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Polyvinyl butyral as a dispersant for barium titanate in a non-aqueous suspension

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Polyvinyl butyral (PVB) was used as a dispersant for $BaTiO_3$ in a toluene–methanol system and its efficiency was evaluated by measuring the zeta potential and by a rheological study of the suspension. Addition of only 1.6 vol% low-molecular-weight (50 000) PVB is effective in making a well-dispersed suspension. But a lower concentration (0.6 vol%) of high-molecular-weight (200 000) PVB is necessary to stabilize the suspension due to the longer chain length of the polymer, which enhances steric stabilization. Dispersion of $BaTiO_3$ by PVB is better in a reverse azeotropic composition of toluene–methanol (72.4:27.6) than in an azeotropic composition.

1. Introduction

Tape-casting technology is one of the important fabrication techniques for multilayer ceramics and ceramic packages. Success in tape casting with the required uniformity and reproducibility is dependent upon the degree of dispersion. The dispersion of solid particles in a liquid generally consists of three stages: wetting of the powder, disintegration of large agglomerates into primary particles and stabilization of the powder against reagglomeration [1]. Interparticle forces influence all stages of the powder-dispersion process. Some of these forces, such as the van der Waals attraction between the solids, which leads to agglomeration, cannot be easily manipulated. One of the ways to improve control during processing is to introduce molecular additives to the system which provide a repulsive force to counteract the other forces active in the system. In principle, this can be achieved via one, or a combination, of two modes: (i) through electrostatic interactions where the necessary repulsive force is provided by a double layer of ions and counterions surrounding the particles in suspension, or (ii) through steric interactions of polymer molecules adsorbed onto the surface of the solids [2]. For the stabilization of concentrated slurry, which is used in processes like tape casting, steric stabilization can be effective whereas the small interparticle spacing in concentrated suspensions may hinder effective electrostatic stabilization [3].

There are very few effective dispersants for $BaTiO_3$, such as Menhaden fish oil and phosphate ester; the latter serves the purpose better than the former [4]. These dispersants have some inherent problems. The composition and the state of oxidation of Menhaden fish oil varies with the place of occurrence [5]. The phosphate ester, on the other hand, does not pyrolyse until the temperature is 800 °C and some phosphorus remains [6] which may hamper the electrical properties of the final products. Further, binders (which are generally high-molecular-weight polymers) have a tendency to be adsorbed on to the particle surface and hence to interfere with the adsorption of the dispersant [6]. This competition for adsorption of two additives effectively reduces the state of dispersion.

So, in this investigation, an attempt was made to study whether a completely organic polymer, polyvinyl butyral (PVB), can act both as a binder and as a dispersant. PVB is the most popular and widely accepted binder used for tape casting. Its slow rate of pyrolysis, in fact, offers an advantage in providing strength during the burn-out period [6]. Moreover, there are two distinct advantages of a dispersantless system in tape-casting processes: (i) no dispersant burn-out problem occurs, and (ii) no separate dispersant is present to interfere with the binder. Further, according to Fowkes [7] a strong bond between a polymer and a powder is made when there is a strong Lewis-acid/Lewis-base interaction. So it is expected that the acidic PVB should attach strongly to the basic $BaTiO_3$ particle surface giving rise to a dense coating on the particle and thus imparting steric stabilization.

Although PVB is a widely used binder [6], there have been some instances where this polymer is also used as a dispersant [8]. In this investigation, an attempt was also made to evaluate its performance as a dispersant for $BaTiO_3$ powder in a toluene–methanol solvent system. The effect of variation of the molecular weight of PVB and of solvent composition on dispersant properties as well as their effects on the properties of cast tapes have been investigated.

2. Experimental procedure

2.1. Raw materials

The main raw material, $BaTiO_3$ powder, used in this investigation was prepared in the laboratory by an

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oxalate-precipitation route. Details of the preparation procedure and powder characteristics have been reported elsewhere [9]. PVB was supplied by Wilson Laboratories, India.

