

Preparation of Concentrated Aqueous PZT Suspension for Wet Processing Methods

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Wet processing methods for fabricating ceramics, such as tape casting, gelcasting, injection molding etc., have been widely used for fabricating ceramic components. Developing concentrated ceramic suspension with still a low viscosity seems necessary for forming high quality components in all these methods. In this paper, based on our experiment results some issues about developing concentrated aqueous PZT suspension, including dispersant type, pH value, solid loading and milling time etc., were discussed. Attentions were mainly paid to a practical way of how to obtain high solid loading ceramic suspensions.

Key words: PZT, suspension, Rheological properties

1. INTRODUCTION

The high hardness and fragility of ceramic make it difficult for mechanical processing. The common die pressing way for forming ceramics is time-consuming and it is difficult to obtain ceramics with homogeneous microstructures by this method. Therefore some "wet processing methods" used for forming of the material, such as tape casting, gelcasting or injection molding etc. have received much attention since their invention. In these methods ceramic phase is dispersed in a solvent, then *in situ* solidification was achieved in a mold by polymerization, coagulation or organic binder etc. Consequently the geometry of the ceramic parts can be obtained without mechanical processing or without dry pressing. However, in these methods, to prepare concentrated stable ceramic suspension or slurries with still low viscosities is a necessary and critical step for forming dense and homogeneous parts. Unfortunately, this is also a very difficult step. Preparation of stable ceramic slurries seems theoretically relatively simple but practically difficult because the rheological properties of the ceramic slurries are nonlinearly related to various conditions. In order to cast a light on the problem, here some issues about developing concentrated aqueous PZT suspension, including dispersant type, pH value, solid loading and milling time etc., were discussed based on our results.

2. Experimental

PZT may be seemed as a classic binary piezoelectric ceramic, which are widely used in various, actuators, micromotors and in transducers etc. Here results of a commercial PZT-5H powder, supplied by the Institute of Acoustics, Academia Sinica, with a mean particle size of 1.3 μm were mainly discussed.

Rheological behavior of the aqueous ceramic slurries were measured by an advanced MCR300 rheometer (Physica, Germany) with a concentric-cylinder setting. Zeta potentials of the powders were measured by a Zetaplus analyzer (Brookhaven Instrument Corp., USA).

The dispersants were produced by Beijing Pinbao Chemical Co.

3. Results and Discussion

3.1 Influence of dispersant type and pH values

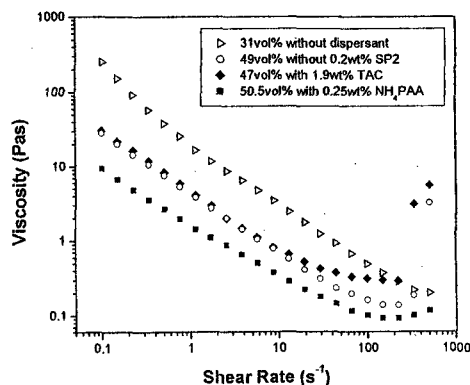


Fig.1 Influence of dispersant on the viscosity of the PZT suspension.

Viscosity versus shear rate curves for the PZT suspension without and with different dispersants are shown in Fig.1 Generally, a viscosity below 100 Pa·s may indicate a flowable slurry. It is impossible to obtain a flowable concentrated PZT suspension without using dispersant, while addition of dispersants can greatly decrease the viscosity. Homogenous dispersion of the powder is determined mainly by attractive and repulsive forces between the particles in the system. The former generally arises from the van der Waals forces while the latter can arise from electrostatic repulsion or steric repulsion of the surfactant material present on the particle surfaces, which effectively broke up the particle agglomerates and thus the viscosities were decreased [1,2]. Polyelectrolyte dispersants (ammonium salt of poly(acrylic acid), NH_4PAA and SP2 (sodium salt of (acrylic acid-co-maleic acid)) exhibited better results in

decreasing the viscosities compared with small molecular TAC (Triammonium citrate), which may be attributed to both electrostatic and steric repulsions of the polymeric molecule [3]. The excellent effect of polyelectrolyte type dispersants for ceramic, especially oxide ceramic, has been widely reported. There are also plenty of polyelectrolyte type commercial surfactant products. But what should be pointed out is that different dispersants' effects to a certain ceramic may vary to a large degree even if they have the same main constitution.

