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PZT-based Suspensions for Tape Casting

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Abstract

A PZT powder of composition $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ *was prepared by conventional mechanical mixing of the raw materials in water, freeze-drying and calcination. Sedimentation tests of four deflocculants in an azeotropic mixture of methyl ethyl ketone/ethanol were carried out to check the dispersing effect. Attention was focused on a phosphate ester based deflocculant. Electrical conductivity and electrophoretic mobility were investigated.*

Slurries for tape casting were prepared with commercial binder and plasticizer and different volumes of solid. The rheological behaviour was recorded as yield stress values and flow curves. The slurries were tape-cast and technological results compared with previous characterization results. © 1996 Elsevier Science Limited.

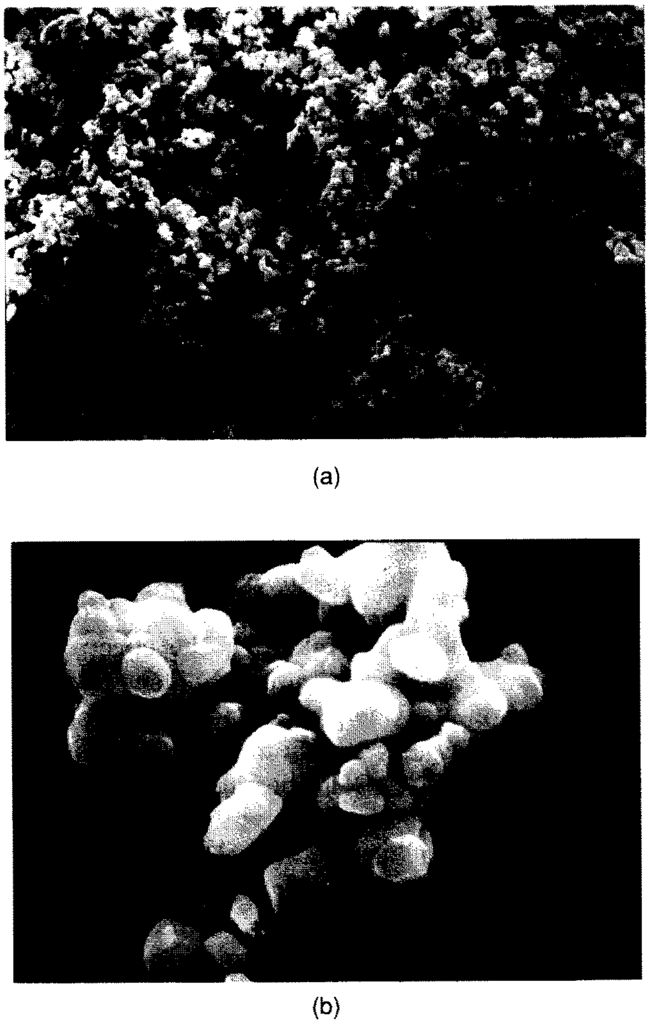
1 Introduction

Thin sheets of piezoelectric materials are applied in sensors, buzzers, actuators, dot-matrix and many other devices for microelectronics. The trend is now to develop very thin (thickness < 0·1 mm) and small pieces (main dimensions < 5 mm), so that extensive optimization of the cold consolidation process is essential. Tape casting is the most efficient and reliable method to produce thin ceramic sheets. The aim of the present study was the evaluation of dispersions of PZT powder in an organic medium upon the addition of deflocculants that promote different stabilizing mechanisms, for a fixed binder–plasticizer system. Tape casting slurries were composed of PZT powders dispersed in an azeotropic mixture of methyl ethyl ketone (MEK)/ethanol (EtOH) that shows an intermediate dielectric constant; many investigators consider that this solvent mixture behaves more like water than do solvents with very low dielectric constant, so electrostatic stabilization can occur when surfactants are introduced into the suspension. The results of a previous study[1] showed that the PZT powder produced by mechanical mixing of the raw materials shows in water an isoelectric region very close to that of the zirconia powder. Consequently, four dispersing agents were chosen from among those known to be suitable for the dispersion of zirconia.[2] Attention has been focused on evaluating the effectiveness of phosphate ester, an additive widely used for the dispersion of oxide powders (especially barium titanate) in organic medium. For the system $BaTiO_3$ in MEK/EtOH solvent, some authors[3] postulate that ceramic particles are charged when a small number of surfactant molecules ionize and are adsorbed onto the polar surface, resulting in a net positive charge. Fowkes *et al.*[4] proposed a variation whereby the surfactants are not extensively ionized until they are adsorbed onto the polar surface of the powder; conductance measurements support this model.

