JOURNAL OF MATERIALS SCIENCE **36** (2001) 2397 – 2403

Colloidal processing of lead lanthanum zirconate titanate ceramics

JEONG-MIN CHO, FATIH DOGAN
Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195, USA
E-mail: fdogan@u.washington.edu

Well-dispersed aqueous slurries of fine ceramic powders with high solids loading are often required for various shape forming techniques such as slip and tape casting in order to fabricate advanced ceramics with a dense and uniform microstructure. Colloidal processing of lead lanthanum zirconate titanate (PLZT) powders was conducted at various pH using ammonium polymethacrylate as a dispersant. Suspensions were characterized by viscosity and zeta-potential measurements. The effect of pH on polymer adsorption and the rheological behavior of the slurries were investigated and stabilization mechanisms discussed. Through optimization of the dispersant concentration and pH, solids loadings of the suspensions up to 50 vol.% with a relatively low viscosity were obtained.

1. Introduction

Piezoelectric ceramics are used in various electronic devices such as actuators, sensors, and transducers. Piezoceramic and polymer composites found applications as ultrasound transducer materials to replace monolithic piezoceramics [1]. Recently, lead zirconate titatanate (PZT) ceramic tapes were utilized as an alternative to traditional dice and fill method to process laminated layered (2-2) structures for ultrasonic transducers [2]. To achieve a reliable performance of piezoceramic/polymer composites, fabrication of dense ceramic tapes is a prerequisite that requires optimized colloidal processing of fine powders during slurry preparation.

Tape casting is a common shape forming technique to process thin and flat ceramics. Tape casting slurries should be well dispersed and have high solids loading in order to process green and sintered bodies with dense and uniform microstructure. In the past, organic solvents were favored to prepare slurries for tape casting due to their low latent heat of evaporation and low surface tension. Recent developments on tape casting gear towards aqueous processing of the slurries in view of the cost, health and environmental considerations. However, hydrogen-bonding linkages in aqueous suspensions can result in flocculation of particles and prevent preparation of ceramic slurries with a high solids loading [3, 4]. Colloidal processing of ceramic powders towards a reliable manufacturing of advanced ceramics is reviewed in several recent articles [5–8].

Extensive studies have been conducted on preparation of aqueous tape casting slurries using e.g. alumina [9–11], mullite [12], $CaCO_3$ [13], SiC [14] and PLZT [15] powders. The objective of this work is to study the electrokinetic and rheological behavior of aqueous PLZT suspensions in order to prepare well-dispersed slurries with a high solids loading. Possible stabilization mechanisms are discussed with regard to the dispersant concentration and pH of the suspensions.

2. Experimental procedure

The dispersion studies of aqueous PLZT suspensions were conducted by viscosity and zeta potential measurements.

2.1. Materials and sample preparation

High purity (99.9%) 5H type PLZT powders (Praxair Specialty Ceramics Inc. Woodinville, WA), with an average particle size 0.51 μm and a specific surface area 7.83 m^2/g, were used in this study. The dispersant was ammonium polymethacrylate (Darvan C, Vanderbilt Co., Inc., Norwalk, CT) with molecular weight of 10,000–15,000. The structure of ammonium polymethacrylate is shown in Fig. 1.

Aqueous suspensions were prepared using deionized water at various pH and dispersant concentration by stirring, ultrasonication as well as milling techniques as described in more detail in the Sections 2.2 and 2.3. Samples, named as "S-A", are the suspensions prepared by adding only dispersant without pH adjustment. Two different methods were used to study the effect of the order of dispersant addition and pH change on the colloidal processing of powders. Samples, which are prepared by first adding of the dispersant into the suspension and followed by the pH change, are named hereafter as "S-B", while the suspensions prepared in

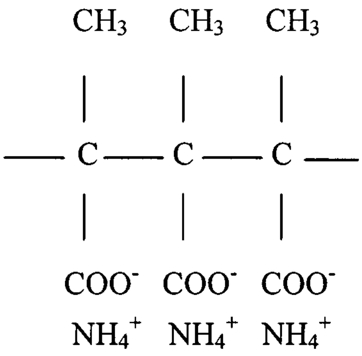

Figure 1 Structure of ammonium polymethacrylate.

a reverse order (first pH adjustment, then dispersant addition) referred to as "S-C".

