Journal of the European Ceramic Society 19 (1999) 2773–2780
© 1999 Published by Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0955-2219(99)00083-7
0955-2219/99/$ - see front matter

Electrokinetic and Rheological Properties of Aqueous TiN Suspensions with Ammonium Salt of Poly(methacrylic Acid)

Chi-Jen Shih* and Min-Hsiung Hon

Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

(Received 1 September 1998; accepted 26 March 1999)

Abstract

The study illustrates how rheology and electrokinetics can be utilized in the investigation and optimization of the properties of ceramic suspensions. Zeta potential studies show that the isoelectric point of TiN particulates is at pH = 4, and for the pH range used, PMAA–NH_4 addition results in a more negative zeta potential value. The rheological behavior of titanium nitride in the presence of PMAA–NH_4 is strongly dependent on pH and three rheological types have been defined. © 1999 Published by Elsevier Science Ltd. All rights reserved

Keywords: TiN, suspensions, rheology, nitrides.

1 Introduction

With high elastic modulus, thermal expansion coefficient and chemical stability, TiN has been widely used as a particulate-reinforcing second phase in ceramic composite. The properties of the ceramic composite are controlled by the dispersion of reinforcements in a ceramic matrix. Inhomogeneous dispersion of reinforcements, such as flocculation or agglomeration, is damaging to the sintering of composite materials and always introduces processing flaws.[1–5]

Flaw minimization and processing optimization can be successfully accomplished by colloidal processing. This processing concept involves the manipulation and control of interparticle forces in powder suspensions to remove heterogeneities and optimize suspension properties.[6–8] Colloidal processing concepts are often applied to forming methods such as slip casting, pressure filtration, tape casting, and injection molding which involve handling of suspensions. During forming, a ceramic powder suspension is subjected to an applied stress to form it into an engineering shape. In all types of suspension forming techniques, ranging from slip casting to injection molding, the rheological properties of the suspension play a key role in controlling shape-forming behavior, and in optimizing the properties of the green body. Fundamentally, the rheological properties of colloidal suspensions are determined by an interplay of thermodynamic and fluid mechanical interactions. This means that an intimate relation exists between the particle interactions, including Brownian motion, the suspension structure (i.e. the spatial particle distribution in the liquid), and the rheological response.

Polyacrylic acids (PAA) are frequently used to disperse oxide particles such as alumina,[9,10] rutile, and hematite.[11,12] The adsorption of polyacrylic acid on these particles was found to be responsible for the dispersion. It was shown that polyacrylic acid strongly adsorbed on positively charged particle surfaces from an acidic pH to pH_{iep} (defined as the pH where the charge at the stern layer is zero). Above pHiep, the particles became negatively charged and started to repel the polymer. Also, it was reported that polyacrylic acid did not adsorb on a negatively charged silica (pH_{iep}~2·5).[11]

On the other hand, the effectiveness of acrylate-based polymers, such as polyacrylic acid and ammonium polymethacrylate, as dispersants for silicon nitride was demonstrated.[13–20] These studies emphasized the general rules of dispersion, and well-dispersed silicon nitride suspensions can only be obtained in both the neutral and alkaline pH range by the application of polyelectrolyte. However these studies have focused on relatively dilute suspensions and narrow ranges of polymer concentration. In our

---

* To whom correspondence should be addressed. Fax: +886-6238-0208; e-mail: n5883110@sparc1.cc.ncku.edu.tw

previous investigation,[21] the electrostatic repulsion between the PAA-NH_4-modified particle surface was found to be the primary mechanism governing the dispersion in both the neutral and alkaline pH range; on the other hand the steric repulsion of PAA-NH_4 in the acidic pH range was demonstrated to make a positive contribution to the dispersion. However, whether the above reported results are applicable to the system of TiN ceramic particles remain to be determined.

This paper describes the results of an experiment focusing on the TiN–H_2O–PMAA–NH_4 system. The ionization chemistry of the ammonium salt of poly(methacrylic acid) was characterized by the potentiometric titration method. Interaction of PMAA-NH_4 with the TiN surface was analyzed using electrokinetic measurements. The rheological characterization was used to determine the degree of stability. The effects of polymer concentration and pH were also evaluated.

Table 1. The chemical compositions of the TiN powders[a]

Composition	*Specification (wt%)*	*Typically (wt%)*
Ti	min 77	77
N	min 20	21
C	max 0·2	0·1
O	max 1·5	1·2
Al	max 0·01	0·008
Ca	max 0·01	0·008
Fe	max 0·2	0·15
S	max 0·01	0·002
Si	max 0·02	0·005

[a] H.C. Starck Inc.

Table 2. The physical properties of the TiN powders[a]

Properties	*Specification*
Density	5·44 (g cm^{-3})
Particle size distribution	95 wt% < 7μm
(cumulative mass, wt%) by X-ray	50 wt% < 1·2μm
Adsorptive	5 wt% < 0·8μm

[a] H.C. Starck Inc.

2 Experimental Procedure

2.1 Powder and dispersant characterization

Commercially available TiN powders and PMAA–NH_4 (R. T. Vanderbuilt Co, Norwalk, C.T.) were used as raw materials in this investigation. The chemical compositions and physical properties of TiN powder are shown in Tables 1 and 2, respectively.

The poly-electrolyte used was the NH_4^+ salt of poly(methacrylic acid). The PMAA–NH_4 structure and dissociation reaction shown below illustrate the functional groups of carboxylic acid that can be COOH or dissociated to COO^-. For each acid group

$$R - COOH + H_2O \leftrightarrow R - COO^- + H_3O^+$$

$$R = -(HC - CH2)-$$

$$K_a = \frac{[R - COO^-][H_3O^+]}{RCOOH}$$

$$pk_a = -\log k_a = pH - \log\left(\frac{\alpha}{1-\alpha}\right)$$

where α is the fraction of dissociated carboxyl groups.