2 Experimental Procedure

The starting PZT powder was prepared by mechanical mixing of PbO (Merck), ZrO_2 (Harshaw SP102), TiO_2 (Degussa P25) and Nb_2O_5 (Fluka) in water, followed by freeze-drying and calcination at 850°C (4 h). The PZT powder, ultrasonically dispersed for 1 h in the solvent, shows the following equivalent diameters of particles at 10, 50 and 90% cumulative weight: $d_{10} = 0{\cdot}8\ \mu m$, $d_{50} = 1{\cdot}4\ \mu m$ and $d_{90} = 2{\cdot}7\ \mu m$ (Sedigraph 5000, Micromeritrics). Scanning electron microscopy (SEM) shows a morphology composed of aggregates of rounded shape with mean diameter 1·4 μm (Fig. 1).

An azeotropic mixture of methyl ethyl ketone and absolute ethanol (MEK/EtOH = 67/33 wt%), dried over 0·3 nm molecular sieve, was used as solvent. Four deflocculants were tested: glycerol trioleate (A), an amine derivative of an oligomeric polyester (B), phosphate ester (C) and polyvinylpyrrolidone (D). The sedimentation tests were performed with 7·6 vol% suspensions of the


(a)

(b)

Fig. 1. SEM morphology of the starting PZT powder.

powder in the azeotropic mixture. The electrophoretic mobility was recorded on diluted suspensions introduced into a capillary cell at 25°C (Rank Brothers Mark II); the conductivity was measured at 25°C using an electronic conductance meter with platinum-coated electrodes (Amel model 134) and the cell constant was determined with 0·1 M KCl standard solution. PZT powder suspensions (7·6 vol%) at different concentrations of deflocculant B and C were obtained after ball-milling for 16 h. The conductivity of the slurry and supernatant obtained after centrifugation was measured; no significantly different values were obtained. Supernatant mixed with a small quantity of centrifuged ceramic powder was used for electrophoretic measurements.

Slurries suitable for tape casting tests were prepared in the above-mentioned azeotropic solvent mixture, the relative dielectric constant (ε_r = 20·5) of which ensures good interaction of the solvent with the charged particles surface and ionized dispersant molecules. For all tape casting slips, two binders (polyvinylbutyral) with different average molecular weights of 55 000 (PVB-1) and 105 000 (PVB-2) were used; butylbenzyl phthalate (BBP) was employed. Slurry formulations at various solid volumes [$X = V_{solid}/(V_{total} - V_{solvent})$], changing the type and quantity of deflocculant, the amount of solvent ($S = V_{solid}/V_{solvent}$), the amount of binder ($B = V_{solid}/V_{binder}$) and the ratio ($Y = V_{binder}/V_{plasticizer}$) of binder and plasticizer, are reported in Table 1.

Table 1. Composition of the tape casting slurries

Slurry	*Deflocculant*		*Solids (vol%)*	X	Y	S	B
	type	*wt%*					
1	A	1·0	20·4	0·46	0·85	0·37	2·0
2	B	1·0	20·4	0·46	0·85	0·37	2·0
3	C	1·0	20·4	0·46	0·85	0·37	2·0
4	B	1·0	24·8	0·50	0·85	0·49	2·4
5	B	1·0	21·5	0·58	2·06	0·34	2·3
6	C	0·5	20·6	0·46	0·85	0·37	2·0
7	C	0·5	21·7	0·58	2·06	0·34	2·3

$X = V_{solid}/V_{total} - V_{solvent}$; $Y = V_{binder}/V_{plasticizer}$; $S = V_{solid}/V_{solvent}$; $B = V_{solid}/V_{binder}$.

