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Effect of type of solvent and dispersant on NANO PZT powder dispersion for tape casting slurry

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Dispersion of PZT powder of average particle size ~75 nm in commonly used solvent systems for tape casting namely, toluene-ethanol and MEK-ethanol (azeotropic), xylene-ethanol (zeotropic) along with triton x-100, menhaden fish oil and phosphate ester as dispersants has been studied using simple sedimentation experiments. The relative merits of these three solvent systems and dispersants in dispersing PZT powder was analyzed. In all the three solvent systems, phosphate ester was found to be the best dispersant. Xylene-ethanol with phosphate ester gave the excellent dispersion characteristics for nano-PZT powder. The results of initial dispersion studies were confirmed by the formation of defect free, denser and smooth green tapes using xylene-ethanol and phosphate ester, while the other two solvent systems gave defective green tapes. The influence of phosphate ester on dispersion is explained by the dissociation and ionization, and the dominance of electrostatic repulsion even though organic solvent systems were used. *© 2002 Kluwer Academic Publishers*

1. Introduction

Lead zirconate titanate $Pb(Zr_xTi_{1-x})O_3$ (PZT) are of interest owing to their ferroelectric and piezoelectric properties [1–3]. Piezoelectric actuators are of great interest as micro-displacement transducers. Multilayer technology is used to fabricate these devices, which brings the drive voltages down to ~75–150 V [4]. The increasing demand for miniaturization of multilayer actuators requires the improvements in processing techniques, the starting materials and their characteristics. There are techno-economic pressures to reduce the layer thickness to around 20 μm, which demands the use of well-dispersed sub-micron sized ceramic powders. Such thin layers are produced using tape casting technique [5]. Tape casting slurry consists of ceramic powders dispersed in solvents and dispersants together with binder and other additives. In achieving uniform, dense, dimensionally accurate ceramic sheets, the colloidal processing of tape casting slurry is the critical step [6]. A well dispersed and highly stable slurry system, shear thinning behavior and optimized low viscosity, high solid content to control the shrinkage during further densification by sintering are the required characteristics of the tape casting slurry to obtain defect free green tapes and hence, the slurry preparation requires a more thorough investigation [7–9].

Slurry preparation usually involves particle deflocculation and dispersion in a solvent using dispersants and slurry homogenization with the aid of binders and plasticizers. The first stage strongly influences green tape characteristics whereas second stage influences the final product properties such as density and microstructure homogeneity [8]. There is ample evidence that systems which are not fully deflocculated contain voids in the cast tape, which are difficult to eliminate during firing and results in porosity in final product [10]. Thus, full dispersion of tape casting slurry is necessary for uniform, high-density dielectrics. It is in this context that recently, stabilization of dispersions of oxide particles in organic liquids has become a major concern in tape casting. Stable suspensions are achieved due to steric stabilization or electrostatic stabilization or both depending upon the type of dispersant used. Steric stabilization is caused by polymeric dispersant of long chain molecule whereas electrostatic stabilization is caused by surfactants [11, 12]. Binders in the slurry may also provide some dispersion effect [13–15].

Measurement of sedimentation height and packing density of particles in suspension is a well-accepted method to establish the degree of particle dispersion and packing. The efficiency of dispersion is evaluated by slower rate of settling of particles and higher final settling density. The state of particle dispersion has very sensitive role to play in the rheological properties of the slurry. Usually the slurry viscosity decreases with increase in flocculation of particles. Powder dispersion is not only dependent on the dispersant but also on the type of solvent used [9]. Tsurumi [16] studied the dispersability of PZT powders in different pure organic solvents. It is well established that a slurry composed of two or more solvents has greater adoptability and solubility for the different additives used for slurry preparation, than a slurry composed of single solvent [9, 17]. Furthermore, adsorption of dispersant molecules can be optimized by using a binary or ternary solvent system [9].

Realizing the importance of dispersion of nano PZT powders for tape casting, the present investigation aims to study the effect of three different binary solvent mixtures namely, toluene-ethanol, MEK-ethanol and xylene-ethanol on the dispersability of PZT powders with different types of dispersants namely, triton x-100, menhaden fish oil and phosphate ester, and compares the green tapes fabricated using the three selected solvent mixtures with common dispersant, phosphate ester. This study also involves the rheological behavior of the selected slurry.