2.2. Electrokinetic analysis and sedimentation tests

Electrokinetic behavior of the slurries was characterized using an Electrokinetic Sonic Amplitude Analyzer (ESA 8000, Matec Applied Sciences Inc., Hopkinton, MA). Zeta potential or dynamic mobility was calculated by measuring the electrokinetic sonic amplitude (ESA), which is the measured pressure amplitude of the sonic wave per unit applied electric field (P/E), and expressed as [13]:

$$\mathrm{ESA}\,(\omega) = \frac{P}{E} = c\Delta\rho\phi f_{\mathrm{G}}\mu_{\mathrm{d}}(\omega) \qquad (1)$$

where ω is frequency, c is sound velocity, $\Delta\rho$ is the density difference between particles and medium, ϕ is the particle volume fraction, f_{G} is a geometrical factor that depends on the electrode geometry and μ_{d} is dynamic mobility. A general guide to calculate the zeta potential can be found elsewhere [15].

For measurement of the zeta potential, the suspensions were prepared by mixing of deionized water and dispersant for 1 minute and adding the powder into the solution at a concentration of 1 vol.%. The suspensions were then dispersed by ultrasonication (550 Sonic Dismembrator, Fisher Scientific, Pittsburgh, PA) at 95 W power for 3 minutes, and subsequently stirred for 15 minutes to remove the trapped air bubbles. The zeta potential of the suspensions was measured by consecutive potentiometric-titration at 2 minutes intervals with acid or base using an automatic titrator (Microlab 500, Hamilton, Reno, NV). A fresh suspension was prepared for each titration with acidic or basic solutions, 1N HCl and 1N NH_4OH, respectively.

To study the effect of dispersant concentration on the zeta potential, the dispersant was added incrementally into the suspension by titration at a constant pH. The slurry was stirred for 3 minutes after each step of dispersant addition. The interval time was determined by the time concentration mode of the system so that any significant change of zeta potential value was not observed after 3 minutes. The pH of the suspension was also monitored during titration with the dispersant and adjusted to the initial value if it was necessary.

Dispersion state of the particles was studied by additional sedimentation tests as a function of the pH and dispersant concentration. The measurement of the sediment- height was conducted using 5 vol% suspensions after a settling time of three days.

2.3. Viscosity measurements

Suspensions with high solids loading were prepared by dispersion of the powders using a roll-mill at a constant pH and dispersant concentration prior to viscosity measurements. Milling was carried out in polyethylene jars using zirconia grinding media for 24 hour. Any pH change during milling was adjusted to the initial set value. A concentric cylinder viscometer (Haake VT550 and sensor MV-1, Germany) was used for viscosity measurements. Viscosity of each suspension was determined at shear rates between 0 to 80 s^{-1} and reported at a shear rate of 20 s^{-1} unless a different rate was indicated.

3. Results and discussion

3.1. Dissociation of dispersant

Dissociation of functional group, $-COONH_4$, of ammonium polymethacrylate to COO^- occurs through the following reactions.

$$\text{R-COONH}_4 \rightarrow \text{R-COO}^- + \text{NH}_4^+ \qquad (2)$$

$$\text{R-COOH} + \text{H}_2\text{O} = \text{R-COO}^- + \text{H}_3\text{O}^+ \qquad (3)$$

Dissociation of the dispersant is strongly affected by the pH of solvent and ionic strength. R-COOH is thermodynamically favorable at acidic pH as shown in Equation 3.

The degree of the polyelectrolyte dissociation was studied by conducting of the ESA measurements, considering that the dispersant molecules are charged species and their density is sufficiently different than that of the solvent. Since the ESA signal is not affected by the particle size or surface area, it is used to investigate the charge of the polymer in aqueous solutions. Fig. 2 shows ESA of ammonium polymethacrylate solution as a function of pH whereas a low signal would indicate a low dissociation of the polyelectrolyte. The ESA continuously decreases below pH 8 and approaches to zero at low pH. Above pH 8, the ESA

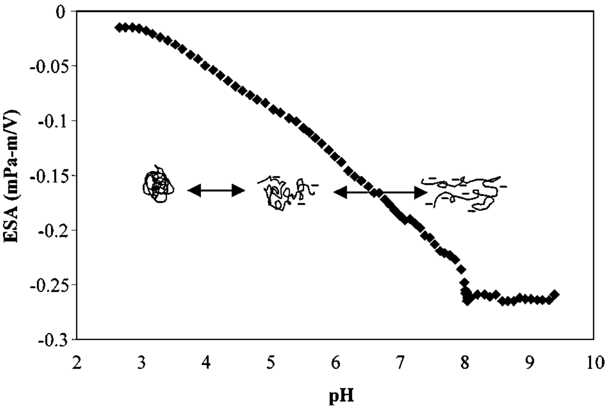

Figure 2 ESA of 5 vol% ammonium polymethacrylate solution at various pH.

remains constant, indicating that dispersant molecules are fully dissociated. It is known that ammonium polymethacrylate is negatively charged and stretched at high pH because of the repulsive forces between the negatively charged segments of the polymer. Similarly, it has been shown using potentiometric titration method that other common dispersants such as polyacrylic acid (PAA) and sodium polymethacrylic acid (Na-PMAA) are negatively charged and stretched in basic aqueous solutions [17, 18].