The PZT powder was first deagglomerated in the solvent with the deflocculant by ball-milling for 1 h in a Teflon jar using zirconia milling media. The first binder was then added and, after a further homogenization (1 h), the second binder and plasticizer were added and ball-milling was continued again for 20 h.

To remove any entrapped air bubbles from the slurry two routes were used: slow rotation (less than 10 rev min^{-1}) on rollers for 10 h (slurries 1–4) or vacuum for 3 min (slurries 5–7). On casting the slurries, the yield stress and flow curves were measured with a Bohlin CS viscometer with the C14 coaxial cylinders measuring system.

Tape casting was performed on a laboratory tape casting bench with a stationary double blade system. Slurries were tape-cast onto a Mylar support moving at a constant speed of 20 cm min^{-1}. The blade height was 1·0 mm. The cast tapes were dried at room temperature without any air flowing.

The tape stripped more or less easily from the Mylar support after drying and all tapes were flexible. The tapes were inspected visually and pre-sintered in closed high-purity alumina crucibles; they were placed on fired setters and a small amount of lead zirconate was added as source of PbO. The heating rate was 20°C h^{-1} until 600°C and 100°C h^{-1} up to 1100°C with 30 min soaking time; the samples were cooled with power off. The density of the tapes, before and after the heat treatment, was calculated from thicknesses measured with a dial micrometer gauge.

3 Results and Discussion

3.1 Dispersing behaviour

The electrophoretic mobility tests reported in Fig. 2 provide evidence that the powder itself is positively charged in the azeotropic mixture and that the phosphate ester deflocculant (C) enhances the surface charge at low concentration; however, the surface charge increases rapidly until a maximum is reached at about 1·0 wt% of deflocculant. The decrease in the electrophoretic mobility for concentrations of phosphate ester higher than 1·0 wt% can be related to the increase in ion concentration, hence to a decrease in the double-layer thickness as suggested previously for the barium titanate system.[5]

Conductivity tests on solvent–deflocculant and solvent–deflocculant–powder systems, Fig. 3(a) and 3(b) respectively, reveal that the ceramic powder surface apparently acts as a catalyst for dissociation of the deflocculant, following the same trend as recorded for barium titanate powders,[6] and an electrostatic stabilization mechanism can be considered, although not sufficient to fully stabilize the suspension. Conductivity tests on the supernatant of the powder dispersed with a deflocculant based on an amine derivative of an oligomeric polyester (b; Fig. 4) show that no significant dissociation of the deflocculant is detected upon addition of powder, compared with the solution of solvent and deflocculant, indirectly confirming the stabilization via a steric mechanism.

The sedimentation tests (Fig. 5) indicate that two deflocculants (B and C) were effective in dispersing the suspensions, while the other two (A and D) produced flocculated suspensions. The deflocculant based on an amine derivative of an oligomeric polyester produces stable suspensions at both concentrations (0·5 and 1·0 wt%), while the phosphate ester disperses the powder only at the lower concentration. The polyvinylpyrrolidone and glycerol trioleate deflocculants produce soft floccules which reduce their volume to about half within 3 h.

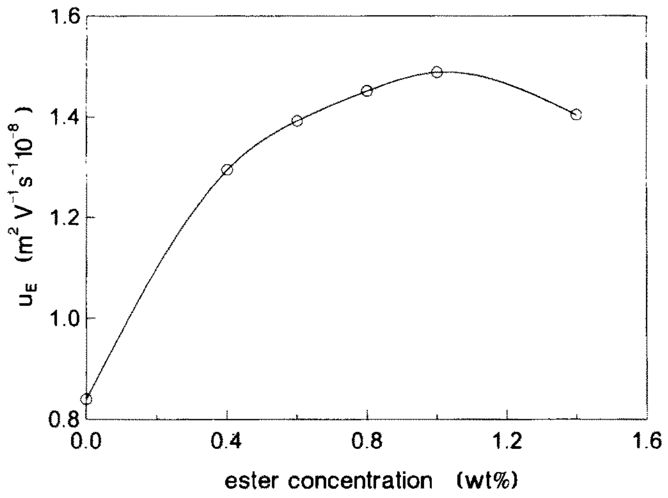


Fig. 2. Electrophoretic mobility versus phosphate ester concentration.