2.2. Zeta-potential measurement

A microelectrophoresis apparatus (Zeta-Meter 3.0 + , Zeta-Meter Inc., USA) was used to measure the electrokinetic mobilities of the powders in a suitable suspending medium. The zeta potentials were determined from electrophoretic mobility values using the Helmhotz–Smoluchowski equation [10]. For electrophoretic-mobility measurement, the powder suspension (4 wt %) was milled for 6 h followed by centrifugation and the supernatant dilute suspension was then taken for measurement.

2.3. Sediment-volume measurement

The sediment volumes in the suspensions of the $BaTiO_3$ powder in different liquids were determined by Mizuta's technique [11]. For this purpose, 2.0 gm of $BaTiO_3$ powder was weighed in a 10 ml glass-stoppered graduated cylinder. Liquid was added so that the total volume was accurately 10 ml; this corresponded to a particle concentration of 3.3 vol % $BaTiO_3$. The cylinder was shaken by hand until the particles were dispersed. The volume of the settled particles was measured after standing for 14 days. The volume of the particles still remaining in the supernatant liquid was neglected.

2.4. Rheological measurement

For rheological measurement, the suspensions were prepared by ball milling a combination of $BaTiO_3$ powder (dried at 150 °C overnight) and solvent (toluene–methanol in different proportions) with different amounts of PVB in a polyethylene jar for 6 h. In all cases the powder concentration was 25 vol % of the slurry. Viscosity, η, versus shear rate, $\dot{\gamma}$, curves were obtained using a concentric-cylinder rotational viscometer (VT 500, Haake, Germany). The shear-stress, τ, values were calculated using the following relationship:

$$\tau = \eta\dot{\gamma}$$

Yield stress, (τ_0), values were determined by extrapolating the high-shear-rate portion of the shear-stress/shear-rate curve down to zero shear rate [8]. The relative viscosity, η_{rel} for particle–liquid suspensions was obtained using the relationship

$$\eta_{rel} = \frac{\eta_{sus}}{\eta_{liq}}$$

where η_{sus} is the suspension viscosity and η_{liq} is the viscosity of the suspension-liquid medium. The relative viscosity is useful in evaluating the effect of additives on the state of the particulate dispersion.

2.5. Determination of adsorption isotherms

Adsorption isotherms of PVB on $BaTiO_3$ particle were obtained by monitoring the change in concentration of the adsorbate in the solution before and after equilibration with the adsorbent. For this purpose, dried $BaTiO_3$ powder of known weight was equilibrated at 25 °C with polymer solutions of different initial concentrations by the suspension for a sufficiently long time (6 h) ball milling. The suspensions were then centrifuged and the polymer concentration in the supernatant liquid was gravimetrically analysed.

2.6. Fabrication of tapes

The preparation of tape-casting slurries involved the following steps.

1. $BaTiO_3$ powder and the solvent (a mixture of toluene and methanol in different proportions) were milled with varying amounts of dispersant (PVB) in a polyethylene jar for 6 h.
2. Then the binder (also PVB) and plasticizers (polyethylene glycol and butyl benzyl pthalate) were added to the slurry and milled for 18 h. It should be mentioned that PVB was used both as a dispersant and as a binder. A typical composition used for the preparation of tape-casting slip is shown in Table I. The total PVB concentration (as a binder and as a dispersant) was always 2.91% of slip.
3. The dissolved air in the slurry was removed by subjecting the slip to a vacuum (10^{-2} torr) and magnetic stirring for 5 min.
4. Finally the slurry was cast onto a glass plate of a tape-casting machine (Integrated Ceramic Technology, Inc., USA, Model 164) at a casting speed of 5 ft min keeping a blade gap of 0.5 mm. The tapes were allowed to dry for 2 h under ambient conditions and then stripped out from the glass plate.