2. Experimental

2.1. Starting materials

The nano-sized PZT powder (75 nm) of composition $Pb(Zr_{0.5}Ti_{0.5})O_3$, used for this study was synthesized using a chemical solution precipitation technique. The powder characteristics are given in Table I. The different raw materials used, their suppliers and their properties are given in Table II. To obtain the better mixing with slurry components and to reduce the milling time for slurry preparation, polyvinyl butyral was predissolved in ethanol.

2.2. Dispersability studies with different solvent mixtures

The dispersability of fine PZT powder particles in three selected binary systems, viz., azeotropic mixtures of toluene-ethanol, MEK-ethanol and zeotropic mixture of xylene-ethanol was studied by conducting the sedimentation tests on 10 vol%. suspensions of powders. Suspensions were prepared by maintaining the constant volume of the solvent mixtures in three cases. Glass measuring cylinder of 10 ml volume with stopper is used to avoid the evaporation of the solvents from the suspension. The tube is well shaken before the sedimentation test and placed in a water bath for ultrasonification for 5 minutes to break up the soft agglomerates of fine PZT powder. Then sufficient time was allowed for the suspensions to settle. Sediment height was recorded at definite intervals from the interface between the dense sediment and supernatant solvent. No significant change of sediment height was observed at longer times. Sediment height was related to packing density by calculating H/H_o (the ratio of instantaneous sediment height to initial height). The values of H/H_o were reported as a function of time.

TABLE I Chemical composition and characteristics of PZT powder

Chemical composition	Equivalent particle size[a] (nm)	Surface area (m^2/g)	Purity (wt%)
$Pb(Zr_{0.5}\ Ti_{0.5})O_3$	75	10.4	99.98

[a] Equivalent particle size is calculated from surface area by using the formula, $d_{av} = 6/\sigma S$, where d_{av} is equivalent diameter in nm, σ is density in g/cc and S is surface area in m^2/g.

2.3. Dispersability studies with different solvent mixtures in combination with three selected dispersants

10 vol% PZT powders suspension is prepared using three selected solvent mixtures of same volume. Three selected dispersants (0.5 wt%) were added to each suspension separately and 30 minutes time was allowed for the dispersant to adsorb on to the particle surface. Then the sedimentation height was recorded at regular intervals by following the procedure described in the preceding sub-section. The values of H/H_o were reported as a function of time.

2.4. Fabrication of green tapes using different solvent systems with common dispersant

Green tapes fabrication from the slurries composed of three selected solvent systems and dispersant, phosphate ester that was proven best in the initial dispersion experiments was taken up. The volume of the solvent mixture was kept constant and the weight of the other slurry components were also maintained constant in all the three components. The composition of the slurry is given in Table III. Tape casting slurry was prepared by following the two stage mixing. In the first stage of mixing, PZT powder, zirconia balls as milling media, dispersant and solvents were added in plastic milling

TABLE II Properties and suppliers of the raw materials

Constituents	Name	Supplier	Properties		
			Viscocity (mPa.s)	Density (g/cc)	Boiling point (°C)
Dispersant	Triton x-100	MERCK, Germany	–	1.064–1.067	63–69
Solvents	Ethanol	Anilax Enterprises Inc., USA	1.2	0.789	78.4
	Toluene	BDH (GPR), India	0.6	0.860–0.866	110.6
	Methylethyl ketone	NICE, India	0.4	0.803–0.805	79–81
	Xylene	BDH (GPR), India	–	0.850–0.865	137–142
Plasticizers	Polyethylene glycol-400	MERCK, India	–	1.126–1.128	–
	Benzyl butyl phthalate	Aldrich, USA	–	1.100	–
Homogeniser	Cyclohexanone	Qualigens, India	–	0.945–0.947	–
Binder	Polyvinyl butyral	Aldrich, USA	–	–	–

TABLE III Slurry compositions for the comparative study with different solvent systems

Constituents	Slurry composition (wt%) Toluene-Ethanol system (32 : 68)	MEK-Ethanol system (60 : 40)	Xylene-Ethanol system (65 : 35)
PZT powder	61.50	61.85	62.97
Phosphate ester	0.30	0.35	0.30
Solvent 1[a]	10.50	18.60	20.15
Solvent 2[b]	22.00	12.45	10.65
Poly ethylene glycol	1.25	1.55	1.35
Benzyl butyl phthalate	1.25	1.55	1.35
Cyclohexanone	0.50	0.55	0.60
Poly vinyl butyral binder	3.20	3.10	2.70

[a] Solvent 1: Toluene/MEK/Xylene.