3.2. Electrokinetic behavior

The change of the zeta potential of 1 vol% PLZT suspension as a function of pH is shown in Fig. 3. The pH and zeta potential of a fresh prepared 1 vol.% suspension were 7.2 and 5 mV, respectively. The isoelectric point (IEP) of the PLZT particles used in this work was measured at pH 8.2. It should be noted that variations of the IEP between 8 and 9.5 were observed, when powders of similar composition but from different lots of the manufacturer were used to prepare suspensions for the zeta potential measurements [15]. This can be attributed to the complex surface chemistry of PLZT particles and the excess PbO phase which is often required to promote the sintering of ceramic parts.

With the decrease of the pH, the zeta potential increased to ∼15 mV. According to Shanefield [19], zeta potential larger than 25 mV is required in order to obtain highly stabilized suspensions. The colloidal stability may become sensitive to pH and ionic strength of the system, which may be affected by the increased solubility of possible free-PbO in acidic PLZT suspensions. Prior to addition of the dispersant, net surface charge of the particles was positive (Fig. 3). Generally, since a polyelectrolyte is electrically charged and composed of long chain polymers, both electrostatic and steric effects control stabilization of the system. Once the dispersant is dissociated and adsorbed on the surface, dispersion of the particles is governed predominantly by polymer/particle interaction.

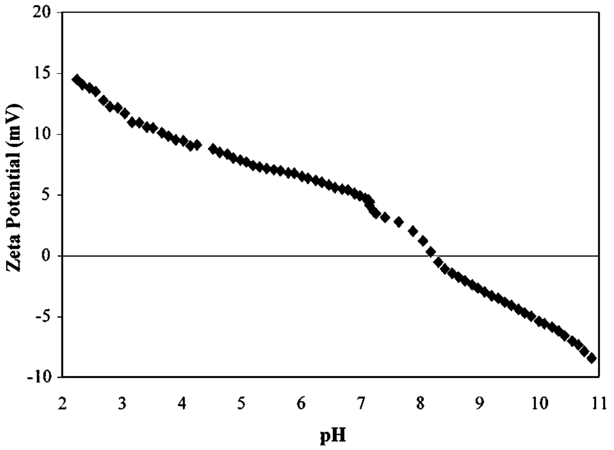

Figure 3 Zeta potential of 1 vol% PLZT suspension as a function of pH (without dispersant).

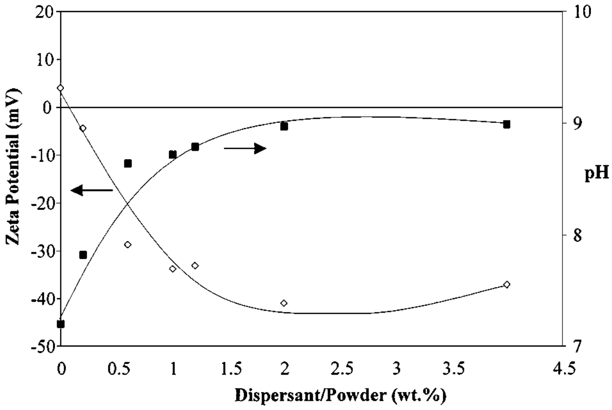

Figure 4 Effect of dispersant concentration on the zeta potential and pH of 1 vol% PLZT suspension.

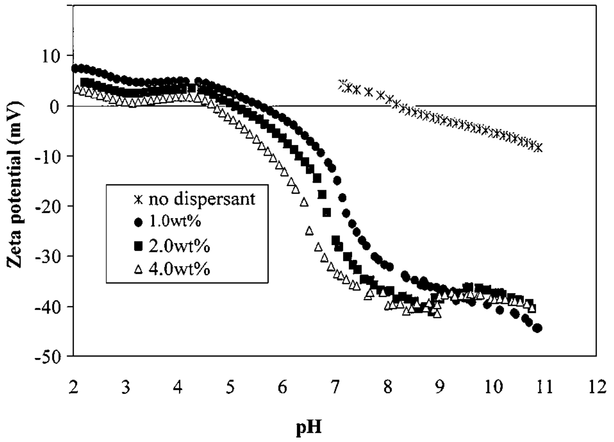

Figure 5 Effect of pH on the zeta potential of suspensions containing different amount of dispersant.