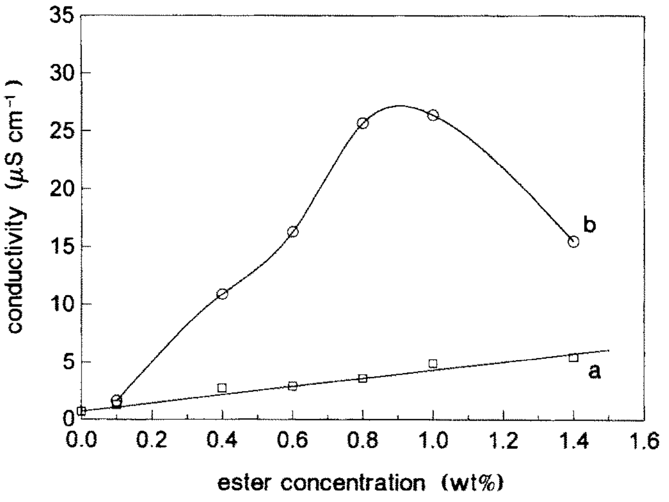


Fig. 3. Electrical conductivity versus phosphate ester concentration: (a) solvent and phosphate ester; (b) supernatant.

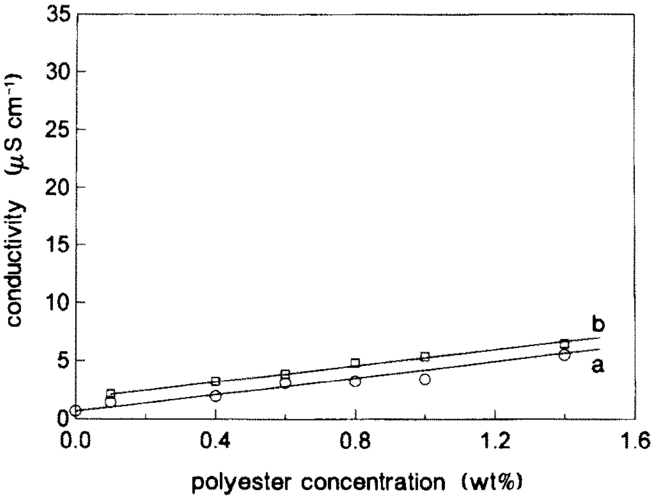


Fig. 4. Electrical conductivity versus concentration of amine derivative of oligomeric polyester: (a) solvent and deflocculant; (b) supernatant.

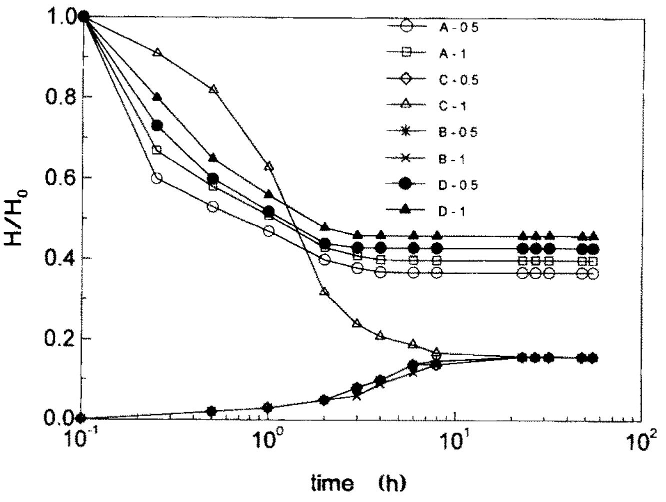


Fig. 5. Plots of sediment height versus time for the deflocculants tested; deflocculant concentration of 0·5 or 1 wt%.

