STABILIZATION OF BIOCERAMIC SUSPENSIONS PREPARED FROM ALUMINA-CONTAINING ZIRCONIA POWDERS

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A stable, agglomerate-free suspension with almost Newtonian flow behavior is one of the basic requirements when slip casting is to be used as a shaping process for bioceramic materials. In this work suspensions of three commercial zirconia powders with different alumina admixtures (Tosoh TZ-3Y, TZ-3YE, TZ-3Y20A) are investigated. The rheological behavior is determined by rotational viscometry, the particle size distribution by low-angle laser light scattering. For the powder types studied the alkali-free polyelectrolyte Dolapix CE64 turned out to be the most effective deflocculant. The optimum deflocculant concentration is approx. 0.6 wt.% in all cases. It has been found that peptization alone is not sufficient for destroying the agglomerates, mechanical dispersion (ball-milling) is also necessary. The concentrational changes during the evacuation step are in the order of several percent and lead to non-negligible viscosity changes.

INTRODUCTION

Bioceramics are special ceramics used in medicine for the replacement or reconstruction of affected or destroyed parts of the skeletal system [1]. Bioceramics can be divided into resorbable (tri-calcium phosphate), bioactive (hydroxyapatite, bioactive glass, bioactive glass-ceramics) and bioinert materials (sintered Al_2O_3, yttria-stabilized ZrO_2) [2].

Bioinert ceramics are used mainly for replacements of bones, hip joints and for dental implants. They have to satisfy strict demands concerning mechanical and corrosion properties, chemical purity and biocompatibility.

The most frequently used bioinert materials so far are ceramic materials based on sintered alumina (α-Al_2O_3, corundum), which exhibit bend strength values of about 380 MPa and higher. Today partially stabilized zirconia ceramics (PSZ or TZP with 3 mol.% or 5 wt.% Y_2O_3) exhibiting bend strengths of up to 1200 MPa as well as mixtures (nanocomposites) of Y-PSZ or Y-TZP ceramics with e.g. 20 wt.% Al_2O_3 (so-called ATZ ceramics, alumina-toughened zirconia), exhibiting bend strengths of up to 2500 MPa, appear as perspective competitors.

Among the main advantages of these zirconia materials are their high values of mechanical strength and fracture toughness, which are attainable due to the phase transformation from the tetragonal to the monoclinic phase of ZrO_2 [3]. The resulting mechanical strength of the material, however, depends largely on the selection of the starting powder and on the final microstructure of the body, which is a result of processing.

Powders used for the preparation of bioceramics (e.g. implants) must be characterized by a small particle size, a narrow particle size distribution, isometric particle shape and high chemical purity, especially the absence of Na, Fe and Si.

One of the main shaping technologies applied for bioinert ceramics is slip casting, where an indispensible condition is the preparation of an appropriate slip, i.e. a slurry or suspension (or possibly sol) without agglomerates or aggregates, exhibiting a rheological behavior close to Newtonian in order to guarantee a homogenous microstructure of the formed body. Dispersion of the material can occur by mechanical milling (milling of particles and agglomerates) or by peptization of floccules. Dispersed colloidal particles, however, have a large specific surface area and tend to minimize the surface energy by flocculation. Generally, there are two ways to avoid this flocculation and to stabilize the suspension, viz. a) sterical stabilization by polymers or b) electrostatic stabilization by electrolytes and polyelectrolytes [4]:

a) Sterical stabilization is dominant in suspensions with a high ion potential (e.g. in gypsum or cement suspensions), where the electrostatic stabilization is hindered [5].
b) Electrostatic stabilization is the usual way of stabilizing ceramic suspensions. It is achieved by a sufficiently large electrostatic potential at the phase boundary (interface) of the colloidal micel - the so-called electrokinetic potential ζ (”zeta-potential”). When the ζ-potential is sufficiently high, repulsive Coulomb forces are exceeding the attractive van der Waals forces, and therefore the particles are repelled, do not flocculate and the suspension becomes stable.

The value of the ζ-potential can be controlled by small changes in the composition of the suspension (by adding electrolytes or polyelectrolytes), and this value

is then responsible for the rheological properties of the ceramic suspension. An increased ζ-potential results in a peptization, which reveals itself in a reduction of the viscosity (because of deflocculation), while a reduced ζ-potential, on the other hand, leads to agglomeration and an increase of apparent viscosity (and to coagulation).

There are essentially two ways to enhance the ζ-potential:

- exchanging the ions adsorbed in the adsorption layer of the electrostatic double-layer while retaining the original value of the surface potential ψ,
- raising the value of the surface potential ψ of the core of the particle.

