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# Effect of TMAH on rheological behavior of SiC aqueous suspension

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## Abstract

Tetramethyl ammonium hydroxide (TMAH) was used as dispersant for SiC aqueous suspension. The effects of dispersant concentration and pH on the rheological behavior of SiC aqueous suspension were studied. TMAH improves dispersion by increasing the negative zeta potential of SiC particles. The recommended amount of TMAH is 0.6 wt.% in order to obtain the minimum viscosity and the maximum negative zeta potential. The optimum dispersion occurs at pH 10. The dispersion mechanism by TMAH is discussed.

*Keywords:* Suspensions; Dispersion; Zeta potential; Grain size; SiC

## 1. Introduction

Silicon carbide is currently used in a number of industrial applications, such as heat engines, gas turbines and high temperature energy conversion systems, due to its high hardness and strength retention at elevated temperatures, good thermal stress resistance and excellent wear and oxidation resistances. At the same time, its excellent combination of the thermal properties (low coefficient of thermal expansion, high thermal conductivity), availability and cost have also made it an arresting class of candidate as reinforcement for high volume fraction metal matrix composites (MMCs).[1]

However, an important aspect of fabrication sequence, which can improve subsequent sintering and final properties of bodies, is obtaining a homogenous structure and good packing of powders at the consolidation stage of the green body. Increasing attention is, therefore, directed on the colloidal processing method, which may result in a more homogenous green microstructure.[2–4] In all of the processing stages preceding firing, a basic step is the control of the rheological behavior of ceramic suspensions.[5] In order to disperse a powder in water, the surface charge properties of the powder have to be controlled.[6] Aqueous ceramic suspensions are dispersed either by adjusting the pH of the slurry away from the $\mathrm{pH_{iep}}$ of the powder (electrostatic stabilization) or by using polyelectrolytes as dispersing agents (electrosteric stabilization).[7] When electrostatic stabilization is used, the pH range in which the particles have a high surface charge has to be known. Steric or electrosteric stabilization requires strongly attached and dense layers of polymer or polyelectrolyte on the powder surfaces. However, powder dispersion characteristics and the flow properties of the resulting suspensions are controlled by the powder surface charge, which varies with the type of powder and even with their sources. Due to this surface property variation it is often necessary to use a specific pH or a certain dispersing agent for each individual powder. Identification of a common pH or dispersing agent becomes difficult especially when different types of powders with different surface properties are used for preparing composite powder suspensions.

A number of studies on colloidal processing of SiC are available. Huang et al.[8] found that the surface modification drastically improved the dispersibility of SiC suspensions. Yang et al.[9] showed that the gelation, consolidation and rheological properties of SiC powder were improved by a boehmite surface layer. Liu et al.[10] studied a dispersant but did not indicate its component. Zhu et al.[11] studied briefly the dispersion of SiC nanoparticles using PEI as dispersant. Little work has been reported on achieving effective stabilization of SiC in an aqueous medium by a simple dispersant control.

In the present work, TMAH was used as dispersant. The purpose of this work is to study the dispersion mechanism of TMAH in aqueous SiC suspension. The effect of dispersant content on rheological behavior (like rheology,

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viscosity and zeta potential) of SiC aqueous suspension was also studied in order to optimize the use of dispersant. The effect of pH on rheological behavior of SiC aqueous suspension was investigated.

## 2. Experimental procedure

β-SiC powders, manufactured by Grinding Wheel Plant, Shenyang, China, were used in this work. Fig. 1 shows the grain size distribution of SiC powders. It can be seen that the grain size distribution shows a bimodal distribution. The thin particles have a larger relative content. SEM observation (Philips SEM 515, Philips Corp., Holland) indicated that the shape of particles was irregular polyhedron. The specific surface area of the powder was measured by a single point BET method (Masterisizer 2000, Malvern Instrument Ltd., UK) to be 6.547 m$^2$/g and the $d_{(0.1)}$, $d_{(0.5)}$ and $d_{(0.9)}$ are 0.366, 1.627 and 3.896 μm, respectively. Chemical composition of the powder from the dealer is given in Table 1. TMAH (Shanghai Chemical Plant, China) were used as dispersant. The pH value of the suspensions was adjusted using HCl.

