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Journal of the European Ceramic Society 27 (2007) 2361–2367
www.elsevier.com/locate/jeurceramsoc

Rheology studies on highly filled nano-zirconia suspensions

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Received 24 June 2005; received in revised form 23 August 2006; accepted 26 August 2006
Available online 7 November 2006

Abstract

The rheological properties of highly filled nano-zirconia suspensions in water and in various water–1,2-propanediol mixtures were investigated. The influence of an electrosteric (polyacrylic acid), an electrostatic (triammonium citrate) and a steric dispersant (2-(2-(2 methoxy ethoxy) ethoxy) acetic acid, TODA) on the viscosity and the elastic properties of the suspensions were also recorded. For any given water–propanediol mixture TODA was the most effective of the investigated dispersants. It resulted in the lowest slurry viscosities and the highest $\tan\delta$ values, indicating best dispersing properties and the lowest elastic shear modulus, respectively. The water–propanediol proportion influenced the properties of the slurries strongly. For all dispersants the relative viscosity of the slurries decreased with increasing propanediol content. This was found to be a non-linear function in the case of TODA, where at a minimum level of 50 wt.% propanediol the properties of the slurries were the best. For the other dispersants this was a linear function, which indicates that the dispersing quality there only depended on the polarity of the dispersing medium. A screen printing paste was produced using TODA as a dispersant and a 75 wt.% propanediol–25 wt.% water mixture dispersing medium and subsequently printed. The printed layer showed 40–50 nm sized particles, indicating that the dispersing properties were also retained.

Keywords: D. ZrO_2; A. Suspensions; Rheology; B. Nanocomposites

1. Introduction

Industrial scale production of thin ceramic layers such as in sensors is typically done by screen printing[1]. Here ceramic or metallic particles are processed into a viscous slurry often referred to as a paste. To minimize shrinkage on drying and sintering slurries with high solids loadings are preferred or even a requirement for economic industrial processing. Due to the constraints induced by cofiring, the particle size effect on sintering temperature is used in order to lower firing temperatures[2]. The lowest sintering temperatures can be achieved when nanoparticles are used. Dispersing nano-sized ceramic particles at high solids loadings in such slurry or screen printing paste, however, is still a challenge. On the one hand, dispersants are to be found, which give a sufficient dispersing force to overcome van der Waals forces[3]. On the other hand, this dispersing force needs to be very short range to allow dense packing of the particles. Thus the desired high solids loading may be reached. Therefore, the right choice of dispersants and dispersion mechanism (electrostatic, steric, electrosteric) is crucial. Furthermore, the dispersing medium is known to influence the interparticle forces[4]. Thus, a stable slurry may only be produced if the dispersing medium and dispersants are tailored to the surface chemistry of the ceramic particles which are to be processed. Recently we have investigated the dispersing quality of electrostatically and sterically stabilized particles using the colloid probe technique[5]. The dispersing medium was varied between a pure d.i. water system and a 75 wt.% 1,2-propanediol–25 wt.% water mixture. The dispersing force created by the steric dispersant was strongly influenced by changing the dispersing medium. In the present work these dispersing media were used to prepare highly filled (20 vol.%) slurries of nano-zirconia particles. Here we present the rheological analysis of these slurries, which are being discussed on the basis of AFM investigations. Triammonium citrate (TAC)

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doi:10.1016/j.jeurceramsoc.2006.08.022

was used as an electrostatic dispersant, 2-(2-(2 methoxy ethoxy) ethoxy)acetic acid (trioxadecanoic acid—TODA) as a steric stabilizer and low molecular weight polyacrylic acid (PAA) as electrosteric dispersant. TODA had been used in previous colloid probe investigations and was therefore also utilized here[5,6].

