 as a function of dispersant concentration. At pH 4, without the polyelectrolyte, the zeta potential of the PZT suspension was positive, which indicated a positive charge on PZT particle surface. The zeta potential value tended to decrease with dispersant addition due to the adsorption of COO^- group on the PZT surface. At Dispex A40 content of ~0.2 wt.%, the zeta potential value was approximately zero and reached a plateau, indicating the absence of electrostatic force between particles. The result is similar to the previous report on PZT-PNN aqueous suspension using lignosulfonate dispersant [16]

At pH 11, for the dispersant-free suspension, the net PZT surface was negatively charged with the absolute zeta potential value ~20 mV. When the APA was introduced to the system, the zeta potential values became more negative, indicating the increase in negative charges caused by adsorption of anionic groups on the particle surface. Theoretically, the high surface charge resulted in high repulsive force and long distance between particles. Therefore, the result suggested that the presence of APA at pH 11 improved the particle dispersion and stability of PZT aqueous suspension. The zeta potential started to reach a plateau at Dispex A40 concentration ~0.6 wt.%. The similar behavior at alkaline pH was reported on $BaTiO_3$ aqueous suspensions prepared with various anionic polyelectrolytes [10,20].

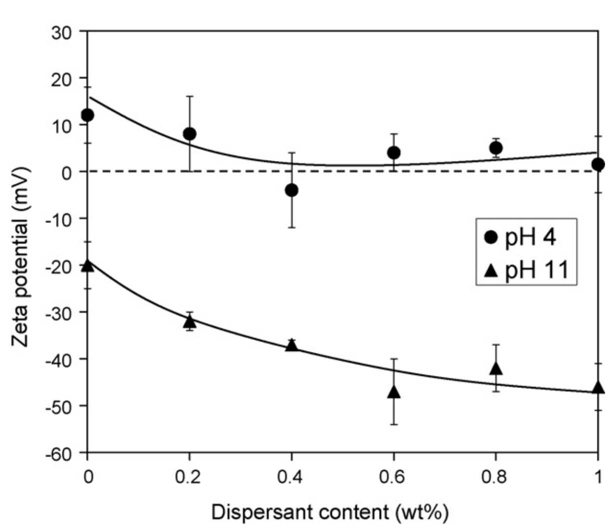

Fig. 2. Zeta potential as a function of dispersant concentration for 10 wt.% solids content PZT aqueous suspension at pH 4 and 11.

3.1.2. Rheological behavior

Viscosity was measured as a function of shear rate for PZT aqueous suspensions containing various amounts of Dispex A40. All suspensions exhibited shear thinning behavior, as shown for examples in Fig. 3 for the suspensions prepared with 0.2, 0.5, 1.0 and 1.5 wt.% Dispex A40. The behavior is desired for fabrication by tape casting process. Low viscosity at high shear rate allows the suspension to flow pass the blade, producing smooth and uniform green tape. After deposited, high viscosity at low shear rate sets the tape on the carrier film. In addition, high viscosity prevents settling of particles, providing stability of the suspension.

Dispersant concentration dependence of viscosity is shown in Fig. 4. Results obtained at the shear rates of 46.5 and 93 s^{-1} were similar. At low dispersant levels (<0.5 wt.% based on powder dried weight basis), viscosity were high due to insufficient amount of APA to separate the particles apart. The optimum dispersant concentration was determined at the lowest viscosity, in which the maximum level of particle dispersion was indicated. For 60 wt.% solids content PZT aqueous suspensions in this study, the optimum Dispex A40 was found to be 0.5 wt.% based on powder dried weight basis. The result was similar to a reported value for PZT aqueous suspension [21]. The optimum dispersant level suggested that there was an adequate amount of APA to cover the particle surface. As a result, particles were distant from each others by electrosteric stabilization. Further increase in the dispersant concentration gradually increased the suspension viscosity due to flocculation.