A series of suspensions containing a certain amount of SiC powders, deionized water and 0.1–0.8 wt.% of TMAH dispersant (based on the weight of SiC powder) were mixed. The suspensions were then blended thoroughly by ball milling for 8 h using SiC spherical grinding media. The suspension was poured into a plastic columned mold with an inner diameter of 15 mm and a height of 3 mm to form a cast compact. For the purpose of uniform casting, the inner wall of the mold was lubricated with silicone grease. After oven-drying at 120 °C for two days, the green density of the compact was measured.

A strain-controlled rheometer (4ARES-9a, Rheometric Scientific, USA) was used to measure the rheological properties of the SiC suspensions at room temperature. Couette (cup diameter: 36.8 mm, bob diameter: 35.0 mm, bob length: 37.37 mm) was used for all these measurements. The samples were protected from drying by adding a thin layer of paraffin oil on top. To avoid undesired influence from different mechanical histories, fresh samples were homogenized by pre-shearing at an identical rate of 100 s$^{-1}$ for 1 min and left standing for an additional 2 min prior to measurement. Steady rate sweep measurement was used to characterize the general flow behavior with shear rates ranging from $10^{-2}$ to 500 s$^{-1}$. Zeta potential measurements were performed on BI-ZetaPlus (Brookhaven Instruments Corp., USA) which uses the Doppler shift resulting from laser light scatter from the particles to obtain a mobility spectrum. The microstructure of the green body was characterized using a S-450 scanning electron microscope (Hitachi Corporation, Japan).

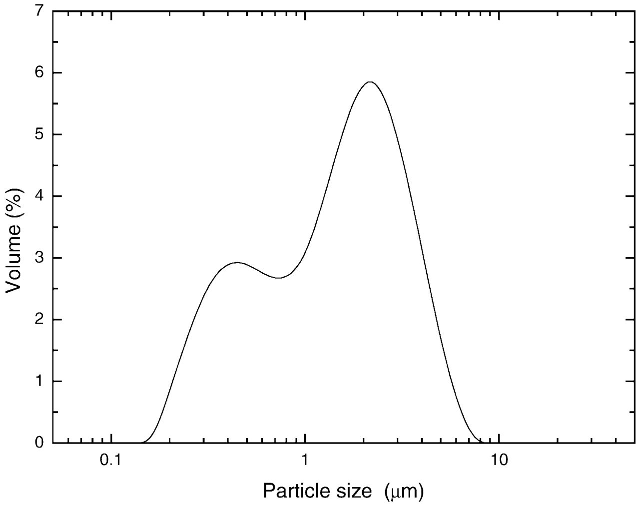


Fig. 1. Particle size distribution of SiC powder.

## 3. Results

Dispersants are added in slurries to improve the dispersibility of ceramic powders. For ceramic slurries, there is a relationship between stability and zeta potential of ceramic powders. Powders with high zeta potential (absolute value) usually exhibit higher stability in slurries than powders with low zeta potential do.[12] Accordingly, the stability of slurries can be characterized by testing the zeta potential of powders in slurries.

The testing results of the zeta potential of SiC powders varied with pH values in slurries are shown in Fig. 2. As can be seen, all the curves show analogous electrophoretic behavior in aqueous media. The isoelectric point (IEP) of as-received SiC powders is 2.5. It is in agreement with the IEP data already reported.[13] With the increasing of pH, a steep increase is observed for the zeta potential. The absolute value of zeta potential reaches the maximum at pH value of about 10. When TMAH is added, the IEP is displaced towards acidic direction. But the maximum of slurries containing 0.3 wt.% and 0.6 wt.% dispersant are 53.3 and 63.6 mV at pH value of about 10, respectively. Compared with the zeta potential of SiC without dispersant, the absolute value of maximum increased with 11.7 and 22 mV, respectively. At pH > 10, the zeta potential decreased with the increasing of pH for all samples.

