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Surface and electrokinetic properties of Y-TZP suspensions stabilized by polyelectrolytes

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Abstract

Yttria-doped tetragonal zirconia (Y-TZP, 3 mol% Y_2O_3) aqueous suspensions with NH_4PAA and NH_4PMAA polyelectrolytes as dispersants were prepared by the ball mill method. Surface chemistry of Y-TZP particles in aqueous suspensions was evaluated via isothermal adsorption, FTIR spectrum and zeta potential analysis. It was found that there was an optimum amount of dispersants absorbed on Y-TZP particles, which changes their surface properties dramatically in the FTIR spectra. Coated with dispersants, the electrokinetic properties of Y-TZP were obviously altered compared with the naked particles, the isoelectric points (IEP) were shifted to pH 2.1 and 2.3 by NH_4PAA and NH_4PMAA, respectively. The rheology of high solids loading Y-TZP suspensions demonstrate dramatic difference with low solids loading suspensions, 47 vol% solids loading suspension showed a viscosity about 600 mPa·s under 20 s^{-1} shear rate.

Keywords: A. Suspensions; C. Chemical properties; D. ZrO_2; Rheology

1. Introduction

In the manufacturing process of advanced materials, much attention was paid to their moulding methods. Colloidal processing is a common and practical pathway for ceramics fabrication, which includes slip casting, injection moulding, gel-casting, direct coagulation casting (DCC) and so on [1–3]. DCC boasts these advantages like low organic substance content, inexpensive moulds and forming of complex-shaped and sizeable structural ceramics parts, thus becomes a focus in materials processing, however, this procedure is very demanding for its suspensions, Gauckle et al.[3] found that successful moulding of Al_2O_3, Si_3N_4 or SiC entailed a stable yet low viscosity suspension with solids loading up to 50 vol% while still maintaining relatively low viscosities of less than 1 Pa·s, so the preparation of high solids loading suspension is a key step in DCC.

Dispersants play an important role in dispersing aqueous suspensions, for instance, that in highly concentrated oxide suspensions, problems related to high viscosity, ageing, and processing of multiphase systems can be drastically reduced by using polyelectrolytes as dispersants or deflocculants, which stabilize suspensions by three mechanisms: electrostatic, electrosteric and steric mechanism [4]. As suggested by I.A. Aksay et al. [5], added polymer compounds such as NH_4PAA and NH_4PMAA (Mw = 10 000∼20 000) as dispersants about 1–2 dwb% (dry-weight basis) can obtain 62 vol% low viscosity Al_2O_3 suspensions, Gauckle et al. [3] prepared 60 vol% Al_2O_3 suspension for DCC and got excellent ceramic green bodies. It was reported that different dispersant structure affected electrokinetic properties and rheology of suspensions drastically. Hidber et al. suggested that dispersants with negative charge shifted the IEP of Al_2O_3 toward acidic area [6], Balmori et al. [7] also found that NH_4PAA changed the IEP of Y-TZP with 2∼3 pH units. But the relationship between dispersants and stability of Y-TZP is still a field in which much fundamental work needs to be done.

The claim of the present paper is to investigate the surface chemistry and rheology of Y-TZP suspensions dispersed by NH_4PAA and NH_4PMAA, correlate the dispersants with surface characteristics and stability of high solids loading suspensions, so that a practical routine of preparing DCC suspensions can be established.

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2. Experimential procedure

Y-TZP powder was prepared by coprecipitation method as follows: $ZrOCl_2{\cdot}8H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were dissolved in distilled water slightly acidified with HCl, then NH_4OH was added when powerfully agitated the mixture, the precipitation was washed with distilled water and then calcinated at suitable temperature, thus Y-TZP powder with a particle size of roughly 600 nm and a BET surface area of 1.05 m^2/g was obtained. The crystal structure was measured by X-ray diffraction (Cu K_α), element analysis was conducted by X-ray fluorescence method (Philips, PW-2400, semiquantity). Dispersants used in the experiment were ammonium poly-methacrylate (NH_4PMAA) with an average molecular weight (Mw) of 10000 and the salts of polyacrylate (NH_4PAA and NaPAA) of various molecular weights (5000, 10000 and 15000) (Aldrich Chemical Co. USA). These polyelectrolyte structures are shown in Fig. 1.