3.2 Rheological characterization

Rheological characterization was carried out on the sample compositions listed in Table 1. The yield stress value was measured directly with the controlled-stress viscometer and the flow curve was detected with the same instrument following the constant rate procedure. Some results are reported in Table 2. The rheological characterization provides evidence that samples 1–4, produced via slow rotation of the slurry, are slightly pseudoplastic with a low yield stress value. Samples 5–7 were prepared in the same way but a careful de-aerating process was introduced, and a higher yield stress value was found. (Solvent evaporation during de-aeration was prevented.) Since the two groups of samples possess significantly different yield stress values corresponding to vacuum/non vacuum de-aerated samples, we can consider that the presence of bubbles greatly influences the yield stress values. However, the flow curves seem to be unaffected by the de-aeration treatment: no sample, except for 7, shows time-dependent properties. The flow curves are reported in Figs 6–9. Figure 6 shows that dispersant B (sample 2) produces a more fluid suspension than dispersants A (sample 1) and C (sample 3) (the sedimentation tests have already indicated that at a concentration of 1 wt% the phosphate ester flocculates rather than disperses the suspension). This confirms the higher effectiveness of the polyester-based deflocculant as expected by the sedimentation tests. Comparing the well dispersed (from sedimentation tests) suspensions at the higher solid loading (Fig. 7, samples 5 and 7) the flow curves are very similar, except that the phosphate-dispersed slurry is slightly thixotropic so evidencing that it is not in a well dispersed state. The comparison of samples 2, 4 and 5 (Fig. 8) evidences the role played by the

Table 2. Rheological parameters and tape characteristics

Slurry	τ_0 *(Pa)*	$\eta_{10\,s^{-1}}$ *(Pa s)*	$\eta_{100\,s^{-1}}$ *(Pa s)*	*Tape thickness (mm)*	*Visual inspection*	ρ^a *(%)*	ρ^b *(%)*
1	3·7	3·2	2·6	0·33	++	44·8	68·0
2	1·7	3·4	2.05	0·44	+++	52·8	—
3	3·5	5·9	3·3	—	—	—	—
4	4·1	8·8	4·9	0·47	+	51·3	87·2
5	15·8	3·1	1·3	0·43	+	48·0	85·0
6	18·1	5·3	2·4	0·41	+++	53·5	88·3
7	20·0	5·3→5·2	1·5→1·4	0·37	+	49·5	84·7

[a] Green body.
[b] Pre-sintered body.

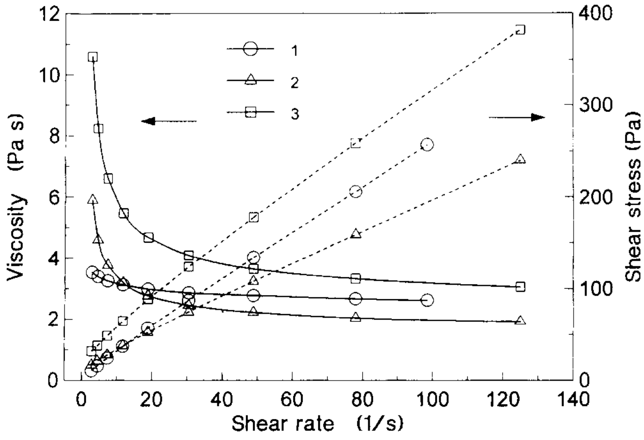


Fig. 6. Flow curves of samples at the same concentration of three deflocculants.