The viscosity of slurries generally depends on its solids volume fraction. With increasing content the particles may form a network, which increases the viscosity until any shearing is blocked at a maximum filling level ϕ_m[7]. This phenomenon is described by a modified semi-empirical Krieger–Dougherty function[8]:

$$\eta_r = \frac{\eta}{\eta_{lp}} = \left[1 - \frac{\phi}{\phi_m}\right]^{-n} \tag{1.1}$$

where η_r is the relative viscosity (with η_{lp} as the viscosity of the liquid media) and n a fitting parameter. Eq. (1.1) is valid for soft sphere systems, in which many body effects between particles are taken into account. There have also been analytical solutions to describe η_r. However, these are only valid for hard sphere systems, where no interaction between particles except elastic repulsion upon surface–surface contact occur. In practice such systems only exist for very low solid contents[9]. To disperse ceramic particles either steric, electrostatic or electrosteric stabilizing mechanisms are used. These mechanisms are based on a polymer layer, a charge or both to form a barrier and hinder agglomeration. The barriers increase the hydrodynamic volume of the dispersed particles. Therefore, the effective solid volume fraction ϕ_{eff} and thus the maximum filling level ϕ_m is reduced. In case of monodisperse spherical particles this can be defined by

$$\phi_{eff} = \phi\left(1 + \frac{\Delta}{r}\right)^3 \tag{1.2}$$

where r is the radius of particles and Δ the thickness of the repulsive barrier[8]. Eq. (1.2) reveals the importance of finding a suitable dispersant for the solid phase particles. It is necessary to form a barrier, which is on the one hand sufficient to act as a dispersant but on the other hand does not hinder high packing of the particles. Fig. 1 illustrates this relation: here the packing of spherical particles is shown as a function of particle diameter and size of the stabilizing barrier ($\underline{\Delta}$). A large barrier will increase the particle radius r to an "effective" radius $r + \Delta$. This barrier influences the particle interaction: if the size of the barrier and the packing density are high enough for the "effective" spheres to touch or penetrate (solid line in Fig. 1), then the particles are repelling each other in every position at any time. Thus an elastic "network" is built up, which increases the elastic modulus. A smaller barrier is desirable, which allows free flow of the particles (dotted line). Tari et al. found a similar effect for alumina suspensions[10] stabilized with electrosteric dispersants.

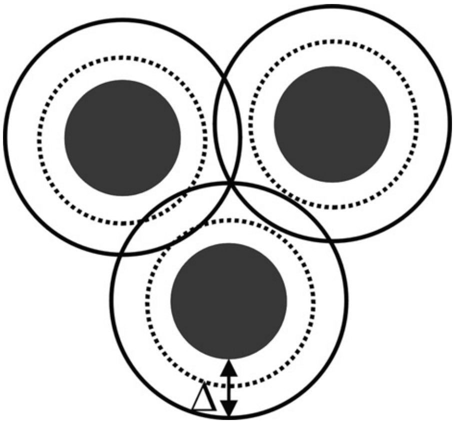

Fig. 1. Discussion of the influence of the size of a stabilizing barrier △ on the packing of particles.

Rheological investigations are suitable to analyze the dispersing quality as well as the elastic modulus as shown by Pugh and Bergström[9]. The sensitivity of this method is particularly high for suspensions with high solid contents. Since the suspensions used in the present work were filled up to 20 vol.%, the viscosity and the tan δ values of the suspensions are being used for discussion[11].

2. Experimental

2.1. Zirconia powder

Nano-zirconia powder was supplied by Degussa, Germany. Fig. 2 shows a TEM picture of the powder. The primary particle size determined from this picture was 13 nm. Agglomerates were present, leading to a size distribution (determined by a Cilas analyzer) as follows: $d_{10} = 68$ nm, $d_{50} = 114$ nm, and $d_{90} = 287$ nm. The surface area was 61 m^2/g and the monoclinic phase proportion 26 wt.%.