The following procedure was adopted for all the preparations of suspensions: spherical balls of zirconia were placed into a certain volume of high-density poly(ethylene) bottle, a known mass of the Y-TZP powder was then added, followed by the addition of a given volume of distilled water, the pH was adjusted with standardized analytical-grade $(CH_3)_4NOH$ to about 10, then a fixed amount of dispersant (2 dwb%) was added in the form of solution. The mixture was ball milled for 24 h at a specific rotational speed. The adsorption of NH_4PAA and NaPAA on Y-TZP was evaluated by a gravimetric technique developed by Baklouti et al. [8], zeta potentials of Y-TZP suspensions were measured on Zeta Plus Analyzer (Brookhaven Instruments Co., USA), sample suspensions were diluted by 1 mM KCl solvent to a low concentration of 0.01 vol% Y-TZP. IR spectra of suspension were studied on FTIR (Nicolet-520 FTIR, USA), samples were prepared with KBr plate; viscosity measurements were conducted with a rotary viscometer (Rheomat mettler 260, Switzerland), flow and relaxation curves were tested in order to determine the stability of the suspensions.

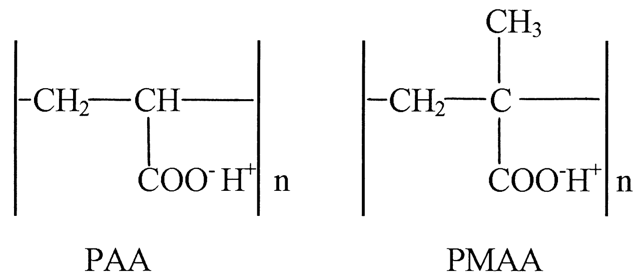

Fig. 1. Schematic of PAA and PMAA polymer segments.

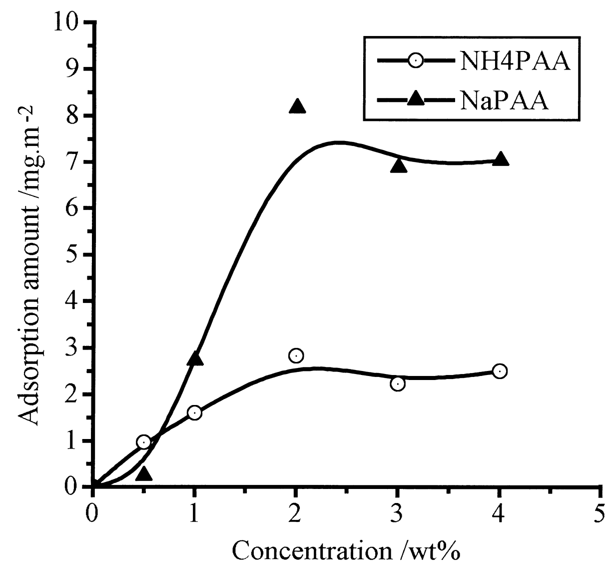

Fig. 2. Adsorption isotherm of NH_4PAA and NaPAA on Y-TZP surface. The pH is 10.

3. Results

Fig. 2 shows the adsorption isotherm of NH_4PAA (Mw = 10 000) and NaPAA (Mw = 15 000) on Y-TZP, it is similar to those reported in the literature [9], the equilibrium quantity of NH_4PAA adsorbed on the surface of Y-TZP powders amounts to 2.5 mg/m^2 at pH 10 on the plateau, while the coverage of NaPAA is 7 mg/m^2, approximately 3 times higher than that of NH_4PAA at pH 10.