2.7. Bulk-density measurement

Bulk densities of green as well as fired tapes were determined by a computerized mercury porosimeter (Autoscan-60 Porosimeter, Quantachrome Corp., USA) in which mercury was forced to penetrate into the pores of the sample under pressure and then the pressure–volume penetration curve was analysed to obtain the bulk density.

3. Results and discussion

3.1. Choice of solvent

Various types of non-aqueous solvents are normally used for the tape casting of ceramics [6, 12, 13]. Among them, the six most popular and widely used solvents are: (i) acetone, (ii) toluene (iii) methyl

TABLE I A typical composition used for tape-casting slip

Ingredient	Function	Weight (%)
$BaTiO_3$ powder	Ceramic	65.63
Toluene + methanol	Solvent	26.52
Polyvinyl butyral	Dispersant	0–0.95
Polyvinyl butyral	Binder	2.91–1.96
Polyethylene glycol	Plasticizer	3.70
Butyl benzyl pthalate	Plasticizer	1.25

ethyl ketone (MEK) + ethanol, (iv) toluene + ethanol, (v) toluene + methanol, and (vi) trichloroethylene + ethanol.

In tape casting, a combination of two solvents is preferred to a single solvent system because the solubility of a polymer is generally greater in an optimized mixed solvent system than in any individual pure solvent [14]. Azeotropic mixtures of solvents are recommended to avoid preferential volatilization during the drying of tapes. As optimization of tape-casting conditions was the primary objective in this investigation, azeotropic mixtures of the above binary solvent systems are used for experimentation. To evaluate the dispersing efficiencies of the six solvents mentioned above for $BaTiO_3$ powder, a sedimentation test was carried out as the first step. The results are presented in Table II, which shows that the maximum sediment density is obtained with toluene–methanol azeotrope, which is consequently considered to be the most effective of the above six solvents as far as the dispersion of $BaTiO_3$ powder is considered. This result is also supported by zeta-potential measurement for these solvent systems. The highest zeta potential (32 mV) was measured for the toluene–methanol –$BaTiO_3$ system, indicating that the electrostatic repulsive force between the particles was a maximum for this solvent system. Again it may be seen (as discussed later) that PVB can also be used as a steric stabilizer whose effectiveness depends largely on the solvent quality. Toluence is a good solvent for PVB, but methanol is a poor solvent [8]. Good solvents enhance the effectiveness of stabilizing moieties by extending "loops" and "tails" from the particle surface into the surrounding liquid. But in poor solvents the probability of adsorption of polymer onto the particle surface increases due to relatively low polymer–liquid interactions giving rise to a dense coverage and thereby inhibiting the close approach of the particles [3]. Based on all this information the toluene–methanol azeotrope was chosen as the most suitable solvent for the present investigation.

3.2. PVB as a dispersant

The effectiveness of PVB as a dispersing agent for $BaTiO_3$ suspensions in toluene–methanol azeotrope was evaluated by studying the rheological properties of the suspension under various conditions. The first set of experiments was carried out using a relatively low-molecular-weight (50 000) polymer (PVB). The viscosity, η, of the suspensions containing a fixed powder loading (25 vol %) was measured as a function of the shear rate. The results are presented in Fig. 1 in which the relative viscosity is plotted against the shear rate for different amounts of the dispersant. In the absence of PVB, the relative viscosity decreases with increasing shear rate (Fig. 1a) which clearly indicates a highly shear-thinning-flow behaviour, a characteristic of a flocculated suspension. A relatively low value of the zeta potential (+32 mV) for the $BaTiO_3$–toluene–methanol system also supports the possibility of flocculation if it is assumed that only an electrostatic stabilization mechanism is operative in this case. It is interesting to note that with increasing additions of PVB, the shear-thinning behaviour of the suspension decreases significantly indicating the effectiveness of the polymer as a good dispersing agent for $BaTiO_3$ in this solvent system. With 1.6 vol % PVB, the viscosity is nearly independent of the shear rate (Fig. 1c), which is characteristic of the approximately Newtonian-flow behaviour of the suspension. This happens only when the suspension is in a highly dispersed condition. On further addition of PVB, the suspension shows dilatant-flow behaviour (Fig. 1d) which is characteristic of a highly loaded suspension in which the interparticle repulsive force is large [15, 16].

