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Binary solvent mixture for tape casting of TiO_2 sheets

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Abstract

Four azeotropic binary solvent mixtures based on ethanol/methyl ethyl ketone, ethanol/toluene, isopropanol/methyl ethyl ketone and isopropanol/toluene were studied for the dispersion of TiO_2 powders. Two different polyvinyl butyral polymers (PVB79 and PVB98) were selected as dispersant and as binder and dibutyl phthalate (DBP) was used as plasticizer. The dispersability of TiO_2 suspensions was characterized by rheological measurements and sedimentation tests. After tape casting, the properties of Green tapes were tested in term of density, surface roughness and strength. Results showed that azeotropic EtOH/MEK mixture is the effective solvent system for tape casting of TiO_2 sheets. The TiO_2 tapes served for multilayer ceramic/metal composite manufacturing.

Keywords: Rheology; Slurry; Tape casting; TiO_2

1. Introduction

Tape casting is an established method for manufacturing wide and flat sheets of ceramic materials. 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 application such as solid oxide fuel cells or laminated composites.[1–5] A tape casting slurry is a complex system in which each component has a substantial effect on the slurry properties. To obtain a reliable processing of high quality products, a homogeneous dispersion of ceramic particles is highly required.[5–14] Stable suspensions are achieved by polymer steric stabilization or electrostatic repulsion or both according the type of dispersant and solvent used. The powder dispersion is not only dependent on the dispersant but also on the type of solvent used.[15] The major function of solvent is to act as a dispersing vehicle and to ensure the dissolution of the organic components. Mixture of solvents may be useful to achieve a good compromise between dielectric constant and surface tension (for dispersion) and low boiling point, and an adequate viscosity (for handling and drying). Azeotropic solvent mixtures were reported to have the advantage of improving the organic solubility, and preventing preferential volatilization and polymeric surface skin formation.[8,15] However, very few works have appeared in the literature dealing with the effect of solvent on the tape casting process.[8,15–18] Although PVB is well known as binder other than dispersant due to its high molecule weight, good disperserbility is also observed with it as dispersant.[17,19]

In the present work, four binary azeotropic solvent mixtures were studied with respect to the dispersability of TiO_2 powders in the presence and absence of dispersant. PVB79 was selected as dispersant. A comparison of dispersability of PVB79 with polycondensed fatty acid, castor oil, phosphate ester and PVB98 was studied, results showed that at low concentration levels (<2 wt.%), PVB79 can be used as effective dispersant.[17,19,20] The slurry properties were characterized in terms of sedimentation tests and rheological measurements. Green tapes were prepared through tape casting process and the influence of solvents on the tape properties was studied. The TiO_2 tapes were subsequently used for manufacturing of multilayer ceramic/metal composites.

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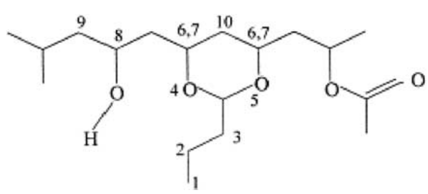
2. Experimental procedure

2.1. Starting materials

TiO_2 powders (Merck Art812, Germany) with a particle size of $d = 1.5$ μm and a specific surface area of 4.91 m^2/g were used for this study. The azeotropic solvent mixtures were prepared from ethyl alcohol (⩾99.8%, Carl Roth GmbHCo, Germany), isopropanol alcohol (⩾99.7%, Carl Roth GmbHCo, Germany), methyl ethyl ketone (⩾99.5%, Carl Roth GmbHCo, Germany) and toluene (⩾99.5, Merck KGaA, Germany). Polyvinyl butyral (B79, Monsanto, USA) was selected as dispersant. For preparing tape casting slurries, a polyvinyl butyral of higher molecular weight (B98, Monsanto,USA) served as a binder and butyl benzyl phthalate (Santicizer 160, Solutia, Inc., St. Louis, USA) were used as plasticizer. The structure of PVB could be shown as following:



PVB79 and PVB98 have the similar average molecue weight, 50,000–80,000 for PVB79 and 40,000–70,000 for PVB98. However, the two polymer are differnet in their hydroxyl contents (18–20% for PVB98 and 10.5–13% for B79). The properties of the starting materials are shown in Table 1.