The pH value was adjusted with standardized analytical-grade HCl and NaOH solutions (0·1 to 1·0 mol. dm^{-3}) and analytical-grade NaCl was used to adjust the ionic strength desired.

2.2 Experimental methods

2.2.1 Potentiometric titration experiments

The procedure of using potentiometric titration to determine polymer behavior is clearly outlined by Arnold and Overbeek[22] and by Hunter.[23] Titrations were completed on a blank electrolyte solution and a corresponding polyelectrolyte solution containing a known amount of sample. The difference between the amounts of titrant added to the blank solution and the sample at a specified pH corresponds to the amount of titrant that reacted with the sample. With this information, the polymer behavior was determined using an automatic titration unit (Orion RSCH 950) in the first-derivative mode and the fraction of functional groups dissociated on poly-electrolyte then can be calculated by the ratio of reacted titrant.[9,23]

The total amount of PMAA–NH_4 dosage was calculated based upon a mass balance for PMAA–NH_4. But it is determined with respect to the amount of TiN particles added. A known amount of the PMAA–NH_4 was diluted with de-ionized water to approximately 25 ml in the range of 0·01~5 wt%. This solution was then sealed in the titration cell and the pH was adjusted to 12 to ensure that PMAA–NH_4 was fully dissociated. The first-derivative titrations were then conducted with 0·5 mol. dm^{-3} HCl and the distance between peaks recorded. The fraction of dissociated carboxyl groups (α) at a specified pH can then be calculated from the ratio of the amount of titrant that reacted with the sample.

$$\alpha = \frac{\text{amount of titrant reacted at a specified pH}}{\text{amount of titrant reacted at pH} = 12\,(\alpha = 1)}$$

2.2.2 Zeta potential measurements

The experimental procedures conducted in the present study were strictly performed and these as-received powders are known to be free of any intentionally added manufacturing aids which might alter their colloidal behavior in a manner uncharacteristic of the pure solid. For the purpose of eliminating the possible unknown history-dependent contamination introduced on the powder surface during normal shipping and handling procedures[24] the following rinse process was taken. To affirm the IEP of the TiN colloid, the as-received powders were first rinsed with de-ionized water, and the washed powder was dried overnight at low temperatures (approx. 40°C) before colloid preparation. Electrophoretic mobility was measured and used to calculate zeta potential, which can be completed in a very dilute suspension (<1000 ppm). Therefore, the 2 vol% TiN samples were centrifuged and the supernatant was carefully decanted into a beaker. Subsequently, a very minute amount of sediment was re-mixed with the supernatant. The samples were ultrasonicated and stirred for 15 min prior to the measurement to ensure that only the mobility of the single particle was measured. The zeta potential of TiN with various amounts of PMAA–NH_4 and pH was determined by Zeta III, zeta meter, USA.

2.2.3 Rheological measurements

Ten vol% TiN suspension with various amounts of PMAA–NH_4 and pH values were milled for 24 h. Each resultant suspension was analyzed directly by measuring viscosity to determine the degree of coagulation of particles in solution. Rheological characterization was performed on a rheometer (model DV II, Brookfield Engineering Laboratories, Inc., USA) at 25°C with a concentric cylinder measurement geometry. Suspensions were subjected to a high shear rate of 100 s^{-1} to break up any initial network structure, then lower rates were employed. A maximum time of 1 h for each sample minimized the effect of sedimentation.

3 Results and Discussion

3.1 Polymer behavior of PMAA–NH_4 in solutions

An important characteristic of the ionizable polymer is its ability to undergo expansion from a coiled to a stretched conformation as charge density increases along the flexible chain. This cooperative transition is due to electrostatic repulsion between neighboring ionized sites. Leyte and Mandel[25] interpreted their titration curves for poly(methacrylic acid) (PMAA) in terms of a similar reversible transition between two stable conformational states and confirmed these results using spectroscopic methods.[26] In PMAA, the transition occurs over a relatively narrow range of ionization, roughly $0{\cdot}1<\alpha<0{\cdot}3$, as evidenced by a fairly abrupt change in the slope of the titration curves in the region. In this case, stabilization of the coiled structure at low α (low pH) is prompted by the hydrophobic interactions of the α methyl groups. Mathieson and Mclaren[27] examined PAA ($Mr=2{\cdot}6\times10^6$),which lacks the hydrophobic side groups of PMAA, and found a similar,although less-pronounced, transition in the titration data that occurs at intermediate α values (roughly $0{\cdot}45<\alpha<0{\cdot}65$). These authors distinguished four regions in the titration curve, analogous to those identified by Wada,[28] and they associated these regions with conformational changes in PAA.

