Dispersion of PZN-PZT powder in organic media with chemically bonded dispersant

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The dispersion of chemically bonded dispersant named di-isopropoxy titanium dioleate in the PZN-PZT powder with organic media was investigated through FT-IR technique and sediment test. The results showed that the dispersant exhibited a good dispersion in the PZN-PZT suspensions. The interaction mechanism between the dispersant and the powder particle surface was involved in the formation of a strongly chemical bond through the reaction of alkoxy groups on the dispersant molecule with the surface hydroxyl of the PZN-PZT powder. The dispersant concentration corresponding exactly to the monomolecule layer coverage onto the PZN-PZT particle surface was determined to be 0.25 wt%. © 2001 Kluwer Academic Publishers

1. Introduction

Piezoelectric PZN-PZT [xPb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ + yPbZrO$_3$ + zPbTiO$_3$, $x + y + z = 1$] thick film is a promising material candidate for micromechanical applications [1, 2]. To produce uniform dense ceramic green bodies, general processing is tape casting [3]. In this processing, a stable, homogeneous powder dispersion is necessary. The state of dispersion is dependent on the dispersion of dispersant in the slurry. For a given slurry with an organic solvent, the dispersing mechanism stems from the steric stabilization [4], that is, the dispersants, which are adsorbed on the particle surface from solution, provide steric repulsive forces and, therefore, help to maintain the dispersion stability. This adsorption is essentially a kind of physisorption, which is usually affected by he polymer-liquid, and particle-liquid interactions. Since both liquid and polymer molecules may compete for adsorption sites on the particle surface, strong adsorption of liquid molecules tend to reduce polymer adsorptions due to fewer available surfaces sites, and the binder added in the following processing procedure also compete for the surface sites, which will cause the desorption of polymer from powder surface [5]. So physisorption is not enough to provide strong adsorption to stabilize the dispersing systems.

To enhance the strength of the dispersant-particle interaction to get a stable, homogeneous dispersing of powders in nonaqueous media, some attemps has been made to investigate so-called chemically bonded dispersant (abbrivated as CBD) [6–8]. These efforts are very beneficial to the application of CBD in the tape casting processings. But up till now, there is no report related to the use of CBD in PZT-PZN slurry.

In the present work, the dispersion of a kind of chemically bonded dispersant called di-isopropoxy titanium dioleate for PZN-PZT powder with an organic media, synthesized by reacting a titanium alkoxide with a long-chain carboxylic acid, was discussed. The interaction mechanism between the dispersant and PZN-PZT particle was investigated by FT-IR technique. The quality of the dispersion was characterized with sediment test, and the dispersant concentration for a single monomolecule coverage was determined based on Green's model.

2. Experimental

The chemical compounds used in this study to synthesize the chemically bonded dispersant were titanium tetraisopropoxide (Ti(O-iPr)$_4$) and oil acid (12-hydroxy steric acid), the synthesizing reaction procedures were as follows: first mixed the two chemicals, and stirred it for 30 minutes, then heated to 90°C, and held at this temperature for 1 hour. One product was removed by the distillation, another product, a viscous brown liquid, was subjected to FT-IR analysis.

