Dispersion and Rheological Characterization of TiO$_2$ Tape Casting Slurry

Abstract

Dispersion behavior of TiO$_2$ in different solvent systems in combination with two different dispersants was studied and optimized for the dispersion of TiO$_2$. Based on sedimentation, viscosity, and rheological characteristics, zeotropic ethanol: xylene with a ratio of 50:50 along with 1 wt% menhaden fish oil is found to be the best solvent–dispersant combination for TiO$_2$. Tape casting slurry was optimized using polyethylene glycol 400 and benzyl butyl phthalate as plasticizers and polyvinyl butyral as the binder. Cyclohexanone was used as homogenizer. TiO$_2$ tapes were obtained by double doctor blade tape casting process and these as cast tapes were dried in air at room temperature. The results show that it is possible to obtain homogenous defect free green tapes of 58.7% solid loading and green density of 55 % having thickness of ~90 mm.
5.1 Introduction

Titanium dioxide is a novel wide band gap material that is exploited for its dielectric, photochemical, catalytic, and other properties [1–5]. TiO₂ as thin films and dielectric ceramic sheets are required for solar cells, photodegradation of organics in water, and in air under ultraviolet illumination and for multilayer ceramic/metal composite components. Tape casting is one of the cheapest methods to produce large ceramic sheets [5, 6]. The doctor blade tape casting is a well established, low cost technique for manufacturing thin ceramic sheets of controlled thickness [7–14]. Tape casting involves dispersion of inorganic ceramic powder in a liquid medium, followed by addition of organic binders and plasticizers to increase the strength and flexibility of the tapes after casting and drying [15,16]. Most applications of tape casting technology refer to the electronic industry, while some authors have also used this technique for obtaining thin ceramic sheets and multilayered structures for different applications such as solid oxide fuel cells or laminated composites [17–20]. Colloidal processing of tape casting slurries is a critical step in achieving uniform and dense ceramic bodies. To make uniform dense green(unfired) tapes, a tape casting slurry should be a well dispersed homogenous stable system with low viscosity, good shear thinning behavior and high solid loading [21,22].

Tape casting slurry preparation involves particle deflocculation and dispersion in a solvent and slurry homogenization with the aid of binders and plasticizers [22]. There are two stages in tape casting slurry preparation, namely deagglomeration and homogenization with
binders and plasticizers. In the first stage, dispersion strongly influences green tape characteristics and later it influences the density and microstructural homogeneity of the final product [23]. Flocculated slurry results in porosity and hence deflocculation/dispersion is the critical step in slurry preparation [22]. Dispersion of ceramic powder in a medium is usually achieved by the addition of an optimum amount of dispersant. Dispersion is achieved by either electrostatic or steric mechanism or a combination of both [13,15,24]. The sedimentation technique, a well accepted method of establishing the degree of particle dispersion and packing, gives a visual representation of deflocculation and dispersion [25]. A low settling rate and a high final packing density represent a high degree of dispersion, which generally corresponds to low viscosity. Powder dispersion is not only affected by the nature and concentration of the dispersant, but also by the type of solvents used [21]. Tape casting slurries are generally prepared using two or three solvent mixtures to facilitate homogenous dispersion of the powder. Another important characteristic of tape casting slurry is its rheological characteristics, that is, flow behavior. During the dispersion stage, as far as the rheological characterization is concerned, the system that gives minimum viscosity and near Newtonian behavior is considered as the best dispersed condition [24–26]. Jingxian et al [11,12] have studied the effect of four different azeotropic binary solvent mixtures for the tape casting of TiO₂ and concluded that ethanol/methane ethyl ketone mixture acts as an effective solvent system. However, in tape casting of other oxide ceramics researchers have used zeotropic solvents which give the flexibility of varying the solvents ratio[13,15].
The aim of the present work is to do a systematic and comprehensive study of a combination of azeotropic/zeotropic solvent systems with well known steric and electrostatic dispersants for TiO$_2$ ceramic and to understand the underlying dispersion mechanism and the role of solvents and dispersants. Hence, the present work attempts to investigate dispersion of TiO$_2$ powder using eight different combinations of binary solvent mixtures with two different dispersants. The study also involves rheological characterization of each dispersed system and that of the tape casting slurry. An optimized slurry combination with 58.78% solid loading was found to exhibit shear thinning rheological characteristics. Based on the optimized slurry composition, tapes free from visible defects with about 90 mm thickness were obtained using the double doctor blade technique.

