ELSEVIER

Ceramics International 30 (2004) 1985–1988

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Dispersion of barium titanate with poly(acrylic acid-co-maleic acid) in aqueous media

Jianling Zhao*, Xiaohui Wang, Zhilun Gui, Longtu Li

Department of Materials Science and Engineering, State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, PR China

Received 22 November 2003; received in revised form 29 November 2003; accepted 23 December 2003

Available online 25 June 2004

Abstract

Dispersing effect of poly(acrylic acid-co-maleic acid) in barium titanate aqueous suspension was studied by means of zeta potential, sediment experiments, rheological behavior, and size analysis etc. Rheological and sediment behavior of the barium titanate was measured as a function of pH and dispersant concentration. Viscosity decreased along with the addition of poly(acrylic acid-co-maleic acid) before its concentration reaching 0.3 wt.%. After that viscosity changed slowly which indicated a saturated adsorption of poly(acrylic acid-co-maleic acid) onto barium titanate. BT suspension without dispersant was badly dispersed with D50 of 3.020 while D50 of BT suspension with poly(acrylic acid-co-maleic acid) was 0.176. As a result, poly(acrylic acid-co-maleic acid) is a potential effective dispersant that can be used in BT aqueous suspension.

Keywords: D. Barium titanate; Dispersant; Rheological behavior; Poly(acrylic acid-co-maleic acid)

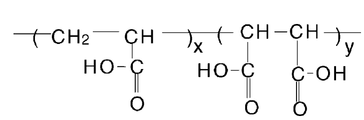
1. Introduction

Tape-casting is a well-established technique used for large-scale fabrication of ceramic substrates and multi-layered structures which involves wet processing of micrometer-sized ceramic particle suspensions to produce green sheets with high packing densities and uniform microstructure. Well-dispersed slurry is the key factor in tape-casting. Dispersing BT powders into organic media, such as toluene, *n*-hexane, acetone, and benzaldehyde has been studied in detail to get well-stabilized suspensions [1,2]. At present many manufacturers are producing BT tapes by this way. In recent years, the environment and health aspects of the tape casting process have received special attention. Use of aqueous media instead of organic solvent is desirable now-a-days due to obvious reasons such as economic and environmental considerations. There are many kinds of dispersants that can be used as dispersants in aqueous media including polyacrylic acid, polyvinyl alcohol, and ammonium citrate [3–8]. But there is little report on the dispersing effect of poly(acrylic acid-co-maleic acid). It was found in our study that poly(acrylic acid-co-maleic acid) was a potential dispersant in aqueous media.

2. Experimental

2.1. Raw materials

$BaTiO_3$ powder (Guoteng Limited Corporation of Functional Ceramics, Shandong, China) with an average particle size of 100 nm, a specific surface area of 8.19 $m^2\,g^{-1}$ (Quantachrome NOVA Automated Gas Sorption System, Quantachrome Instruments Corporation) and a Ba/Ti ratio of 1.000 ± 0.002 was used as-received form. Structural formula of poly(acrylic acid-co-maleic acid) was shown as follows:



Deionized water was used as solvent to prepare BT suspensions and the pH was adjusted via addition of HCl and $NH_3{\cdot}H_2O$.

* Corresponding author. Tel.: +86-10-62784579; fax: +86-10-62771160.

E-mail address: zhaojl02@mails.tsinghua.edu.cn (J. Zhao).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.12.177

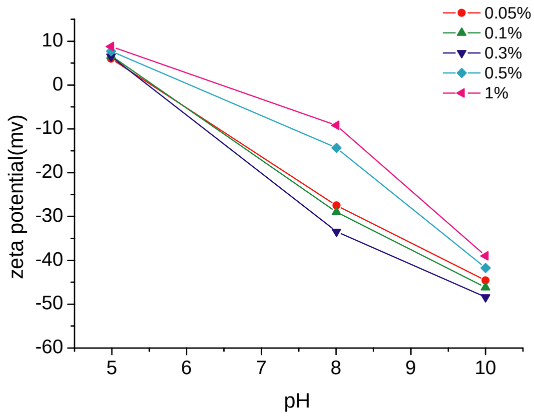


Fig. 1. Zeta potential at different pH value and different concentration.

2.2. Experimental method

In the sediment experiment, 10 wt.% BT suspensions with different dispersant concentration and different pH value were prepared in 10 ml graduated cylinders. After ultrasonic dispersing the suspension were left untouched. Supernatant volumes were taken down at fixed intervals. The supernatant liquids were also used to determine their zeta potential. 60 wt.% BT suspensions with different dispersant concentration and different pH value were prepared in plastic bottle and ball-milled for the rheology experiment. Zeta potential was determined by zetaplus, Zeta Potential Analyzer (Brookhaven Instruments Corporation, USA).The rheological behaviors of BT suspensions at different conditions were studied using Modular Compact Rheometer (PHYSICA MCR300, Physica, Germany). Particle size distributions of BT suspension were measured with BI-XDC Sizing Analyzer (Brookhaven Instruments Corporation).