The PZN-PZT powder was prepared by conventional solid-solution-reaction with the mixture of Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$, PbZrO$_3$, PbTiO$_3$, the specific surface area of PZN-PZT powder measured by Micromeritics ASAP 2010 (U.S.A.) was found to be 2.337 m^2/g, the particle size distribution analized by Zeta Potential (Zetaplus, Brookhaven Instruments Corp., U.S.A.), indicated a mean particle size of 1.02 μm with 90% of the cumulative mass of the sample having a particle size of less than 1.2 μm. The powders were dried at 120°C prior to use in the dispersion tests. Dispersion tests were carried out in 10 ml graduated
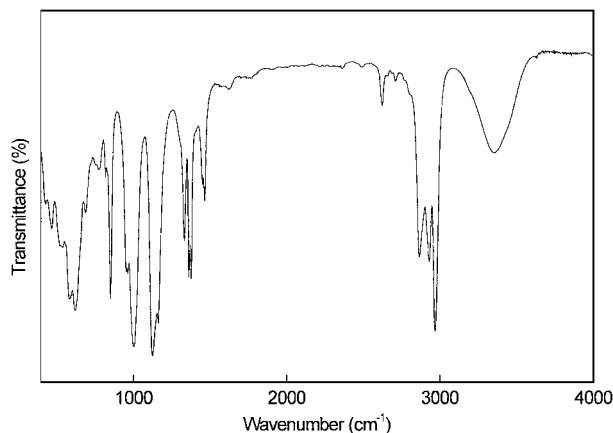
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Figure 1 FT-IR spectrum of Ti(O-iPr)$_4$.

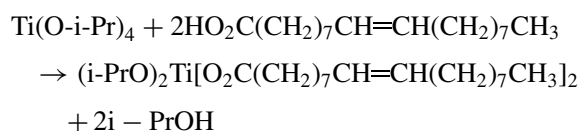*Figure 2* FT-IR spectrum of chemically bonded dispersant.

cylinders: 5 g of the PZN-PZT powder were added to 10 ml solutions of the chemically bonded dispersant in hexane solvent. The suspensions were ultrasonicated to 30 minutes to break up agglomerates, then milled for 20 hours to ensure complete coating of the particles by the dispersant. The suspensions were then allowed to stand undisturbed, and the sediment height as a function of dispersant concentration was measured periodically at room temperature until there was no further change in height.

To reveal the interaction mechanism between the dispersant and PZN-PZT particle surface, the PZN-PZT powder treated by the chemically bonded dispersant was subjected to FT-IR analysis (Bio-Rad FTS-185, U.S.A.), but it is necessary to wash the treated powder with pure hexane solvent and dried at 60°C before analysis.

3. Results and discussion
3.1. FT-IR characterization of chemically bonded dispersants

To determine the structure of chemical structure of CBD, the reaction raw material Ti(O-iPr)$_4$ and the resulting viscous brown liquid were subjected to FT-IR analysis. Fig. 1 shows the IR spectrum of Ti(O-iPr)$_4$, the peak at 1004 cm^{-1} has been attributed to ν_{sym}Ti(O-C) stretching vibration of the isopropoxy groups of titanium isopropoxide. The IR spectrum of the product is given in Fig. 2, four peaks at 1111 cm^{-1}, 1455 cm^{-1}, 1550 cm^{-1}, 1735 cm^{-1}, corresponds to the ν_{sym}(C=O), ν_{sym}(Ti-CO$_2$), ν_{asym}(Ti-CO$_2$), ν_{asym}(C=O), respectively [9]. From these IR results, a possible chemical reaction happening in the systems is as follows:

$$Ti(O\text{-}i\text{-}Pr)_4 + 2HO_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3$$
$$\rightarrow (i\text{-}PrO)_2Ti[O_2C(CH_2)_7CH{=}CH(CH_2)_7CH_3]_2$$
$$+ 2i - PrOH$$

i.e. two isopropyl group in Ti(O-iPr)$_4$ are replaced by the carboxylic acid group in oleic acid, thus form a compound named di-isopropoxy titanium dioleate (namely chemically bonded dispersant).
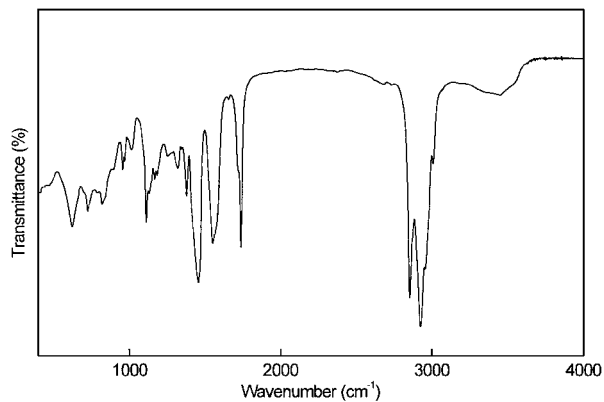
3.2. FT-IR results for interaction mechanism between CBD and PZN-PZT particle surfaces