Figure 1 depicts the typical behavior of the fraction of dissociated functional groups as a function of pH. Similar behavior was observed for the range of PMAA–NH_4 concentration 0·01~5 wt% in this study. The one shown in Fig. 1 is plotted for 2 wt% PMAA–NH_4 added. As pH increases the fraction dissociated (α) increases from ~0 to ~1. The curve in Fig. 2 is qualitatively similar to those reported by Mathieson and Mclaren[27] for PAA dissociation, the region labeled 'A' and characterized by a sharp upward curvature is attributed to instabilities that are possibly caused by precipitation of the coiled form of PMAA–NH_4. Region 'B' represents ionization of the coiled ('a') state, region 'C' is the transition region that is associated with coil expansion, and 'D' represents ionization of the stretched ('b') state. The values of α and pH that roughly correspond to these four stability regions are listed in Table 3. An interesting point is that

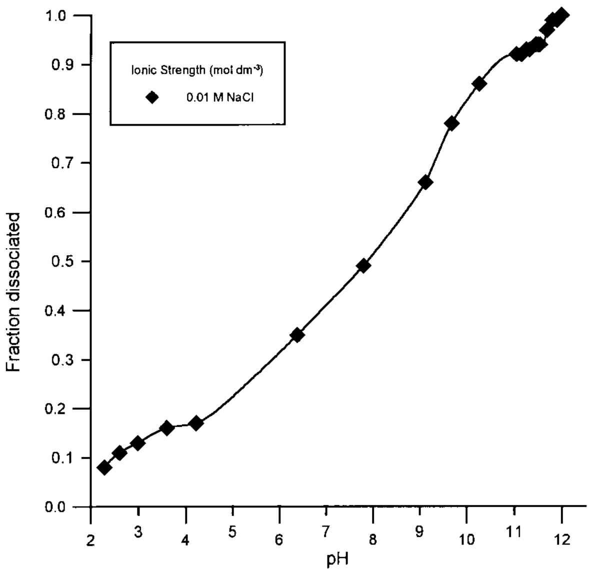

Fig. 1. Typical behavior of fraction of dissociated carboxyl groups as a function of pH plotted for PMAA–NH_4 concentration of 2 wt%.

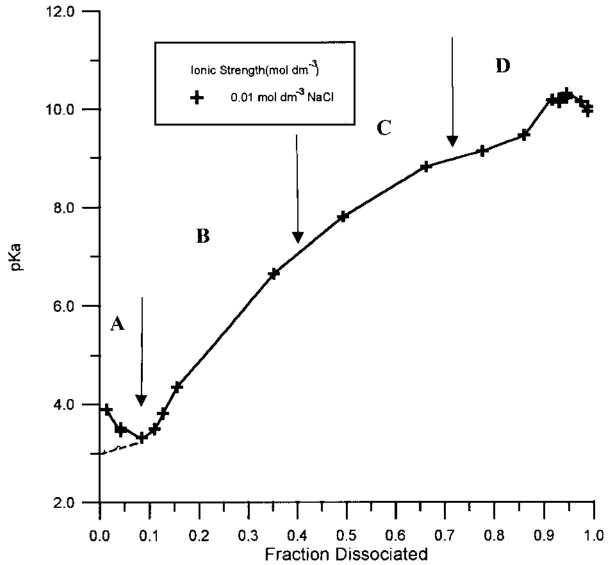

Fig. 2. Dissociation reaction constant ($pk_a = -\log k_a$) of carboxyl group for PMAA–NH_4 as a function of fraction of dissociated.

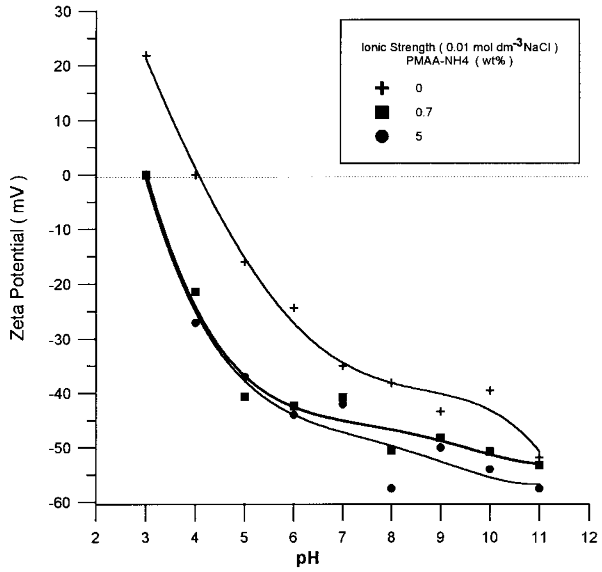

Fig. 3. Effect of pH on the zeta potential of TiN suspension with 0·7 wt%, 5 wt% and without PMAA–NH_4 additions.

Table 3. Approximate conformational stability regions for PMAA–NH_4, based on analysis of potentiometric titration data

Region	*α range*	*pH range*	*State*
A	$\alpha < 0{\cdot}08$	$< 2{\cdot}3$	Unstable
B	0·08–0·4	2·3–6·7	Coiled (a state)
C	0·4–0·7	6·9–9·3	Transition
D	$> 0{\cdot}7$	$> 9{\cdot}3$	Stretched (b state)

extrapolation of pk_a values to $\alpha = 0$ yields a value of 3·0. This value is constant with those for simple organic acids which only have one acid group. In this condition the polyelectrolyte chains approach insolubility and are unstable for region A. As pH is increased, the number of negatively charged sites also continually increases until the polyelectrolyte is effectively ionized near pH12 and $\alpha \sim 1$ for region D, where the polyelectrolyte is in the form of relatively large expanded random coil (~10 nm) in solution.[22]

3.2 Interaction of PMAA–NH_4 with TiN

For electrostatic stabilization it is vital to know the position of the isoelectric point (IEP) so a pH region can be identified where there is sufficiently high surface charge density to generate a strongly repulsive double-layer force. Figure 3 shows the dependence of zeta potential of TiN suspension on pH value for 0, 0·7, and 5 wt% PMAA–NH_4 additions. The zeta potential changes from −53 mV at pH = 11 to +28 mV at pH = 3, with an isoelectric point(IEP) at about pH = 4. For 0·7 wt% PMAA–NH_4 addition, the zeta potential changes from −55 mV at pH = 11 to 0 mV at pH = 3. For the pH range used, PMAA–NH_4 additions result in a more negative zeta potential. The IEP value measured for TiN in the present study is similar to that obtained by Nass *et al.*[29] The IEP value for their as-received powder (marketed by the same manufacturer of H. C. Starck, Inc.) was pH~4, and higher negative zeta potentials were observed for pH values greater than 4. Their systematic investigations also revealed that the suspension could be stable for several months at pH~8–9.

