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Deflocculants for tape casting of TiO_2 slurries

Zhang Jingxian[a,*], Jiang Dongliang[a], Lars Weisensel[b], Peter Greil[b]

[a]*The State Key Lab of High Performance Ceramics and Superfine Structure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, Ding-Xi Road, 200050, PR China*

[b]*Department of Materials Science, Glass and Ceramics, University of Erlangen-Nuremberg, Martensstr. 5, D-91058 Erlangen, Germany*

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Abstract

Five dispersants, polycondensed fatty acid, castor oil, phosphate ester, polyvinyl butyral (B79), polyvinyl butyral (B98) are used as dispersant. The dispersability of TiO_2 slurries is studied through ESA measurement, rheological characterization and FTIR test. ESA measurement shows that the adsorption of PVB79 and phosphate ester is of physical and chemical type, respectively. Rheology, TG–DTA and sedimentation measurements show that in the absence of binder, PVB79 is the best dispersant; after the addition of binder, phosphate ester is the best one. The adsorption of dispersants on powder surface is also characterized by FTIR. The dispersion and stability mechanism is discussed.

Keywords: Deflocculants; Rheology; Suspensions; Tape casting; TiO_2; Zeta potential

1. Introduction

Tape casting is a well-established technique for making large, thin and flat sheets for preparation of high-quality substrates and laminated materials.[1–4] Tape casting involves the dispersion of inorganic ceramic powders in a liquid medium, followed by the addition of organic binders and plasticizers to increase the strength, flexibility and viscosity of the tapes after casting and drying.[5,6] In achieving uniform, dense, dimensionally accurate ceramic green tapes, the preparation of a stable, well-dispersed slurry is a critical step.[7–11] The role of dispersant, binder and plasticizer in tape casting processing are well studied and documented.[4,5,12,13] Stable suspensions are achieved by steric stabilization or electrostatic repulsion or both according to the type of dispersant and solvent used. Steric stabilization is caused by polymeric dispersant of long chain molecular whereas the electrostatic stabilization is caused by surface-active agents, usually called surfactants.[5,14] In general, it has been accepted that steric stabilization is the only effective mechanism in organic solvents. Nevertheless, even in nonpolar media, the particles are charged so that there is an electrostatic repulsion when polymer is present.[15]

The present work was initiated with the aim of studying the effect of different dispersants including polycondensed fatty acid, Castor oil, Phosphate ester (PE), Polyvinyl butyral (B79), Polyvinyl butyral (B98) on the dispersability of TiO_2 powders. The stability of slips were characterized and studied by rheological measurement, sedimentation and FTIR measurement.

2. Experimental

2.1. Starting materials

TiO_2 powder (Merck Art812, Germany) with the particle size as $D_{50} = 1.497$ μm and the specific surface area as 4.91 m^2/g was used for this study. For preparing tape casting slurries, a polyvinyl butyral of higher molecular weight (B98, Monsanto, USA) was used as binder and butyl benzyl phthalate (Santicizer 160, Solutia, Inc., St. Louis, USA) as plasticizer. The different solvents and dispersant used, their suppliers and their properties are given in Table 1.

2.2. Electrokinetic measurement

The ESA characterization was conducted at 1.231 MHz (27 °C) using a Electrokinetic Sonic Amplitude

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* Corresponding author.
E-mail address: jx_zh@yahoo.com (Z. Jingxian).

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Table 1
Properties and supplier of the solvents and dispersants

Constituents	Name	Supplier	Properties		
			Viscosity (mPa s)	Density (g/cm^3)	Dielectric constant
Solvent	Ethyl alcohol	Carl Roth GmbHCo, Germany	1.2	0.789	24
Solvent	Methyl ethyl ketone	Carl Roth GmbHCo, Germany	0.4	0.805	18
Solvent	Isopropanol	Carl Roth GmbHCo, Germany	2.4	0.785	18.8
Solvent	Toluene	Merck KGaA, Germany	0.6	0.867	2.4
Dispersant	Polycondensed fatty acid	Uniqema, Belgium	–	–	–
Dispersant	Castor oil	Henry Lamotte GMBH, Germany	–	0.961	–
Dispersant	Phosphate ester	Zschimmer&Schwarz GmbH&Co Chemische fabriken, germany	200	1.02	–
Dispersant	Polyvinyl butyral(B79)	Monsanto Company, USA	–	1.08	–
Dispersant	Polyvinyl butyral(B98)	Monsanto Company, USA	–	1.08	–