2.2. Dispersability studies with binary solvents

Four binary azeotropic mixtures of solvents were selected for the dispersability study, see Table 2. Suspensions containing 16 vol.% of TiO_2 powder were prepared using different solvents in the absence of dispersant. The slips were ball milled with Al_2O_3 balls for 24 h. Slightly high concentrated suspension with 18 vol.% TiO_2 were also prepared with PVB (B79) as dispersant. The concentration of PVB (B79) was hold as 1 wt.% of the solid to assure all the suspensions with different solvent mixture are well stabilized. An interval of 24 h was allowed by ball milling to achieve equilibrium between the powder surface and the dispersant in the suspension. Then binder and plasticizer were added with the content as 8.56 wt.% and 8.32 wt.% (of the solid) respectively. The slurries were ball milled for another 48 h. Rheological behavior of the suspensions was characterized at 25 °C using a stress-controlled rheometer (UDS 200, Paar Physica, Austria). Shear dependence behavior of the suspensions under steady shear conditions were evaluated by ascending and descending shear rate ramps from 0.01 to 1000 s^{-1} in 5 min, and from 1000 to 0.01 s^{-1} in 5 min, respectively.

Table 1
Properties of raw materials

Constituents	Name	Properties			
		Density (g/cm^3)	Dielectric constant	Viscosity (mPa s)	Solubility parameter (MPa)
Solvent	Ethyl alcohol	0.789	24	1.2	26.2
Solvent	Isopropanol	0.785	18.8	2.4	24.9
Solvent	Methyl ethyl ketone	0.805	18	0.4	19.3
Solvent	Toluene	0.867	2.4	0.6	18.3
Dispersant	Polyvinyl butyral(B79)	1.08	3.1	–	23.12
Binder	Polyvinyl butyral(B98)	1.08	–	–	
Plasticizer	Butyl benzyl phthalate	1.05	–	–	

Table 2
Physical properties of four binary azeotropic solvent mixtures

Azeotropic solvent	Composition	Properties		
		Density		
(g/cm^3)			Dielectric constant	Solubility parameter (MPa)
Ethyl alcohol/methyl ethyl ketone	34:66	0.799	20.07	21.68
Ethyl alcohol /toluene	68:32	0.812	17.52	23.83
Isopropanol/methyl ethyl ketone	30:70	0.799	18.24	21.01
Isopropanol/toluene	69:31	0.810	14.06	22.99

2.3. Sedimentation tests

Glass cylinders of 10 ml volume covered with a lid were used to test the sedimentation behavior of 18 vol.% TiO_2 suspensions with PVB (B79). The position of the interface between the clear and supernatant solvent was recorded at regular time intervals. A month later, the volume of the sediment was determined before it was removed and the adsorption of dispersant on TiO_2 powder surface was characterized by TG-DTA, which measured the amount of released deflocculant upon heating in air.

2.4. Tape casting

After milling, the homogenous slurry was transferred to a vacuum chamber where it was de-aired at 30 kPa for 30 min. Tape casting was performed on a silicone coated polyethylene substrate foil with a gap height of 500 and 300 μm for 18 and 30 vol.% TiO_2 slurries, respectively. After drying, green sheets were removed and the density was measured using Archimedes method.

3. Results and discussion

3.1. Interaction between solvent and TiO_2 powder surface

The physical properties of the four azeotropic solvents are listed in Table 2. The rheological properties of 16 vol.% TiO_2 slurries (without dispersant) are characterized, see Fig. 1. The four azeotropic solvent systems reveal shear thinning behavior with a non-linearity of the viscosity at a shear rate of 10 s^{-1}. The irregular shape and break points suggest the lack of uniformity of slurries, which can be characterized as an agglomerated/flocculated structure. In non-aqueous solvent systems with low to moderate dielectric constant, the electrostatic repulsion between particles might not be high enough to overcome the van Der Waals attraction, so it's difficult to efficiently reduce flocculation/agglomeration in the absence of dispersant.