The electrokinetic behaviors of TiN in the presence of PMAA–NH_4 is strongly dependent on pH, Fig. 4 shows that for pH = 3~5 the PMAA–NH_4 addition results in a more negative zeta potential than pH = 9~11. At pH = 3~5, where approaches zero the coiled polymer is essentially neutral. It is evident, as reflected by the electro-kinetic curves, that increasing the concentration of PMAA–NH_4 results in a reduction of the positive shear plane potential. There are two possible causes for this behavior. First, according to the proposed model by Bohmer *et al.*,[30] dissociation of carboxyl sites increases as the proximity to the surface increases in response to the local potential field that is generated by the charged surface sites. The ionization of near-surface segments then partially screens the charge on the particles, thereby decreasing the shear plane potential. Second, the presence of polymer chains may disturb the hydrodynamic plane of shear, shifting it further out from the particle surface. Because potential decreases exponentially with distance,[23] the modified shear plane will experience a lower potential. The second interaction type,which is found at strongly alkaline pH values where α approaches a value of 1 and the stretched polymer is essentially charged as shown

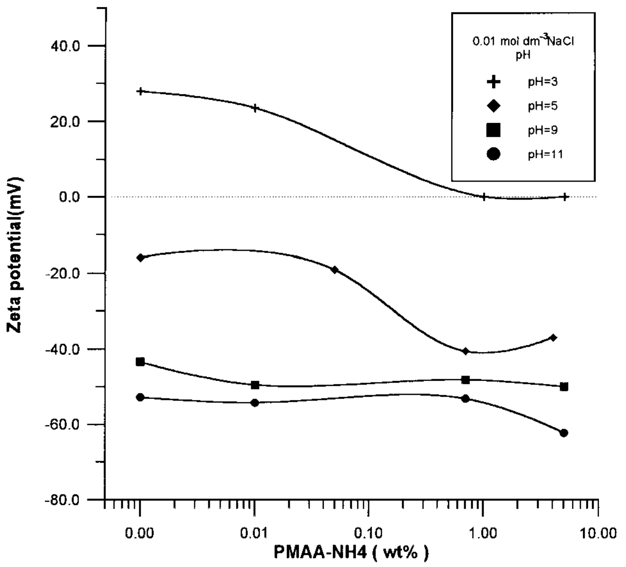

Fig. 4. Effect of PMAA–NH$_4$ concentration on the zeta potential of TiN suspension at pH = 3, 5, 9,11, respectively.

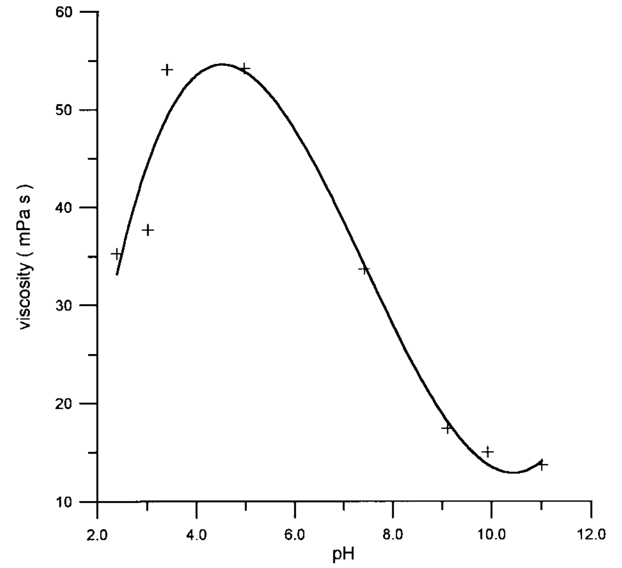

Fig. 5. Effect of pH on the viscosity under a steady shear rate (100 s^{-1}) for 10 vol % TiN suspension in the pH range 2·4–11.

for pH = 9~11 in Fig. 1. The weak interaction revealed by this electro-kinetic curve is attributed to the mutual repulsion between the highly ionized PMAA–NH$_4$ and negative charged particle surface.

3.3 Rheological properties of titanium nitride using PMAA–NH$_4$ at various pH value

The surface charge on the particles is also reflected in the rheological behavior as Figs 5 and 6 show the dependence of viscosity on shear rate for 10 vol% titanium nitride slurries without PMAA–NH$_4$. The suspension formed in the range of pH (= 9·9~11) has nearly Newtonian flow, i.e. the viscosity is independent of shear rate up to the limit of instrument resolution. In this range, there is a strong electric double-layer repulsion between the titanium nitride particles which inhibits agglomeration. Suspensions formed in the range of pH (= 3·4~5) with no surfactant exhibit a viscosity maximum at any shear rate, and viscosity decreases ('shear thinning') with increasing shear rate. No repulsive forces exist in the pH range near the iso-electric point (Fig. 3), and the large attractive van der Waals force produces an attractive, touching particle, network. Michaels and Bolger,[31], Firth and Hunter[32,33] and Hoffman[34] describe a number of mechanisms to explain the viscosity of particulate slurries. When the network is sheared, it breaks into agglomerates that decreases in size with increasing shear rate. The liquid within each agglomerate is relatively immobile since it must flow with the agglomerates. Based on this model, Firth and Hunter[32,33] explained that the decrease in viscosity with increasing shear rate was a result of the increasing liquid volume released by the agglomerates as they became smaller.