(ESA) measurement apparatus (ESA9000 Zeta Potential Analyzer, Matec Applied Science, Northboro, USA). Details of the ESA technique have been well documented.[16,17] Slurries were prepared by dispersing TiO_2 powders in ethanol with required solid loading (5 vol.%), followed by ball mixing for 24 h. During the ESA experiments, the pH was adjusted with 2 M HCl and 2 M NaOH solutions.

2.3. Dispersability with different dispersants

TiO_2 slips (16 and 20 vol.%) were prepared with azeotropic EtOH/MEK (34:66) mixture as solvent. The slurries were ball milled for 24 h in the absence of dispersant. After rheological measurement, five selected dispersants were added, the concentration of which was hold as 1 wt.% of the solid to assure all the suspensions are well stabilized. High concentrated TiO_2 slips (30 vol.%) were also prepared in the presence of various dispersants. The slurries were ball milled for another 24 h to allow the equilibrium adsorption of dispersants on to the powder surface. After rheological measurement, binder and plasticizer were added to 30 vol.% TiO_2 slips according to fixed mass ratios between binder/plasticizer and binder/TiO_2 powders. The slurries were further ball milled for 48 h.

The rheological behavior was characterized using a stress-controlled rheometer (UDS 200, Paar Physica, Austria) with a cone-plate system at 25 °C. Shear dependent behavior of the examined suspensions was 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.

2.4. Sedimentation and FTIR test

Sedimentation measurements were made on suspensions of 18 vol.% TiO_2 in the presence of dispersants (phosphate ester, B79 and B98). After ball milling (24 h), the suspensions were pored into glass cylinders. The position of the interface between the clear and unclear supernatants was recorded at regular intervals. A month later, the sediment was removed and dried at 80 °C to remove the solvent. The adsorption of dispersants on the TiO_2 surface was determined by TG–DTA and FTIR (Nicolet Impact 420T, Nicolet Instrument Corporation, Madison/USA) measurement. The starting TiO_2 powders are also characterized for comparison.

3. Results and discussion

3.1. Effect of deflocculants

Azeotropic ethanol/methyl ethyl ketone systems were evidenced to have effective wettability on TiO_2 particle surface. Details about the characterization of solvents were reported in another paper.[18] In this work, the azeotropic EtOH/MEK mixture is used as solvent. TiO_2

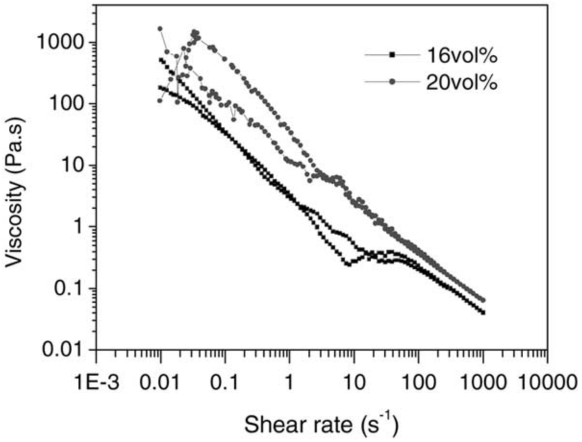


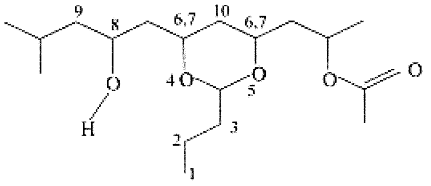
Fig. 1. Rheological properties of TiO_2 slurries in the absence of dispersant.