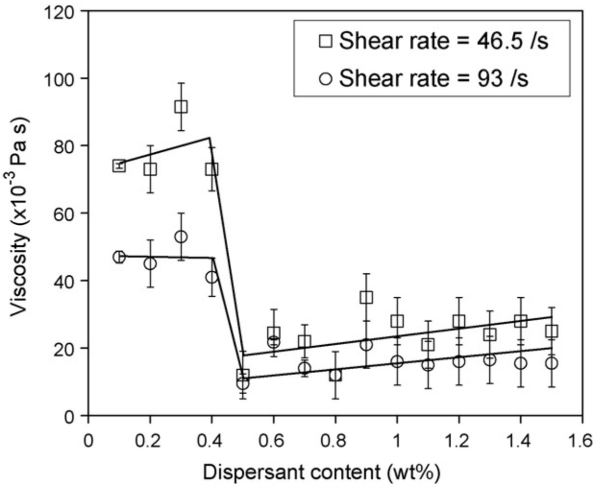

Fig. 4. Viscosity of PZT aqueous suspensions as a function of Dispex A40 concentration.

3.1.3. Sedimentation behavior

The sedimentation height to the initial suspension height (h/h_0) ratios at 7 days after ball milling of the suspensions prepared with various APA amounts is shown in Fig. 5. While the suspensions with less than 0.5 wt.% Dispex A40 exhibited high h/h_0 ratios, the suspensions with 0.5 wt.% Dispex A40 and higher revealed low h/h_0 ratios. The suspensions with high dispersant contents also showed relatively cloudy supernatants. Since low precipitation height and cloudy supernatant indicated a well-dispersed suspension [6], it can be concluded that APA dispersant promoted particle dispersion, which was in agreement with the zeta potential measurement. The result of sedimentation behavior also confirmed the optimum dispersant level of 0.5 wt.% Dispex A40 determined by the deflocculation curve in Fig. 4.

3.2. Effects of pH on properties of PZT aqueous suspension

3.2.1. Particle dispersion

Particle size distributions of suspensions with various pH were illustrated in Fig. 6. Both pH 3.2 and 10.1 suspensions

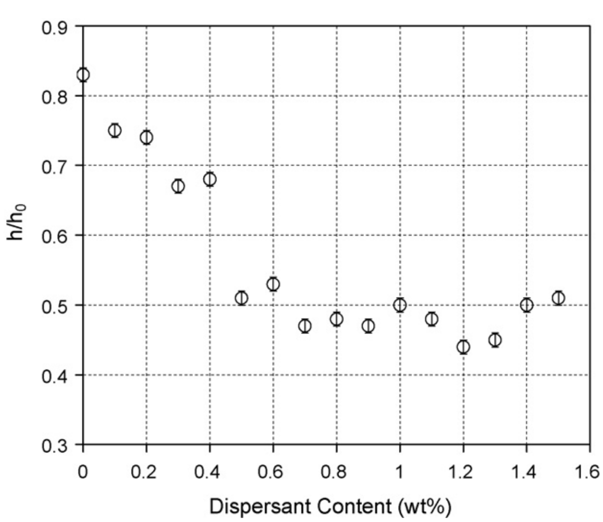

Fig. 5. Sedimentation height to the initial suspension height (h/h_0) ratios of PZT aqueous suspensions prepared with various APA levels.

