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Forming nanometer TiO_2 sheets by nonaqueous tape casting

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Abstract

The condition for the preparation of stable nanometer TiO_2 slurries by nonaqueous tape casting was indentified. To acquire stable low-viscosity slurries, the influences of solvent, dispersant and solid content on the rheological properties were investigated. The azeotropic mixtures (ethanol/methyl ethyl ketone) and Polyester/Polyamine Copolymer (KD-1) could serve as good solvent and dispersant, respectively. The slurries of nanometer TiO_2 behaved as near Newtonian up to a solid loading of 34 vol.%. Films of TiO_2 had very good qualities, such as homogeneity, surface quality, absence of bubbles and cracks, which indicated that slurries at selected conditions met the needs of tape casting process. The relative density of 24 and 34 vol.% sintered sheet was 51 and 69%, respectively. Results indicated the density increased with the solid content, sintering temperature and pressure.

Keywords: A. Tape casting; A. Films; Nano-TiO_2

1. Introduction

In the past decades, much attention had been paid to nanometer TiO_2 owing to its special dielectric, photochemical catalysis properties and good mechanical performances, such as super-plasticity in hypothermy and good ductility with high hardness [1–3]. Some applications including the use of TiO_2 in solar cells and for the photodegradation of organics present in polluted water and air under ultraviolet light illumination [4,5] had been researched.

Recently, much work has been focused on the preparation of TiO_2 films. The most-common fabrication methods are sol–gel, vapor deposition process, ion-beam sputter [6–8]. Tape casting can be also used to prepare TiO_2 films, which is a prominent technique for preparation of large dimension ceramic films with lower price [9,10]. It has been used in electronic devices and tailored structural parts, such as multilayered composites. In tape casting processing, an appropriate choice of the dispersant type and concentration is essential to obtain adequate stability of the suspension and ensure acceptable quality of the products [11]. However, nanosized powder is difficult to be deflocculated [12,13].

To our understanding, little work has been reported on the preparation of TiO_2 film by nonaqueous tape casting process. The work was aimed to identify the conditions for the preparation of stable nanometer TiO_2 slurries for nonaqueous tape casting. Effects of pH, dispersant type and powder concentration on the rheological behavior of the slurry were investigated by employing Zetaplus particle sizing distribution, sedimentation, viscosity and rheological measurements.

2. Experimental procedure

Nanometer TiO_2 (HTTi-01, Nanjing Haitai, China) with the particle size as $D_{50} = 10$ nm and the specific surface area as 120 m^2/g was used. The crystal structure was anatase identified by X-ray diffraction. TiO_2 powder ultrasonically treated in ethanol for 1 h was used as raw material. Azeotropic mixture was prepared with ethanol/methyl ethyl ketone (EtOH/MEK = 33/66 wt.%). Five kinds of dispersants including olein, oleic acid, polyethylenimine (PEI, BDH Laboratory supplies, England), potassium polyacrylate (Lopon 895, Bk Guiulini Chemic representative office), and hypermer KD-1 (Uniqema) were studied. polyvinyl-butyral (PVB) and butyl benzyl phthalate (BBP) were used as binder and plasticizer, respectively. The apparent pH was adjusted with 2 M HCl and 2 M NaOH solutions.

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Slurries of TiO_2 were prepared with TiO_2 powder dispersed in EtOH/MEK mixture with dispersant by ball milling in a plastic jar with ZrO_2 balls for 24 h. Then the viscosity and rheology of slurries were measured. After adding the binder and plasticizer to the slurries, tape casting was performed on a polypropylene film using Procast Precision Tape Casting Equipment (Division of the International, Inc., Ringoes, New Jersey) with a blade height of 500 μm. The casting speed is 100 cm/min and the temperature of the chamber is 25 °C. In order to avoid the particles agglomeration on the surface of films that resulted from poor dispersibility of PVB, the PVB ethanol solution was used as binder. The content of PVB (based on ethanol solvent) was 30 wt.%. Drying and removing binder were conducted at room temperature in open air and at 500 °C for 2 h in vacuum, respectively. The TiO_2 sheet was sintered by spark plasma sintering (SPS) at 700 °C with 35 MPa for 3 min.