Fig. 2 shows the amount of PVB adsorbed on the surface of the $BaTiO_3$ particles plotted against the total quantity of PVB added to the suspension. With increasing PVB concentration in the suspension, the adsorbed amount initially increased, as expected, and then reached a saturation value at around 1.6 vol % of the polymer, which probably corresponds to the completion of the monolayer coverage of the particle surface with PVB molecules. A good correlation between the quantity of PVB required for complete coverage of the particle surface and observation of Newtonian-flow behaviour from viscosity measurements (Fig. 1c) clearly indicates that steric stabilization due to adsorption of the polymer onto the particle surfaces is the primary cause for dispersion in this suspension.

TABLE II Sedimentation density of $BaTiO_3$ powder in different solvent systems

Solvent system	Powder density (%)
Acetone	13.50
Toluene	13.80
MEK + methanol	21.36
Toluene + methanol	23.65
Toluene + ethanol	21.30
Trichloroethylene + ethanol	20.07

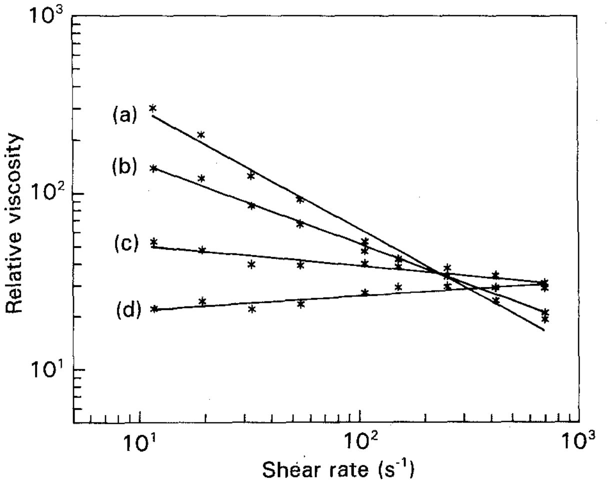

Figure 1 The relative viscosity plotted against shear rate of a 25 vol % $BaTiO_3$ suspension in a toluene–methanol azeotrope with different concentrations (vol %) of PVB (molecular weight 50 000): (a) 0.0, (b) 0.2, (c) 1.6, and (d) 2.0.

Good dispersion with increasing PVB concentration is also reflected in the bulk densities of the tape-cast samples (Table III). The bulk density of the green tapes using PVB as the dispersant increased from 36 to 45% of the theoretical value as the dispersant concentration was increased from 0 to 2.0 vol %, whereas for fired tapes (1350 °C for 2 h) a maximum bulk density of 92% of the theoretical was achieved using the same quantity of PVB as the dispersant.