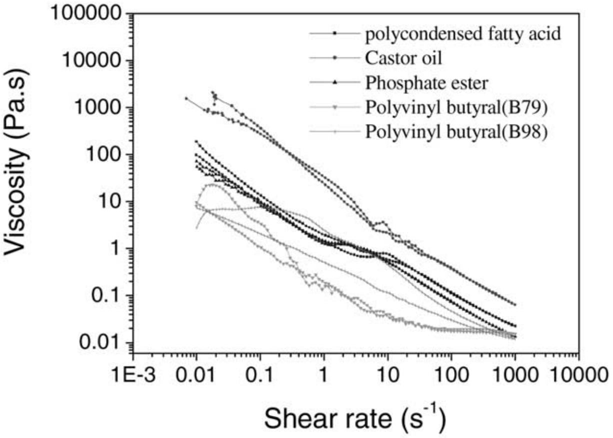
suspensions in the absence of dispersant are characterized by rheological measurement, see Fig. 1.

As shown in Fig. 1, with the increase in solid content from 16 to 20 vol.%, the TiO_2 slurries exhibit a transition from weak to agglomerated state. This result indicates the limited dispersing effect of solvent.

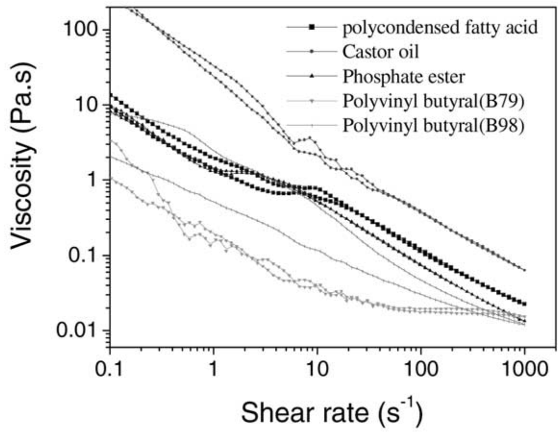
Five dispersants, polycondensed fatty acid, castor oil, phosphate ester, PVB98 and PVB79, are studied in this work. The reason for using PVB98 and PVB79 as dispersant is that they could also provide well-dispersed slurries though their molecule weight is high.[18,19] After the addition of dispersant, TiO_2 slurries show an apparent improvement in stability (Fig. 2).

As shown in Fig. 2(a) and (b), castor oil exhibits a limited dispersing effect characterized as a higher viscosity, indicating that castor oil is not a suitable dispersant for TiO_2. Both polycondensed fatty acid and phosphate ester show a similar dispersability. Slurries with PVB98 and PVB79 exhibit an inertial effect at low shear rate due to the high molecular weight of them. In comparison to other dispersants, slurries with PVB79 provide the best stability. The structure of PVB is shown as the follow:





(a) $0.01\text{-}1000 s^{-1}$



(b) $0.1\text{-}1000 s^{-1}$

Fig. 2. Flow curves of TiO_2 slips dispersed with 1 wt.% of different deflocculants.

For slurries with PVB98 as dispersant, due to the higher hydroxyl contents (18%–20% for PVB98 and 10.5–13% for B79), polymer bridging (hydrogen bonding between adsorbed molecule chains)and agglomeration will be highly enhanced,[20] as evidenced by a strong time-dependence behavior.

3.2. ESA of TiO_2

The effect of phosphate ester and PVB79 on the state of dispersion was studied, Fig. 3. In the absence of dispersant, TiO_2 particles are positively charged, similar to PZT particles in EtOH/MEK.[21] The ESA of TiO_2 particles decreases with the increase of pH in the pH = 2–7.50 range, and increases again in basic region. After the addition of PVB79, a similar trend is observed in the whole pH range, indicating a physical adsorption mode other than a chemical one (high affinity type). This kind of adsorption has very limited effects on the surface charge properties.[22] In comparison with PVB79, phosphate ester showed a different effect on the ESA of TiO_2 particles. This may be due to the dissociation of the polymer, from which the H^+ ions are liberated into solvent and the polymers are negatively charged. This negatively charged polymers is likely to adsorb onto TiO_2 particle surface.[5,22–25] In alkaline region, the phosphate ester may dissociate more completely and counterpart the surface charge of TiO_2 particles. Therefore, this kind of adsorption is supposed to be of a chemical type.