Zetaplus particle sizing distribution (Brookhaven Instruments Corp.) was used to survey the particle existence state. A rotating-cylinder viscometer (Model NDJ-7, Shanghai Balance Instrument Factor, China) was used to determine the apparent viscosity of slurries. The rheological behavior was measured on Model SR5 (Scientific, Piscataway, NJ) by the rotating cylinder method. Scanning electron microscopy (SEM) system (JSM-6700F, JEOL, TOKYO, Japan) was used to observe the microstructure of green films. The infrared spectrum analyzer (Nicolet-7199, USA) was used to search the valence bond on the surface of powders. The crystal structure was obtained from X-ray diffraction (Rigaku D/max 2550V X, Cu Kα).

3. Results and discussion

3.1. Influence of powder and solvent on the stability of slurries

For the unbalance of Ti–O, the water adsorbed on the surface of nano-TiO_2 powder can dissociate and easily form the hydroxyl. It is to say pure nano-TiO_2 is easily dispersed in the polar medium such as water and ethanol. But considerable impurities such as metals and metal oxides (induced during the preparation process) in the powder will decrease the dispersibility of TiO_2. Fig. 1 shows the FTIR spectrograms of treated and untreated powder. The intensive absorption peak near 500 cm^{-1} corresponds to the bond of Ti–O. Treated powder has stronger absorption than untreated powder, which indicates treaded powder losing cations has more naked surface.

The major function of solvent is to act as a dispersing vehicle and to ensure the dissolution of the organic components. Nonaqueous solvents tend to be preferentially used for tape casting due to its low surface tension and dielectric constant compared with water. Azeotropic mixtures are reported to have the advantage of improving the organic solubility, and preventing preferential volatilization and polymeric surface skin formation [14]. EtOH/MEK are selected as azeotropic mixtures. Fig. 2 shows the particle sizing distribution of original powder in water and in azeotropic solvent and treated powder in azeotropic solvent, which is important for understanding the dispersibility of ceramic particles in a liquid medium. Results indicate that untreated powder in water has the largest particle size and in azeotropic mixtures has smaller particle size. EtOH/MEK mixture has been evidenced to have effective wettability on TiO_2 particle surface [15]. The treated powder does not have the larger secondary generation agglomerate that exists in the untreated powder. Treated powder losing cations has bigger specific surface and more hydroxyl groups on the surface, which cause better consistency in nonaqueous and the interaction between the hydrocarbon chain in solvent and hydroxyl on the surface of TiO_2. Results indicate that the treated powder has better dispersity in water and EtOH/MEK. In following experiments, the treated TiO_2 powder and EtOH/MEK mixture is used as material and solvent, respectively.

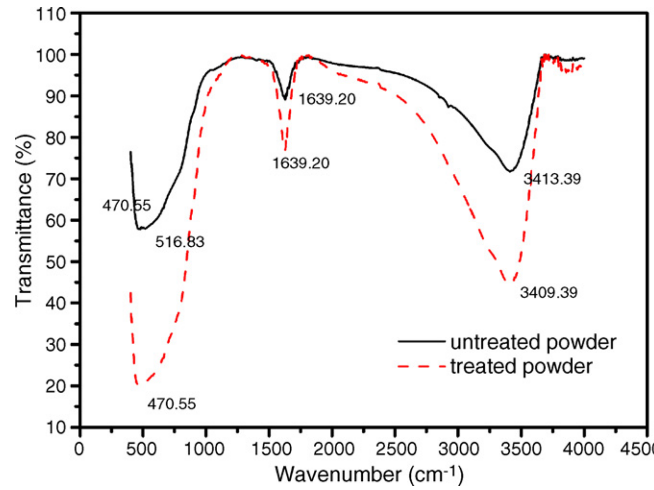

Fig. 1. FIR spectrograms of nano-TiO_2 powder.

3.2. Influence of dispersants on the stability of slurries

Viscosities of slurries with 10 vol.% powder concentrations and 2 wt.% dispersant (based on the powder) are shown in Table 1. Of all slurries, only the slurry with KD-1 dispersant does not settle after 24 h. Results indicate that KD-1 has the best dispersity. Fig. 2 indicates that the particle size of the slurry with KD-1 as dispersant is smaller than that of the slurry without KD-1. After putting KD-1 in slurries, it may dissociate positively charged long-chains, which adsorb on the surface of TiO_2 and form the electrostatic and steric hindrance. The Zeta potential curve of TiO_2 treated powder with KD-1 shift to alkality, which indicates that the KD-1 has adsorbed on surfaces of TiO_2 powders.