Table 1
Chemical composition (wt.%) of SiC powder

| SiC | Free Carbon | Oxygen | Calcium | Aluminum | Magnesium | Iron | Sodium |
|---|---|---|---|---|---|---|---|
| 98 | 0.2 | 0.9 | 0.05 | 0.05 | 0.04 | 0.04 | 0.03 |

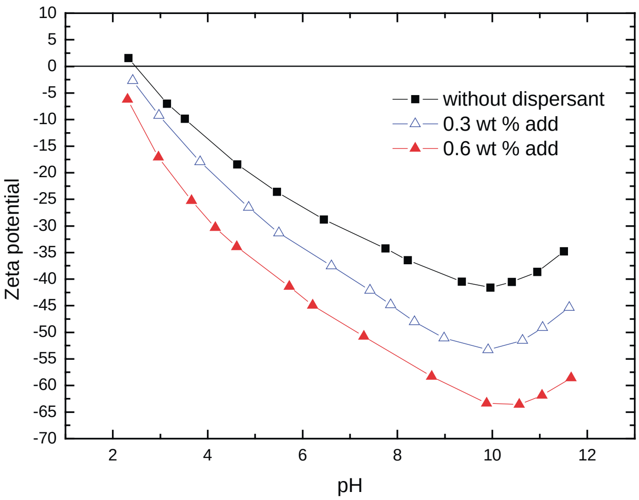


Fig. 2. Comparison of zeta potential vs. pH for adding different dispersant.

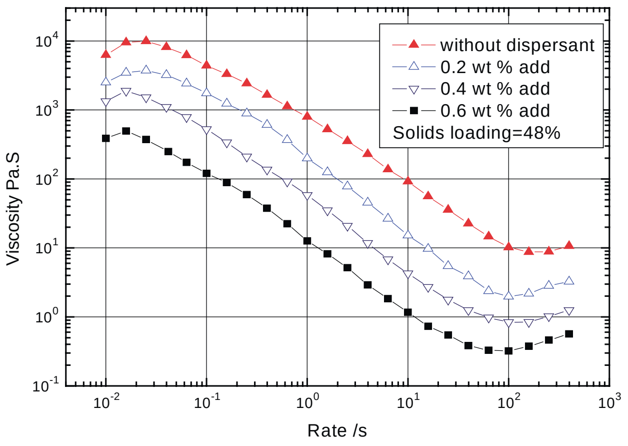


Fig. 4. Comparison of viscosity for adding different dispersant.

The influence of pH value on rheological property of suspension is very important and a suitable pH value is helpful for enhancing the solids loading of slurry.[14] To identify the optimum pH value for stable slurries, the pH value is adjusted to review the variation of viscosity of the suspension. Fig. 3 shows the testing results of viscosity of SiC suspension at different pH values. Lower viscosities are observed in the pH range 9.5–10 with a minimum at pH value of 9.8. According to the results of zeta potential versus pH, the pH value was adjusted to about 10 in the following experiments.

The change in zeta potential indicates strong differences in interparticale forces, from adhesive at the IEP to strongly repulsive at lower and higher pH values, respectively. Their influence on the rheological behavior of the SiC suspension was analyzed by viscosity measurements. Fig. 4 shows the viscosity as a function of shear rate with different dispersant contents. It can be observed that the rheological properties of the suspensions are strongly dependent on the amount of the dispersant added. The suspension with 0.6 wt.% dispersant addition has the lowest viscosity. Fig. 5 shows the viscosity of SiC suspension as a function of dispersant content with different solid loadings. The lowest viscosity can be obtained at the amount of 0.6 wt.% no matter of the solids loading in suspension. Therefore, 0.6 wt.% of the TMAH seems to be the optimum concentration to disperse the SiC powder, which gives the minimum viscosity value and the maximum zeta potential. This situation should correspond to the maximum coverage of the particles' surface by the dispersant, as proposed by Briscoe et al.[15]

Fig. 6 shows the microstructure of the broken surface of the green bodies cast from suspensions with different dispersant concentrations. Serious agglomeration and large pores exist in the green body prepared from original powder (Fig. 6a). The agglomeration slightly reduced when 0.3 wt.% TMAH was added (Fig. 6b). The above phenomenon indicates that the amount of TMAH is not enough to efficiently disperse the powder. At dispersant content of 0.6 wt.%, a well-defined and more uniform microstructure can be observed (Fig. 6c).