3.3. Effect of the molecular weight of PVB

Fig. 3 plots the relative viscosity against the shear rate of a 25 vol % $BaTiO_3$ suspension in a toluene–methanol azeotrope, for varying amounts of PVB with a molecular weight of 200 000 rather than 50 000 as was used in the earlier case (Fig. 1). The initial addition of this high-molecular-weight polymer resulted in an increase of viscosity together with increased shear-thinning behaviour in comparison to the flow behaviour of suspensions containing no PVB (Fig. 3a and b). This is a typical behaviour of a polymer-bridging flocculation, which occurs at a very low concentration of PVB. The increased viscosity because of this bridging flocculation is due to the formation of a floc structure of low average packing density resulting in a higher effective solid loading in the suspension. This behaviour of the suspension is further supported by the results of Fig. 4 where the yield stress of the suspension is plotted against the PVB concentration for both the low and high molecular weight polymers. Fig. 4 clearly shows that the yield stress increases as the high-molecular-weight polymer increased from a volume percentage of 0 to 0.2 (Fig. 4a). But for the low-molecular-weight polymer, the yield-stress value continuously decreased with increasing polymer concentrations (Fig. 4b). However, in the high molecular-weight polymer–liquid–powder system further additions of PVB decreased the relative viscosity and the suspension showed nearly Newtonian-flow behaviour when the PVB concentration was 0.6 vol % of the suspension (Fig. 3c). The yield-stress values also decreased to zero at this concentration of the polymer (Fig. 4a). This behaviour indicated a transition from polymer-bridging flocculation to steric stabilization. A similar type of transition was earlier reported for a Poly Vinyl Alcohol (PVA)–SiO_2–H_2O system [8]. The Newtonian-flow behaviour and zero yield stress of the $BaTiO_3$ suspension were observed when the total PVB concentration was around 0.6 vol % which is much lower than the concentration (1.6 vol %) needed for the low molecular-weight PVB to disperse the same suspension. The increased effectiveness of the

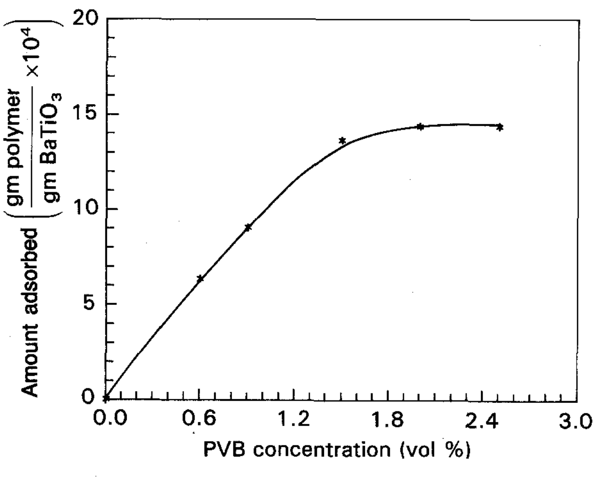

Figure 2 Variation of the amount of PVB adsorbed on $BaTiO_3$ particles with overall PVB (molecular weight 50 000) concentration.

TABLE III Variation of bulk densities of green and fired tapes with PVB concentration (as dispersant) of the suspension

PVB concentration (vol %) (as dispersant)	Bulk density (%)	
	Green	Fired
0.0	36.0	85.0
0.6	39.0	89.0
1.6	44.5	92.0
2.0	45.0	92.0

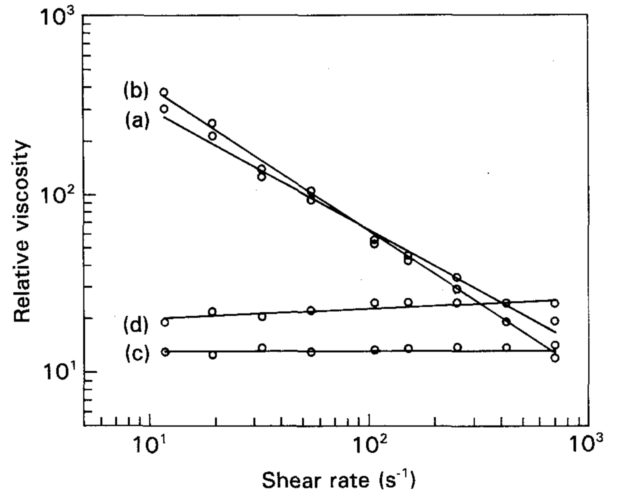

Figure 3 Relative viscosity versus shear rate of a 25 vol % $BaTiO_3$ suspension in a toluene–methanol azeotrope with different concentrations (vol %) of PVB (molecular weight 200 000): (a) 0.0, (b) 0.2, (c) 0.6, and (d) 0.8.