As shown in Fig. 1(b), in the 0.01–10 s^{-1} shear rate range, suspensions show different dropping rate in viscosity: at low shear rate of 0.01 s^{-1}, the ETOH/MEK suspension exhibits the highest viscosity of all solvent mixtures; however, with the increasing of shear rate to about 10 s^{-1}, it drops quickly to the lowest one. This cannot be explained mainly using the surface dissociation phenomena of TiO_2 particles because suspensions with ETOH/MEK systems show the highest viscosity at low shear rate (0.01 s^{-1}). The main reason for the difference in dropping rate of viscosity versus shear rate is the difference in polarity of the solvent system. As shown in Tables 1 and 2, EtOH is polar liquid, whereas isopropanol and MEK are weakly polar, so the ethanol has a strong hydrogen bonding and has strong preference to oxide particle surface.[22] Similar, isopropanol has the second strongest preference to TiO_2 particle surface. This polarity can be further correlated to the wettability(other than dispersability) of solvent because the surface of oxide particle is also polarized.[21,22] The difference in wettability between solvent and powders lead to the agglomerates with different properties. For ETOH/MEK systems, due to the strong interaction, agglomerates are relatively weak and can be broken easily under shearing. So with the increase of shear rate, the viscosity drops faster than other systems and show the lowest viscosity at about 10 s^{-1}, see Fig. 1(b). This wetting behavior can not be evidenced by viscosity measurement at very low shear rate because different solvent system showed different viscosity level due to hydrogen bonding, see Table 1. Based on the rheological measurement, it can be concluded that EtOH/MEK system shows the best wettability on TiO_2 powder surface.

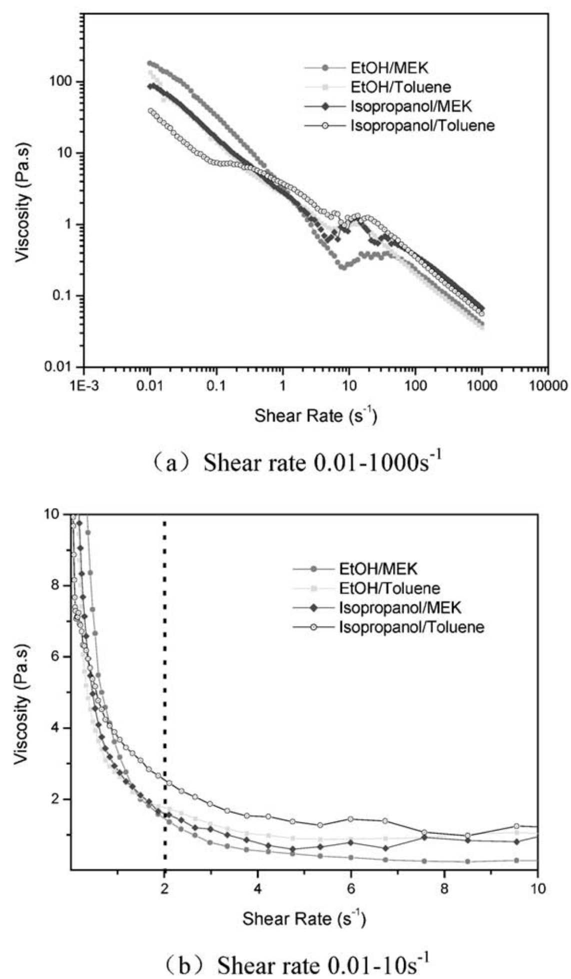


Fig. 1. Rheological properties of 16 vol.% TiO_2 slurries in the absence of dispersant.

3.2. Interaction between solvent and dispersant

The EtOH/MEK mixture shows a relative dielectric constant of 21.3 and effective electrostatic stabilization can be achieved when ionic polyelectrolyte surfactants are introduced into the suspension, as is the case for aqueous suspensions.[23,24] To avoid any influence of polarity, PVB79 was selected as dispersant. The rheological properties of 18 vol.% TiO_2 slurries in the presence of PVB79 are shown in Fig. 2. A considerable decrease in viscosity is observed for TiO_2 suspensions after the addition of dispersant, see Fig. 1(b) and 2(b). The curves for EtOH/MEK and isopropanol/toluene systems show a relatively stable character with a near-Newton rheological behavior, where the irregular shape at low shear rate might be due to the formation of weak agglomerates due to the high molecule weight of dispersant.[25]