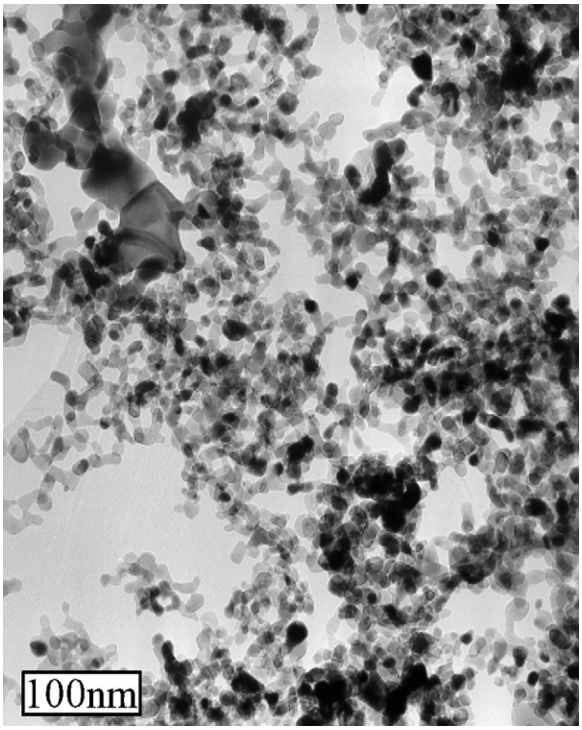

Fig. 2. TEM picture of the zirconia nano-particles. Primary particle size determined from this picture was ≈13 nm.

2.2. Reagents and apparatus

All water (di-water) used in the presented experiments was filtered by a Millipore water purification system (“Milli-Q”), which increases the resistance of the water to well above 10^6 Ω/cm. 1,2-Propanediol, (2-(2-(2 methoxy ethoxy) ethoxy) acetic acid (TODA), triammonium citrate (TAC), polyacrylic acid (PAA) with molecular weight 2000 g/mol, NaOH and HCl (33 wt.%) were supplied by Sigma–Aldrich (analytical reagent grade) and used as delivered. NaCl was taken as a background electrolyte for all measurements at a concentration of 10^{-3} M. The pH values of the solutions were adjusted using HCl and NaOH (for solutions of pH 3, no NaCl was added to keep the electrolyte concentration also at 10^{-3} M). The propanediol–water mixtures were made as follows: first a 10^{-1} M NaCl solution in “Milli-Q” water was produced. This solution was then diluted with water and propanediol according to the desired concentration. This way the overall electrolyte concentration was kept at approximately 10^{-3} M (for pH 3 no background electrolyte was added). The optimal pH with regard to stability for the dispersants TODA (pH 3), TAC (pH 9.5) and PAA (pH 9.5) were determined in separate rheological and zeta-potential investigations[6].

The solutions of TODA were produced by adding TODA to the water–propanediol mixture directly at a concentration of 0.01 wt.%. This solution had a pH 3 due to the acidic character of the TODA. Therefore, no electrolyte was added and the pH was not adjusted any further.

2.3. Slurry preparation

For screen printing pastes and suspensions with solids loading of 20 vol.% or higher the surface of the zirconia nano-powder needed to be modified prior to processing. Zirconia and the chosen dispersant were milled in an APS-dispermat(R) dissolver (by VMA-Getzmann GmbH, Germany) together with water for at least 4 h. The dissolver was equipped with a double milling impeller made of polyamide. The speed of the agitator was set between 1500 and 2500 rpm depending on the filling level of the slurries. Zirconia milling balls (diameter 2 mm) were added in a volume relation to the slurry 1:1 (e.g. to 250 ml slurry 250 ml milling balls were added). Due to the rotation of the impeller, the milling balls also rotate and perform impacts with each other. Agglomerates which are trapped between the balls will be cracked. The pH was adjusted to the appropriate value depending on the dispersant (using HCl or NaOH). This batch was processed in a double wall container, which was connected to a cooling device (set to 15 °C). The slurry was then freeze-dried and the pretreated surface modified powder was subsequently used to prepare pastes and suspensions for further characterization.

For slurry and paste preparation the dissolver was used again. First, a solution was prepared. In case of slurries, this was the water–propanediol mixture, in case of a paste, a polymer binder was mixed in. Subsequently the pH was adjusted. Zirconia milling balls (diameter 2 mm) were added as described above. The freeze-dried powder was then mixed to this phase in small incremental amounts of 0.5–0.8 g. After each increment the slurry was milled for at least 40 min up to 1 h before more powder was added. Thus, the whole mixing process took up to 30 h. The last milling step after all powder was mixed in, was set to 5 h.

2.4. Rheological measurements

A Haake RS150 and a Physica MCR500 rheometer were used to record rheological data. For samples with high solid loadings a plate–plate and a cone–plate (cone: 2°) system of 25 and 35 mm diameter were utilized. Samples with low viscosity were measured in a cylinder system. Both rheometers were set to controlled shear rate mode and the temperature to 20.5 °C.