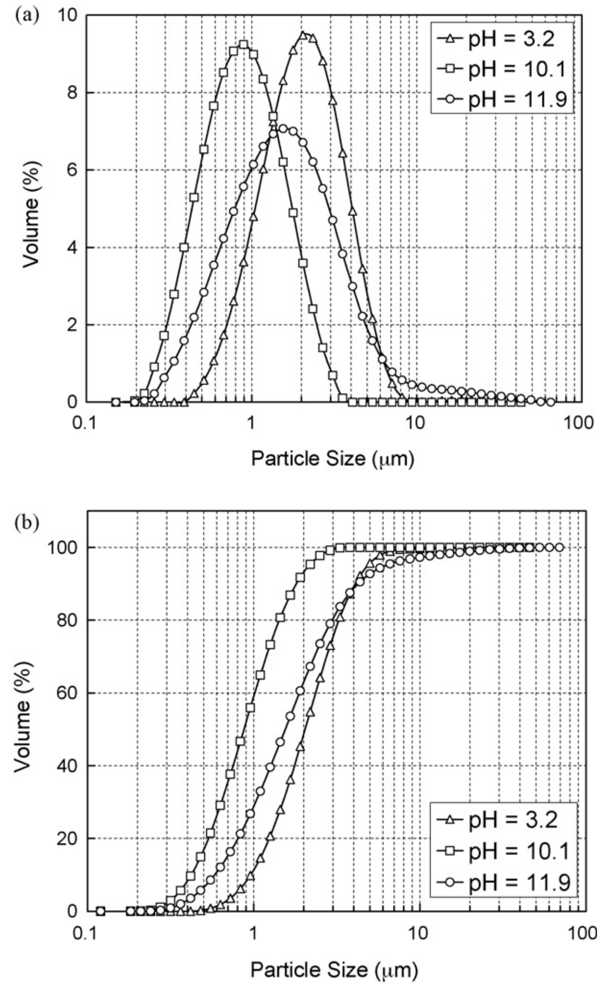

Fig. 6. Particle size distribution of PZT suspension with 1 wt.% Dispex A40 at pH 3.2, 10.1 and 11.9 (a) frequency curves and (b) percent finer than curves.

showed narrow particle size distributions compared to the suspension of pH 11.9. Particle size in the pH 3.2 suspension was the largest with the median diameter around 2 μm (Fig. 7). The smallest particle size (median diameter) of 0.87 μm was found for pH 10.1 suspension. Since the suspensions were obtained from the same ball milled batch, the effects of mixing process were eliminated. Therefore, it can be verified from the results that particles were agglomerated in the suspensions of pH 3.2 and 11.9.

To confirm the agglomeration of particles, the SEM pictures of particle dispersion in the suspensions of different pH were acquired. It is obviously illustrated in Fig. 8 that particles were well-dispersed at pH 10.1 while at pH 3.2 particles agglomerated, and at pH 11.9 particles formed network or, in other word, flocculation. Dispersion of particles in the suspensions of various pH can be explained based on the dissociation of polyelectrolyte in water and the adsorption of the polymer chain on particle surface as shown in Figs. 1 and 9. High concentration of hydronium ions in pH 3.2 suspension produced –COOH functional group, which rollup on itself. The coiled polymer with –COOH group was repelled by water and anchored on PZT surface caused a decrease in electrostatic force between particles. When

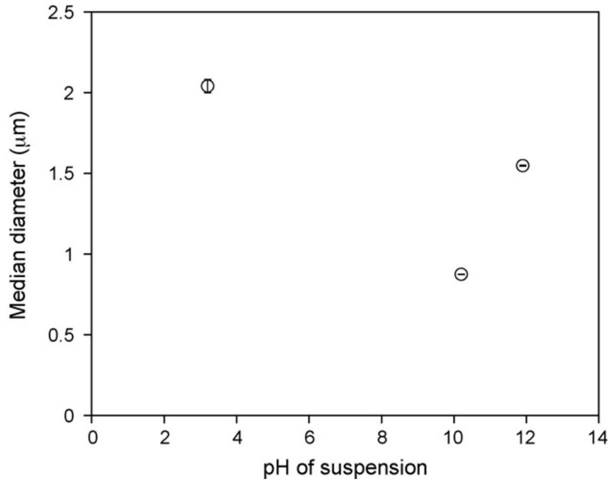

Fig. 7. Median diameters of PZT suspensions with 1 wt.% Dispex A40 at pH 3.2, 10.1 and 11.9.