The rheological properties of the suspensions can be related to the solubility behavior using the Hansen parameters and Hansen graph of solubility areas,[22] see

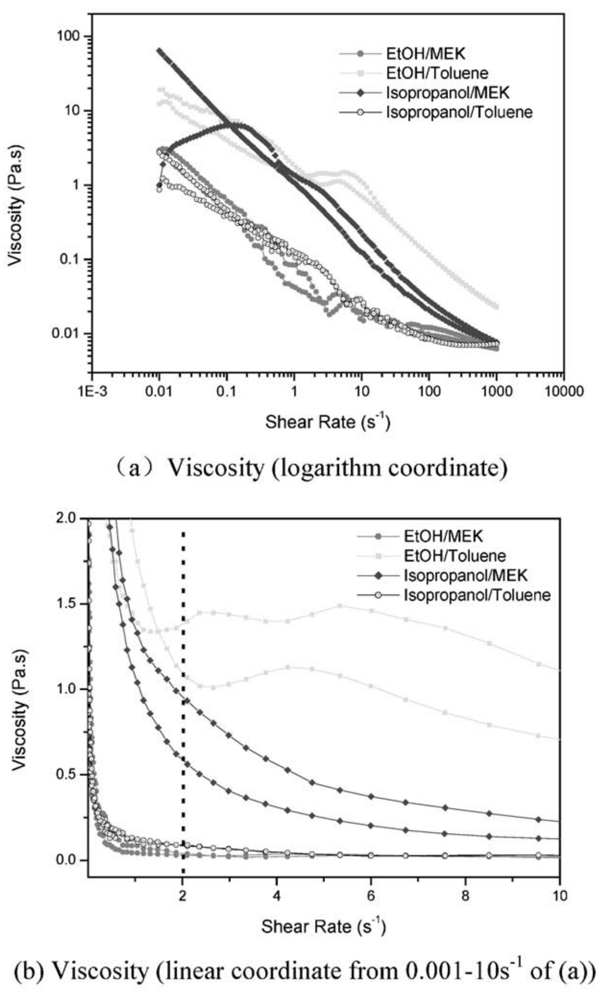


Fig. 2. Rheological properties of 18 vol.% TiO_2 slurries in the presence of dispersant.

Fig. 3. The miscibility between polymer and solvent can be predicated using a three-parameter system,

$$\partial_t^2 = \partial_d^2 + \partial_p^2 + \partial_h^2 \quad (1)$$

where the total Hildebrand value ∂_t (solubility parameter) is given by three parts: a dispersion force component ∂_d, a hydrogen bonding component ∂_h, and a polar component ∂_p. Hansen also used a three-dimensional model to plot polymer solubilities in various solvents. He found that, by doubling the dispersion parameter (∂_d) axis, an approximately spherical volume of solubility would be formed for each polymer, with solvent locations nearest the edge of a solubility area being the least predictable. When a solvent lies within the sphere for a given polymer, a reasonable solubility of the polymer in this solvent is predicated, see Fig. 3(a). Hansen's three dimensional volumes can be similarly illustrated in two dimensions by plotting a cross-section through the center of the solubility sphere on a graph that uses only two of the three parameters for three different polymer additives, PVB, PVC and PVA, see Fig. 3(b).

As evidenced by Hansen model, isopropanol is located near the center of PVB while toluene is outside the polymer area of solubility. Therefore, isopropanol is expected to be the most effective solvent for PVB, while toluene is the least effective one. This corresponds well with the Hildebrand solubility parameter, see Table 1.

For isopropanol/toluene systems, the dispersion can be related to the following two possible factors: (1) As isopropanol has the least difference in internal energy as PVB, a stretched configuration of dispersant molecules will be preferred; (2) the difference in solubility parameter between toluene and PVB79 will enhance the adsorption of dispersant on powder surface.[17] Therefore, TiO_2 suspensions with isopropanol/toluene as solvent show relatively stable state see Fig. 2. For EtOH/Toluene system, due to the considerable competition adsorption between solvent and dispersant, a relatively high viscosity is expected though PVB79 shows obvious dispersing effect (see Figs. 1(b) and 2(b) at shear rate 2 s^{-1}). For isopropanol/MEK system, the high viscosity may be due to the swelled and well-stretched configuration of dispersant, which could be evidenced by rheological measurement, Fig. 2(a).