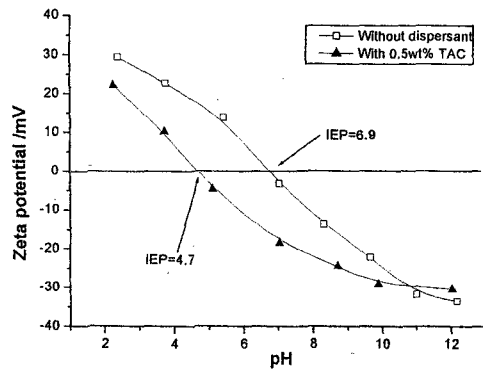


Fig.2 Zeta potentials of PZT suspension at different pH values

Table 1 Influence of pH values on the viscosities of 31 vol% suspension at low shear rate of 0.1 s^{-1}

pH value	2.1	7.0	12.2
Initial viscosity/ Pa·s	250	255	238

Electrostatic repulsion is directly dependent on the zeta potential of the powders. It seems from zeta potential values in Fig.2 that either acid or basic pH values can greatly enhance the electrostatic repulsion of the particles. Based on this consideration, many suspensions were reported to have an optimum pH condition [4]. However, it is obvious from the PZT data in Table 1 that only changing pH value has little effect in decreasing viscosities. In fact, our results of other ceramic powders were similar. A higher electrostatic repulsion (zeta potential) may not promise a good dispersion. At high zeta potential values, the increase of the electric double layer thickness may increase the "effective particle diameter" although the real "hard diameter" of the particle is constant, which in turn result in a higher effective solid phase volume. As a result the viscosities may be increased, especially when high solid loading or small particles are used [5].

3.2 Influence of dispersant concentration

Theoretically there is an optimum concentration for a dispersant at which just enough dispersant is present in solution to provide maximum coverage of the PZT powder and any excess dispersant may be harmful in decreasing viscosity. But practically it may be very difficult to find out the optimum value because the colloidal properties of the solution are relevant to various conditions, such as the ion strength, impurity ions, particle size and distribution and even particle

geometry etc., and the optimum value may vary substantially for different dispersants for the same material. From Fig.3 we can see that TAC has a much higher optimum use level than NH_4PPA . In practical operation, we may be disappointed at TAC because only at more than 1.9 wt% can we obtain a suspension with a usable solid loading. This value seems surprising to those who use TAC for dispersion of alumina where a level of about only 0.2wt% is enough [6].

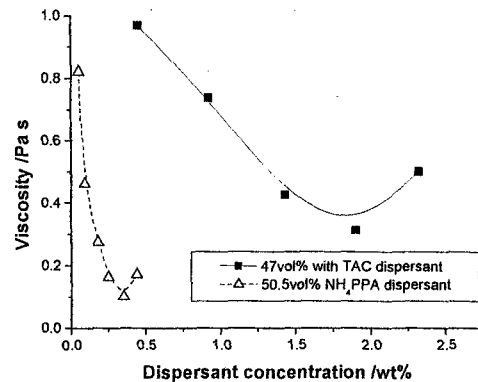


Fig.3 Effect of dispersant concentration on the viscosities under a steady shear rate of 99 s^{-1} .

3.3 Influence of milling time

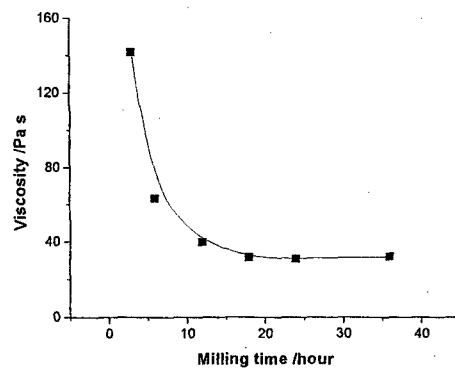


Fig.4 Viscosities of 47vol% PZT suspension versus milling time by using TAC as the dispersant.

During the preparation of the ceramic suspension, milling is a necessary step to achieve stable and well dispersed suspension. Here we use ball milling as an example. From the result of the milling time dependence of viscosities shown in Fig.4 we can see that at beginning the viscosity of the system decreases quickly as milling proceeds, then after a certain time of milling viscosity keeps almost constant. This may be partly attributed to the variation of effective dispersant amount adsorbed by the PZT particles at different milling stage. A decreasing dispersant adsorption trend with milling time has been confirmed by TGA measurement of the actual dispersant amount adsorbed by the ceramic particles after different milling time [7]. It was also observed that after a certain period of milling the adsorption seemed to achieve an equilibrium and more milling produced no obvious change in the adsorption. As a result, a stable viscosity appeared as shown in

Fig.4. There also seems to exist a critical milling time of about 12~20 hours. This critical milling time may be different at different milling conditions, but it reveals that a certain amount of milling is necessary for good dispersion of the suspension.