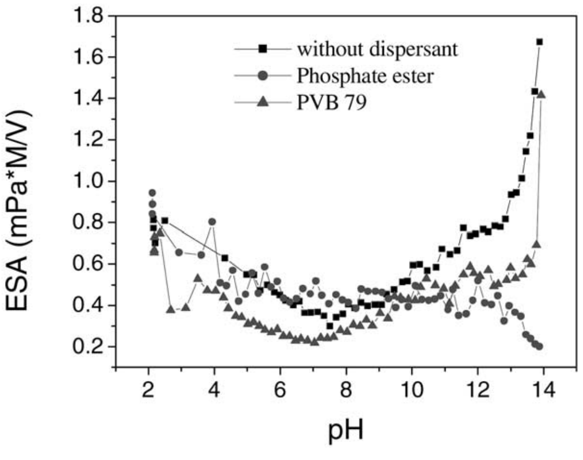


Fig. 3. ESA curves versus pH for TiO_2 particles in ethanol media.

As shown in Fig. 3, in acid and weak basic pH range, phosphate ester did not show obvious influence on the surface charge of TiO_2 particles, suggesting the low adsorption amount in this region.

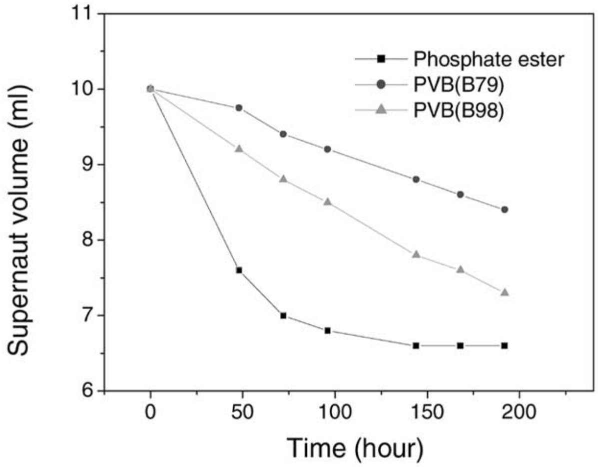
3.3. Sedimentation and adsorption behavior

Sedimentation test is in good agreement with the rheological measurement, see Fig. 4(a). Slurries with PVB79 as dispersant are well stabilized characterized as a high volume of unclear supernatant. In comparison with PVB98 and PVB79, phosphate ester produces relatively unstable suspensions. This result is in good agreement with the TG–DTA measurement, see Fig. 4(b).

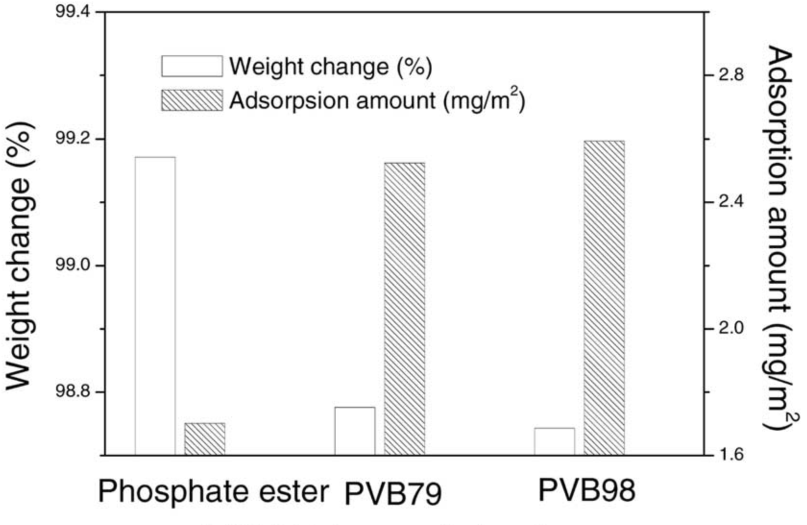
As shown in Fig. 4(b), the adsorption amount of PVB98 is higher than that of PVB79. This can be attributed to the difference in hydroxyl contents (18–20% for B98 and 10.5–13% for B79), similar results were also reported for the adsorption of PVB on ferrite powder surface.[28] However, this high adsorption amount did not enhance the stability of TiO_2 slurries, as evidenced by sediment [Fig. 4(a)] and rheological test (Fig. 3), because of the strong polymer bridging effect caused by hydrogen bonding of PVB98.[20]