Fig. 4 shows the results of sedimentation and adsorption measurements of the slips. The criteria used for evaluation of the dispersability are the settling rate and the settling density. As shown in Fig. 4(a), the isopropanol/toluene mixture exhibits the best dispersability in the presence of the dispersant represented by the highest supernatant volume and the lowest sediment volume (e.g. highest sediment density). This finding is in good agreement with the rheological behavior shown in Fig. 2. Fig. 4(b) corresponds well with Figs. 2 and 3 too.

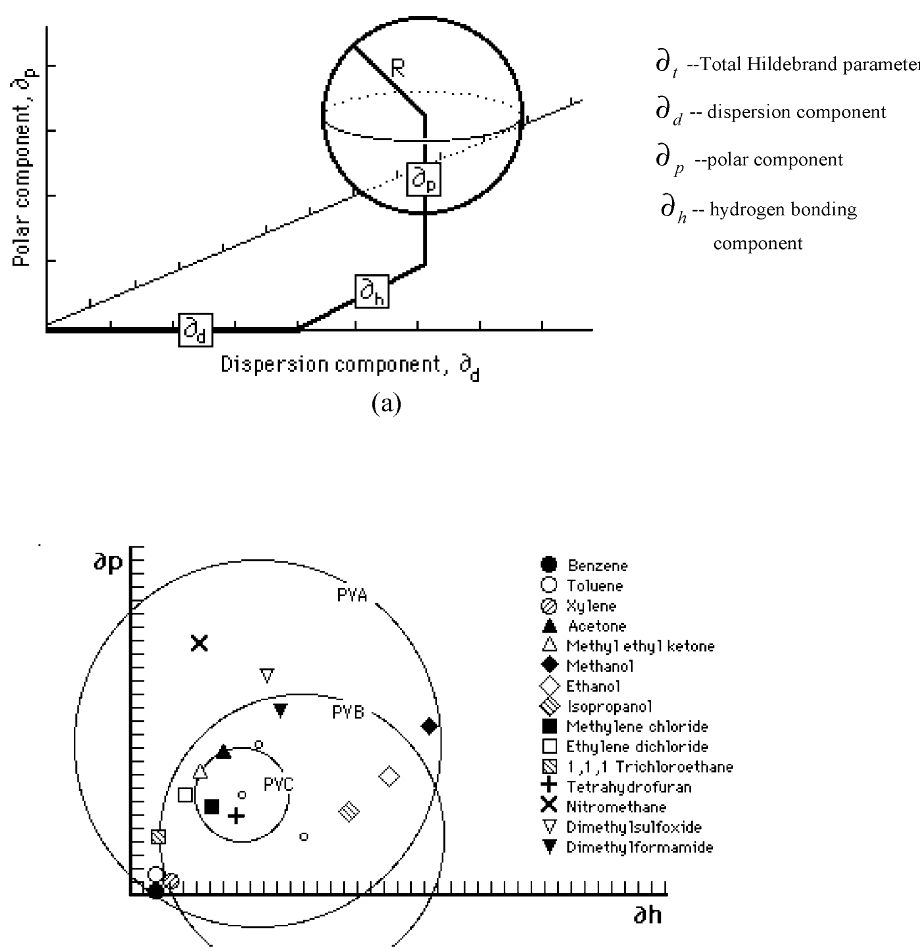
Although the adsorption amount is high for isopropanol/MEK system, due to the well-stretched configuration and high molecule weight of PVB79, polymer bridging and agglomeration will be highly possible.[25] For EtOH/MEK system, the competition adsorption between solvent and dispersant takes effect, therefore, a relatively low adsorption amount is observed.