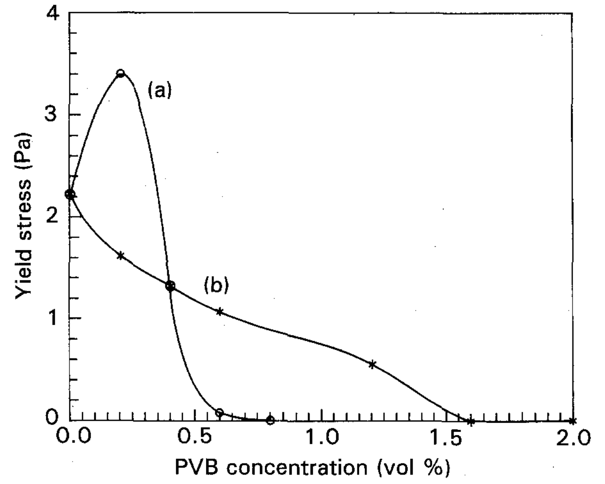

Figure 4 Variation of the yield stress with the overall PVB concentration for two different molecular weight of PVBs: (a) 200 000, and (b) 50 000

high molecular-weight polymer may be due to either or both of the following reasons.

1. Due to the longer chain length of the high molecular-weight polymer, the number of attachments on the particle surface (adsorption density) is more than that for a low-molecular-weight polymer. As a result, the monolayer coverage is expected to be completed at a lower concentration of the high-molecular-weight polymer.

2. According to Flory's equation [3] the radius of gyration of a polymer chain, R_g, is related to the degree of polymerization, N, in the following manner

$$R_g = KN^g$$

where K and g are constants.

So, for high-molecular-weight polymers, which have larger values of N and hence of R_g, the action of stabilizing moieties is much more effective due to the larger spatial extension in comparison to that of a low-molecular-weight polymer.

3.4. Effect of solvent composition

All the above experiments were carried out with the same solvent system, that is, an azeotropic mixture of toluene and methanol (27.6% + 72.4%). The effect of variation of the solvent composition on the rheological properties of the suspension is discussed in this section. The values of the shear-rate exponent as the PVB concentration increases are listed in Table IV for an azeotropic solvent composition of toluene and methanol (solvent A) and also for the reverse azeotropic mixture (solvent B) of the same components. The powder loading was kept constant at 25 vol % of the suspension in all cases. The shear-rate-exponent values, m, are obtained by fitting shear-rate, $\dot{\gamma}$, and shear-stress, τ, data to the following equation [17]

$$\tau = k\dot{\gamma}^m$$

where k is a constant.

The value of m gives an indication of the flow behaviour in the following manner:

$m < 1$, indicates shear thinning,
$m = 1$, indicates Newtonian flow, and
$m > 1$, indicates dilatancy (shear thickening).

The results presented in Table IV indicate that with no PVB addition the suspension containing solvent B shows more shear-thinning behaviour than the suspension with solvent A. This is due to the relatively low zeta potential of the solvent B system (7 mV) compared to that of solvent A (32 mV). Consequently, it may be concluded that a relatively low electrostatic repulsive force exists in the solvent B system causing more shear-thinning behaviour. However, on addition of increasing amounts of PVB, both the suspensions become Newtonian and finally show dilatancy. It is interesting to note that the solvent B system exhibits Newtonian flow at a much lower concentration of PVB (0.7 vol %) than that of solvent A for which the value is 1.6 vol %. This behaviour is supported by the adsorption isotherm curves for the two solvent systems presented in Fig. 5 which clearly shows significantly higher adsorption densities for solvent B than for solvent A, throughout the whole range of PVB concentration.