[b] Solvent 2 : Ethanol.

jar in the same order. This mixture is then ultrasonificated for 10 minutes and milled for 30 minutes to ensure the uniform mixing of constituents. In second stage of mixing, the remaining additives viz., plasticizers, homogeniser and binder were added and ultrasonificated for 10 minutes and milled for 48 hours. This slurry was cast to a thin tape on a glass substrate of laboratory batch type tape caster with doctor blade initial gap setting of 250 μm. This gap is kept constant in all the experiments, as it affects the solid content of tapes due to differential shrinkage rate during drying [18]. After 25 minutes of drying, the green tape is stripped off the glass substrate. This fabricated green tape was used for comparative study based on visual inspection, solids content, green density and flexibility.

The green density of the tape was determined using a geometrical technique. Three samples (2.4 cm × 2.4 cm) are taken from different locations of green tape. The thickness of the sample tapes was measured by using a micrometer accurate to 0.001 mm at different locations on the samples and average was taken for the calculation of the volume. By knowing the mass and volume, the green density was calculated. Solid content was calculated based on weight ratios between the ceramic powder and other organic additives. Rheological behavior was studied by measuring the viscosity of the slurry using a viscometer (Brookefield Viscometer, HBTDV-11CP) at shear rates between 0 to 150 s^{-1}. The slurry for viscosity measurements was prepared by the same procedure used in the fabrication of green tapes. The composition of the slurry is given in Table IV.

TABLE IV Composition of the slurry for viscosity measurements

Constituents	Composition (wt%)
PZT powder	66.0
Phosphate ester	0.8
Xylene	15.6
Ethanol	8.4
Polyethylene glycol	2.4
Benzyl Butyl phthalate	2.4
Cyclohexanone	1.1
Polyvinyl butyral	3.3

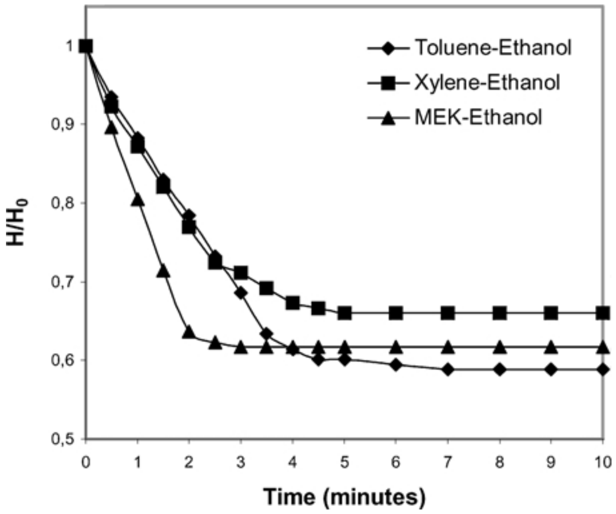

Figure 1 Dispersability of PZT powder in different solvent systems.

3. Results and discussion

3.1. Dispersability with different solvent systems

Comparison of sedimentation height as a function of time in 10 vol% PZT powder suspensions of three selected solvent mixtures without dispersant is shown in Fig. 1. The criterion used for better dispersability is more time for settling and higher settling density represented by lower H/H_0 value. It can be seen from the Fig. 1 that the time for initial settling in toluene-ethanol and xylene-ethanol mixtures is same, but toluene-ethanol mixture shows high settling density (low H/H_0 value) with time. In case of MEK-ethanol system, the initial settling is too fast, which is not acceptable for tape casting slurries.

3.2. Dispersability with different dispersants

The dispersability data of 10 vol% PZT powder suspensions in the three selected solvent systems with the combination of three dispersants are shown in Figs 2–4. From Figs 2–4, it can be inferred that phosphate ester and xylene-ethanol combination shows far better dispersion characteristics than others (In Fig. 4, the data points for phosphate ester dispersant are only two,

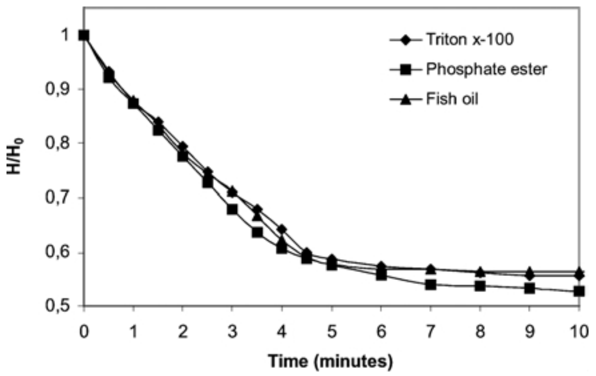

Figure 2 Effect of type of dispersant on the dispersability of PZT powder in toluene-ethanol solvent system.