3.3. Slurry structure in the presence of binder

After the addition of binder and plasticizer, the slurries show a near Newton flow behavior in a wide shear rate range, Fig. 5. There is evidence that the binder (PVB98) will compete with dispersant for the adsorption sites on the powder surface.[26] As the amount of binder is quite large in comparison to that of the dispersant, the rheological behavior of the suspensions is mainly governed by the binder. The isopropanol/MEK and isopropanol/toluene solvent systems are effective for PVB98, so these slurries show high viscosity. On the contrary, in EtOH/toluene system, due to the relatively poor solubility of the solvent, the molecule chain of PVB98 is somewhat coiled, and a low viscosity is observed. Therefore, the viscosity level cannot be directly related to the dispersion state of TiO_2 particles, though it may influence the solid content of slurries and the properties of final green tapes.

3.4. Processing of green tapes and laminated composites

To further characterize the effect of solvent on the properties of green sheets, TiO_2 slurries are cast and dried in controlled conditions. After drying, the four kinds of sheets exhibit a great shrinkage, see Table 3. The systems with EtOH/MEK and isopropanol/MEK as solvent show a high density, smooth surface and good strength. For isopropanol/toluene and EtOH/toluene systems, rough surface and low strength are observed, though isopropanol/toluene system is on a relative stable state before the addition of binder. In



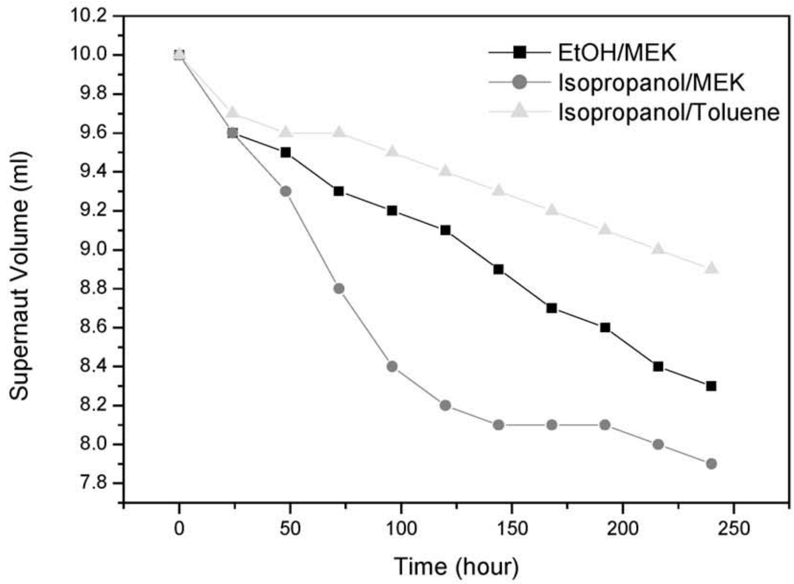
(b)

Fig. 3. A three-dimensional Hansen model (a) and (b) Hansen graph of solubility areas.

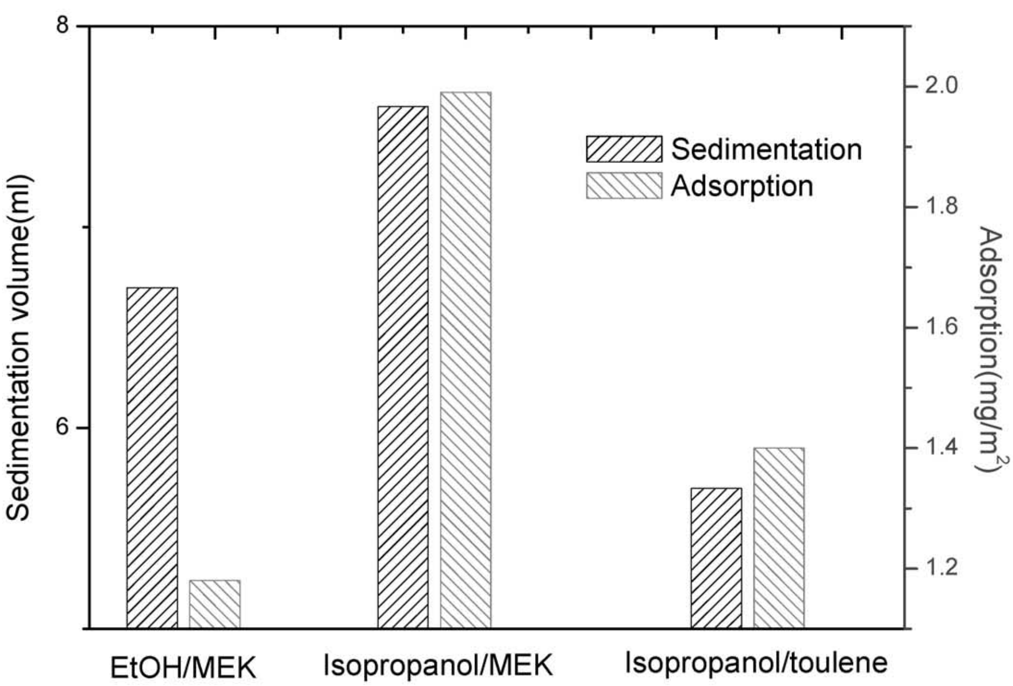
combination with Fig. 1, it can be concluded that solvent systems play an important role on the slurry stability and final properties of green tapes.