Flow and viscosity curves were obtained using the continuous shear method: either a loop test (where also thixotropy was detected) or a simple increase of shear rate. Prior to the experiments each sample was pre-sheared followed by a rest for 2 min. Each test was repeated three times. To determine the viscoelastic properties an oscillation frequency sweep was performed. Only very small stresses or strains were applied to ensure that all measurements were done within the linear viscoelastic region (lvr). The range of the lvr was determined by an oscillation strain or stress sweep before the frequency experiments were performed. Also, the structure build-up time after pre-shearing the slurry was examined. All samples were allowed to rest the appropriate amount of time before the oscillation experiment was started.

3. Results and discussion

A liquid phase consisting of water only is inadequate for screen printing. The high vapor pressure of water leads to fast evaporation during the screen printing process. To prepare suspensions suitable for this technology, water was mixed with 1,2-propanediol, which lowers the vapor pressure. The rheology of these mixtures is important when suspensions are prepared. Therefore, rheology curves were taken as a function of liquid composition (left plot in Fig. 3). Mixtures containing more than 25 wt.% propanediol exhibited Newtonian behavior throughout the investigated shear rate range. Therefore, in this work all further analysis of suspensions or liquids were performed at $\dot{\gamma} = 100\,\mathrm{s}^{-1}$. It is worth noting that the viscosity of liquid phase mixtures as a function of water content fitted well to an exponential function. The right plot in Fig. 3 shows this fit. The resulting function is $\eta = 0.035 \exp(-3.49 c_{\mathrm{H_2O}})$ where $c_{\mathrm{H_2O}}$ is given in wt.%. The reliability of this fit is $R^2 = 0.993$.

High ceramic solids content in screen printing pastes is desirable for industrial applications to reach a high sinter activity, low shrinkage, or a small pore distribution. Therefore, zirconia suspensions with a solids volume fraction of $\phi = 20$ vol.% were prepared using the three different dispersants PAA, TAC and TODA. First, the influence of the liquid phase composition on the rheological behavior of these suspensions was investigated. In Fig. 4 the viscosity curves (left plot) for two different liquid phases are shown, in which PAA was used as dispersant.

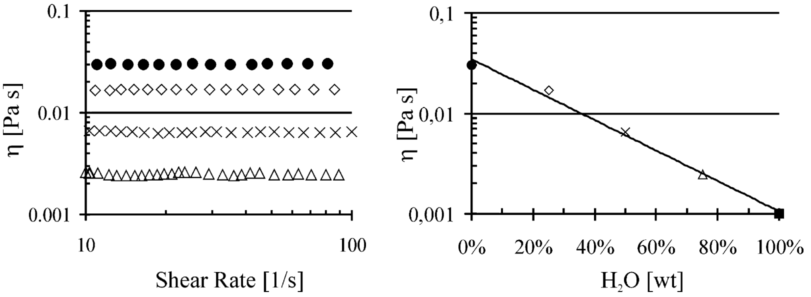

Fig. 3. Rheology of liquid phase mixtures. The left plot gives the viscosity curve of 100 wt.% propanediol (●), 75–25 wt.% propanediol–water (◇), 50–50 wt.% propanediol–water (×), and 25–75 wt.% propanediol–water mixture (△). The right plot shows the viscosity at shear rate $100\,\text{s}^{-1}$ as a function of liquid phase composition (■I, 100 wt.% water). The line represents an exponential fit to the data. The standard deviation for all measurements is ±10%.

Both suspensions exhibited a Newtonian region at low shear rates and a shear thinning behavior beginning at $\dot{\gamma} > 1\,\text{s}^{-1}$. If more propanediol was present in the liquid phase (75 wt.% propanediol sample) the viscosity decreased one order of magnitude (i.e. for $\dot{\gamma} = 0.8\,\text{s}^{-1}$ η decreased from 2300 to 340 Pa s). This result is surprising. As discussed above in the pure liquid phase (3) the viscosity increased with increasing propanediol content. The viscosity decreases in the suspension therefore cannot be explained by the viscosity of liquid medium. Instead, the influence of the Hamaker constant of this medium needs to be taken into account. This has been discussed in an earlier publication[5]: due to a lower Hamaker constant in a less polar medium, the van der Waals attraction is reduced and less agglomeration may occur. Further, the degree of dissociation of PAA depends on the dielectric constant $\in_r$, which is also a function of the polarity of the medium[5]. A less dissociated PAA molecule, which adsorbs to a zirconia surface, will lead to a smaller "effective" particle size. Thus the dispersion quality and the viscoelastic properties of the suspension will be improved.