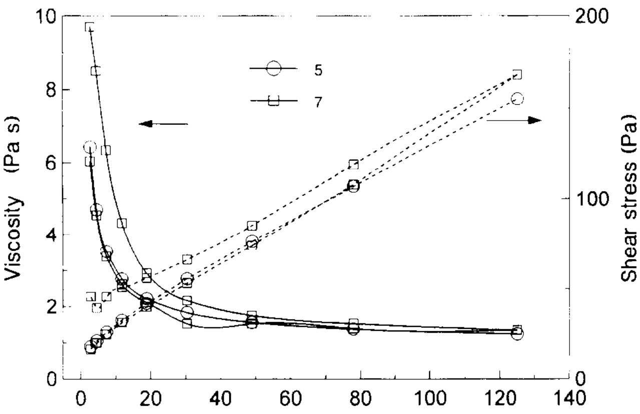


Fig. 7. Comparison of the flow curves for the highest solids loading and different deflocculants.

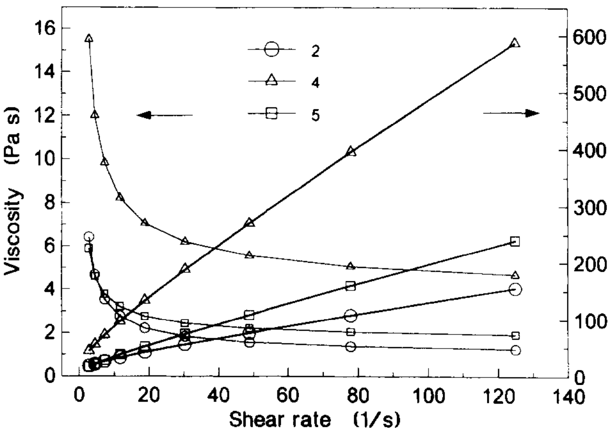


Fig. 8. Flow curves of suspensions with 1 wt% of polyester-based deflocculant and different solids loadings (see Table 1).

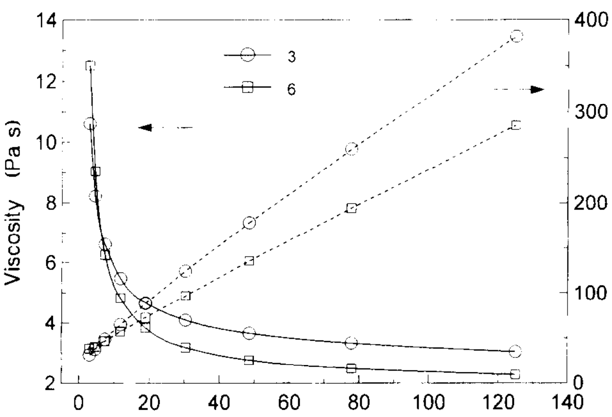


Fig. 9. Flow curves of suspensions with two concentrations of phosphate ester.

solvent content (viscosity increases with increasing value of the parameter S), while in Fig. 9 the effect of the phosphate content is compared (samples 3 and 6). In Table 2 some rheological data are reported together with several parameters of the green and pre-sintered bodies.

3.3 Tape casting test

All the slurries, except for 3, were tape-cast and the tapes obtained were evaluated visually on the basis of ease of removal from the support, brittleness and smoothness, and the results are reported in Table 2. Samples 2 and 6 performed best, with the highest green density. After the thermal treatment sample 2 stuck to the support and there was no chance to measure its final density; for sample 6 the density increased after pre-sintering, so confirming the quality of the cold consolidation procedure and the dispersion effectiveness of the phosphate ester deflocculant.

4 Conclusions

This study has shown that both phosphate ester and an amine derivative of an oligomeric polyester are suitable deflocculants for MEK/EtOH-based tape casting slurries of PZT powder. The slurries show pseudoplastic behaviour with a yield stress value and time dependency arises at high solids loading when phosphate ester deflocculant is used. The tapes produced are suitable for final densification. Tapes with higher green and pre-sintered densities, good flexibility and no sticking on the support were obtained using phosphate ester (0·5 wt%) with a solids loading of 20·6 vol%; the variation of the parameters X, Y, S and B involves a decrease of the final density.

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