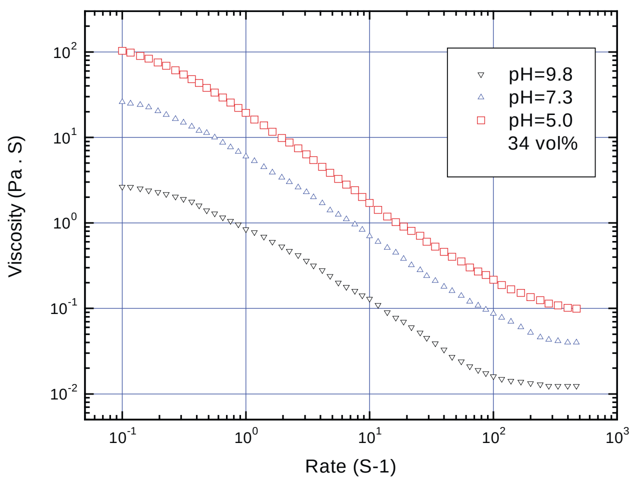


Fig. 3. Viscosity of SiC suspension at different pH.

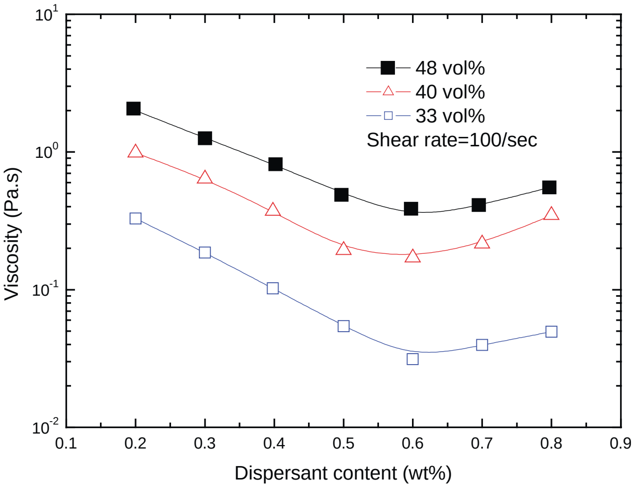


Fig. 5. Viscosity of SiC suspension with different solid loadings.