The IR spectra of Y-TZP suspensions are shown in Fig. 3, pure Y-TZP shows a broad peak at 490 cm^{-1} (curve a in Fig. 3), however, the dispersant treated powder shows typical signals of N–H bond at 3400 cm^{-1} and C=O bond at 1080 cm^{-1}, respectively, the distinctive peak of Y-TZP occurring at 490 cm^{-1} displays a minor shift and its intensity descends slightly (curve b in Fig. 3), these results demonstrate some changes of surface chemistry of Y-TZP particles in the solvent induced by the addition of NH_4PAA, which would be discussed in more detail later.

The isoelectric point (IEP) of pure Y-TZP used is approximately 5.8 (Fig. 4), a little lower than the reported pH = 7 [10]. Yttrium has a significant solubility below pH 7, and can reprecipitate as hydroxide on the particle surface, greatly affecting the surface chemistry and IEP. The impurity in Y-TZP as shown in Table 1, also inevitably displaces the IEP of the powder. Dramatic shift of IEP occurs when the suspension is doped with polyelectrolytes, when NH_4PAA (Mw = 5000, 10 000) is added (0.01 vol% in suspensions), the zeta potential becomes more negative and the IEP is displaced towards acidic values, reaching a pH value of 2.3; meanwhile, NH_4PMAA can affect the surface charge of

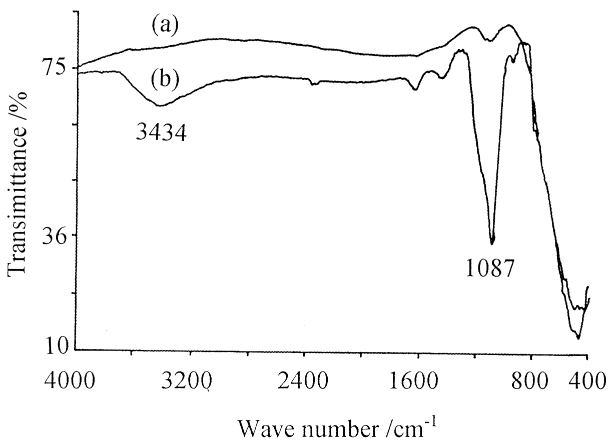

Fig. 3. IR spectra of Y-TZP suspensions (a, pure Y-TZP; b, dispersed by NH_4PAA).

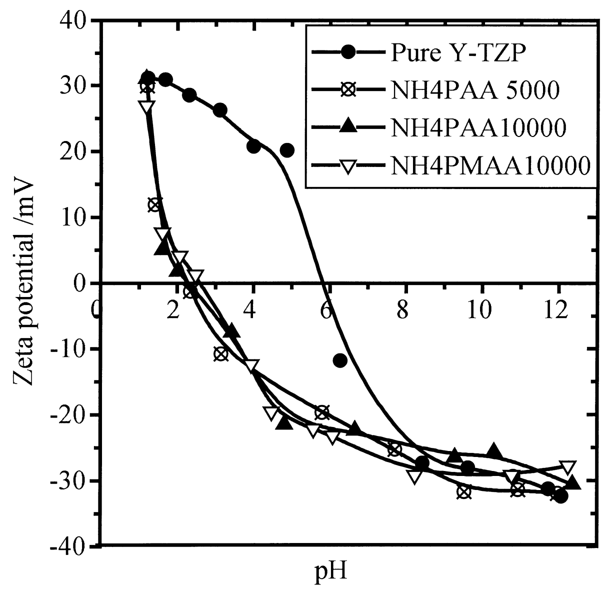

Fig. 4. Zeta potential of Y-TZP suspensions.

Y-TZP in the same way, the IEP alters to pH 2.6. The apparent differences of curve appearances between pure Y-TZP and those of dispersants doped occur in the range of pH 2–5, in which ζ potential becomes more sensitive to pH changes, obviously, polyelectrolyte dispersants interact with colloid particles in the aqueous suspensions [11].