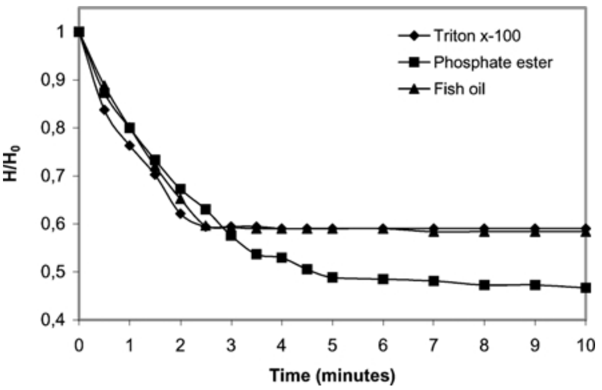

Figure 3 Effect of type of dispersant on the dispersability of PZT powder in MEK-ethanol solvent system.

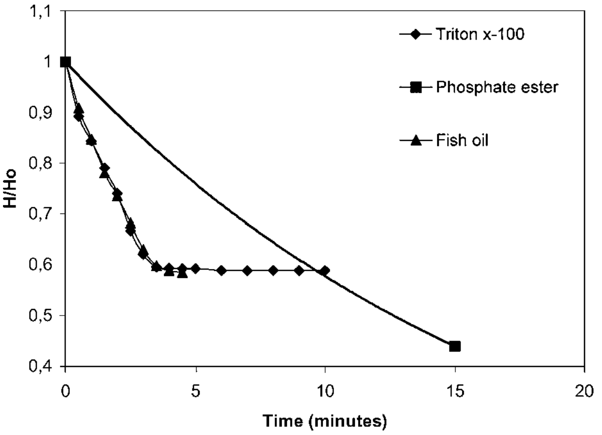

Figure 4 Effect of type of dispersant on the dispersability of PZT powder in xylene-ethanol solvent system.

because we could not see the interface between powder and solvent supernatant till 15 minutes). Adsorption on the particle surface is a competitive process between solvents and dispersants [19, 20]. It is well known that ethanol is a polar liquid, whereas toluene and xylene are non-polar liquids. Hence, ethanol has a strong hydrogen bonding capacity and has stronger preference to oxide particle surface [21]. In the case of MEK-ethanol system, since MEK ($CH_3{-}CO{-}C_2H_5$) is weakly polar, the solvents MEK, ethanol and dispersant competes for the oxide surface. In the case of toluene-ethanol and xylene-ethanol, because xylene and toluene are non-polar, only the ethanol and dispersant competes for the oxide surface, i.e., the adsorption effect of solvent is diluted giving preference to the dispersant to attack the surface. Comparing the toluene-ethanol and xylene-ethanol, the former has 68 wt% ethanol, while the later has only 35 wt% ethanol i.e., the dilution effect of xylene as a non-polar liquid is higher in xylene-ethanol. This may be one of the reasons why xylene-ethanol system shows much better dispersion characteristics for the given dispersant, phosphate ester.

From Figs 2–4, it can also be seen that irrespective of the solvent system, phosphate ester acts as an effective dispersant than fish oil or triton x-100. Dispersion can be because of electrostatic repulsion mechanism or steric hinderance mechanism. In the case of fish oil, it has been stated that steric hinderance mechanism is operative. Menhaden fish oil contains polyunsaturated ester molecules, basically glycerol esters of fatty acids such as oleate and linoleate. This dispersant cannot be considered as a surfactant and steric stabilization is most likely to occur since no variation in zeta potential occurs when this dispersant is added to slurry [12]. It has also been reported that fish oil is not much soluble in ethanol [22]. Triton x-100, because of its larger molecular size and longer chain seems to act as a steric hindrant. On the other hand, in the case of phosphate ester electrostatic repulsion mechanism is possible for oxides. The mono and dialkyl esters are highly acidic and exist as anions in aqueous and non-aqueous media. Acidity in the both aqueous and non-aqueous was confirmed by a measurable decrease in pH on addition of phosphate ester [23] indicating some degree of dissociation and ionization of the phosphate ester. The free photons liberated during dissociation of the phosphate ester are subsequently adsorbed onto the surface of the PZT causing the metal oxide to take on positively charged surface.