To further study the properties of dispersants, TiO_2 slurries with high solid loading (30 vol.%) are characterized using rheometer, see Fig. 5. As shown in Fig. 5, PVB79, PVB98 and phosphate ester exhibit a comparable dispersing effect. In the case of ionic phosphate ester, this dispersing effect is due to a combination of electrostatic and steric mechanisms, which has been well documented in literature.[10,21,23,26,27] For PVB98 and PVB79, due to the high molecule weight, an inertial effect at low shear rate is observed and polymer bridging is highly possible.[4]

The adsorption of the dispersant on the TiO_2 powder surface is detected by FTIR, see Fig. 6. The spectra of TiO_2 in the wavelength range of 893–937 cm^{-1} is due to



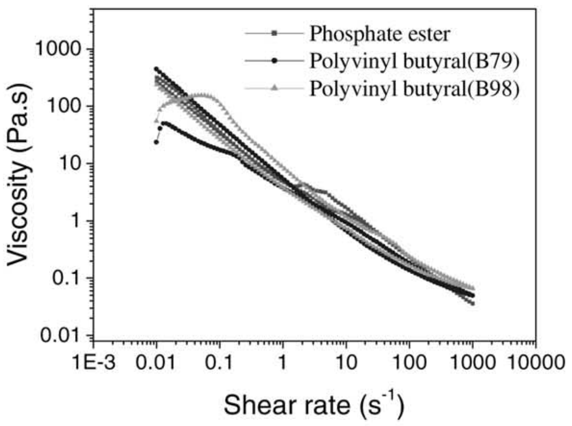
(a) Sedimentation test



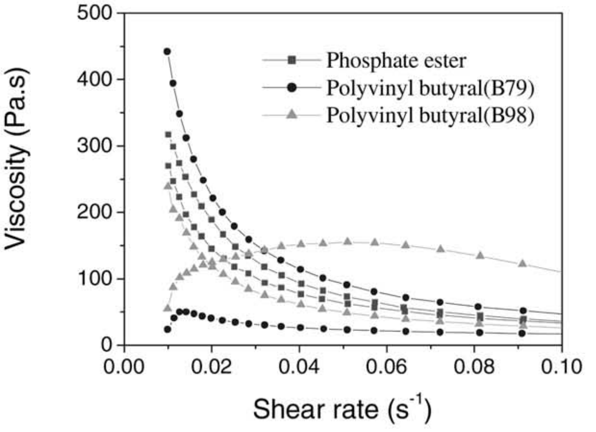
(b) Weight change and adsorption

Fig. 4. Sedimentation test of 18 vol.% TiO_2 slips and the relevant TG-DTA measurement.