5.2 Experimental

TiO$_2$ powder used for the present study was obtained from Sigma Aldrich, with a purity of 99.91%. The average particle size, as given by the manufacturer, is < 5 nm. In the case of oxides, the most common solvent combination used for tape casting was azeotropic mixtures of solvents with alcohol as one of the constituents. The solvent systems used for the present study were mixtures of ethanol (EtOH) with toluene (Tol), methyl ethyl ketone (MEK) or xylene (Xyl), while toluene/ethanol and ethanol/ methyl ethyl ketone were taken in the azeotropic ratio, xylene/ethanol was taken at 50:50 ratio. This ratio was arrived at after preliminary experiments with different ratios. The most effective dispersants for oxides that were commonly used in tape casting such as menhaden fish oil (MFO) and phosphate ester
(PE) were chosen for the present study. For the preparation of tape casting slurry, polyethylene glycol 400 (PEG) and benzyl butyl phthalate (BBP) were used as plasticizers. 20 wt% polyvinyl buyral (PVB) was used as binder.

5.2.1 Slurry Preparation

Dispersion studies were carried out with 33 wt% of solid content in different solvent mixtures with varying wt% of dispersant. Slurry was ultrasonicated for 10 min and then ball milled for 24 hour with zirconia balls as milling media for effective deagglomeration and dispersion. Further sedimentation and rheological studies were carried out.

5.2.2 Sedimentation Studies

For sedimentation study, 10mL of the ultrasonicated and ball milled slurry was immediately transferred to a graduated measuring cylinder and then the slurry was allowed to settle undisturbed for a day. The sediment height (H) was recorded at regular intervals as a function of time against the initial height (H₀). For better clarity sedimentation up to 1 hour and the value after 24 hour alone is plotted.

5.2.3 Rheological Studies

Rheological characterization was carried out using a shear-controlled rheometer (Brookfield programmable DV III1Rheometer) using UL adapter for dispersion studies and small sample adaptor (Spindle SC4-18, Brookfield) for tape casting slurry. The general flow behavior was studied by plotting the variation of viscosity with shear rates. These viscosity data were tested by fitting with different mathematical models using the Rheocalc Software (Brookfield
In the case of final tape casting slurry shear thinning behavior is desirable as the tape casting slurry experiences shear force under the action of moving blade/carrier.

5.2.4 Tape Casting and Dielectric Studies

Tape casting slurry was prepared with optimum concentration of the selected solvents and dispersant. Double step slurry preparation was carried out. In the first stage, powder was ball milled for 4 hour in solvent with dispersant using zirconia balls as milling media. This treatment was effective in breaking up the soft agglomerates and in ensuring equilibrium adsorption of dispersant on the powder surface. Other tape casting additives (binders, plasticizers) were then added and the slurry was rolled for 24 hour in the second step. Tape casting was carried out using double doctor blade technique on a clean glass bed using laboratory batch type tape caster (EPH Engineering). The blade gap was kept at 250 µm. After natural drying, tapes were released and inspected for potential defects. Thickness and green density were measured. Green tapes were cut, stacked and laminated at 80 ºC and 1.6 ton/cm² pressure. A slow binder burn out cycle up to 600 ºC was carried out for removal of organic contents. For densification, these samples were sintered in a platinum crucible at different temperatures of 1200 ºC, 1250 ºC, 1300 ºC, 1350 ºC for 2 hour. The density of the ceramic sheets was measured by Archimedes principle. Dielectric studies were performed using Gain Phase analyzer (Agilent Technologies). Room temperature silver paste was applied on both sides of the ceramic and acts as ohmic contact. The capacitance and dielectric constants were measured.
Chapter 5

5.3 Results and Discussion

5.3.1 Influence of Solvents and Dispersants

The sedimentation technique, a well-accepted method of establishing the degree of particle dispersion and packing, gives a visual representation of deflocculation and dispersion. A low settling rate and a high packing density represents a high degree of dispersion and generally corresponds to low viscosity. The rate at which the dispersed powder settles under gravity is also a clear indication of the state of dispersion and stability. The settling rate and viscosity measurements for TiO$_2$ with 1 wt% of MFO with different solvent systems are shown in Figures 5.1 and 5.2. From Figure 5.1 it is clear that the initial rate of sedimentation differs considerably for the different solvent systems.