Such an effect of solvent composition on the rheological properties of the suspension can be explained by considering the polymer–liquid, polymer–particle and particle–liquid interactions. PVB resins contain a significant fraction of hydroxyl side groups (i.e. PVB segments) [8] and it is reported [18] that PVB resins attach themselves to oxide particles via hydrogen bonding between hydroxyl side groups of the polymer and hydroxyl side groups on the particle surface. Fig. 5 shows that higher adsorption densities are obtained with solvent B containing a relatively large quantity of toluene, which is a better solvent for PVB. Since polymer adsorption tends to be reduced when the polymer–liquid interaction is strong, this result indicates that the particle–liquid interactions must be playing a significant role. The latter interactions are important because both the liquid and the polymer may compete for adsorption sites on the particle surface. Strong adsorption of liquid on particle surfaces reduces the possibility of adsorption of the polymer due to the lower availability of surface sites. In this investigation methanol is expected to be adsorbed on $BaTiO_3$ particles via hydrogen bonding. This tends

TABLE IV Comparison of the shear-rate exponent, m, of a 25 vol % $BaTiO_3$ suspension in two solvent systems (an azeotrope, A, and a reverse azeotrope, B, of toluene–methanol)

PVB concentration (vol %)	Shear-rate exponent, m	
	Solvent A	Solvent B
0.0	0.29	0.26
0.4	0.60	0.81
0.6	0.73	0.96
0.7	–	1.00
1.2	0.90	1.21
1.6	1.00	–
2.0	1.10	–

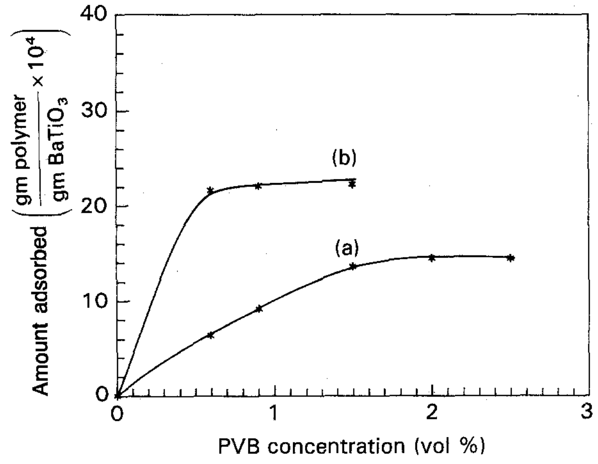

Figure 5 Variation of the amount of PVB adsorbed on $BaTiO_3$ particles with overall PVB (molecular weight 50 000) concentration (vol %) for two different compositions of toluene–methanol: (a) an azeotropic mixture (27.6% + 72.4%), and (b) a reverse azeotropic mixture (72.4% + 27.6%)

to reduce the adsorption of PVB on $BaTiO_3$ in solvent A containing large amounts of methanol. But in solvent B, containing smaller amounts of methanol, less liquid adsorption occurs and more surface sites are available for PVB adsorption.

Higher adsorption densities with solvent B are also reflected in the bulk densities of the tape-cast samples. A maximum bulk density of 48 per cent of the theoretical for the green tapes has been achieved with the solvent B system, whereas in solvent A the maximum bulk density is around 45 per cent of the theoretical value.

However, one major disadvantage of preparing tapes with the solvent B system is that the cast tapes show a greater adherence to the glass surface on which the tapes are cast, and it is difficult to remove the tapes from the glass plate without tearing. This is possibly due to the incompatibility of polyethylene glycol (used as a plasticizer) with solvent B, as Karas *et al.* [19] have observed that polyethylene glycol is primarily responsible for the smooth stripping of $BaTiO_3$ tape from the glass surface.

4. Conclusions

1. Addition of a small amount (1.6 vol %) of PVB (average molecular-weight 50 000) to a 25 vol % $BaTiO_3$ slurry in a toluene–methanol azeotrope produces a well dispersed system. The adsorption isotherm curve also indicates that the monolayer coverage is complete at 1.6 vol % of the polymer.