3.4 Influence of preparation procedure and other relevant conditions

Generally, the relationship between the viscosity and the solid volume percentage for monodisperse suspension can be modeled by Krieger-Dougherty (K-D) equation (see equation (1)) or similar equations^[2].

$$\eta = \eta_0 (1 - \phi / \phi_m)^{-[\eta] \phi_m} \quad (1)$$

Where, η is the viscosity of the suspension and η_0 is the viscosity of the solvent. The true volume fraction of the powder dispersed in the suspension is represented by the variable Φ and Φ_m represents maximum packing fraction. The intrinsic viscosity $[\eta]$ of the suspension is a function of particle geometry. A maximum packing fraction of 0.63 ± 0.002 is appropriate for random close packing at low shear rate^[8]. Although there may exist discrepancies between the experimental curves and the K-D model curve, the model predicts a typical situation of solid loading versus viscosity: low viscosity at low solids loading and very sharp increase at high solids loading as shown in Fig.5, where a with $[\eta]$ value of 2.5 is adopted.

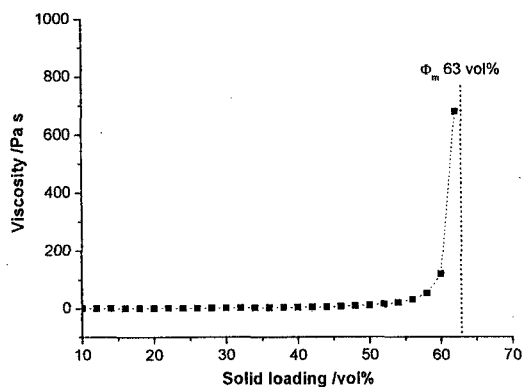


Fig. 5. Predication of the relationship between solid loading and viscosity by K-D model at 0.1 s^{-1} shear rate

An useful experience for practical preparation of ceramic suspension based on this predication is that much attention should be paid if you want to obtain a suspension with a solid loading as high as possible. It may occur that a suspension exhibiting a very good flowability may "solidify" if you just want to add a very little more powder to the suspension. Once a "solidified" slurry has formed, it is relatively difficult to disperse it again even after adding much water to a lower solid loading than that of the previous flowable suspension.

Preparation of flowable ceramic suspension seems to be a very complicated problem because there are also many other conditions that can also greatly influence the situation.

Concentrated aqueous ceramic suspensions generally exhibit shear-thinning behavior as shown in Fig.1, which is due to that the flow will lead to particle structure rearrangement. It was generally accepted and has been

verified that the flow-induced structure is an layered structure, which can result in a low resistance of the particle movement between different layers thus a low viscosity is obtained^[8,9]. This shear-shinning behavior suggests that a "solidified" slurry may become flowable under a shear stress (pouring down or casting). This may give us a hint on how to judge and control the maximum solid loading based on our special application purpose.

We found that the milling ball has an "abstruse" effect on the viscosity. It was found that milling with agate balls at higher solid volume fraction resulted in an aggregated slurry. The agate balls were found to be covered with a thick layer of slurry after milling. However, ZrO_2 balls can provide a suspension with good flowability just at the same conditions. This difference may be ascribed to the different surface physical and chemical properties of the ZrO_2 and agate. Milling with mechanical stirrer could greatly decrease the time before achieving the lowest viscosity, but ball milling could provide a more homogenous slurry with lower viscosity, although it might require a much longer milling time to achieve this.

Moreover, different dispersants' effects may vary for suspensions with different solids loading, so that selection of a suitable dispersant should be based on the solid loading one requires.

4. Conclusions

In summary, preparation of high solid loading ceramic suspension for successful application of the "wet processing" methods seems to be a theoretically relatively simple but practically complicated process. Although we should set out by using theories as the guideline, there are still much to be depended on experience in order to obtain stable and well dispersed concentrated ceramic suspension. And much care should be paid to the preparation procedure and preparation conditions etc.

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