distance between particles was small, agglomeration occurred with the aid of polymer bridging. At pH 10.1, high concentration of hydroxide ions resulted in the dissociation of the polyelectrolyte to produce –COO$^-$ functional group. The stretch polymer chains covered the particle surface, providing electrosteric stabilization. At pH 11.9, although high concentration of –COO$^-$ functional group from the polyelectrolyte dissociation, the net particle surface charge was highly negative. Therefore, most of the stretch polymer chains were dispersed in the suspension with only small amounts adsorbed on the particle surface. Particle stabilization mechanism at pH 11.9 was mainly electrostatic, which was insufficient to separate particles apart, leading to flocculation.

3.2.2. Suspension viscosity

Viscosity of the suspensions with pH 3.2, 10.1 and 11.9 were shown in Fig. 10. The results can be explained based on particle dispersion in the suspension. Presence of agglomerates at pH 3.2 as confirmed by particle size distribution (Figs. 6 and 7) and SEM micrograph (Fig. 8) resulted in relatively high viscosity. At pH 10.1, particles were well-dispersed as a result of the electrosteric stabilization; therefore, the suspension exhibited low viscosity. At pH 11.9, the viscosity of the suspension was slightly higher than that of pH 10.1 due to flocculation.

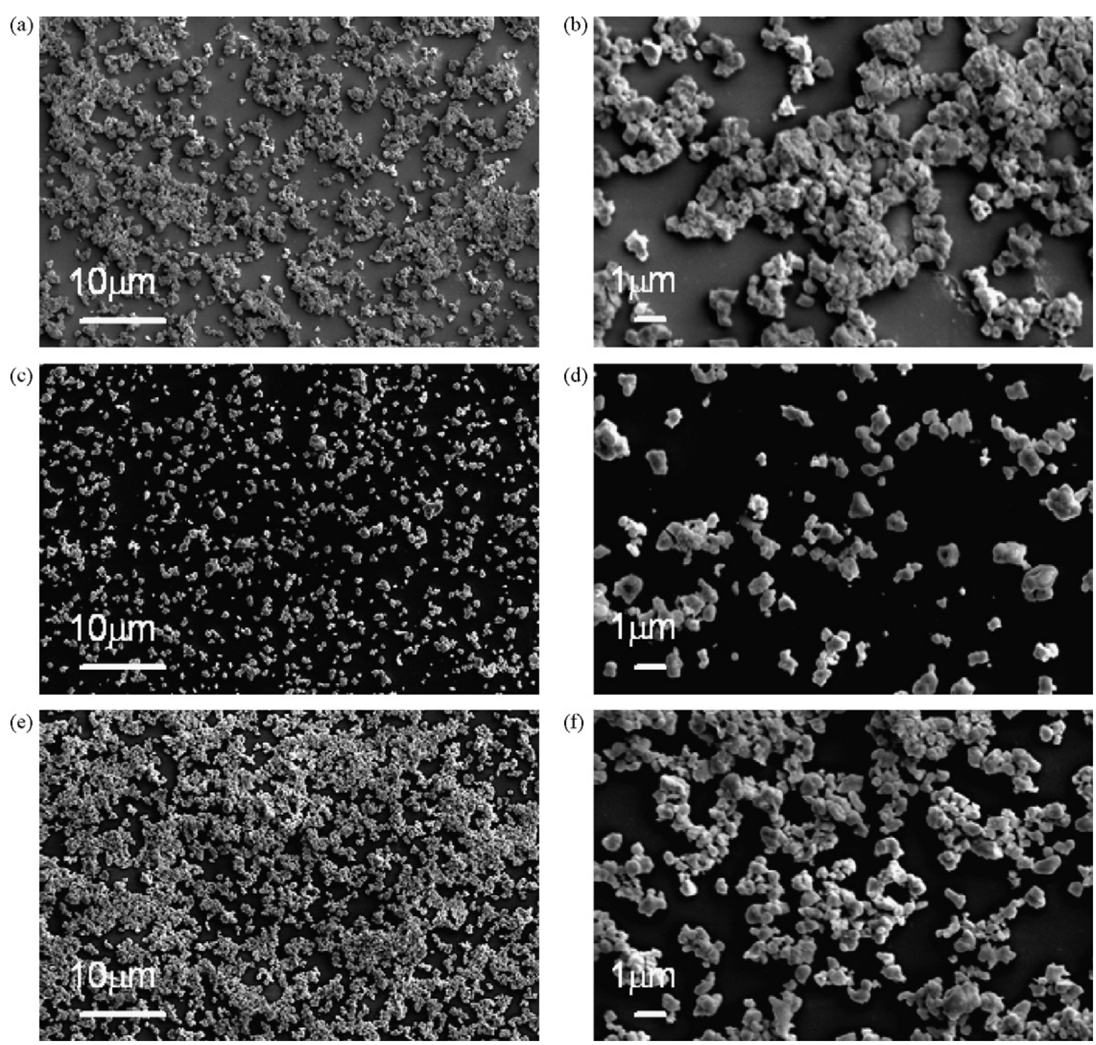

Fig. 8. Particle aggregation state after the suspension drying. Dispex A40 content 1 wt.%. (a and b) pH = 3.2, (c and d) pH = 10.1 and (e and f) pH = 11.9.

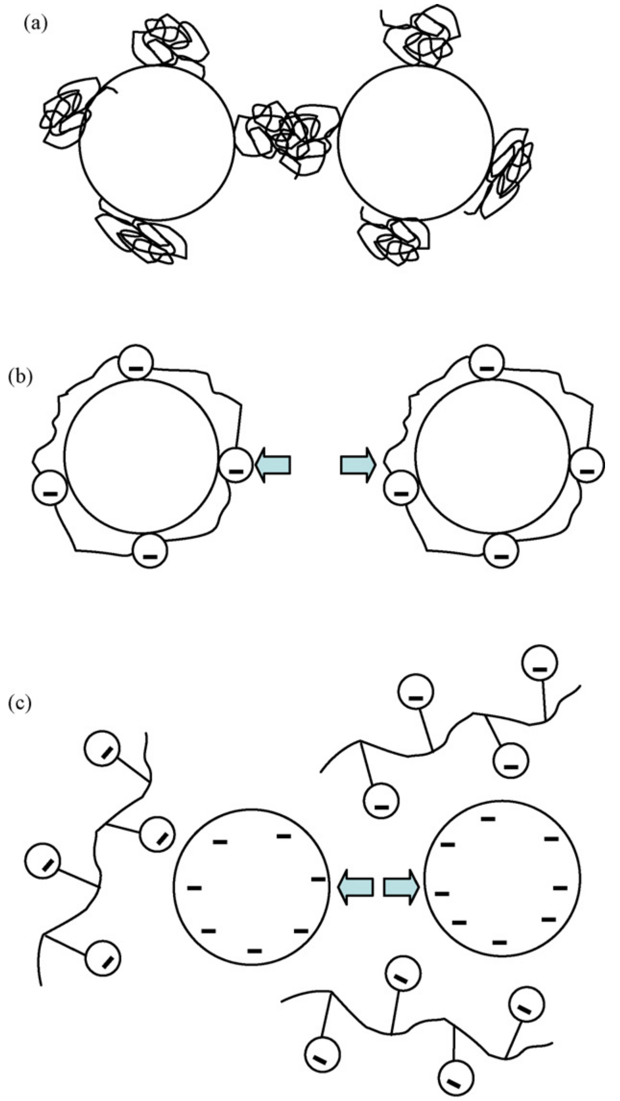

Fig. 9. Adsorption models of the polymer chain on PZT particle surface in suspensions with various pH (a) pH 3.2, (b) pH 10.1 and (c) pH 11.9.