Based on the study above, azeotropic EtOH/MEK mixture was selected as effective solvent. Further study of different dispersants on the stability of TiO_2 slurry is reported in another paper.[20] Finally a formulation for tape casting of TiO_2 slurries is obtained, see Table 4. Green tapes prepared from this formulation are used for the subsequent lamination and infiltration process.

The concept of laminated composite for improved performance of brittle materials is well established.[27–31] Multilayer design is a powerful, flexible approach since the microsturcture of individual layers with different properties (mechanical, thermal or electrical properties) can be well tailored to meet various structural and



(a) Sedimentation of the 18vol% TiO_2 slips.



(b) Sediment volume and adsorption after 240 hours

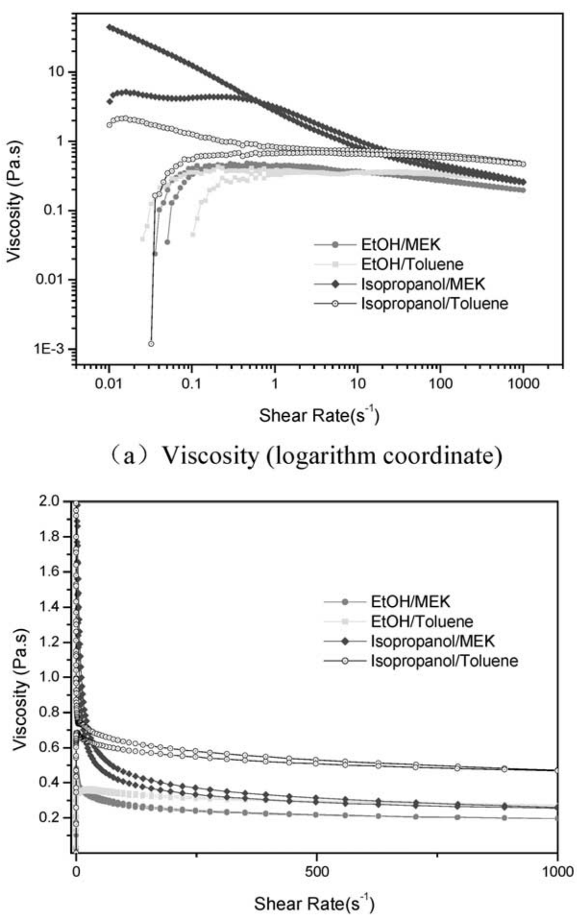
Fig. 4. Sediment volume and adsorption of PVB79 on powder surface.

functional requirement such as strength, toughenss, thermol conductivity etc. Based on multilayer disign, a new processing technique is utilized to develop tailored ceramic multilayer blanks using controlled ceramic–metal reaction. This process can be expressed in the following.