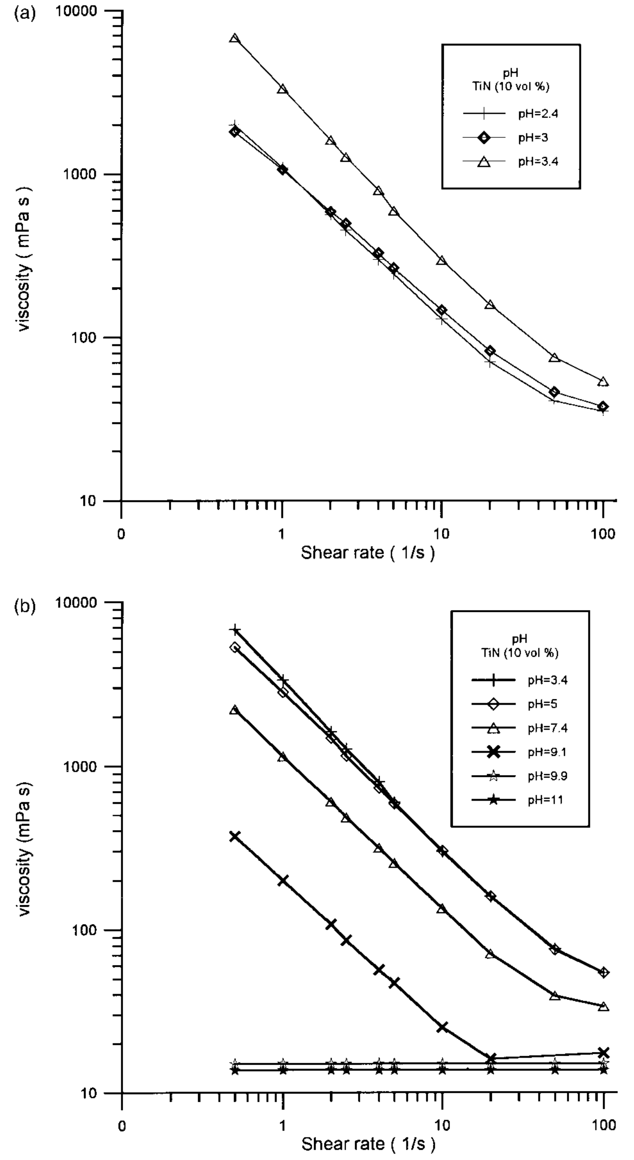

Fig. 6. (a) Effect of pH on the rheology of a 10 vol % aqueous TiN suspension in the pH range 2·4 to 3·4 (b) effect of pH on the rheology of aqueous TiN suspension (10 vol%) in the pH range of 3·4–11.

The rheological behavior of TiN in the presence of PMAA–NH$_4$ is strongly dependent on pH. As shown in Fig. 7 the three pH values chosen for further discussion can well represent the corresponding three characteristic types of rheological behavior of titanium nitride suspensions. The rheology of a titanium nitride suspension as a function of the amount of PMAA–NH$_4$ added at pH = 3 is shown in Fig. 8. The results display an abrupt change from a shear thinning behavior at low additions to Newtonian behavior with a very low viscosity (ν = 15 mPa s) at higher additions of PMAA–NH$_4$.The decrease in viscosity and degree of shear thinning with the addition of more PMAA–NH$_4$ implies that the degree of flocculation decreases.

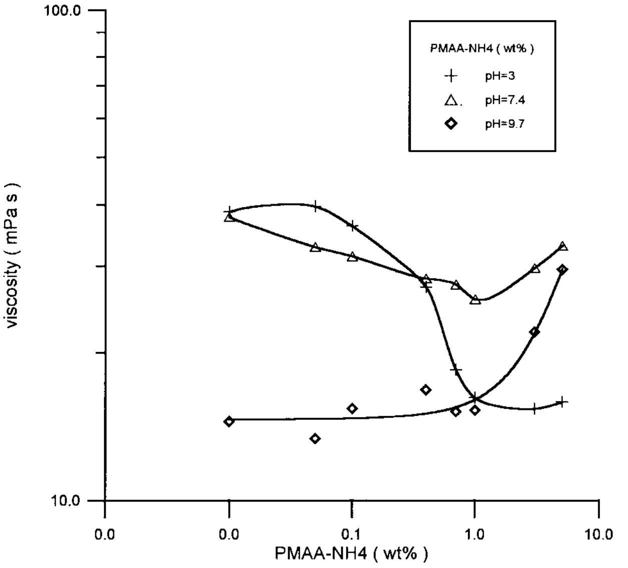

Fig. 7. Effect of PMAA–NH$_4$ concentration on the viscosity under a steady shear rate (100 s^{-1}) for aqueous TiN suspension (10 vol%) at pH = 3, 7·4 and 9·7, respectively.

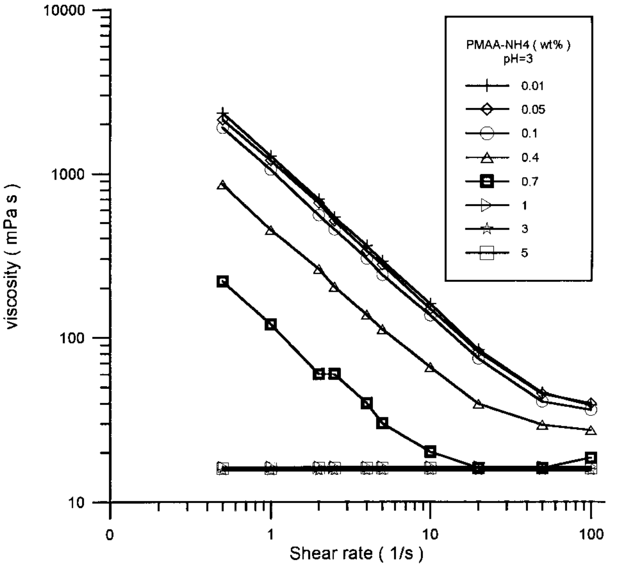

Fig. 8. Effect of PMAA–NH$_4$ concentration on the rheology of aqueous TiN suspension (10 vol%) in the range of 0·01 to 5 wt% at pH = 3.