Both systems exhibited inferior processing qualities. The tackiness was high. During preparation of the suspension a poor processing quality was noted. This indicated that the dispersing process was insufficient. Also a low tan (δ) values (see right plot of Fig. 4) were detected (i.e. at $f = 10$ Hz $\tan\delta = 0.37$ for 75 wt.% propanediol sample and 0.13 for 25 wt.% propanediol sample). Obviously the elastic modulus dominated the viscoelastic properties, which may be explained by Eq. (1.2): for the suspensions in the present work (solids volume fraction $\phi = 20$ vol.% and particle sphere diameter of 13 nm) the maximum layer thickness for the particles not to touch may be calculated as

$$\Delta = r\left[\sqrt[3]{\left(\frac{\phi_{\max}}{\phi}\right)} - 1\right] = 3.1\,\text{nm} \qquad (3.1)$$

where r is the radius of sphere (6.5 nm), $\phi_{\max} = 0.64$ (for random close packing) and ϕ is the solids volume fraction (0.20).

Biggs and Healy[12] investigated the steric interaction length of PAA ($M_w = 2000$ g/mol) on ZrO_2 in water. They report changes in the conformation of the PAA molecule with pH, due to the different dissociation rate. At pH 9.0 the molecule is fully dissociated, resulting in a tail conformation. They determined the barrier size to be 5–8 nm. Also a shift of the plane of charge (electrostatic contribution) of about 0.8 nm is discussed. This would increase the repulsive barrier size of PAA even more. This is clearly far too big for the suspension system investigated in the present work. Therefore, the conclusion is drawn that PAA is not a suitable dispersant for highly filled suspensions of nanozirconia powder in a propanediol–water matrix at pH 9.0. The dispersant was not investigated further.

The influence of the liquid phase composition has also been studied for suspensions stabilized by TAC. The results are shown in Fig. 5. At low shear rates (left plot) the 25 wt.% water sample indicates a Newtonian region, which is confirmed by the flow curve data (not shown here). The 50 and 75 wt.% samples both exhibit a yield stress. At higher shear rates ($\dot{\gamma} > 10\,\text{s}^{-1}$) there is no significant difference in the viscosity data of the samples. However, one should keep in mind that the background viscosity of the liquid phase also varied with propanediol content, which will be discussed in Fig. 8. The right plot in Fig. 5 represents the

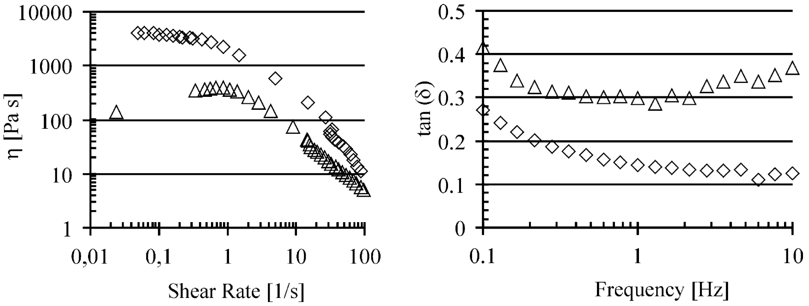

Fig. 4. Influence of liquid phase composition on rheological properties of zirconia suspensions. Left plot shows the viscosity curve for zirconia solids loading of 20 vol.% using PAA as dispersant. Propanediol content in the liquid phase was 25 wt.% (◇) and 75 wt.% (△) and pH was set to 9.5. The right plot exhibits the tan δ value as a function of oscillation frequency. The standard deviation for the viscosity data is ±10% and for tan δ ± 20%.