Fig. 4 shows the change of the zeta potential and pH of a 1 vol.% PLZT suspension as a function of dispersant concentration. When a small amount of dispersant was added, zeta potential decreased and approached to zero due to the charge neutralization. With the addition of 0.2 wt.% dispersant, pH of the system increased to 7.8 approaching to the IEP at 8.2. Flocculation can occur at low dispersant concentrations due to the effects of charge neutralization as well as polymer bridging. With the increase of dispersant concentration, the zeta potential (negative value) increased and reached a maximum at about 2 wt.% dispersant. The slight decrease of the zeta potential at higher dispersant concentrations can be attributed to the decrease of dynamic mobility due to the increasing concentration of NH_4^+ ions, which may compress the double layer and/or shield the negative charge of the adsorbed polymer.

The pH dependency of the zeta potential of 1 vol.% “S-B” suspensions is shown in Fig. 5. The zeta potential at low pH decreases slightly as the amount of dispersant increases. This behavior can be explained based on a model by Böhmer *et al.* [20] suggesting that some segments of polymer may dissociate at the near surface of particle due to the local potential field generated by surface charge of the particle.

Sedimentation experiments (Fig. 6) reveal a good agreement between the dispersion state of the particles and the zeta potential results in Fig. 5. While flocculated particles at low pH result in a larger sediment-volume with a clear supernatant, dispersed suspensions