Fig. 3 shows the viscosities of the 15 vol.% slurry (powder concentration) with 0.1–3.0 wt.% KD-1 (based on the powder), recorded at a shear rate of 350 s^{-1}. Fig. 3 shows that the viscosity of the slurry with around 0.5 wt.% KD-1, reaches its lowest value, which concentration is the optimal content. With excessive dispersant, the stretched molecular chain tends to tangle, which results in a thick double-charge layer and high viscosity [16]. The settling volume of

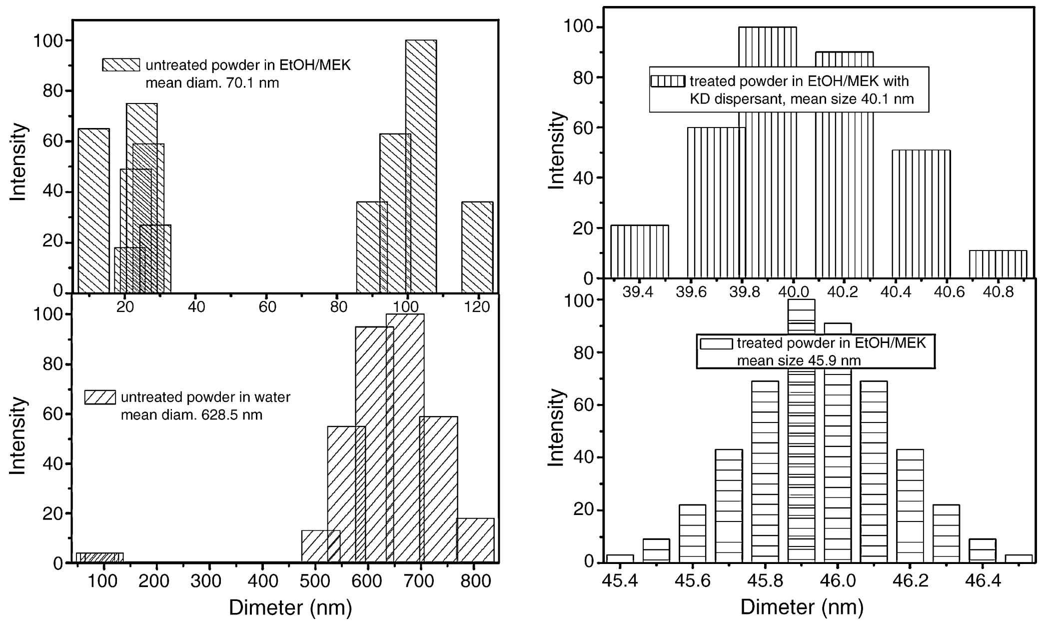

Fig. 2. Zetaplus particle sizing distribution of TiO_2 powder.

Table 1
Viscosities of 10 vol.% slurries with different dispersants (added to a concentration of 2 wt.% based on the dry powder)

Dispersant	Viscosity (mPa s)
Olein	6.5
Oleic acid	4.8
Lopon 895	8
PEI	33
KD-1	1

10 vol.% TiO_2 with 2 wt.% and 0.5 wt.% KD-1 measured as a function of slurry pH is shown in Fig. 4. Variation of sedimentation volumes at different pH values is due to the different extents of agglomeration/dispersion of the particles, which leads to different levels of particles packing in free space. The lowest settling volume of both TiO_2 suspensions occurs near pH 6.8. The good dispersion of TiO_2 with the pH range is attributed to the moderate adsorption of dispersant on the surface of TiO_2. The settling volumes of suspensions decrease with the pH range from 2 to 7. The reason is that at lower pH, the number of dispersant KD-1 dissociating in the solution and adsorbing on the surface of TiO_2 is less, which causes the aggregation of the nano-TiO_2 particles with larger surface. The settling volumes increase with pH in the range from 7 to 10, which is caused by the excess adsorption of KD-1.

Based on the above results, the 0.5 wt.% KD-1 (based on the powder) and pH 6.8 is selected as dispersant agent and pH value, respectively.

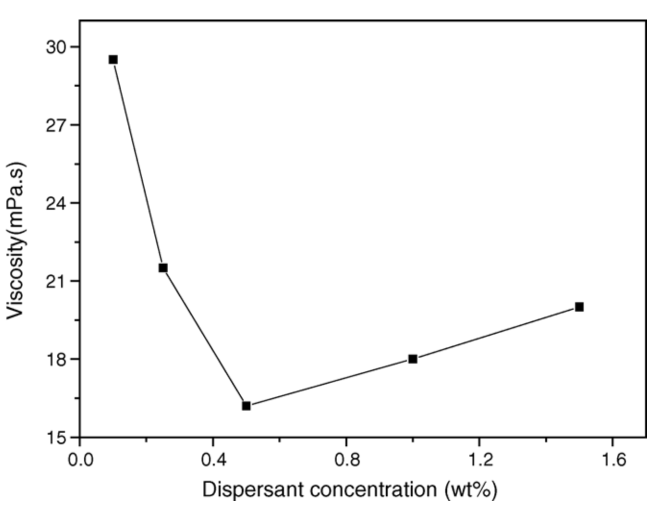

Fig. 3. Effect of KD-1 content (based on the powder) on the viscosity of 15 vol.% slurries.