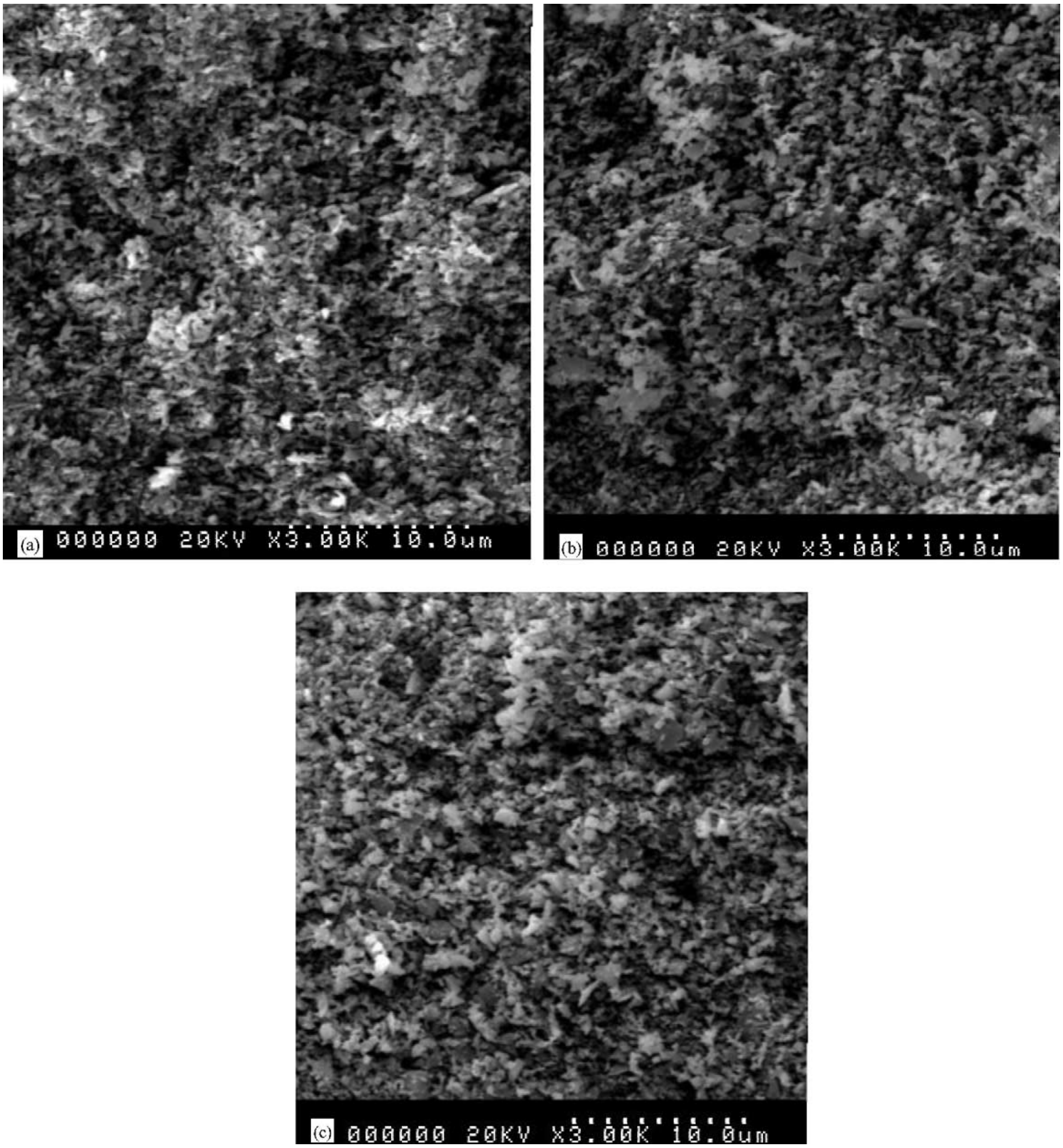


Fig. 6. SEM of the broken surface of the green body prepared at (a) 0, (b) 0.3% and (c) 0.6% dispersant.

It is also found that there is a relationship between the concentration of dispersant and the green density which is shown in Fig. 7. The maximum green density for SiC powder also occurs when the dispersant concentration is about 0.6 wt.%. This value correlates very well with the data obtained through zeta potential and viscosity measurements.

## 4. Discussion

Van der Waals attraction between particles is responsible for holding agglomerates together. In order to enhance colloidal stability, it is necessary to create repulsion force between particles. This repulsion must be at least as strong as, and comparable in range to, the attractive interaction.

It is generally accepted that the SiC powder surface consists of an oxide film and the major functional group on the surface of SiC powder is silanol group.[16] The surface charging of SiC powder in water is attributed to the dissociation of the silanol group according to the following reactions:

$$[\mathrm{SiOH_2}]^+ \xleftarrow{\mathrm{H}^+} [\mathrm{SiOH}] \xrightarrow{\mathrm{OH}^-} [\mathrm{SiO}]^- + \mathrm{H_2O}$$

The addition of TMAH, a strong organic base, can promote the dissociation of the silanol group inducing more negative charge to SiC surface. As a consequence, the maximum of zeta potential tends to increase up to 63.6 mV (with 0.6 wt.% TMAH) at pH value of about 10, decreasing afterwards due to the compressive effect on the electrical double layer by the excess ion remaining in the solution.

