Study on Stability of $\text{Si}_3\text{N}_4$- nano BN Aqueous Suspension using Polyethylenimine as Dispersant

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Abstract—In this paper, a novel colloidal forming process has been developed to prepare silicon nitride –nano Boron nitride composites. In the present work, the dispersion of mixed silicon nitride –nano Boron nitride powders in aqueous media was investigated by adjusting the concentration of dispersant, pH value of the solution and other parameters. polyethylenimine (PEI) was used as dispersant for $\text{Si}_3\text{N}_4$ and BN powders in water. Well-dispersed $\text{Si}_3\text{N}_4$ and BN aqueous suspensions were obtained using 1 wt% PEI at pH 9. It depends upon the synthetic effects of dissociation of PEI and sufficient positive adsorption sites on the particle surfaces in aqueous media. The rheological behavior of $\text{Si}_3\text{N}_4$– BN aqueous suspensions was also investigated. Finally, a high solid loading (42 vol%), low viscosity (380 mPa s at 100 s$^{-1}$) $\text{Si}_3\text{N}_4$–BN aqueous suspension was successfully prepared. It was observed that the suspensions exhibited shear thinning behaviours with relatively low viscosity which could satisfy the gelcasting process.

Keywords— dispersant, rheology, silicon nitride, zeta potential, Aqueous Suspension

I. INTRODUCTION

CERAMIC gelcasting has rapidly developed in the past decade due to its capability of near-net-shape processing of fine ceramic pieces. The advantages of the technique include dimensional accuracy and complex shaping capabilities, as well as reducing the cost of manufacturing. A slurry made from ceramic powder and a water-based monomer solution is poured into a mold, polymerized in-situ to immobilize the particles in a gelled part, removed from the mold while still wet, then dried and sintered [1]–[4]. Gelcasting is near net shaping process of ceramics to overcome some of the problems in the existing processing routes, such as injection molding (e.g., long removal times and/or flaw generation during binder thermolysis) and slip casting (e.g., slow casting rates, inadequate strength for green machining). This new process for making high-quality, complex-shaped ceramic parts shows promise for manufacturing ceramics at a lower cost than conventional forming techniques. In addition, gelcasting appears attractive for an increasing number of applications ranging from accelerator magnets to artificial bone. The Principal advantages include near-net-shape forming, high green strength, shorter molding time, and low organic levels in the dried green ceramics. Therefore, a wide variety of ceramic materials have been prepared using gel casting process [1], [3]–[8].

A prerequisite for successful colloidal process is to produce a stable suspension with a high content of solid and a low viscosity. Due to vander Waals forces, the particles in the suspension have a tendency to coarsen or aggregate, which causes a relatively high suspension viscosity that may make colloidal process rather difficult. Therefore, it is essential to increase the repulsive forces to a high level to overcome vander Waals forces between the particles. The repulsive forces in the suspension usually result from three different mechanisms: (1) the electrostatic repulsion force due to the development of an electrical double layer around the particles; (2) steric hindrance related to the adsorbed long polymer chain on particle surface; (3) electrosteric mechanism as a combination of the above two mechanisms.

In gelcasting process, preparing a ceramic suspension with high solid loading and low viscosity is the most key issue. In order to obtain such a ceramic suspension, the choose and control of dispersant, dispersant concentration and pH value must be paid more attention. Compared with other polymer dispersants, branched polyethylenimine (PEI) has a chemical structure as shown in Fig. 1, which may exhibit better steric stabilization behavior. Besides, it has a high positive charge density that allows it to adsorb tightly on negatively charged substrates, resulting in a higher electrostatic force in a suspension. Therefore, as a strongly cationic branched polymer, PEI has been applied to disperse many kinds of ceramic suspensions [9], [10].

Many literatures on colloidal process of $\text{Si}_3\text{N}_4$ are available [11]–[13] but the colloidal process of $\text{Si}_3\text{N}_4$/BN composites has not been reported much. In this present work, PEI was used as dispersant. The purpose of this work is to optimize and prepare a $\text{Si}_3\text{N}_4$–BN aqueous suspension with a high solid loading and low viscosity. The effects of PEI concentration, pH value on dispersion of $\text{Si}_3\text{N}_4$ and BN in water, and rheological behavior of $\text{Si}_3\text{N}_4$–BN aqueous suspensions were investigated in detail. Finally, a high solid loading, low viscosity $\text{Si}_3\text{N}_4$–BN aqueous suspension was successfully obtained.
II. EXPERIMENTAL PROCEDURE

A. Materials

Commercially available Si$_3$N$_4$ powders (SN E-10, Ube industries Ltd, Japan) and nano BN powders were used as raw materials. The Si$_3$N$_4$ and BN powders had the same purity of 99%. The median volume diameter (D50) for the as-purchased Si$_3$N$_4$ and BN powder was about 0.5 mm and 100 nm, respectively, reported by manufacturers. Polyethyleneimine (PEI, Aladdin Co. Ltd., Shanghai, China), a cationic polymer with an average molecular weight of 10,000 was used as dispersant.