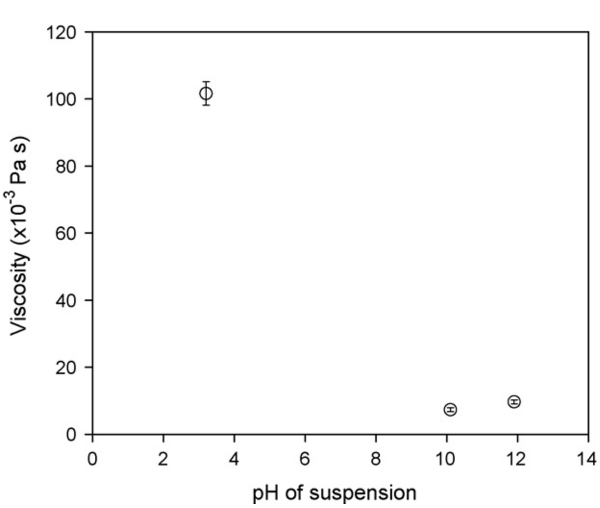

Fig. 10. Viscosity of the suspensions with pH 3.2, 10.1 and 11.9 measuring at shear rate of 46.5 s^{-1}.

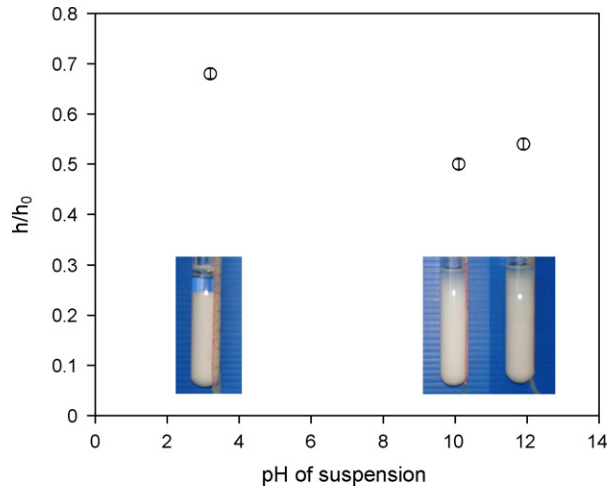

Fig. 11. Sedimentation behavior of the suspensions with 1 wt.% Dispex A40 at pH 3.2, 10.1 and 11.9.

3.2.3. Sedimentation behavior

Fig. 11 showed the h/h_0 ratios and sedimentation characteristics of the suspensions with pH 3.2, 10.1 and 11.9 investigated at 7 days after ball milling. Similar to the effect of pH on viscosity, the results can be explained in terms of particle dispersion in the suspensions of various pH. Relatively large agglomerates in pH 3.2 suspension tended to deposit disorderly and completely within a short period of time, while well-dispersed particles in suspensions of pH 10.1 and 11.9 were more stable. Therefore, the suspension of pH 3.2 exhibited a high h/h_0 ratio and clear supernatant, indicating poor dispersion and instability. On the other hand, the suspensions of pH 10.1 and 11.9 showed low h/h_0 ratios and cloudy supernatants, suggesting well-dispersed and highly stable suspensions.

4. Conclusions

It was found that APA dispersant promoted particle stabilization in PZT aqueous suspension under alkaline pH condition. The optimum dispersant concentration to produce a well-dispersed and highly stable suspension of 60 wt.% solids content was 0.5 wt.% Dispex A40 based on powder dried weight basis. The pH of the suspension affected particle dispersion and, therefore, viscosity and sedimentation behavior. In acidic pH suspension, particle agglomeration due to a decrease in electrostatic force and polymer bridging lead to high viscosity and unstable suspension. On the other hand, particle dispersion by electrosteric and electrostatic stabilization in alkaline pH suspensions resulted in low viscosity and high stability.

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