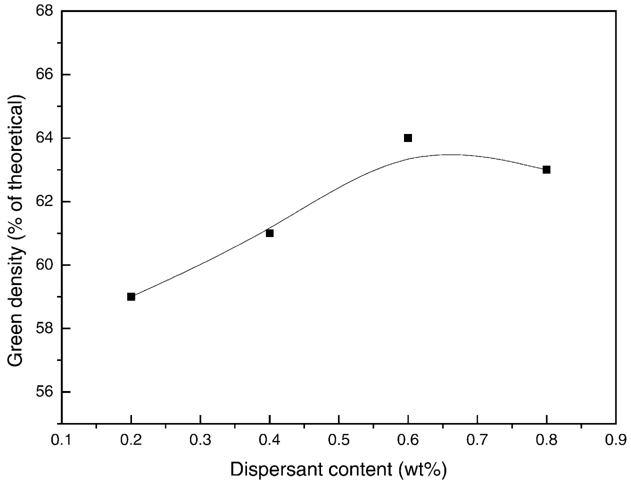
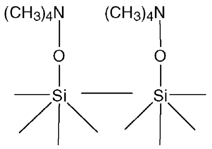


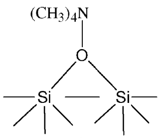
Fig. 7. Green density of SiC as a function of dispersant.

The low molecular weight of the dispersant would result in negligible steric effect on the stabilization of the suspension, suggesting that electrostatic forces would dominate the stabilization in the present situation. Therefore, the intermediate amount of dispersant (0.6 wt.%), with highest zeta potential, should be more favorable for the stabilization of the suspensions than any other concentrations do. The large magnitude of repulsive forces among the suspended particles would decrease the probability of flocculation at this dispersant concentration.[17] These results are in good agreement with other previous reports.[18,19]

When TMAH is added, there is a trend for the electrophoretic curves to shift toward the acidic direction as the amount of dispersant increases. The shifting of the curves in the acidic direction indicates that the organic cation (TMA$^+$) dispersant has been adsorbed onto the particles' surface.[18] The cations can bond with either free surface silanol (1) or siloxane (2).



(1)



(2)

The adsorption of the bulky TMA$^+$ leads to thickening of stern layer resulting in the increase of the electrostatic repulsion potential, which succeedingly leads to a decreased suspension viscosity. Adding further amounts of dispersant would result in an excess of dispersant remaining in the solution, which would exert a detrimental effect on rheology by two mechanisms: (i) acting as a free electrolyte, increasing the ionic strength and thus disturbing the electrostatic force among particles; (ii) forming a bridging effect between separated particles, causing a slightly flocculated suspension.

After the viscosity is lowered through the addition of TMAH, a more stable suspension with less powder agglomeration is formed. Therefore, a better particle packing efficiency[20] and higher greed density are obtained.

## 5. Conclusions

The effects of TMAH on the rheological behavior of SiC aqueous suspension were studied. The results proved that TMAH can increase the zeta potential of SiC suspension. The organic cations TMA$^+$ could be adsorbed onto SiC surface by electrostatic adsorption. The adsorption of the bulky TMA$^+$ leads to the thickening of stern layer and the increasing of electrostatic repulsion potential. Thereby, TMAH can efficiently improve the dispensability of SiC powder and the fluidity of the suspension. The content of dispersant affects the rheological behavior of SiC suspension. The recommended amount of TMAH is 0.6 wt.% of the weight of dry SiC powder. At this content the green density reached a maximum and the lowest viscosity can be obtained no matter of the solids loading in suspension. Further increase of the dispersant will enhance the ion strength of suspension inducing the increase of suspension viscosity.

The dispersion of SiC powders in deionised water was studied in the pH range of 3–12. It is revealed that the stability of SiC suspension in an aqueous medium could be controlled by adjusting the pH of the medium. The optimum dispersion was observed at the pH value of 10, as revealed by the minimum in viscosity and by the maximum in zeta potential for this suspension.

These results demonstrate that the colloidal processing through the control of dispersant content and pH of SiC suspension could be used as a recommended route for obtaining high solid, well dispersed suspension, which will assure the uniform and dense green bodies.