At a critical addition of dispersant the viscosity is at a minimum and the suspension becomes Newtonian, implying the suspension is now colloidal stable. Examination of the results presented in Figs 4 and 8 reflects that at pH = 3, a lower α value (Fig. 1), the polyelectrolyte is constant with those for simple organic acids which only have one acid group. In this condition the polyelectrolyte chains are insoluble and unstable. The amount of PMAA–NH$_4$ required for mono-layer coverage from the zeta potential measurements using electrokinetics correlate very well with the amount required for reaching the minimum in viscosity. It reflects that minimum viscosity occurs at mono-layer coverage of the polyelectrolyte on the particles, which corresponds to no charged polyelectrolyte-coated particles. This implies that no electric repulsive forces exist in the presence of PMAA–NH$_4$ and in acidic

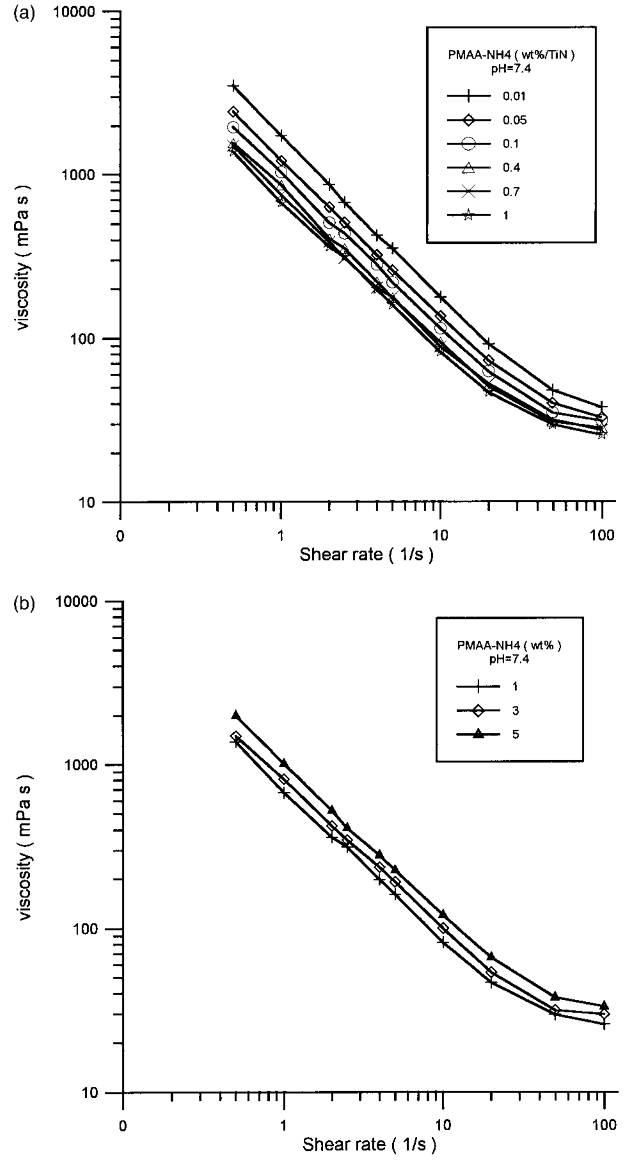

Fig. 9. (a) Effect of PMAA–NH$_4$ concentration on the rheology of aqueous TiN suspension (10 vol%) in the range of 0·01 to 1 wt% at pH = 7·4 (b) effect of PMAA–NH$_4$ concentration on the rheology of aqueous TiN suspension (10 vol%) in the range of 1 to 5 wt% at pH = 7·4.

pH range the steric repulsion of PMAA–NH$_4$ has a positive contribution to the dispersion.

Figure 9(a) and (b) show the effect of the amount of PMAA–NH$_4$ on the rheological properties of 10 vol% titanium nitride suspensions at pH = 7·4. The initial additions of PMAA–NH$_4$ [Fig. 9(a)] result in a further decrease in viscosity and shear-thinning flow behavior. This is also indicated by decreased yield stress values as the amount of polymer dosage from zero to 1 wt%. With further PMAA–NH$_4$ addition, the trend observed in Fig. 9(b) is reversed. Relative viscosities increase and suspensions become more shear thinning as the amount increases above 1 wt%. Examination of the results presented in Figs 3 and 9 shows a decrease in degree of flocculation decreases with an increase in the zeta potential (i.e. became more negative) except for very high concentrations. However, at this pH value, PMAA–NH$_4$ interactions with the particle surface resulted in a complex array of suspension effects including electrosteric stabilization and polymer-bridging flocculation. Figure 10 shows the effects of the amount of PMAA–NH$_4$ on the rheological properties of 10 vol% suspensions at pH = 9·7. This implies that the suspension is a colloid stable at a critical addition of PMAA–NH$_4$. With further PMAA–NH$_4$ addition, it reflects a transition from stabilization to flocculation. As shown for pH = 9·7 in Fig. 1, at strongly alkaline pH values α approaches a value of 1. The weak interaction revealed in Fig. 4 suggests that the electro-kinetic curve is attributed to the mutual repulsion between the highly ionized PMAA–NH$_4$ and negatively charged particle surface. In this alkaline pH range, non-adsorbed PMAA is appreciably present in solution, and dispersion properties of the titanium nitride suspension with the presence of PMAA–NH$_4$ were basically dominated by the surface (interfacial) charge primarily between the titanium nitride particles.