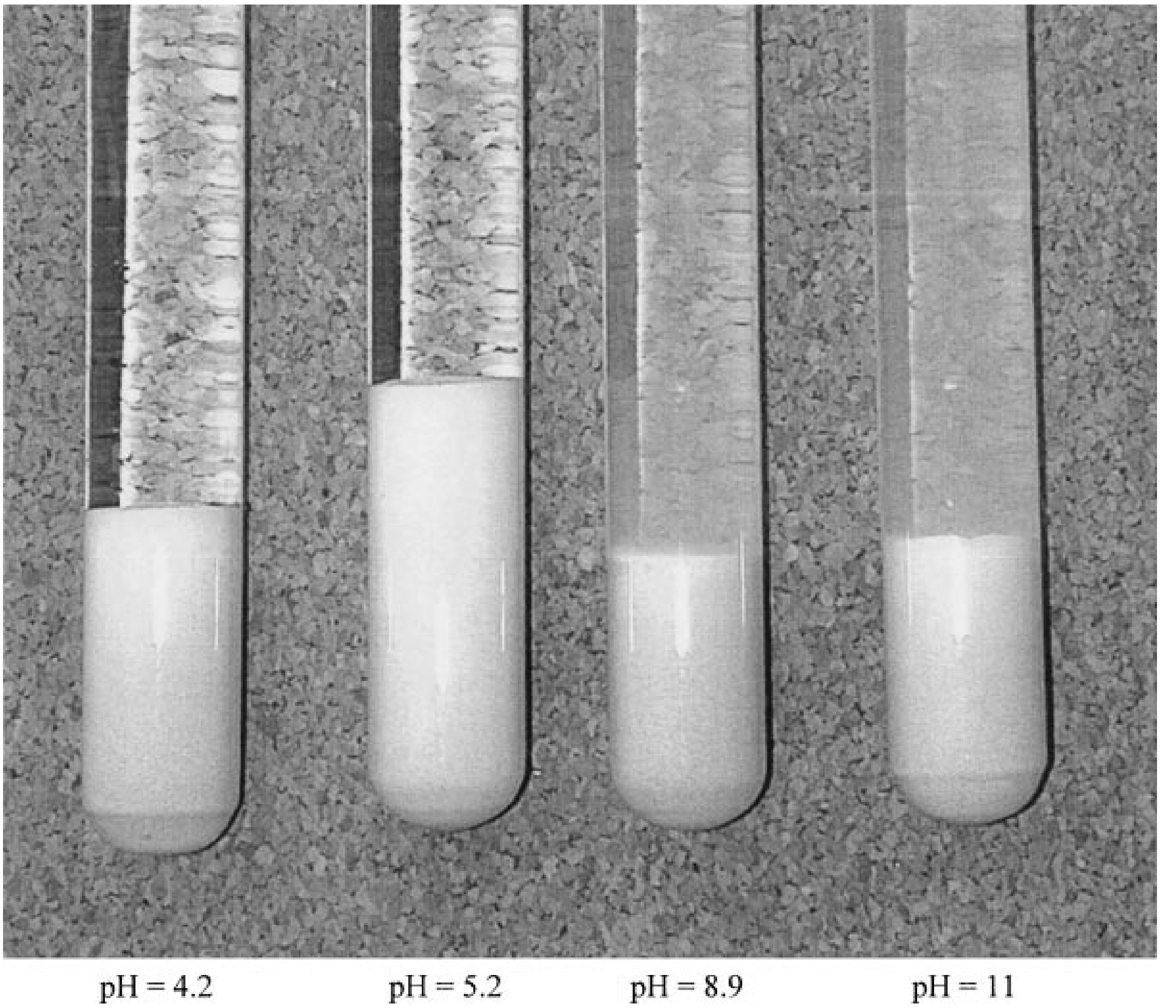

Figure 6 Comparison of the sedimentation height of 5 vol% "S-B" suspensions containing 2 wt% dispersant at various pH.

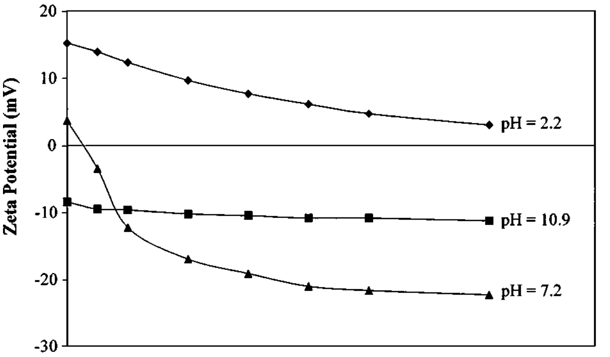

Figure 7 Effect of dispersant concentration on the zeta potential of 1 vol% "S-C" suspensions at various pH.

at higher pH reveal a low sediment-height and a cloudy supernatant.

The behavior of polymer adsorption depending on the order of dispersant addition and pH adjustment was studied by zeta potential measurements (Fig. 7). The zeta potential of the "S-B" samples where the dispersant was added first and followed by the pH adjustment, showed a larger value than that of the "S-C" samples with the reverse order of titration. This indicates that adsorbed polymers at lower pH are highly stable against desorption as the pH increases. On the other hand, adsorption of negatively charged polyelectrolytes on the particles with highly negative charge is hindered at high pH. Similarly, reversible and irreversible adsorption behavior of Na-PMAA on alumina particles was observed in basic suspensions [18]. As discussed in the previous section, anionic polymers are easily attached on the positive surface sites at pH 2.2 so that sequential adsorption of dispersant lead to a decrease of the zeta potential and dispersibility. At pH 7.2, a significant increase of the zeta potential is observed with the increase of dispersant concentration due to the steric effect of adsorbed polymers. At pH 10.9, the zeta potential is not significantly affected by the amount of dispersant that can be attributed to a hindered adsorption of polymers on the surfaces with a high negative charge. However, when the dispersant was added prior to the pH increase, significantly higher values of the zeta potential were obtained as shown in Fig. 5. Similar dispersion behavior of the particles has been observed in suspensions of barium titanate dispersed in solutions containing PAA as a dispersant [21].

3.3. Rheology

Fig. 8 shows the viscosity of a 40 vol.% PLZT suspension as a function of dispersant concentration. The decrease of the viscosity with addition of the dispersant

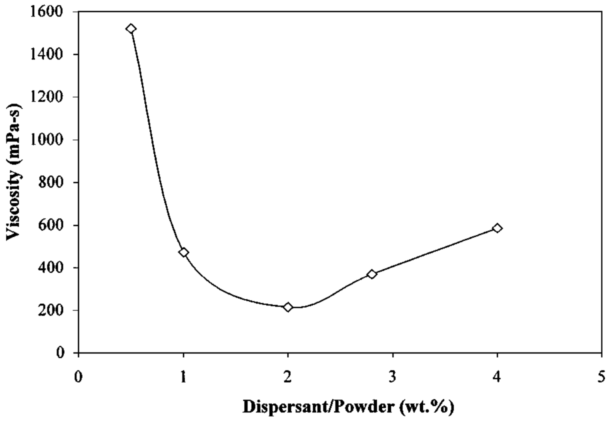

Figure 8 Effect of dispersant concentration on the viscosity of the suspensions.