The TiO_2 green tapes were stacked with aluminum foil (AlMg3, Cochius, Nuremberg, Germany) with a thickness of 300 μm. After lamination at 90 °C and an applied pressure of 10 MPa the organic components of the TiO_2 green tape were burned out in air atmosphere and the multiplayer stack was subsequently heated to 1000 °C in inert atmosphere. Above the melting temperature of Al the metal melt will penetrate into the porous green tape by capillary driven infiltration and react to form a laminar ceramic/metal composite according to

$$3/2TiO_2 + (2+x)Al \rightarrow Al_2O_3 + 3/2TiAl_x \quad (2)$$

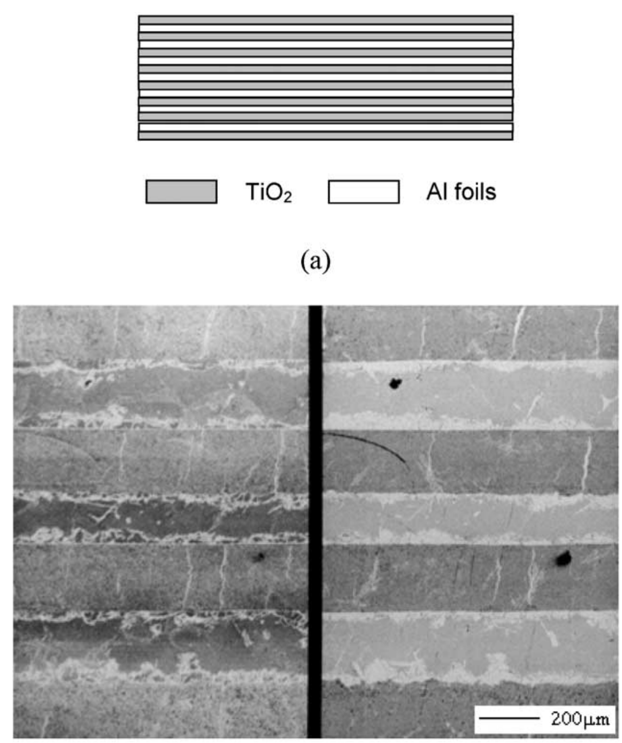
Depending on the excess of Al with respect to the stoichiometric reaction a residual metal or intermetallic phase (with x ranging from 1 to 3) will be formed. Fig. 6 shows the green TiO_2/Al-stacks and typical laminar microstructure of the resulting laminar composite. Based on the metal–ceramic reaction, multilayer materials with tailored toughness, anisotropic thermal and electrical behavior are currently under development.



(a) Viscosity (logarithm coordinate)

(b) Viscosity (logarithm coordinate)

Fig. 5. Rheological properties of TiO_2 slurries in the presence of dispersant, binder and plasticizer.



(a)

(b)

Fig. 6. Green TiO_2/Al stacks and laminar microstructure of the resulting laminar composite (a) Schematic illustration of the laminar structure of the green TiO_2/Al-stacks (b) SEM micrograph of the resulting $Al_2O_3/TiAl_3$ structure.

Table 3
Green sheet properties

Properties	EtOH/MEK	EtOH/Toluene	Isopropanol/MEK	Isopropanol/toluene
Average tape thickness (μm)	108±9	112±24	93±11	114±13
Green density (g/cm^3)	2.34	2.12	2.38	2.19
Strength	High	Very low	High	Low
Flexibility	Good	Good	Good	Good
Surface roughness	Smooth	Rough	Smooth	Rough

Table 4
Slurry formulation

Component	Function	vol.%	wt.%
TiO_2	Powder	24.70	59.36
Dispersant		0.88	0.59
PVB(B98)	Binder	8.40	5.68
DBP(santicizer)	Plasticizer	8.40	5.52
EtOH/MEK	Solvent	57.63	28.85

4. Conclusions

The effects of solvent composition on the tape casting of TiO_2 slurries were examined for four different azeotropic binary solvent systems. The EtOH/MEK had the highest dielectric constant of the systems investigated and showed the lowest viscosity of the TiO_2 slips. Green tapes prepared from the EtOH/MEK systems exhibited a high packing density with smooth and defect free surface. Results showed that azeotropic EtOH/MEK mixture is the effective solvent system for tape casting of TiO_2 sheets. The TiO_2 tapes can be combined with Al foils to form TiO_2/Al stacks which can be converted into a multilayer $Al_2O_3/TiAl_x$ reaction product. The multilayer $Al_2O_3/TiAl_x$ composites offer an interesting potential for engineering applications.

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