The rheology of suspensions is greatly influenced by the solids loading of Y-TZP, at low solids loading, for instance, 25 and 30 vol% (Fig. 5), the suspensions show Newtonian properties, their viscosities remain constant as the shear rate changes, the flow curves are flat; however, up to 47 vol% solids loading, the flow curve deviates Newtonian fluid, its viscosity descends when shear rate ascends, which is the so called 'shear thinning' phenomenon in rheology [12,13]. At certain shear rate

Table 1
Result of Y-TZP powder by X-ray fluorescence analysis

Ingredient	ZrO_2	Y_2O_3	HfO_2	Na_2O	Nd_2O_3	Fe_2O_3
Concentration/wt%	90.2	6.0	2.6	0.5	0.3	0.07

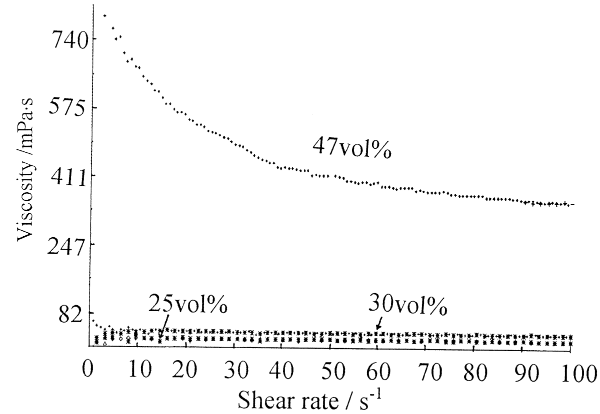

Fig. 5. Flow curves of Y-TZP suspensions with various solids loading.

(20 s^{-1}), with solids loading below 35 vol%, viscosity shows minor changes, in the range of 25 to 35 vol%, viscosity increases approximately 60 mPa·s; on the other hand, as the solids loading increases, the viscosity increases accordingly, at solids loading of 47 vol% (equals 80 wt%), its viscosity is about 600 mPa·s (Fig. 6). Those results indicate that solids loading exerts a stronger effect on rheology of high solids loading suspensions in comparison to its low counterparts.

4. Discussion

Powder surface chemistry such as adsorption coverage, surface charges and surface bond structure affects the rheology and stability of suspensions [14]. In the suspension, the powder forms a solid/liquid interface, it is obvious that the surface has a strong impact on the deagglomeration of a powder in a liquid to form a desired suspension. The consistency of the suspension is very important, since only small forces occur during pressureless casting such as DCC and tape casting [1,3]. According to Guo et al. [12], beyond the optimum adsorption coverage, excessive polymer will affect the rheology and stability of suspensions significantly, Takahashi [9] classified the polymer conformation adsorbed on the particle surface, interactions between particles depend on the conformation of absorbed polymer. In Y-TZP suspensions, adding a trace amount of PAA or PMAA could balance the interactions between particles and form consistent suspensions. However, as shown in Fig. 2, there exists an optimum value for

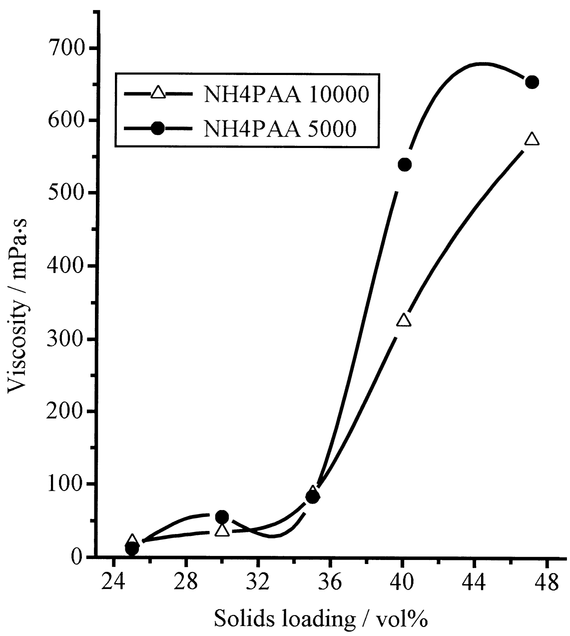

Fig. 6. Viscosity of Y-TZP suspensions vs solids loading.