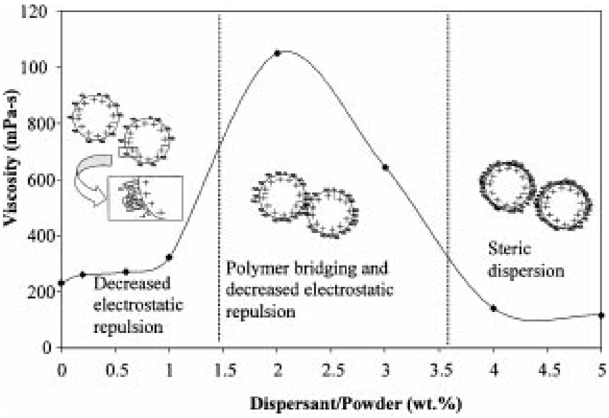

Figure 9 Viscosity of 10 vol% suspensions as a function of dispersant concentration at pH 4.2 and proposed stabilization mechanisms.

to a minimum value and the increase of that at higher dispersant concentrations are in good agreement with the zeta potential measurements in Fig. 4. This can be attributed to the increase of the ionic strength due to NH_4^+-ions and/or the effect of depletion flocculation [22]. Nonadsorbed dispersants are not able to penetrate into the space between particles since the interparticle distance is smaller than the stretched polymers in highly concentrated suspensions. Thus, osmotic pressure develops between the polymer-free and polymer-rich regions and induces attractive forces between particles. It has been reported that the viscosity of alumina suspensions with excess dispersant increases dramatically with increasing molecular weight of the polymer [23].

The effect of the order of pH adjustment and dispersant addition on the viscosity of 40 vol.% suspensions at a shear rate of 20 s^{-1} is depicted in Table I. In analogy to the zeta potential measurements using 1 vol.% PLZT suspensions, viscosity results indicate the irreversible desorption of adsorbed polymer at high pH.

Suspension "S-A" was prepared by addition of dispersant without pH adjustment and resulted in the lowest viscosity. Preparation of suspension "S-B" was carried out by adding the dispersant first, ball-milling for 1 hour and followed by the increase of pH. Suspension "S-C" was prepared by adding the powder into the dispersant solution at pH 11. Suspension "S-B" represents a dispersed state where polymers are already adsorbed at lower pH and subsequent increase of pH does not lead to a significant increase of the viscosity. The lower viscosity of suspension "S-B" than that of "S-C" can be attributed to the hindered desorption of the pre-adsorbed polymers at pH 11 [14].

3.4. Dispersion mechanisms

Well-dispersed suspensions with high solids loading are difficult to achieve at low pH due to weak electrostatic repulsion and "coiled-up" configuration of the dispersant. At low pH, anionic dispersants are hardly dissociated, but they still carry sufficient negative charge along the polymer chain allowing them to adsorb on the surfaces. Thus, adsorbed polymers screen the positive surface charge of particles and reduce electrostatic repulsion.

TABLE I Viscosities of 40 vol.% PLZT suspensions depending on the order of dispersant addition and pH adjustment

Sample	Addition of 2.0 wt% dispersant	Viscosity [mPa-s]
S-A	Dispersant only, pH 8.9	223.7
S-B	First dispersant, then pH to 11	246.1
S-C	First pH to 11, then dispersant	315.3

Fig. 9 shows the viscosity of 10 vol.% PLZT suspensions as a function of dispersant concentration at pH 4.2. It is suggested that both mechanisms, the reduction of surface charge and polymer bridging, are effective up to 3.0 wt% dispersant concentration. At low dispersant concentrations, <1 wt.%, electrostatic stabilization is effective to overcome the polymer bridging due to repulsion between the positively charged surface sites of particles at which polymers are not attached. As the dispersant concentration increases, apparent surface charge is reduced resulting in flocculation, which is also be affected by polymer bridging. On the contrary, as the dispersant concentration increases, >4 wt.%, total surface coverage of the particles with adsorbed polymers leads to deflocculation of the suspension. This behavior of particle-particle interaction can be attributed to the transition from polymer bridging to steric stabilization. With increasing amount of adsorbed polymer, steric dispersion becomes the dominant mechanism whereas the electrostatic effect decreases.

Viscosity of 40 vol.% PLZT suspensions at pH 11 as a function of dispersant concentration and proposed stabilization mechanisms are depicted in Fig. 10.