3. Results and discussion

3.1. Zeta potential

Results of zeta potential at different dispersant concentration and different pH value were shown in Fig. 1. At the same

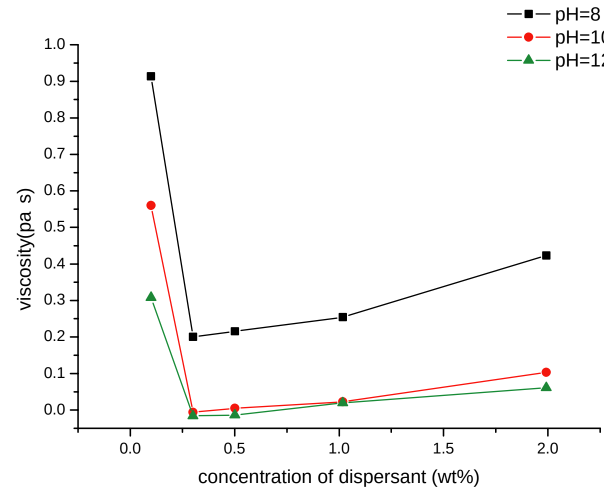


Fig. 3. Effect of dispersant concentration and pH value on suspension viscosity.

concentration of poly(acrylic acid-co-maleic acid), zeta potential decreased along with the increase of pH. It was due to the unbalanced adsorption of H^+ and OH^- by BT particles. Similarly zeta potential decreased along with the addition of poly(acrylic acid-co-maleic acid) before its concentration reaching 0.3 wt.%. Poly(acrylic acid-co-maleic acid) was anionic surfactant and would dissociated at higher pH and be adsorbed onto particle through electrostatic and intermolecular force. When dispersant concentration was over 0.3 wt.%, adsorption equilibrium of dispersant onto BT was reached and zeta potential decreased slightly with the addition of poly(acrylic acid-co-maleic acid).When dispersant concentration was over 0.5%, zeta potential increased abnormally. This phenomena was probably caused by excess dispersant in free state which might interconnected with dispersants adsorbed onto BT particles and refrained their directional motion in the electric field.

3.2. Sediment experiment

Results of sediment experiment at different dispersant concentration and different pH value were shown in Fig. 2.

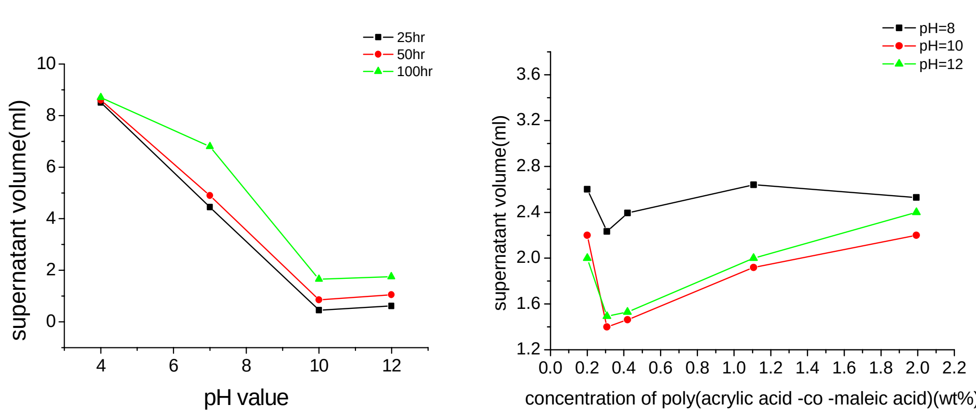
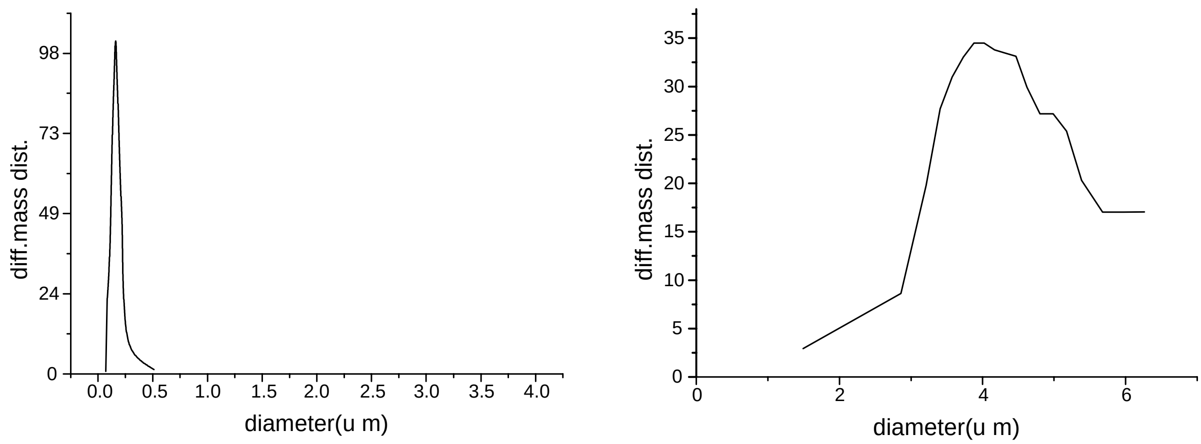


Fig. 2. Results of sediment experiments.



a. 0.3wt% poly (acrylic acid-co-maleic acid)

b. without dispersant

Fig. 4. Differential distribution curves with and without poly(acrylic acid-co-maleic acid) acid.