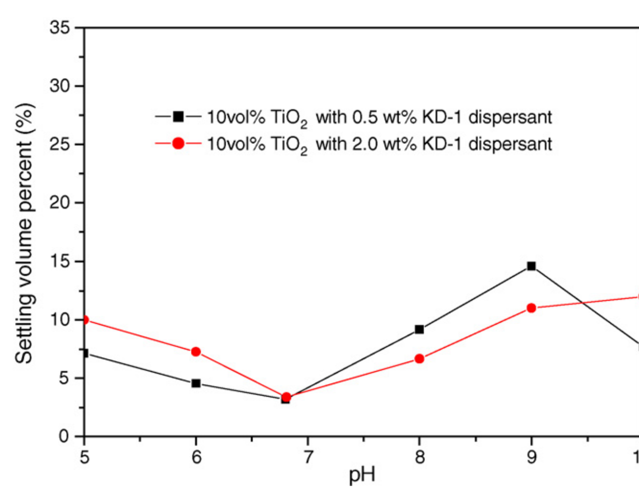

Fig. 4. Settling volume of 10 vol.% TiO_2 slurry with 2 and 0.5 wt.% KD-1dispersant as a function of pH.

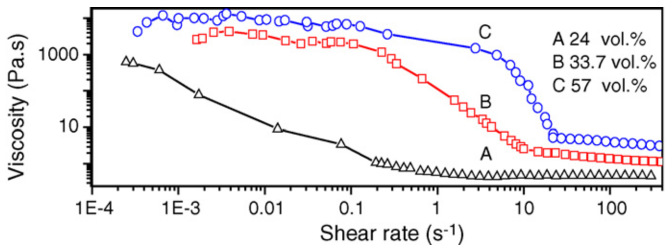

Fig. 5. Rheological curves of TiO_2 suspensions.

3.3. Influence of the solid content on the stability of slurries

Fig. 5 shows the rheological curves of slurries with solid contents of 24–57 vol.%. All slurries show slight shear thinning. With increasing the shear rate, viscous force may destroy the structure, increasing the suspension fluidity due to the release of immobile liquid within agglomerates. Based on the Woodcock formula, which gives the average distance h between first neighbors in terms of the particle size d and the volume fraction ϕ as follows [17]:

$$\frac{h}{d} = \left[\frac{1}{3\pi\phi} + \frac{5}{6}\right]^{1/2} - 1$$

when $\phi = 0.3$, $h = 0.0895d$. If $d < 20$ nm, then $h < 1.8$ nm. So the short distance between particles hindrances the relative flow of suspension and then causes the high viscosity at the low shear rate. As the solid content of the slurries increases, the gap of viscosity between the two Newtonian regions is sharper and the viscosities of slurries reach a plateau above the shear rate of 200 s^{-1}. The viscosity plateau value of A and B slurries is lower than 1 Pa s, and that of slurry C is higher than 1 Pa s. Slurries with the solid content of 24 and 34 vol.%, at the selected condition meet the demands of tape casting process. The slurry with 57 vol.% TiO_2 powder having a high viscosity is unsuitable for tape casting, since no thoroughly mixing would occur at the same rotational speed.

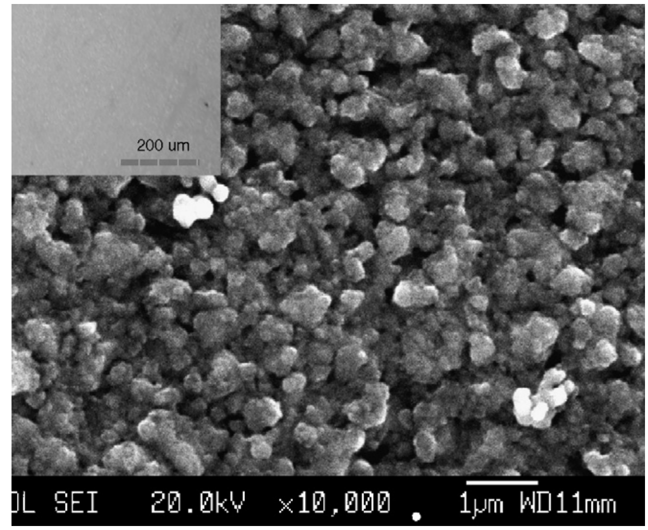

Fig. 6. SEM micrograph of TiO_2 green films after binder removal (left upper: optical graph of TiO_2 green film).