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## References

1. Zweben, C., Advances in composite materials for thermal management in electronic packaging. *JOM* 1998, **6**, 47–51.
2. Sun, J. and Gao, L., Dispersing SiC powder and improving its rheological behaviour. *J. Eur. Ceram. Soc.* 2001, **21**, 2447–2451.
3. Millán, A.J., Nieto, M. I. and Moreno, R., Near-net shaping of aqueous alumina slurries using carragreenan. *J. Eur. Ceram. Soc.* 2002, **22**, 297–303.
4. Sigmund, M., Bell, N. S. and Bergström, L., Novel powder-processing methods for advanced ceramics. *J. Am. Ceram. Soc.* 2000, **83**(7), 1557–1574.
5. Gutiérrez, C.A. and Moreno, R., Interparticle potentials in nonaqueous silicon nitride suspension. *J. Am. Ceram. Sci.* 2003, **86**(1), 59–64.
6. Tartaj, P., Reece, M. and Moya, J. S., Electrokinetic behaviour and stacility of silicon carbide nanoparticulate dispersions. *J. Am. Ceram. Sci.* 1998, **81**(2), 389–403.

7. Prabhakaran, K., James, J. and Pavithran, C., Surface modification of sic powders by hydrolysed aluminium coating. *J. Eur. Ceram. Soc.* 2003, **23**, 379–385.
8. Huang, Q., Chen, P., Gu, M. Y., Jin, Y. P. and Sun, K., Effect of surface modification on the rheological behavior of concentrated, aqueous SiC suspensions. *Mater. Lett.* 2002, **56**, 546–553.
9. Yang, C. Y., Shih, W. Y. and Shih, W. H., Gelation, consolidation, and rheological properties of bohemite-coated silicon carbide Suspensions. *J. Am. Ceram. Soc.* 2000, **83**(8), 1879–1884.
10. Liu, D. M. and Fu, C. T., Effect of rheological behavior on properties of cast and sintered silicon carbide. *Ceram. Int.* 1996, **22**, 101–106.
11. Zhu, X., Tang, F., Suzuki, T. S. and Sakka, Y., Role of the initial degree of ionization of polyethylenimine in the dispersion of silicon carbide nanoparticles. *J. Am. Ceram. Soc.* 2003, **86**(1), 189–191.
12. Oliveira, A. I. R., Sepulveda, P. and Pandolfelli, V. C., Deflocculation of $Al_2O_3$–SiC Suspensions. *Am. Ceram. Soc. Bull.* 2001, **80**(2), 47–53.
13. Si, W., Graule, T. J., Baader, F. H. and Gauckler, L. J., Direct coagulation casting of silicon carbide components. *J. Am. Ceram. Soc.* 1999, **82**(5), 1129–1136.
14. Jun-hui, X., Yong, H. and Zhi-peng, X., Study of gel-tape-casting process of ceramic materials. *Mater. Sci. Eng. A* 2002, **323**, 336–341.
15. Briscoe, B. J., Khan, A. U. and Luckhan, P. F., Optimising the dispersion on an alumina suspension using commercial polyvalent electrolyte dispersants. *J. Eur. Ceram. Soc.* 1998, **18**, 2141–2147.
16. Huang, Q., Gu, M., Sun, K. and Jin, Y., Effect of pretreatment on the properties of silicon carbide aqueous suspension. *Ceram. Int.* 2002, **28**(7), 747–754.
17. Greenwood, R. and Kendall, K., Selection of suitable dispersants for aqueous suspensions of zirconia and titania powders using acoustophoresis. *J. Eur. Ceram. Soc.* 1999, **19**, 479–488.
18. Mei, S., Yang, J. and Ferreira, M. F., Effect of dispersant concentration on slip casting of cordierite-based glass ceramics. *J. Colloid. Inter. Sci.* 2001, **241**, 417–421.
19. Baklouti, S., Pagnoux, C., Chartier, T. and Baumard, X., Processing of aqueous $\alpha$-$Al_2O_3$, $\alpha$-$SiO_2$ and $\alpha$-SiC suspensions with polyelectrolytes. *J. Eur. Ceram. Soc.* 1997, **17**, 1387–1392.
20. Liu, D.-M., Influence of dispersant on powders dispersion and properties of zirconia green compacts. *Ceram. Int.* 2000, **26**, 279–287.