2. The $BaTiO_3$ tapes (green as well as fired) which are prepared with PVB as a dispersant show an appreciable bulk density.

3. Use of high-molecular-weight PVB (200 000) rather than a low-molecular-weight PVB causes bridging flocculation when the polymer concentration is very low (0.2 vol %). However, the flocculation behaviour changes to steric stabilization at a relatively higher concentration (0.6 vol %) of the polymer. The relatively low PVB (high-molecular-weight) concentration (0.6 vol %) required to stabilize a 25 vol % $BaTiO_3$ suspension compared to that (1.6 vol %) with the low-molecular-weight polymer is due to the longer chain length of high-molecular-weight polymers.

4. So far as the dispersibility of $BaTiO_3$ suspensions with PVB is concerned, a reverse azeotropic composition of toluene–methanol (72.4:27.6) is a much better solvent than an azeotropic concentration. However, the tapes cast with slurries containing the former solvent show strong adherence to the glass surface.

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References

1. G. D. PARFITT, "Dispersion of powders in liquids", (Elsevier, London, 1969) p. 82.
2. J. TH. G. OVERBEEK in "Colloid science", Vol. 1, edited by H. R. Kruyt, (Elsevier, Amsterdam, 1952) p. 58.
3. D. H. NAPPER, "Polymeric stabilisation of colloidal dispersions", (Academic Press, New York, 1983) p. 21.
4. K. MIKESKA and W. R. CANNON in "Advances in ceramics", Vol. 9, edited by J. A. Mangles and G. L. Messing, (The American Ceramic Society, Westerville, Ohio, 1985) p. 164.
5. W. R. CANNON, J. R. MORRIS and K. R. MIKESKA in "Advances in ceramics", Vol. 19, (The American Ceramic Society, Westerville, Ohio, 1987) p. 161.
6. W. R. CANNON, R. BECKER and K. R. MIKESKA in "Advances in Ceramics", Vol. 26, (The American Ceramic Society, Westerville, Ohio, 1989) p. 525.
7. F. M. FOWKES, *J. Adhesion* **4** (1972) 155.
8. M. D. SACKS, C. S. KHADILKAR, G. W. SCHEIFFELE, A. V. SHENOY, J. G. DOW and R. S. SHEU in "Ceramic powder science", Advances in Ceramics, Vol. 21, (The American Ceramic Society, Westerville, Ohio, 1987) p. 495.
9. SUBIR BHATTACHARJEE, M. K. PARIA and H. S. MAITI, *Ceram. Int.*, communicated.
10. J. T. G. OVERBEEK in "Colloid science", edited by H. R. Kruyt, (Elsevier, Amsterdam, 1952) p. 202.
11. S. MIZUTA, M. PARISH and H. K. BOWEN, *Ceram. Int.* **10** (1984) 43.
12. R. E. MISTLER, D. J. SHANEFIELD and R. B. RUNK in "Ceramic processing before firing", edited by G. Y. Onoda and L. L. Hench, (Wiley, New York, 1978) p. 411.
13. J. C. WILLIAMS in "Ceramic fabrication processes", edited by F. F. Y. Wang, (Academic Press, New York 1976) p. 173.
14. H. BURREL, *Int. Chem. Rev.* **14** (1955) 3.
15. M. D. SACKS, *Amer. Ceram. Soc. Bull.* **63** (1984) 1510.
16. R. J. MORGAN, *Trans. Soc. Rheol.* **12** (1968) 511.
17. T. C. PATTON "Paint flow and pigment dispersion", (Wiley, New York, 1964).
18. K. NAKAMAE, K. SUMIYA, T. TAII and T. MATSUMOTO, *J. Polym. Sci.* **71** (1984) 109.
19. A. KARAS, T. KUMAGAI and W. R. CANNON, *Adv. Ceram. Mater.* **3** (1988) 374.

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