B. Zeta Potential Measurements

Firstly, the dispersion of Si$_3$N$_4$ and BN powders in water was investigated by zeta potential measurements. Then, Si$_3$N$_4$–BN composite suspensions were prepared by adding 80 vol% Si$_3$N$_4$ plus 10 vol% BN powder mixtures to deionized water. A series of Si$_3$N$_4$–10 BN aqueous suspensions with different solid loading containing 0–0.8 wt% PEI dispersant (based on the powder mixture weight) were ball-milled for 12 h using ZrO$_2$ spherical grinding media in a planetary mill (PM 100, Retech GmbH, Han, Germany) at 240 rpm (revolutions per minute). Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH value, and the zeta potential was determined as a function of pH. Zeta potential measurements of Si$_3$N$_4$ and BN in the presence of PEI were conducted separately as a function of pH value (in the range of 2–12) via Zeta potential analyzer (Zetasizer Nano ZS, Malvern, UK) using very dilute suspensions (0.01 vol%). The ionic strength was adjusted with 0.001M KCl solutions.

C. Rheological Properties Measurement

A Rotational rheometer (Physica MCR 51, Antonpaar GmbH) was used to measure the rheological behavior of the Si$_3$N$_4$–BN suspensions at room temperature. To avoid the undesirable influence from different mechanical histories, the fresh samples were homogenized by shearing at an identical rate of 100 s$^{-1}$ for 2 min and left standing for an additional 3 min before measurement. The measuring configuration adopted was a cone and plate (4°, 40 mm, and gap of 1 mm), and the flow measurements were conducted between 0.1 and 400 s$^{-1}$ at a constant temperature 25°C. Before carrying out the viscosity measurements, bubbles were removed by slow speed agitation from the suspensions. Rheological behavior of the suspensions was determined using a rotational viscometer (4ARES-9a, Rheo-metric Scientific Inc., USA).

D. Gelcasting Process

For further processing silicon nitride and nano Boron nitride powder are used. 3%Alumina and 2%Yttrium oxide are used as sintering aids. These powders were dispersed in a premix solution of low-toxicity monomers to obtain a suspension with powder loading of 42 vol%. A commercial dispersant, polyethylenimine, was used (1 wt% of ceramic powder) to stabilize ceramic particles in the suspension. The premix monomer solution was prepared by dissolving 5-10 wt% monomers in deionized water. Methacrylamide (MAM) (Sigma-Aldrich Chemie, Germany) and N, N′-methylene bisacrylamide (MBAM) (Sigma-Aldrich Chemie) were used as the linear monomer and cross-linker, respectively. The ratio of the linear monomer to the cross-linking monomer is 10:1. Ammonium persulfate (APS, 99.99%, Aldrich) and N,N,N’,N’-tetramethylethylenediamine (TEMED, 99%, Aldrich) were added to the slurry as a catalyst and an initiator, respectively. The ceramic suspensions were mixed for 24 h prior to the addition of initiator and accelerator. APS was added to the suspension as a 5 wt% water solution. The APS solution was always prepared fresh before use and the pH of the solution was adjusted by using ammonium hydroxide and Hydrochloric acid. A flow chart of the gel-casting process is shown in Fig. 2.
III. RESULTS AND DISCUSSION

A. Effect of pH on Zeta potential of suspensions

One of the widely used methods to stabilize the ceramic suspension is electrostatic stabilization caused by the repulsive forces of net surface charges between the particles. Fig. 3 shows Zeta potential of Si$_3$N$_4$ or BN powders as a function of pH value. The isoelectric point (iep) for Si$_3$N$_4$ and BN powder with PEI locates at the pH value of 6.9 and 2.4 respectively. With the increase of pH value from 2 to 12, Zeta potential negatively increases up to -50.8 mV for Si$_3$N$_4$ powder and -53.2 mV for BN powder, respectively. When 1wt% PEI is added into the suspensions, the pH$_{iep}$ for each powder moves to a more acidic range. And Zeta potential becomes more negative, especially in the case of pH<6. It indicates that the variation of Zeta potential value and pH$_{iep}$ of each particle is caused by the introduction of the dispersant, which reverses the positive charge or increases the negative charge on the particle surfaces[14][15]. The stronger effect of the dispersant on the particle surface charge in lower pH range indicates that, the cationic PEI has higher affinity to the negatively charged surface sites than the positive ones due to the electrostatic attraction between the particle and the dispersant.