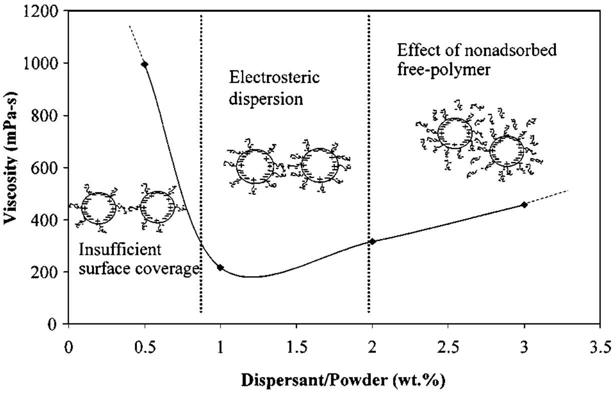

Figure 10 Viscosity of 40 vol% suspensions as a function of dispersant concentration at pH 11 and proposed stabilization mechanisms.

Suspension with 1 wt.% dispersant revealed the lowest viscosity, which is in good agreement with the zeta potential measurements as shown in Fig. 5. The increase of the dispersant concentration led to an increase of the viscosity that is attributed to the non-adsorbed free polymers in the solution. As mentioned previously, polymer adsorption on particles at high pH is hindered due to the repulsive interaction between the negatively charged dispersant molecules and negatively charged surface sites of the particles. However, polymer adsorption can still take place on the surface sites with a positive charge although the net charge of the particles is strongly negative. Hence, both electrostatic and steric repulsion (electrosteric) are the proposed stabilization mechanisms at pH 11 and a dispersant concentration of about 1 wt.%. However, in suspensions at higher pH, only electrostatic repulsion may become dominant since positively charged surface sites are not existing. It has been reported that stabilization of negatively charged Si_3N_4 suspensions at pH 10.5 with PAA as a dispersant is governed only by the electrostatic repulsion [17].

3.5. Effect of pH on solids loading

Slurries suitable for ceramic shape forming often require high solids loadings to achieve high green densities with a uniform microstructure. Fig. 11 shows the effect of pH on the solids loading of a suspension containing 2 wt.% dispersant. Note that a different batch of PLZT powders was used in these studies, and therefore, the measured data are comparable but not in exact agreement with the results in the previous sections. The viscosity of the suspensions becomes more pH dependent, as the solids loading increases from 20, 45 to 50 vol.%. Flocculation of 50 vol.% suspension at pH 10.2 can be attributed to the effect of polymer bridging as discussed in the Section 3.4. It is considered that polymer bridging is most effective when the half of the particle surface is covered by polymer adsorption [24]. Hence, the particles become more negatively charged as the pH increases to 11, reduced polymer adsorption may lead to a less effective polymer bridging and a lower viscosity of 50 vol.% suspension.

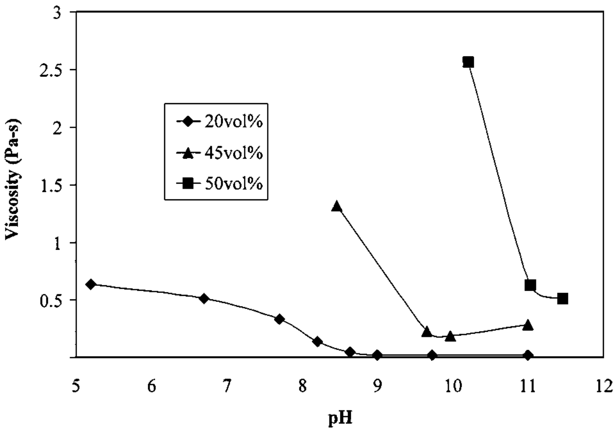

Figure 11 Effect of pH and solids loading on the viscosity of the suspensions with 2 wt% dispersant.

4. Conclusions

Dispersion and electrokinetic behavior of aqueous PLZT suspensions were investigated at various pH using ammonium polymethacrylate as a dispersant. Possible stabilization mechanisms were discussed depending on the pH and the amount of the dispersant. Freshly prepared suspensions showed a positive zeta potential and pH ∼ 7 whereas IEP was measured at ∼8.2. It was pointed out that the PLZT slurries were sensitive to lot-to-lot variations of the powders due to the complex surface chemistry of the particles and possible formation of free-PbO phase. Because of the positive charge of PLZT particles below pH 8.2, adsorption of the non-streched polymers increased with the decrease of pH.