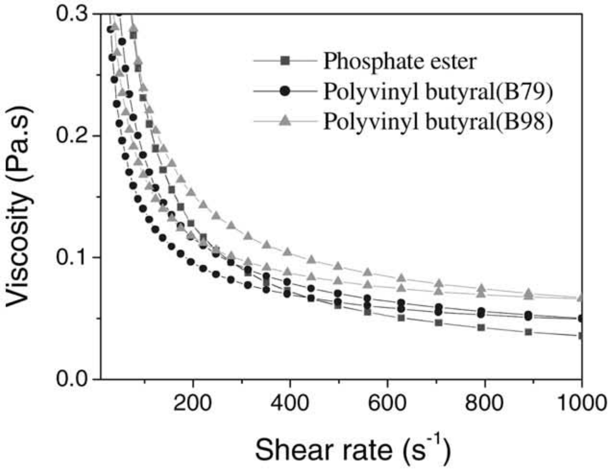
the skeletal vibration of TiO$_2$.[28] The C–O ether and the P–O band of phosphate group, located at 1150–1085cm^{-1}, could not be detected, maybe due to the overlapping of Ti–OH stretching motions at 1095 and 1039 cm^{-1}.[10,29] For TiO$_2$ powders with PVB79 and PVB98 as dispersant, the peak over the 1500–1900 cm^{-1} range is enhanced, which may be due to the carbonyl groups of PVB.[10,30,31] The peak at 2370 cm^{-1} is assigned to the adsorption of CO$_2$.[32] Two peaks at 2825 and 2904 cm^{-1} are observed for TiO$_2$ powders in the



(a) 0.01-1000s^{-1}



(b) 0.01-0.1s^{-1}



(c) 0.1-1000s^{-1}

Fig. 5. Flow curves of 30 vol.% TiO$_2$ slips dispersed with 1 wt.% of different deflocculants.

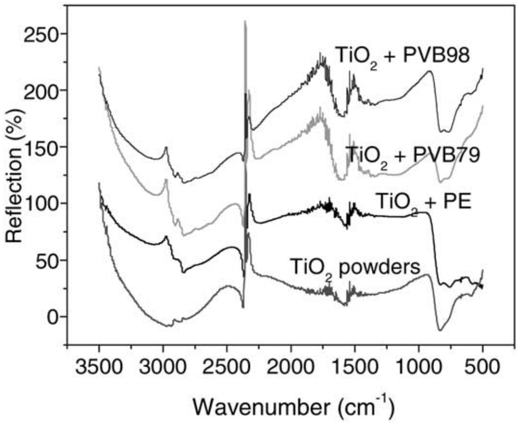
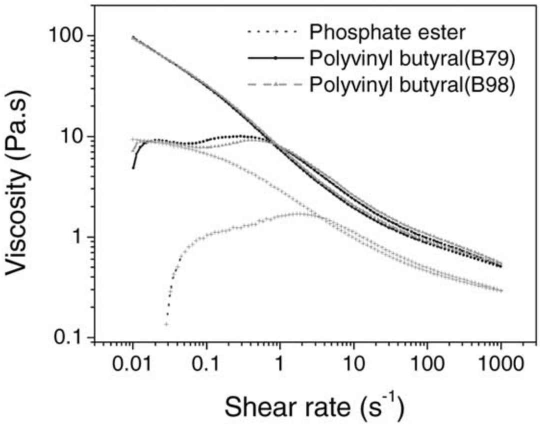
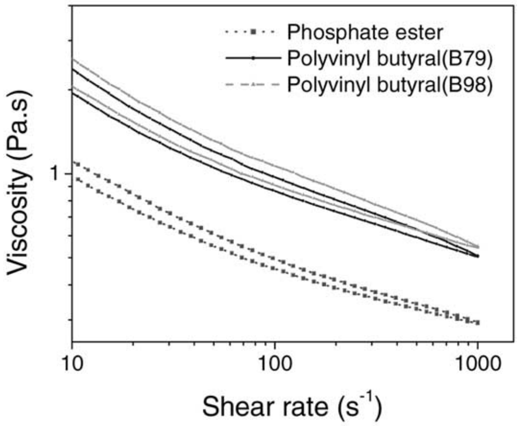


Fig. 6. Infrared spectra of the TiO$_2$ powders in the presence and absence of dispersant.