3.4. Property of TiO_2 green film and sintered sheet

The qualities of green film, such as homogeneity, surface quality, absence of bubbles and cracks greatly affect the properties of TiO_2 ceramic. Optical graphs of TiO_2 green films and SEM micrographs after binder removal are given in Fig. 6. The thickness of green film after drying is 110 μm. The apparent density and porosity of green film (34 vol.%) measured by mercury intrusion method (Poresizer 9320, USA) is 1.6 g/cm^3 and 12.53%, respectively. The dark areas in SEM micrographs are holes formed during the organic matter removal, especially PVB. These films have very good strength and flexibility, and can be easily cut and stacked together.

Fig. 7 shows the SEM micrographs of TiO_2 sintered sheet (24 and 34 vol.%). The sheet is stacked by green films and sintered by SPS at 700 °C with 35 MPa for 3 min. The relative density of 24 and 34 vol.% sheet is 51 and 69%, respectively. Results indicate the density increases with the solid content, sintering temperature and pressure. In sintering process, small

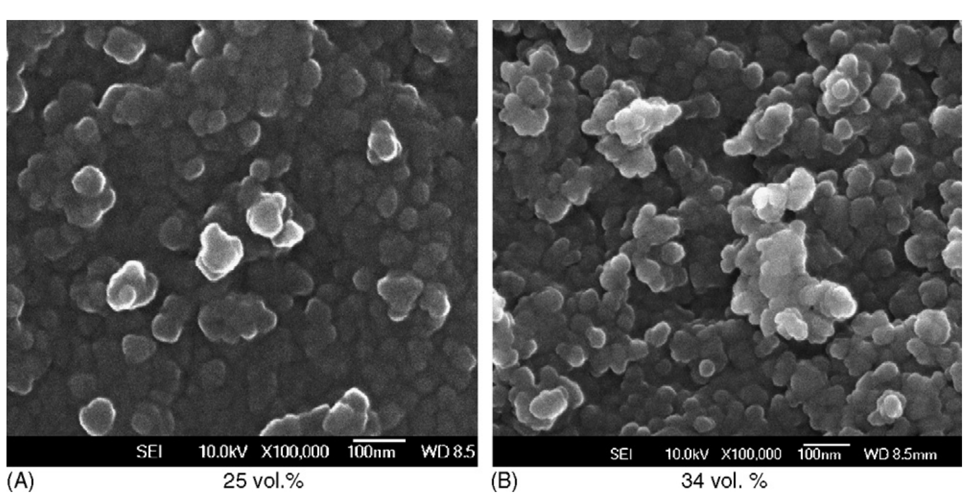

Fig. 7. SEM micrographs of TiO_2 sheets.

pores (3–15 nm) are difficult to remove. Thus it is difficult to get dense TiO_2 ceramics at low pressure, and crack is easy to grow [18]. Sintering process of nanocomposite should be researched more carefully. XRD indicates that the grain of TiO_2 sintered sheet is the anatase crystal, and the grain size is 26.12 nm according to Scherrel formula.

4. Conclusions

Zetaplus particle sizing distribution shows the TiO_2 powder ultrasonically treated in ethanol particles has better dispersity in azeotropic mixtures of EtOH/MEK solution. The TiO_2 slurry with 0.5 wt.% KD-1 with pH 6.8 reaches the lowest sediment volume and viscosity. Rheological quality of slurries depends strongly on the TiO_2 concentration. Slurries of TiO_2 with solids content up to 34 vol.% presents near Newtonian. TiO_2 green films exhibit good qualities, such as the homogeneity of composition, smooth surface, being free from bubbles and cracks, which show that the condition of slurry is credible. The apparent density and porosity of green film (34 vol.%) is 1.6 g/cm^3 and 12.53%, respectively. The relative density of 24 and 34 vol.% sintered sheet is 51 and 69%, respectively. The grain size of sintered sheet is 26.12 nm. Results indicate the density increases with the solid content, sintering temperature and pressure.

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