Different electrokinetic behavior and rheology of the suspension were observed depending on the order of dispersant addition and the pH adjustment. Addition of dispersant, followed by pH increase, led to higher zeta potential values. Thus, once the polymer adsorption takes place at low pH, reversible desorption is strongly hindered at higher pH.

Adsorption of the dispersant was reduced at high pH due to the repulsive forces between the highly negatively charged particles and the ionized dispersant molecules having a negative charge. Electrosteric stabilization mechanism was effective in preparation of well-dispersed slurries at high pH. PLZT suspensions with solids loading up to 50 vol.% and relatively low viscosities were prepared at pH 11.5 with addition of 2 wt.% dispersant.

Acknowledgment

This work was supported by the Washington Technology Center under Contract No. 97-A6 and Praxair Specialty Ceramics, Inc.

References

1. V. F. JANAS, T. E. MCNULTY, F. R. WALKER, R. P. SCHAEFFER and A. SAFARI, *J. Amer. Ceram. Soc.* **78** (1995) 2425.
2. J. W. STEVENSON, M. R. REIDMEYER and W. HUEBNER, *ibid.* **77** (1994) 2481.
3. E. S. TORMEY, R. L. POBER, H. K. BOWEN and P. D. CALVERT, in "Forming of Ceramics," edited by J. A. Mangels (The American Ceramic Society, Westerville, OH, 1984) p. 140.
4. P. NAHASS, W. E. RHINE, R. L. POBER, H. K. BOWEN and W. L. ROBBINS, in "Ceramic Transactions," Vol. 15, edited by K. M. Nair, R. Pohanka and R. C. Buchanan (The American Ceramic Society, Westerville, OH, 1990) p. 355.
5. F. F. LANGE, *J. Amer. Ceram. Soc.* **72** (1989) 3.
6. E. CARLSTRÖM, in "Surface and Colloid Chemistry in Advanced Ceramics Processing," edited by R. J. Pugh and L. Bergström (Marcel Dekker, New York, 1994) p. 1.
7. W. M. SIGMUND, N. S. BELL and L. BERGSTRÖM, *J. Amer. Ceram. Soc.* **83** (2000) 1557.
8. J. A. LEWIS, *ibid.* **83** (2000) 2341.
9. C. PAGNOUX, T. CHARTIER, M. F. GRANJA, F. DOREAU, J. M. FERREIRA and J. F. BAUMARD, *J. Eur. Ceram. Soc.* **18** (1998) 241.
10. K. NAGATA, *J. Ceram. Soc. Jpn.* **101** (1992) 1271.
11. Y. HIRATA, A. NISHIMOTO and Y. ISHIHARA, *J. Cer. Soc. Jpn.* **100** (1992) 972.

12. N. USHIFUSA and M. J. CIMA, *J. Amer. Ceram. Soc.* **74** (1991) 2443.
13. G. TARI, S. TOUCHAL and J. M. FERREIRA, *Key Eng. Mat.* **132–136** (1997) 289.
14. M. F. GRANJA, F. DOREAU and J.M. FERREIRA, *ibid.* **132–136** (1997) 362.
15. J.-H. FENG and F. DOGAN, *Mater. Sci. Eng. A* **283** (2000) 56.
16. R. W. O'BRIEN, *J. Flu. Mech.* **212** (1990) 81.
17. V. A. HACKLEY, *J. Amer. Ceram. Soc.* **80** (1997) 2315.
18. J. CESARANO III, I. A. AKSAY and A. BLEIER, *ibid.* **71** (1988) 250.
19. D. J. SHANEFIELD, in "Organic Additives and Ceramic Processing" (Kluwer Academic Publishers, Norwell, MA, 1996).
20. M. R. BÖHMER, O. A. EVERS and J. M. H. M. SCHEUTJENS, *Macromolecules* **23** (1990) 2288.
21. Z. CHEN, T. A. RING and J. LEMAITRE, *J. Amer. Ceram. Soc.* **75** (1992) 3201.
22. D. H. NAPPER, in "The Effect of Polymers on Dispersion Properties" edited by T. F. Tadros (Academic Press, London, 1982) p. 8.
23. J. CESARANO III and I. A. AKSAY, *J. Amer. Ceram. Soc.* **71** (1988) 1062.
24. SACKS, M. D. C. S. KHADILKAR, G. W. SCHEIFFELE, A. V. SHENOY, J. H. DOW and R. S. SHEU, in "Dispersion and Rheology in Ceramic Processing" edited by G. L. Messing (The American Ceramic Society, Westerville, OH, 1987) p. 495.

Received 24 July
and accepted 27 November 2000