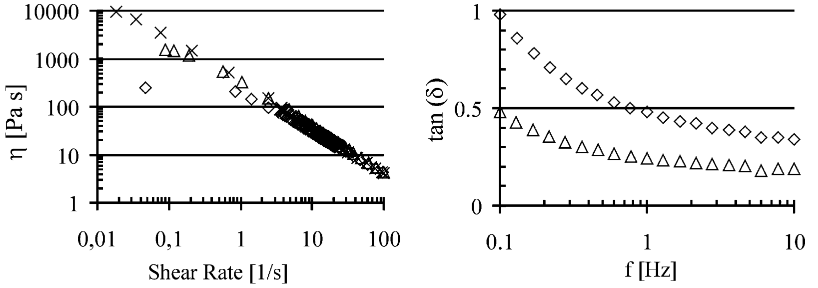

Fig. 5. Influence of liquid phase composition on rheological properties of zirconia suspensions. The left plot shows the viscosity curve for zirconia solids loading of 20 vol.% using TAC as dispersant. Water content in the liquid phase was 25 wt.% (◊), 50 wt.% (×) or 75 wt.% (△) and pH was set to 9.5. The right plot exhibits the tan δ value as a function of oscillation frequency. The standard deviation is given in Fig. 4.

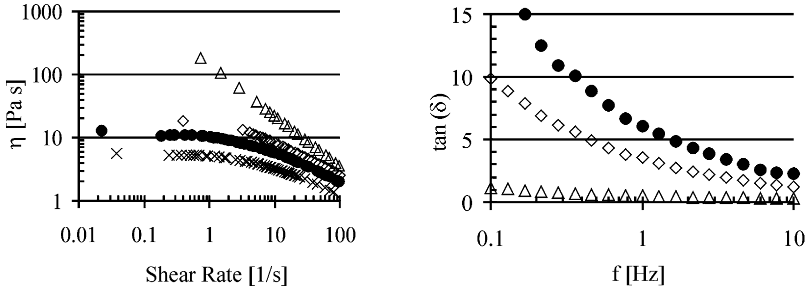

Fig. 6. Influence of the liquid phase composition on rheological properties of zirconia suspensions. Left plot shows the viscosity curve for zirconia solids loading of 20 vol.% using TODA as dispersant. Water content in the liquid phase was 20 wt.% (●), 25 wt.% (◊), 50 wt.% (×) or 75 wt.% (△) and the pH was set to 3.5. The right plot exhibits the tan δ value as a function of oscillation frequency. The standard deviation is given in Fig. 4.

tan δ value as a function of the oscillating frequency. For both investigated TAC samples, 25 and 75 wt.% propanediol content in liquid phase, tan $\delta < 1$ at all frequencies. Only for very low frequencies ($f \rightarrow 0$) the value approaches 1. This means that the elastic modulus dominated the viscoelastic properties of all samples. Without further additives, such systems cannot be well processed by screen printing.

Using TODA as a dispersant this is not the case. Fig. 6 shows the plots for the TODA dispersed suspensions. The viscosity values (left plot) are well below 10 Pa s for all background solutions (from 20 to 75 wt.% water) at a shear rate of $100\dot{\gamma} = 1\ \mathrm{s}^{-1}$. Obviously these samples were dispersed better than the TAC samples. Also the tan δ values are above 1 in the investigated frequency region except for the 75 wt.% water sample. These suspensions were easily processed and could also be screen printed.

In Fig. 7 all absolute values of the viscosity for the investigated dispersants are compared. As stated above, TODA samples exhibited the lowest viscosity values: in the left graph viscosity curves are plotted for all suspensions containing 75 wt.% propanediol in the liquid phase. At all shear rates, suspensions prepared with TODA show the lowest η values. The viscosity of TAC samples is one order of magnitude higher than the one of TODA. As mentioned before, PAA suspensions show the highest viscosity values. Since the liquid phase is identical for all samples in that figure, it can be concluded that TODA is the most suitable dispersant of for nano-zirconia particles in water–propanediol mixtures. TAC works better than PAA but is clearly not as effective as TODA.