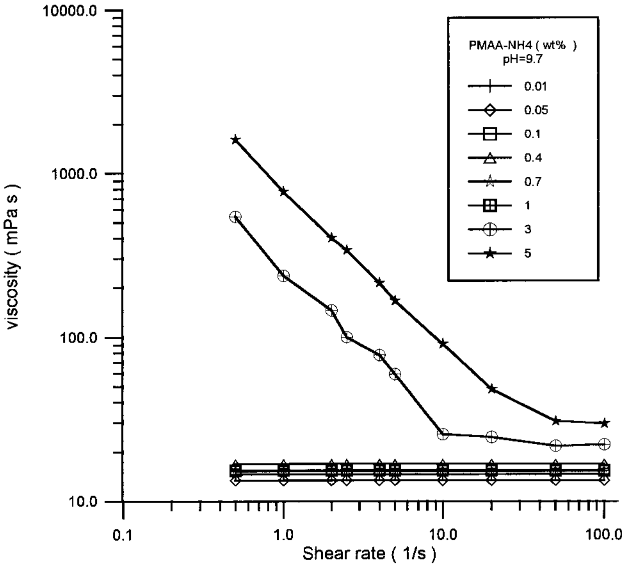

Fig. 10. Effect of PMAA–NH$_4$ concentration on the rheology of aqueous TiN suspension (10 vol%) in the range of 0·01 to 5 wt% at pH = 9·7.

4 Conclusions

Based on the above experimental results and discussion, the following conclusion can be drawn. Characterization of the stabilization of aqueous titanium nitride suspensions with the ammonium salt of poly(methacrylic acid) at various pH values was conducted in order to understand the basic mechanisms of dispersion.

1. Zeta potential studies show that the isoelectric point of the TiN used is at pH = 4 and PMAA–NH$_4$ addition results in a more negative zeta potential value in the pH range of 3 to 11. The surface charge of TiN in the presence of PMAA–NH$_4$ is strongly dependent on pH and shows that for pH = 3~5 the PMAA–NH$_4$ addition results in a more negative zeta potential than pH = 9~11.
2. The rheological behavior of TiN in the presence of PMAA–NH$_4$ is strongly dependent on pH, three characteristic types may be defined.

   i. The rheology as a function of the amount PMAA–NH$_4$ added at pH = 3 shows an abrupt change from shear thinning at low additions to Newtonian behavior with a very low viscosity (η = 15 mPa s) at higher additions. Examination of the results show a transition from polymer-bridging to steric stabilization and in acidic pH range the steric repulsion of PMAA–NH$_4$ has a positive contribution on the dispersion.
   ii. The rheology of a titanium nitride suspension as a function of the amount PMAA–NH$_4$ at pH = 7·4 shows that the initial additions of PMAA–NH$_4$ result in a further decrease in viscosity and shear-thinning flow behavior. This is also indicated by decreased viscosity as the amount of polymer dosage increases from zero to 1 wt%. With further PMAA–NH$_4$ addition, the trend observed is reversed. Relative viscosities increase and suspensions become more shear thinning as the amount increases above 1 wt%.
   iii. Studies of the effect of the amount of PMAA–NH$_4$ on the rheology of 10 vol% titanium nitride suspensions at pH = 9·7 show that the suspension is deflocculated at a critical addition of PMAA–NH$_4$. With further PMAA–NH$_4$ addition, a transition from stabilization to flocculation occurs. In this alkaline pH range, non-adsorbed PMAA is appreciably present in solution, and dispersion properties of the titanium nitride suspension with the presence of PMAA–NH$_4$ were basically dominated by the surface (interfacial) charge primarily between the titanium nitride particles.