![Fig. 3: Effect of pH on Zeta potential of suspensions](image)

B. Rheological properties of Si$_3$N$_4$-BN suspensions

B.1. Effect of pH on Viscosity of suspension

As for Si$_3$N$_4$–BN composite suspensions, the influence of pH values on rheological properties is very important and a suitable pH value is helpful for enhancing the solid loading as well as reducing the viscosity of the suspension. To identify the optimum pH value for stable suspensions, the pH value was adjusted to review the variety of viscosities of the Si$_3$N$_4$–BN aqueous suspensions containing 40vol% of solid loadings, as shown in Fig. 4. The viscosity decreases with the increase of pH values from 5 to 9, followed by a slight increase with the increase of pH value from 9 to 10. The lowest viscosity was obtained at the pH value of 9. This agreed with the results of zeta potential measurements and particle size distribution measurements, indicating the optimum pH value of Si$_3$N$_4$–BN aqueous suspension was 9. At pH > 9, the suspensions exhibit shear thinning behavior at low shear rate due to a perturbation of the suspension by shear[16]. At pH = 9, the suspension exhibits a slight shear-thickening behavior at low shear rate. All slurries exhibit Newtonian behaviors at high shear rate to generate a well-dispersed, homogeneous suspension by shear. In an aqueous-based system, the additional parameter of pH can be controlled to achieve good dispersion. This becomes the unique advantage of aqueous processing, especially for ceramic-polymer composites [6], [17].

![Fig. 4: Viscosity of the suspension versus shear rate with 1wt% PEI.](image)

B.2. Effect of PEI concentration on viscosity of suspension

As discussed above, the changes in zeta potentials of Si$_3$N$_4$ and BN particles indicated strong differences inter-particle forces, from adhesive at the IEPs to strongly repulsive at lower and higher pH values, respectively. Thus, the changes in zeta potentials would affect the rheological behavior of Si$_3$N$_4$–BN aqueous suspensions. Fig. 5 exhibits the viscosities of Si$_3$N$_4$–BN aqueous suspension as a function of shear rate with different concentrations of PEI. The rheological properties of the Si$_3$N$_4$–BN aqueous suspensions were strongly dependent on the amounts of PEI added. The suspension with 1 wt% PEI had the lowest viscosity. Using 1 wt% PEI as dispersant seemed to be the optimum dispersant concentration to disperse the Si$_3$N$_4$–BN powder mixture, which also induced the minimum viscosity value (as shown in Fig. 6) and the maximum zeta potentials. For every group, the flow curve deviates from a Newtonian behavior, its viscosity becomes lower as the shear rate is increased, which is known as shear-thinning in rheology [18]. Besides, it is found that the viscosity of slurry decreases with increase in dispersant dosage, and an optimum value of the dispersant dosage was found.
Finally, just as a note, when a green body of the mixed powders prepared from a suspension with 40 vol% solid loading was sintered at 1700°C for 2 h under nitrogen atmosphere, the relative density was around 99% as shown in figure 6 (a) & (b). This confirms that the nano BN powder is distributed homogeneously around the Si$_3$N$_4$ particles, and thus pressureless sintering at a relatively low temperature can produce a high sintered density.

IV. CONCLUSIONS

In this paper, PEI was selected as the dispersant for the aqueous dispersion of Si$_3$N$_4$–10v%BN powder mixture. The effects of the dispersant concentrations and pH values on zeta potentials of Si$_3$N$_4$–BN powders were investigated in detail. Zeta potential values for both powders become more negative with the increase of pH value from 2 to 12 or with the addition of 1wt% PEI. Well-dispersed Si$_3$N$_4$ suspension and BN suspension were obtained by using 1 wt% PEI at pH 9. The rheological behavior of Si$_3$N$_4$–15BN aqueous suspensions was also studied and discussed. It was found that the 40 vol% suspension had a lower viscosity and exhibited a slighter ‘shear thickening’ behavior, whereas the 45 vol% suspension had a much higher viscosity and exhibited a more obvious ‘shear thickening’ behavior. Considering high solid loading and low viscosity are desirable for the following colloidal forming processes, a high solid loading, low viscosity Si$_3$N$_4$–BN aqueous suspension was successfully prepared by using 1 wt% PEI at pH 9 and ball milled at 240 rpm for 12 h. We believe that this study will be helpful for the preparation of high quality Si$_3$N$_4$–BN suspension and lay the foundation for aqueous colloidal forming of Si$_3$N$_4$–BN composites.

REFERENCES