From the oscillation experiments (right graph in Fig. 7) it can also be concluded that TODA is the most suitable dispersant. Here PAA and TAC (in suspensions with 75 wt.%

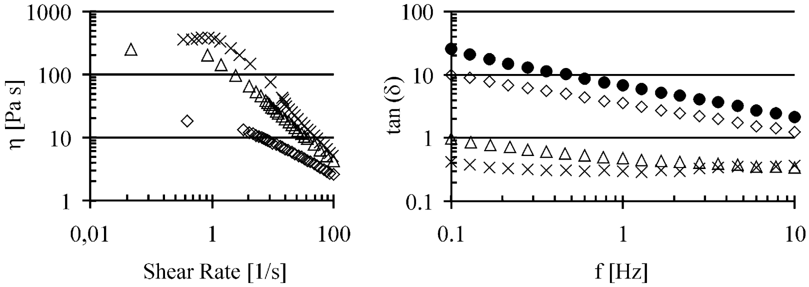

Fig. 7. Comparison of different dispersants and the liquid phase composition on rheological properties of zirconia suspensions. Left plot shows the viscosity curve for zirconia solids loading of 20 vol.%. The propanediol content in the liquid phase was 75 wt.% for all samples. Different dispersants were used: TODA (◊), TAC (×) and PAA (△). The pH was set to 9.5 for TAC and PAA, and 3.5 for TODA. The right plot exhibits the tan δ value as a function of oscillation frequency, where the 80 wt.% propanediol (TODA) sample (●) is added. The standard deviation is given in Fig. 4.

propanediol) exhibit the lowest tan δ values, which indicates that the elastic modulus G' dominated their viscoelastic properties. For TODA samples this is not the case. If 75 wt.% propanediol is used as liquid phase, tan δ increases above unity for frequencies $f < 13$ Hz. If the propanediol content is increased to 80 wt.% this tendency is amplified and G'' dominates the viscoelastic behavior (tan $\delta > 1$) at all investigated frequencies. Obviously the choice of dispersant as well as the composition of the matrix (liquid phase) determine the dispersing quality and the viscoelastic properties. The size of the stabilizing barrier and the Hamaker constant of the suspension system are the key elements. Both need to be optimized and suit to each other. If the repulsive forces are too high and long ranged, they may cause processing problems just as strong adhesive forces will.

Fig. 8 confirms the superiority of TODA for all liquid phase compositions. Here the relative viscosity $\eta_r = \eta_{\text{suspension}}/\eta_{\text{liquidphase}}$ (taken at $\dot{\gamma} = 100\,\text{s}^{-1}$) is plotted as a function of water content in the liquid phase. It is obvious from this graph that TODA exhibits the lowest viscosity values and therefore the best dispersing properties. It also becomes apparent that the dispersing quality rises with propanediol content in the liquid phase for all investigated dispersants. For TAC this seems to be a linear function. For TODA this is clearly a non-linear function. Between 50 and 75 wt.% water content the viscosity decreases strongly. For higher propanediol contents η_r seems to be constant. These results correspond very well with previous AFM investigations[5]. There it was found that the dispersing forces in the propanediol–water mixtures are depending strongly on the propanediol content. Also, when using TODA as a dispersant in a propanediol–water mixture, the best dispersing properties were achieved at a minimum propanediol content of 50 wt.%. This is now confirmed by Fig. 8. It is worth noting that the dispersing quality depends strongly on the liquid dispersing medium. There are two opposite tendencies overlapping each other. The viscosity of the liquid medium and the Hamaker constant of the system are both a functions of the propanediol content. The viscosity of the liquid medium may be decreased by adding water. However, due to the high dielectric constant of water this addition will increase the Hamaker constant of the system. This leads to agglomeration and thus an increase of the viscosity[9]. Obviously the Hamaker constant effect exceeds by far the liquid medium effect.

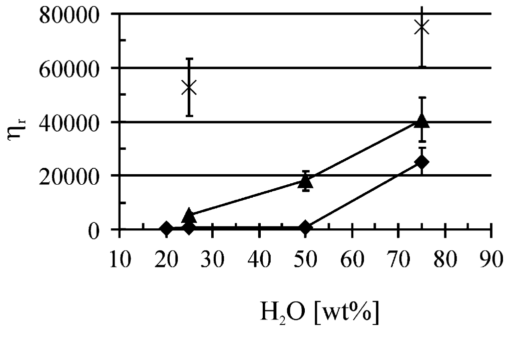

Fig. 8. Relative viscosity η_r of suspensions prepared with PAA (×), TAC (▲) and TODA (♦) as a function of water content in the liquid phase. The values were calculated at a shear rate $\dot{\gamma} = 100\,\text{s}^{-1}$. TODA exhibits the lowest values for all compositions. However, the trend is non-linear, whereas for TAC it is clearly linear. Lines are for clarifying reasons only.