Fig. 3 shows a IR spectrum of CBD-treated PZN-PZT. The powder had been washed with pure hexane to remove weakly adsorbed CBD. The spectrum exhibits a small, broad peak near 1560 cm^{-1} which has been attributed to adsorption by the organotinate carbonyl. This peak is not seen in the spectrum for untreated PZN-PZT shown in Fig. 4. The results reveal a chemical reaction between the CBD molecule and the surface
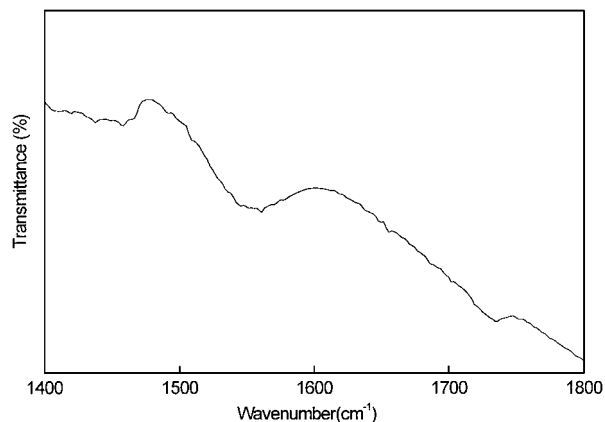

Figure 3 FT-IR spectrum of PZN-PZT powder treated by chemically bonded dispersant.
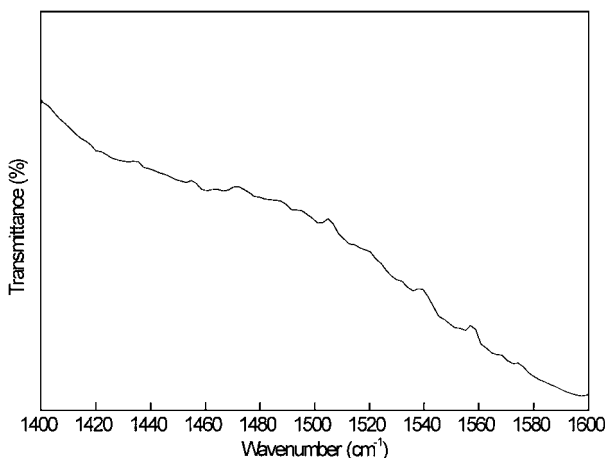

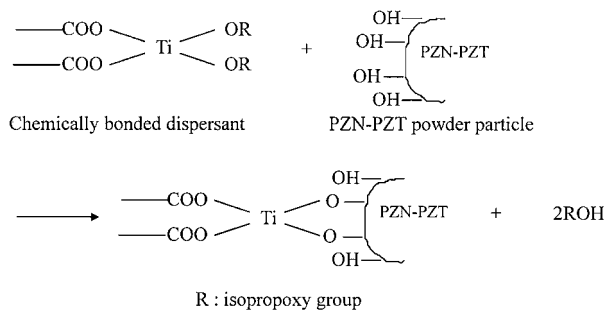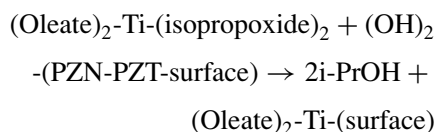*Figure 4* FT-IR spectrum of pure PZN-PZT powder.