The ability of cations to disperse a given suspension containing agglomerates is described by the so-called Hofmeister series:

$Li^+ > Na^+ > K^+ > NH_4^+ > Mg^{2+} > Ca^{2+} > Al^{3+} > H^+$

From this sequence it can be concluded that alkali cations are the most effective in raising the ζ-potential. Their use, however, is undesirable especially from the viewpoint of further heat processing of biomaterials, because they lead to melts in a ceramic body, and the resulting inhomogeneities (e.g. glassy boundary phases or recrystallization products) dramatically decrease mechanical strength. Furthermore they may possibly affect the biocompatibility of the materials. Therefore it is not advisable to apply an exchange adsorption of alkali ions in order to achieve stabilization of the slurry. Thus for the electrostatic stabilization of bioceramic suspensions only the second route for enhancing the ζ-potential is feasible (enhancing the surface potential ψ by alkali-free electrolytes or polyelectrolytes).

EXPERIMENTAL DETAILS, RESULTS AND DISCUSSION

The rheological character of suspensions made from three powder types (labelled TZ-3Y, TZ-3YE and TZ-3Y20A, produced by TOSOH Corporation / Japan) was studied. The powders, which can all be used for the preparation of bioceramics, differ with respect to their overall content of zirconia, alumina, yttria and impurities. Two of them are essentially zirconia powders (containing yttria), while one is a typical ATZ (alumina-toughened zirconia) powder mix. Characteristic parameters of the powders are shown on table 1. The harmonic mean diameters were calculated from literature data [6].

Aqueous suspensions of the respective powders were prepared in PVC bottles by mixing an adequate amount of dry powder (28-38 g) with the corresponding amount of deflocculant (wt.% based on dry solid mass) and adding the necessary amount of distilled water. The water content of the deflocculant was duely taken into account. The suspensions thus prepared were homogenized by shaking for 90 min with alumina balls (mass ratio of balls to dry solids 1:2). Entrapped air was eliminated from the suspensions by 10 min evacuation, followed by 10 min sonication and a further evacuation period of 10 min.

Table 1. Basic parameters of the powders used.

Powder type	TZ-3Y	TZ-3YE	TZ-3Y20A
ZrO_2 content (wt.%)	94.68	94.65	75.32
Al_2O_3 content (wt.%)	<0.1	0.253	20.72
Y_2O_3 content (wt.%)	5.15	5.07	3.93
Impurities (wt.%)			
SiO_2	<0.02	0.005	0.005
Fe_2O_3	<0.01	<0.002	<0.002
Na_2O	<0.04	0.022	0.019
Specific surface area ($m^2\ g^{-1}$)	16	15.4	16
Harmonic mean diameter (calculated) (μm)	0.062	0.064	0.068
Density (10^3 kg m^{-3})	6.05	6.05	5.5
Particle size (median) x_{50} (μm)	0.6	0.6	0.6
Agglomerate size (median) x_{50} (μm)	60	60	60

Aqueous ceramic suspensions can be characterized by their rheological properties, most completely expressed by their flow curve, which is a graphical representation of the dependence of the shear rate (D) (deformation rate, velocity gradient) on the shear stress (τ) (or vice versa). In the present work this dependence was measured with a rotational viscometer (RHEOTEST 2, Medingen / Germany) in a shear rate range from 3 to 1312 s^{-1} (with the corresponding shear stresses ranging from 0 to 350 Pa). The necessary sample volume for one measurement was 10 ml (double-gap cylinder system "N"). The apparent viscosity η_a was determined from the dependence D (τ) at D = 48.6 s^{-1} (in the case of time-dependence, i.e. a flow curve with hysteresis, always read off from the increasing branch).

Properties of the suspensions prepared from the as-received powders

Three frequently recommended deflocculants were tested for the stabilization of the aqueous suspensions: Dolapix CE64 and Dolapix ET85 (Zschimmer & Schwarz, Lahnstein / Germany) and Sokrat 32A (Chemické závody Sokolov / Czech Republic). All

Table 2. Basic parameters of the deflocculants used.

Deflocculant tipe	Dolapix CE64	Dolapix ET85	Sokrat 32A
pH	7	7	6-8
Density (g cm^{-3})	1.10	1.14	-
Content of active agent (%)	70	65	40
Chemical character	Organic acids	Esters of organic acids	Ammonium salt of polyacrylic acid

these electrolytes are alkali-free deflocculants. Table 2 lists some of their further characteristic features [7, 8].

For easier and more precise addition in practice the deflocculant was diluted to a 50 % solution in distilled water. Note, however, that all deflocculant contents presented in this paper are retransformed to the undiluted deflocculant (i.e. to the deflocculant with a concentration of active agent as delivered by the producer).