polyelectrolyte dispersants. In our work, the total concentration of NH_4PAA should be no higher than 2 dwb%, otherwise excessive polymers dissolve in the solvent, their stretched molecular chains tend to tangle, inducing an unexpected high viscosity and yield value or even weak flocculation [12], for this reason, free polymers were intentionally avoided in present studies by adding only 2 %dwb dispersants. The mechanism by which the dispersants act with particles in suspensions were probed by Khan et al. [15] via atomic force microscopy (AFM), their results illustrate that at pH 7, the addition of dispersant induces a significant repulsive interaction between the particles in Al_2O_3 dispersion, which is important to stabilize the dispersion. Roosen et al. [14] found out that surface functional group of Al_2O_3 were largely affected by the dispersants, in our case, FTIR spectra were carried out in order to analyse the adsorption effect of dispersants, NH_4PAA acts with the surface functional groups of Y-TZP, the polymer chains dominate the surface of the particles by adopting various conformations at low or high polymer coverage, causing changes in the FTIR results as described above. Simultaneously, obvious displacements of surface charge were observed in polyelectrolytes dispersed Y-TZP suspensions under ζ potential measurements. Adsorbing on the surface of the particles, NH_4PAA or NH_4PMAA attributes more negative charges to the particle double layer, since the dispersants of this kind can dissociate in aqueous solution with pH value higher than 3 according to the following reaction [7]:

$$RCOO - NH_4 \overset{H_2O}{\Leftrightarrow} RCOO^- + NH_4^+ \quad (1)$$

With such an enhanced negative surface charge, the suspension can be stabilized more easily and sustains a fairly long time, which is the very desired property of suspensions for colloidal shaping. At low pH, the undissociated $RCOO\text{-}NH_4$ can also adsorb thereby influencing the ζ potential [7]. At pH close to IEP, the ζ potential decreases faster because every adsorbed RCOO- neutralizes a positive site increasing the negative density of an almost zero charge or slightly negative surface.

PAA and PMAA, together with their sodium or ammonium salts are highly effective dispersants for Al_2O_3, ZrO_2 and Y-TZP high solids loading aqueous suspensions [5,16]. The suspensions can be deflocculated with a solids loading up to 50 vol% yet retain a relatively low viscosity [4]. For Y-TZP used in our study, 47 vol% uniformly deflocculated suspension was obtained and kept under ambient surroundings for about 2 weeks without any sedimentation, and rheology tests also clarify that low solids loading suspensions are newtonian fluids, since particle separation distance is fairly large and interactions between particles are vastly repulsive potential according to DLVO theory, the ubiquitous van der Waals attractive potential is weak compared to the double-layer repulsive potential; at high solids loading like 47 vol%, however, Y-TZP powder dominates the great part of the suspension, liquid content is no higher than 15 wt%, the suspension gradually turns to be non-Newtonian fluid, and correspondingly its viscosity increases sharply, evincing the reinforced van der Waals attractive potential within a low particle separation distance, eventually, the suspension demonstrates the pronounced 'shear thinning' character as the shear rate is increased. Fortunately, dispersed with NH_4PAA, the viscosity is still no higher than 1 Pa·s at 20 s^{-1} shear rate, which means the suspension closely meets the demand of most colloidal processing methods [3,12,15,17].

5. Conclusions

Surface properties of Y-TZP aqueous suspensions are greatly influenced by dispersants. At pH 10, the optimum coverage of NH_4PAA and NaPAA is 2.5 and 7.0 mg/m^2, respectively. The surface bond structure and IEP of the suspension are obviously changed with the addition of polyelectrolytes. 47 vol% Y-TZP suspensions with low viscosity of 600 mPa·s are obtained by carefully controlling the process.

Acknowledgements

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