Figure 5 Reaction processes of chemically bonded dispersant with PZN-PZT powder surface.

group of the PZN-PZT powder. The reaction form is as follows:

$$(Oleate)_2\text{-Ti-}(isopropoxide)_2 + (OH)_2$$
$$\text{-}(PZN\text{-}PZT\text{-}surface) \rightarrow 2i\text{-}PrOH +$$
$$(Oleate)_2\text{-Ti-}(surface)$$

the detailed reaction processes are illustrated in Fig. 5 i.e. the alkoxie groups on the CBD reacted with surface hydroxyl groups of the PZN-PZT powder, forming isopropyl alcohol and two surface-oxygen-titanium-oleate bonds, resulting in the covalent bonding of Ti-oleate groups to the surface of the PZN-PZT powder. The formation of strongly chemical bond between the CBD molecule and the PZN-PZT surface would enhance the adsorption strength between the dispersants and particles, thus avoiding beneficially the desorption of dispersants from the particle surface affected by other organic molecules (which usually take place for the physorped systems). Another end of the chemically bonded dispersant, the long hydrocarbon chains extending fully into the solvent, produces a more effective steric barrier, so that the equilibrium particle seperation is greater, and the system reach a more homogeneous, stable state.

3.3. Sedimentation tests

Fig. 6 presents the measured sediment heights for PZN-PZT powder dispersed in hexane solvent with CBD. The addition of CBD gives consistently much lower
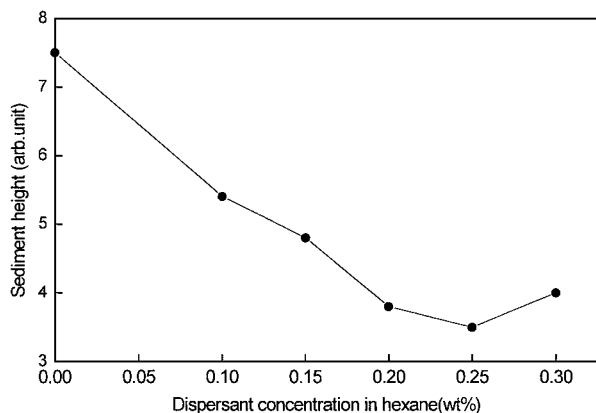

Figure 6 Sediment height as a function of dispersant concentration in hexane (wt%).

sediment height compared to the case of no CBD addition, which indicates the CBD do stabilize PZN-PZT suspensions. Generally, there is a trend of decreasing sediment height with increasing concentration of CBD. The minimum sediment height occurs at 0.25 wt% concentration, at which a good PZN-PZT suspension with a cloudy, homogeneous, stable state was observed in the sediment experiment. But when the dispersant concentration was above 0.25 wt%, the suspension system, when compared to that of the former, gave a poorer state with an increasing sediment height.

Green *et al*. [6] calculated the surface area of BaTiO$_3$ powder covered by a single molecule of CBD, assuming the CBD molecule bonded to two hydroxyl surface sites and considering the configuration of the least area possible, the bond lengths, and the bond angles, the result gave a minimum occupied area of around 0.53 nm^2 (53 Å^2) per CBD molecule. But the corresponding experimental value was found to be 0.75 nm^2 (75 Å^2). The large difference between the theoretical value and experimental one may result from the two possible factors. One is that the practical interaction configurations between the CBD molecules and the particle surface are more complicated than the theoretical one. The other, the repulsive force arising from chemically bonded molecules adsorbed onto a single particle surface may yield large effective coverage for CBD bonded to the particle surface sites.

Using Green's model and the following expression with the related parameters shown in Table I,

$$C = \frac{\gamma}{A}\frac{M}{N_o} \times 100\% \qquad (1)$$

the total adsorbed CBD contents for stabilizing 5 g of PZN-PZT powder was estimated to be 0.534 wt% for theoretical *A* value of 0.53 nm^2, while for experimental *A* value of 0.75 nm^2, the corresponding *C* value is 0.375%. It is clear that the latter is much lower than the former. Considering this decreasing trend, the possible reasons mentioned above, and the more complex structure of multi-component PZN-PZT as compared to that of BaTiO$_3$, we can follow that the coverage for a CBD molecule onto the PZN-PZT particle is largerer than that onto the BaTiO$_3$ (i.e. 0.75 nm^2). Naturally, the resulting *C* value for PZN-PZT suspensions is smaller than that for BaTiO$_3$ system (i.e. 0.375 wt%). Since our calculation expression (1) is based on Green's monomolecule layer model, it was reasonable to conclude that 0.25 wt% in Fig. 6 was