References

1. Jang, H. M., Moon, J. H. and Jang, C. W., Homogeneous fabrication of Al_2O_3–ZrO_2–SiC whisker composite by surface-induced coating. *J. Am. Ceram. Soc.*, 1992, **75**, 3369–3376.
2. Lim, B. C. and Jang, H. M., Homogeneous fabrication and densification of cordierite–zirconia composite by a mixed colloidal processing. *J. Am. Ceram. Soc.*, 1993, **76**, 1482–1490.
3. Kimura, T. and Yamaguchi, T., Consolidation of alumina–zirconia mixtures by a colloidal process. *J. Am. Ceram. Soc*, 1991, **74**, 625–632.
4. Werent, J. and Feke, D. L., Effects of solids loading and dispersion schedule on the state of aqueous alumina/zirconia dispersions. *J. Am. Ceram. Soc*, 1994, **77**, 2693–2698.
5. Lee, H. W. and Sacks, M. D., Pressureless sintering of SiC-whisker-reinforced Al_2O_3 composites: I, Effect of matrix powder surface area. *J. Am. Ceram. Soc.*, 1990, **73**, 1884–1893.
6. Lange, F. F., Powder processing science and technology for increased reliability. *J. Am. Ceram. Soc*, 1989, **72**, 3–15.
7. Aksay, I. A., Microstructure control through colloidal consolidation. In *Advances in Ceramics*, Vol. 9, *Forming of Ceramics*, ed. J. A. Mangels and G. L. Messing. American Ceramic Society, Columbus, 1984, pp. 94–104.
8. Pugh, R. J., Dispersion and stability of ceramic powders in liquids.. In *Surface and Colloid Chemistry in Advanced Ceramic Processing*, ed. R. J. Pugh and L. Bergstrom. Marcel Dekker, New York, 1994, pp. 127–192.
9. Cesarano III, J., Aksay, I. A. and Blier, A., Stability of aqueous αAl_2O_3 suspensions with poly(methacrylic acid) polyelectrolye. *J. Am. Ceram. Soc.*, 1988, **71**, 250–255.
10. Cesarano III, J. and Aksay, I. A., Processing of highly concentrated aqueous α-alumina suspensions stabilized with polyelectrolte. *J. Am. Ceram. Soc.*, 1988, **71**, 1062–1067.
11. Gebhardt, J. E. and Fuerstenau, D. W., Adsorption of polyacrylic acid at oxide/water interfaces. *Colloids and Surface.*, 1983, **7**, 221–231.
12. Foissy, A., Attar, A. and Lamarche, J. M., Adsorption of polyacrylic acid on titanium dioxide. *J. Colloid. Int. Sci.*, 1983, **96**, 275–287.
13. Hackley, V. A., Premachandran, R. and Malghan, S. G., Surface chemical interactions of Si_3N_4 with polyelectrolyte deflocculants. *Key Engineering Materials*, 1994, **89-91**, 679–682.
14. Liu, D. and Malghan, S. G., Role of polyacrylate in modifying interfacial properties and stability of silicon nitride particles in aqueous suspensions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1996, **110**, 37–45.
15. Premachandran, Pradip, R. S. and Malghan, S. G., Electrokinetic behaviour and dispersion characteristics of ceramic powders with cationic and anionic polyelectrolytes. *Bulletin of Materials Science*, 1994, **17**, 911–920.
16. Lum, L.-S. H., Malghan, S. G. and Schiller, S. B., Standard reference materials for particle size analysis of ceramic powders by gravity sedimentation. *Powder Technology*, 1996, **87**, 233–238.
17. Malghan, S. G., Hackley, V. A. and Wang, P. S., Intelligent processing of ceramic powders and slurries. *Ceramic Engineering and Science Proceedings*, 1994, **154**, 527–535.
18. Hackley, V. A., Colloidal processing of silicon nitride with poly(acrylic acid): I, adsorption and electrostatic interactions. *J. Am. Ceram. Soc*, 1997, **80**, 2315–2325.
19. Hackley, V. A. and Malghan, S. G., Surface chemistry of silicon nitride powder in the presence of dissolved ions. *Journal of Materials Science*, 1994, **29**, 4420–4430.
20. Malghan, S. G., Silicon nitride powders and their processing. *Key Engineering Materials*, 1991, **56–57**, 243–264.
21. Shih, C. C. and Hon, M. H., Stabilization of aqueous Si3N4 suspensions with ammonium salt of poly(acrylic acid) at various pH. *Materials Chemistry and Physics*, 1998, **57**, 125–133.
22. Arnold, R. and Overbeek, J.Th.G., The dissociation and specific viscosity of polymethacrylic acid. *Rec. J. R. Neth. Chem. Soc*, 1950, **69**, 192–206.
23. Hunter, R. J., Applications of the zeta potential. In *Zeta Potential in Colloid Science–Principles, Applications*, ed. R. J. Hunter. Academic Press, London, 1981, pp. 219–257.
24. Bergstrom, L. and Bostedt, E., Surface chemistry of silicon nitride powders: electrokinetic behaviour and ESCA studies. *Colloids and Surface*, 1990, **49**, 183–197.
25. Leyte, J. C. and Mandel, M., Potentiometric behavior of polymethacrylic acid. *J. Polym. Sci. PartA: Polym. Chem.*, 1964, **2**, 1879–1891.
26. Mandel, M., Leyte, J. C. and Stadhouder, M. G., The conformational transition of poly(methacrylic acid) in solution. *J. Phys. Chem*, 1967, **71**, 603–612.
27. Mathieson, A. R. and McLaren, J. V., Potentiometric study of the conformation transition in poly(acrylic acid). *J. Polym. Sci. PartA: Polym. Chem.*, 1965, **3**, 2555–2565.
28. Wada, A., Helix-coil transformation and titration curve of poly-l-glutamic acid. *Mol. Phys.*, 1960, **3**, 409–416.
29. Nass, R., Albayrak, S., Aslan, M. and Schmidt, H., Colloidal processing and sintering of nano-scale TiN. In *Ceramic Processing Science and Technology, Proceedings of the Fifth International Conference on Ceramic Processing Science and Technology*, ed. H. Hausner, G. L. Messing and S. I. Hirano. Friedrichafen, Germany, 1994, pp. 591–595.
30. Bohmer, M. R., Evers, O. A. and Scheutjens, J. M. H. M., Weak poly-electrolytes between two surfaces: adsorption and stabilization. *Macromolecules*, 1990, **23**, 2288–2301.
31. Michaels, A. S. and Bolger, J. C., The plastic flow behavior of flocculated kaolin suspensions. *Ind. Eng. Chem. Fundam*, 1962, **1**, 153–162.
32. Firth, B. A. and Hunter, R. J., Flow properties of coagulated colloidal suspensions, I. Energy dissipation in the flow units. *J. Colloid Interface Sci.*, 1976, **57**, 248–256.
33. Firth, B. A. and Hunter, R. J., Flow properties of coagulated colloidal suspensions, III. The elastic floc model. *J. Colloid Interface Sci*, 1976, **57**, 266–275.
34. Hoffman, R. L., Rheology of concentrated latexes and dispersions. In *Science and Technology of Polymer Colloids*, Vol. 2, Series E, No. 68, ed. G. W. Poehlein, R. H. Ottewill, and J. W. Goodwin. Nishoff, Boston, MA, 1983.