From the results of sediment experiments, it could be concluded that pH value played the most important role in suspension stabilization. When pH value was below 7, poly(acrylic acid-co-maleic acid) did not add any favorable contribution to the stability of the suspension. When pH was above 7, suspensions with dispersants were more stable than those with no dispersants. Because dispersants used in this experiment are anionic surfactant, dissociation becomes more complete when pH increases. This means dispersants adsorbed on the ceramic particles stretch and repel to form stable suspension by both the electrostatic and steric mechanism. When pH value was 10, the best dispersing effects were reached as could be found in Fig. 2. Similarly dispersant concentration was also a key factor for stable suspension. As it was shown in Fig. 2 supernatant volume decreased along with the addition of poly(acrylic acid-co-maleic acid) and reached its minimum when the dispersant concentration was 0.3 wt.%.

3.3. Rheological behavior

Fig. 3 showed the effect of dispersant concentration and pH value on suspension viscosity. As it could be concluded from Fig. 3 viscosity of $BaTiO_3$ suspension decreased at low dispersant concentration and reached a minimum at 0.3 wt.%. More dispersant adsorbed on to the BT surface along with the increase of dispersant concentration at the beginning that resulted in the decrease of viscosity. It reached a saturated adsorption at the concentration of 0.3 wt.%. After that too much dispersants might cause a slight increase of viscosity due to tangled chain of the polyelectrolytes.

3.4. Particle size distribution

Optimum conditions drawn from the above experiments were applied to prepare suspensions to study the particle size distribution in order to get a direct view of dispersing effects of these dispersants. The results were shown in Fig. 4. BT suspension without dispersant was badly dispersed with D50 of 3.020 while D50 of BT suspension with poly(acrylic acid-co-maleic acid) was 0.176. As a result, poly(acrylic acid-co-maleic acid) is a potential effective dispersant that can be used in BT aqueous suspension.

4. Summary

The effect of poly(acrylic acid-co-maleic acid) on the dispersion of barium titanate in aqueous media was investigated through zeta potential, sediment experiments, rheological behavior, and size analysis etc. Rheological and sediment behavior of the barium titanate was measured as a function of pH and dispersant concentration. Optimum conditions drawn from the above experiments were applied to prepare suspensions to study the particle size distribution in order to get a direct view of its dispersing effects. BT suspension without dispersant was badly dispersed with D50 of 3.020 while D50 of BT suspension with poly(acrylic acid-co-maleic acid) was 0.176. As a result, poly(acrylic acid-co-maleic acid) is a potential effective dispersant that can be used in BT aqueous suspension.

Acknowledgements

This work was supported by the High Technology Research and Development Project, China under grant no. 863-2001AA325010 and the Ministry of Sciences and Technology of China through 973-Project under grant no. 2002CB613301.

References

[1] B.I. Lee, Chemical variation in barium titanate powders and dispersants, J. Electroceram. 3 (1) (1999) 53–63.

[2] N.L. Bars, P. Levitz, A. Messier, Deagglomeration and dispersion of barium titanate and alumnia powders in an organic medium, J. Colloid Interf. Sci. 75 (1995) 400–410.
[3] M.C. Blanco, B.R. Lopez, F.L. Riley, The properties of aqueous phase suspensions of barium titanate, J. Eur. Ceram. Soc. 17 (1997) 281–287.
[4] C.-C. Li, J.-H. Jean, Interactions between dissolved $Ba^{2+}$and PAA–NH_4 dispersant in aqueous barium titanate suspensions, J. Am. Ceram. Soc. 85 (6) (2002) 1449–1455.
[5] J.-H. Jean, H.-R. Wang, Dispersion of aqueous barium titanate suspensions with ammonium salt of poly(methacrylic acid), J. Am. Ceram. Soc. 81 (6) (1998) 1588–1599.
[6] A.W.M. De Laat, A.W. de Bruijn, G.L.T. Van den Heuvel, The adsorption of polyvinyl alcohols with caboxylate groups on $BaTiO_3$, Colloids Surf. A 82 (1994) 99–110.
[7] X.Y. Wang, S.W. Lu, B.I. Burtrand, et al., Dispersion and aging behavior of $BaTiO_3$ and PZT in water, Mater. Res. Bull. 35 (2000) 2555–2563.
[8] X. Wang, B.I. Lee, L. Mann, Dispersion of barium titanate with polyaspartic acid in aqueous media, Colloids Surf. A: Physicochem. Eng. Aspects 202 (2002) 71–80.