Figure 5.1 sedimentation study of TiO$_2$ with 1% MFO as dispersant
The sedimentation height after 24 hour also shows a clear difference bringing out the fact that xylene–ethanol solvent system is better than methyl ethyl ketone–ethanol or toluene–ethanol system. Xylene–ethanol solvent system shows a minimum settling rate compared with methyl ethyl ketone–ethanol and toluene–ethanol solvent systems.

The same experiment was also performed with 1wt% of PE as dispersant. Figures 5.2 and 5.3 show viscosity and the settling rate measurements for TiO$_2$ with PE as dispersant. From Figure 5.2 it is observed that, slurries with MFO as dispersant have low viscosities compared with that of PE as dispersant. Hence MFO was chosen for
the present study as dispersant. From Figure 5.3 it is observed that xylene–ethanol system has a low settling rate compared with methyl ethyl ketone-ethanol and toluene–ethanol solvent systems. It is also observed from Figure 5.2 that methyl ethylketone-ethanol system has slightly low viscosity than xylene–ethanol system, but from sedimentation study its settling rate is faster. Hence xylene–ethanol was chosen as the solvent system for the present study.

To understand the effect of concentration of MFO as dispersant, its content was varied from 0.5% to 1.5% in xylene–ethanol system.
Dispersion & rheological characterization of TiO₂

Figure 5.4 Sedimentation Study of TiO₂ in Xyl-EtOH system with different concentrations of MFO

Figure 5.5 Effect of different MFO concentrations on rheology of TiO₂ dispersed in Xyl-EtOH system
From Figures 5.4 and 5.5 it is found that lowest settling rate and minimum viscosity is observed for 1 wt% MFO concentration. Finally 1 wt% MFO with xylene–ethanol solvent system is found to be the optimum for dispersion of TiO₂. Tape casting slurry composition was optimized using PEG and BBP as plasticizers, PVB as binder, using ethanol–xylene as the solvent and MFO as dispersant. Cyclohexanone was used as the homogenizer. The optimized slurry composition is shown in Table 5.1. Here the weight percent of dispersant is taken with respect to powder loading in the tape casing slurry. As expected the final tape casting slurry exhibited shear-thinning pseudoplastic behavior (Figure 6). Using the optimized slurry composition, green tapes free from visible defects of ~ 90 mm thickness were obtained.

![Figure 5.6 Rheological Characterisation of final tape casting slurry](image-url)
Figure 5.7 shows the flow chart diagram of the tape casting process.
5.3.2 Properties of TiO$_2$ Green Tapes and Sintered Ceramic Sheet

The qualities of green tapes, such as homogeneity, surface quality, absence of bubbles, pinholes, transparent dots, agglomerates, and cracks greatly affect the properties of TiO$_2$ ceramic sheet. Dried tapes were cut at a size of 1" X1" and 20 numbers were stacked at a pressure of 1.6 ton/cm$^2$ at a temperature of 80$^\circ$C(1 hour) and pressure was continuously applied till it cooled down to room temperature. For binder burn out of samples, slow heating rate (4$^0$/min) up to 600$^\circ$C with a dwell time of one hour was adopted. Density of the sample sintered at 1300 $^\circ$C was measured by Archimedes principle and the value obtained (4.19 g/cm$^3$) is very close to its theoretical value of 4.23 g/cm$^3$.

![Figure 5.8 FTIR spectra of TiO$_2$ powder and green tape](image)
Figure 5.8 shows FTIR spectra of TiO\textsubscript{2} powder and tape. The material was mixed with KBr and pelletized. FTIR spectrum was recorded on a Shimadzu Spectrophotometer. The bands at 1350, 458, 2783 cm\textsuperscript{-1} are due to C–H stretching of methyl groups present in organic constituents of the tape. The bands at 1284 cm\textsuperscript{-1}, 1130 cm\textsuperscript{-1} are C–O stretching of PEG and the bands at 1728 cm\textsuperscript{-1} due to carbonyl group present in MFO [27–30]. In Figure 5.9 the SEM micrograph shows dense ceramic with almost uniform microstructure.