TABLE I The parameters for calculating monolayer chemically bonded dispersant coverage on PZN-PZT powder surface

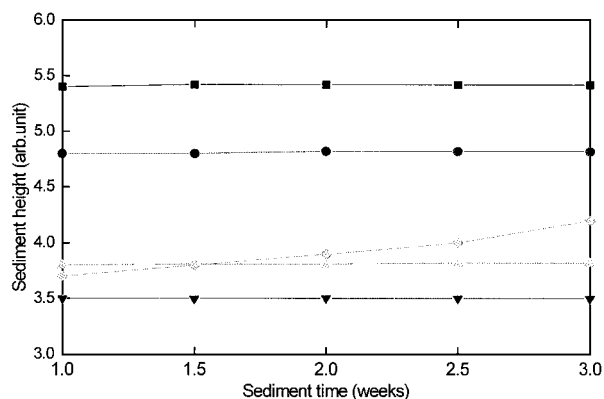| Parameters	Discriptions	Values
γ	Specific surface area of PZN-PZT powder	2.337 m^2/g
A	Coverage area of per molecule CBD on BaTiO$_3$ powder surface	53 Å^2 (theoretical) 75 Å^2 (experimental)
M	Molar weight of CBD	728 g/mol
N_o	Avogadro constant	6.02×10^{23}

Figure 7 Sediment height as a function of sediment time for systems with different dispersant concentration, (■) 0.1 wt%, (●) 0.15 wt%, (▲) 0.2 wt%, (▼) 0.25 wt%, (♦) 0.3 wt% in hexane.

just the required concentration for CBD achieving a monomolecule layer coverage onto the surfaces of 5 g of PZN-PZT powder in the dispersing systems. Substituted *C* with 0.25 wt% in expression (1), the corresponding *A* value is calculated to be 1.13 nm² (113 Å²). This result reflects in another side that the PZN-PZT dispersions with 0.25 wt% of CBD concentration corresponds exactly to the monomolecule layer coverage onto the PZN-PZT particle surface.

As for the increasing of the sediment height above 0.25 wt%, this may be due to the excess dispersant molecules which were unbonded to the particle surface, the excess dispersant molecules may sometimes have a deleterious effect on the stability of the dispersion systems [6].

Fig. 7 shows the sedimental stability as a function of time for different systems. For the dispersion system with 0.30 wt% concertration of dispersant, it is obvious that there is an remarkable increase of sediment height with increasingly settling time, which demonstrates that excess dispersants have a negative effect on the stability of the system. But for the 0.1 wt%, 0.15 wt%, 0.20 wt%, 0.25 wt% system, there is no observable change in sediment height with time, which reveals that the systems are very stable. In practice, these systems were very homogeneous. So such dispersant shows a promising application prospects in tape casting.

4. Conclusions

The dispersion of chemically bonded dispersant named di-isopropoxy titanium dioleate in the PZN-PZT powder with organic media was studied through FT-IR technique and sediment test. The results showed that the dispersant exhibited a good dispersion in the PZN-PZT suspensions. The interaction mechanism between the dispersant and powder particle surface was involved in the formation of a strongly chemical bond through the reaction of alkoxy groups on the dispersant molecule with the surface hydroxyl of the PZN-PZT powder. The dispersant concentration corresponding exactly to the monomolecule layer coverage onto the PZN-PZT particle surface was determined to be 0.25 wt%. The chemically bonded dispersant exhibit a promising application prospects in the tape casting processing.

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