(a) 0.01-1000s^{-1}



(b) 10-1000s^{-1}

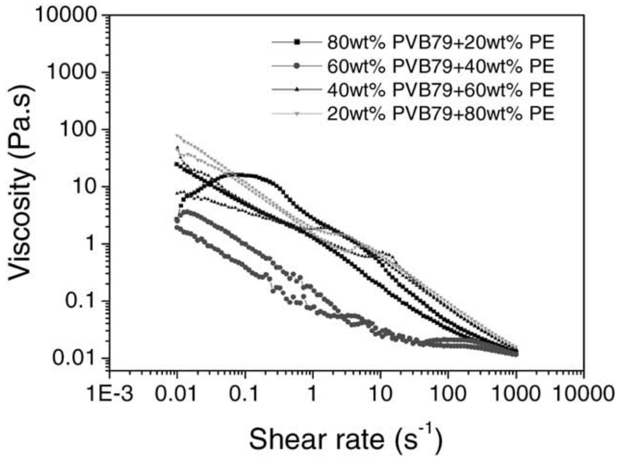
Fig. 7. Flow curves of TiO$_2$ slips in the presence of dispersant, binder and plasticizer.

presence of dispersants, corresponding to the C–H stretching vibrations. It is believed that these peaks are related to the adsorbed dispersants (PE, PVB79 and PVB98). All the above results indicate that the adsorption of dispersants (PE, PVB79 and PVB98) has taken place.

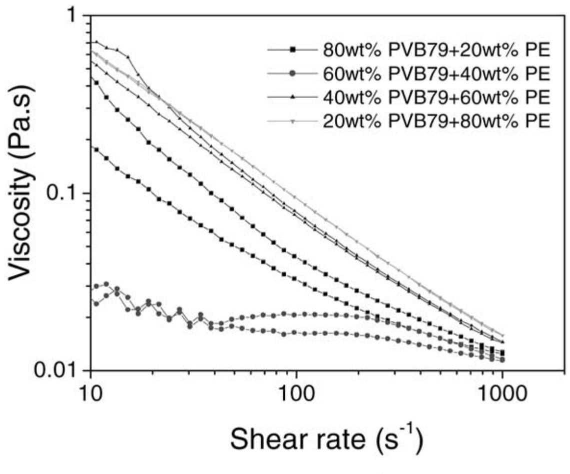
3.4. Interaction between dispersant and binder

After the addition of binder, all slurries exhibit the inertial effects at low shear rate, which is a common case,[33] see Fig. 7. It should be noted that phosphate ester produces a more fluid suspension than PVB79 and PVB98. This might be due to the co-adsorption of some binder molecules on powder surface, though polymer bridging is commonly expected due to the adsorption of binders.[4,24]

To confirm this assumption, a mixture of PVB79 and phosphate ester is used as dispersant for 20 vol.% TiO_2 slurries, see Fig. 8. Viscosity of TiO_2 slurries shows a decrease trend with the increase of PVB79 to 60 wt.%; further increase in PVB79 content to 80 wt.% will lead to an increase in slurry viscosity. This variation in viscosity can be related to the co-adsorption behavior (PVB79 and phosphate ester), which could increase the saturation amount of polymers on powder surface and decrease the slurry viscosity. In addition, similar to that in SiO_2 systems, due to the mutual interaction (hydrogen bonding), the adsorption of phosphate ester first on TiO_2 surface might augment the adsorption of PVB and vice versa.[34,35] Further study in this area is necessary.



(a) 0.01-1000s^{-1}



(b) 10-1000s^{-1}

Fig. 8. Flow curves of TiO_2 slips with different composition of PVB79 and phosphate ester.

4. Conclusion

On the basis of the discussion above, the following conclusions are made:

1. ESA measurement shows that the adsorption of PVB79 and phosphate ester is of physical and chemical type, respectively.
2. Rheological and sedimentation measurement show that in the absence of binder, PVB79 is the best dispersant; after the addition of binder, phosphate ester is the best one.
3. A combination of PVB79 and phosphate ester as dispersant could produce well dispersed slurries.

Acknowledgements

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