Figure 5.9 SEM image of TiO\textsubscript{2} sintered sheet

Figure 5.10 shows an optical photograph (Olympus BX51) of a defect free tape. Dielectric constant (K) of the TiO\textsubscript{2} pellet was measured by applying silver paste as electrode. K is obtained using the conventional equation $K = Cd/\varepsilon_0 A$, where C is the capacitance of
the TiO$_2$ pellet, d and A represent the thickness and area of the pellet and $\varepsilon_0$ is the permittivity of free space. The obtained $K$ value of 106 is in agreement with the theoretical value of 109.

![Figure 5.10 Optical Photograph of the green tape](image)

**Table 5.1. Optimized tape casting slurry composition**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Role of constituent</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>Powder</td>
<td>58.95</td>
</tr>
<tr>
<td>MFO</td>
<td>Dispersant</td>
<td>0.58</td>
</tr>
<tr>
<td>Xylene</td>
<td>Solvent</td>
<td>17.83</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Solvent</td>
<td>8.21</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>Homogenizer</td>
<td>0.21</td>
</tr>
<tr>
<td>PEG 400</td>
<td>Plasticizer</td>
<td>1.18</td>
</tr>
<tr>
<td>BBP</td>
<td>Plasticizer</td>
<td>0.95</td>
</tr>
<tr>
<td>PVB</td>
<td>Binder</td>
<td>12.05</td>
</tr>
</tbody>
</table>
Fish oil is a natural product that contains, among other things, 20 or more different types of fatty acids. MFO is primarily \[22,31\] a steric hindrance deflocculant, though the dielectric nature of the solvent can significantly affect this. In the case of nonpolar solvents MFO ordinarily can act only as a steric hinderant and in polar liquids ionization of acids can lead to electrosteric dispersant mechanism \[22,31\]. PE functions as an electrosteric dispersant. PE is the corresponding ester of phosphoric acid. Phosphoric acid contains three hydroxyl groups and can form esters in which one, two, or three of the P–OH hydroxyl groups can be replaced by alkoxy groups to form mono-, di- and tri alkyl esters. The P–OH groups of the monoalkoxy and dialkoxy PEs contain acidic hydrogens, which undergoes ionization in aqueous medium. A monoalkoxy ester, for example, could exist as a dianion, monoanion, or neutral ester. The ionization of the esters in aqueous medium allows the polymer to act as an electrosteric dispersant \[22,31\]. However, in nonaqueous medium because of low dielectric constant ionization of PE is not effectively taking place. Hence PE is not acting as a good dispersant. On the other hand MFO imparts steric hindrance and hence is an effective dispersant for TiO\(_2\) in nonaqueous solvent medium. The present study also highlights the fact that zeotropic xylene–ethanol systems with MFO as dispersant acts as a better solvent–dispersant combination for TiO\(_2\).
5.4 Conclusion

The dispersion, viscosity and rheological characteristics of the tape casting slurry for TiO$_2$ were studied systematically at every stage of the slurry preparation. Based on these studies, a combination of 50:50 ratio of xylene–ethanol zeotropic solvent system and 1wt% MFO as the dispersant were used for achieving optimum dispersion. MFO acts as a steric dispersant and effectively disperses TiO$_2$ in nonaqueous medium. Using the optimized slurry with 58.7% of solid loading, which exhibits pseudo plastic behavior, visibly defect-free tapes of ~ 90 mm thickness and 55% green density were obtained. The sintering cycle of TiO$_2$ ceramics was also optimized and the properties were evaluated. The qualities of green tapes, such as homogeneity, surface quality, agglomerates and cracks greatly affect the properties of TiO$_2$ ceramic sheet. Dried defect free tapes were cut into desired shapes and 20 numbers were stacked at a pressure 1.6 ton/cm$^2$ and at a temperature of 80$^\circ$C for one hour. The pressure was continuously applied till the tape cooled down to room temperature. The sintering temperature of the TiO$_2$ laminated sheets was optimized at 1300$^\circ$C. The experimental values of density and dielectric constant for the sheets sintered at 1300$^\circ$C are in agreement with theoretical values.
References