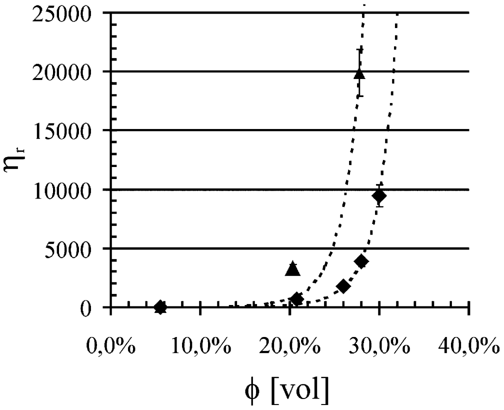

Fig. 9. Krieger–Dougherty plots for TODA (♦) and TAC (▲) suspensions. Dotted lines represent modified Krieger–Dougherty fits.

On the basis of the above results, suspensions were produced with solids volume contents well above 20 vol.%. Fig. 9 shows the relative viscosity η_r as a function of solids content. The lines in the graph are Krieger–Dougherty fits according to Eq. (1.1). It is obvious from the plot that the fit for TAC is not very good. This indicates that these samples did not follow the Krieger–Dougherty theory. It may be concluded that the particles were not well dispersed and most likely not spherical. The fitting parameter n is determined to be 18.66 and the maximum package density is set to $\phi_m = 0.64$. The fit for TODA samples is much more accurate. The parameters here are $\phi_m = 0.43$ and $n = 8.24$. Eq. (1.1) seems to describe the curve quite well. Although, the low packing density indicates that the particles are not densely packed and thus may not be spherical. Comparing the viscosities at different solids content shows that TODA exhibits much lower η_r values. By extrapolating the curves in Fig. 9 it may also be concluded that the repulsive barrier created by TAC is far bigger than the one created by TODA. Thus the maximum

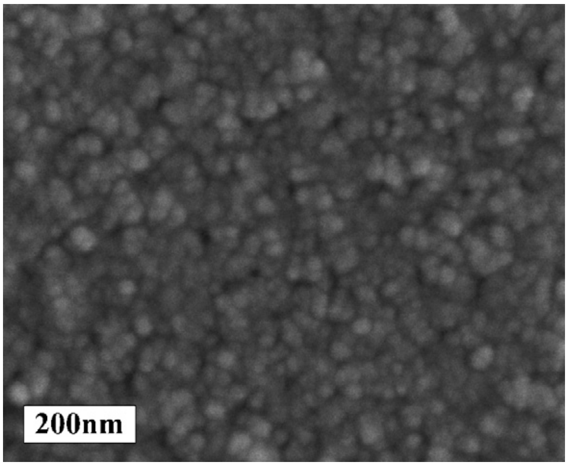

Fig. 10. SEM picture of a green paste layer with 100,000× magnification. The spherical agglomerates are clearly visible and have an approx. size of 40–50 nm. Note that a polymer layer is surrounding these agglomerates, implying that their effective size is even smaller.

achievable filling level of TAC suspensions is much lower than the one of TODA.

Finally, as an example for application purposes, the results were used to prepare a screen printing paste. Here a filling level of 11 vol.% zirconia, 75 wt.% propanediol–25 wt.% water mixture as dispersing medium, TODA as dispersant and an additional polymer binder PVP were used. Fig. 10 shows a picture of the dried green layer. The agglomerated zirconia particles are clearly visible. The approx. size is now 40–50 nm. This is much smaller then the original d_{50} value of 110 nm. These agglomerates therefore consist of only two–three primary particles in diameter. Note that a polymer layer is surrounding the agglomerates, implying that the effective size is even smaller.

4. Conclusion

The preparation of nano-zirconia dispersions in water with high solids loadings showed that "TODA" is a useful dispersant surpassing citric acid and polyacrylic acid in achieving low viscosities. The efficiency of TODA can further be raised by moving from pure water to mixtures of water–propanediol as dispersing medium. Even though the viscosity of the dispersing medium increases with higher propanediol content a steady decline in viscosity for the slurry was observed. There might be several reasons responsible for this. The presented data suggests that the largest contribution to this unexpected behavior stems from the change in Hamaker constant, i.e. lowering of attractive forces due to the organic solvent when it exceeds 50 wt.%.

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