The anionic end of the amphipathic phosphate molecule is attracted to the positively charged surface of the particle by coulombic forces. The non-polar hydrocarbon tail extends into the non-polar organic media. In this system the hydrocarbon tail is lyophilic and soluble in the non-polar bulk solution. Therefore, there is no attraction of additional amphiphatic molecules as in the case of the aqueous system. The strong positive charge arise because the negative charge of the anionic end of the hydrocarbon molecule is small in comparison to the strongly positive particle surface and is not strong enough to offset the positive charge, therefore it migrates towards the cathode. The adsorption of hydrogen ions onto the surface to achieve a strong positive charge is important to the dispersion properties. First, a strongly positive surface aids in anchoring the phosphate ester molecule to the particle by attracting the negatively ionized end of the phosphate ester molecule. Second, double layer repulsion is possible and further stabilizes the suspension [23]. Hence, in the case of PZT powder electrostatic repulsion mechanism seems to dominate over other mechanism even in the case of non-aqueous solvent system.

3.3. Comparative study of green tapes

The comparison of the green tapes is shown in Table V. The comparative study shows that xylene-ethanol

TABLE V Comparison of green tapes with phosphate ester as dispersant in three selected solvent systems

Parameters	Toluene-Ethanol (32 : 68) system	Xylene-Ethanol (65 : 35) system	MEK-Ethanol (60 : 40) system
Shrinkage (%)	68.51	59.6	67.32
Green density (g/cc)	3.0964	3.1585	3.0771
Solid content (wt%)	61.47	62.97	61.84
Strength	Poor	Good	Very poor
Flexibility	Low	Good	Very low
Surface roughness	Rough	Smooth	Smooth
Agglomeration	High	Very low	Less

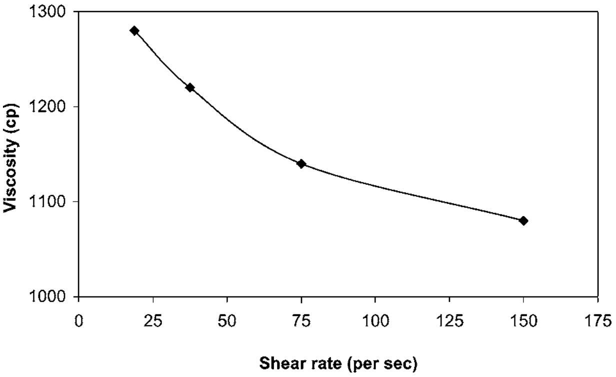

Figure 5 Viscosity vs Shear rate curve for PZT slurry based upon xylene-ethanol solvent mixture with phosphate ester as dispersant.

solvent system with phosphate ester as dispersant yield better green tapes than the other two solvent systems supporting the initial dispersion studies. Lower drying shrinkage in xylene-ethanol system indicates better dimensional stability compared to other two systems. High green density and solid content indicates that the powder is filled in the green tape uniformly. Good strength and flexibility is the indication for the better handling ability for the further processing of green tape. Smooth surface and low agglomeration shows the better dispersion and distribution of the powder.

3.4. Viscosity of the slurry

Fig. 5 shows the rheological behavior of the tape casting slurry in which the effect of shear rate on viscosity is presented. As the shear rate increases, the viscosity decreases, indicating the shear thinning behavior of the slurry, which is highly desirable to have the dimensional accuracy, as most of the electronic devices requires maintenance of close dimensional tolerances.

4. Conclusions

It was found that among the three selected solvent systems, toluene-ethanol and xylene-ethanol are better than MEK-ethanol for nano PZT powder. In the experiments with the three selected dispersants, phosphate ester was found to be better than the other two dispersants, namely, triton x-100 and fish oil. The combination of xylene-ethanol and phosphate ester showed better dispersion characteristics among all the selected combinations. It is believed that electrostatic stabilization is dominant for nano PZT powders for the xylene-ethanol solvent mixture and phosphate ester, later being anionic disperasant. Solvent system, adsorption of dispersant, interaction among other additives seem to influence the dispersability of powder particles. Adsorption of dispersant in turn depends on type of solvent systems used. The low concentration of ethanol in xylene-ethanol system resulted in more particle surface sites for the dispersant adsorption to the surface, which is essential for better dispersion.

The slurry prepared for tape fabrication showed shear thinning behavior. Visual inspection, packing density and solids content of green tapes confirmed the results of initial dispersion experiments. Xylene-ethanol solvent system with phosphate ester as dispersant showed higher particle packing density and solids content.

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