The influence of the various deflocculants on the peptization of the respective zirconia powder suspensions was tested for suspensions with an initial solid content of 71.3 wt.% for the powders TZ-3Y and TZ-3YE, while for the powder TZ-3Y20A the content had to be reduced to 62.5 wt.% (with higher solids contents these suspensions did not flow except when CE64 was used). The optimum deflocculant content was found to be 0.6 wt.% (based on dry solid mass) for all suspensions. Figures 1 through 3 show the dependence $D(\tau)$ for a given powder and a given deflocculant, while table 3 lists the apparent viscosities at a shear rate of 48.6 s^{-1}. The initial solid content of 71.3 wt.% (before evacuating) was selected according to literature data [9] (note that here and in the following text all solids contents are meant to denote initial solid contents calculated from the masses of the components weighed in during the preparation of the suspension, i.e. solids contents before the evacuation step, if not stated otherwise).

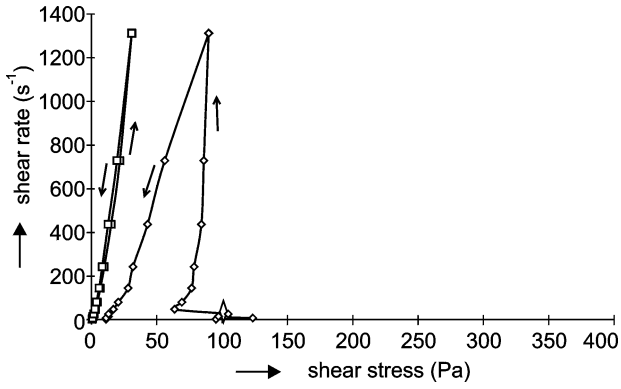

Figure 1. Flow curves of the 71.3 wt.% suspension with TZ-3Y and addition of 0.6 wt.% Dolapix CE64 and Sokrat 32A, respectively.
□ – TZ-3Y (0.6 % CE64), ◊ – TZ-3Y (0.6 % S32A)

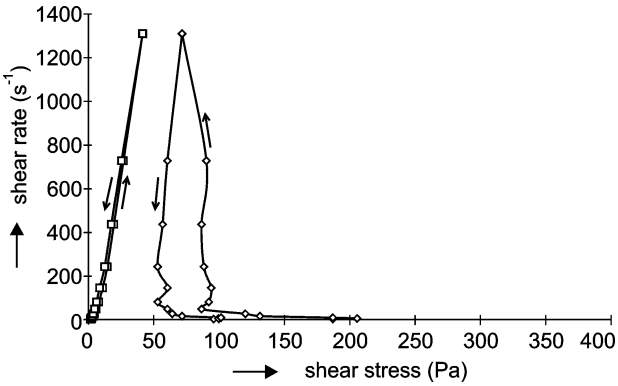

Figure 2. Flow curves of the 71.3 wt.% suspension with TZ-3YE and addition of 0.6 wt.% Dolapix CE64 and Sokrat 32A, respectively.
□ – TZ-3YE (0.6 % CE64), ◊ – TZ-3YE (0.6 % S32A)

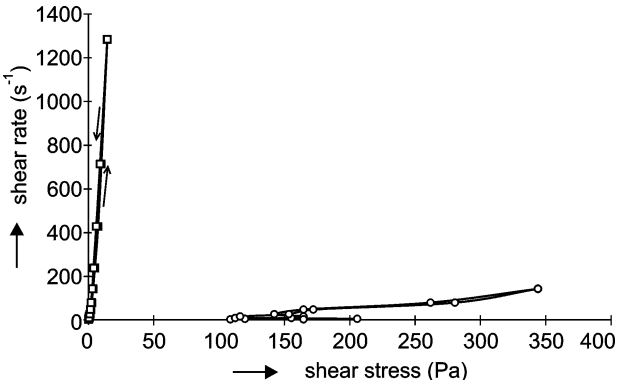

Figure 3. Flow curves of the 62.5 wt.% suspension with TZ-3Y20A and addition of 0.6 wt.% Dolapix CE64 and Dolapix ET85, respectively.
□ – TZ-3Y20A (0.6 % CE64), ◊ – TZ-3Y20A (0.6 % ET85)

Considering the measured flow curves, Dolapix CE64 (in the following abbreviated as CE64) appears as the most promising deflocculant, because the rheological character of suspensions with this deflocculant seems to be closest to that of Newtonian liquids (compare, however, figure 5 below). Therefore this deflocculant has been used in all further experiments. From the flow curves it can also be concluded that, when an inappropriate deflocculant is chosen, the hyseresis loop is too wide and the apparent

Table 3. Apparent viscosities η_a for suspensions with different deflocculant types (deflocculant content 0.6 wt.%).

Powder type	(solids content)	Dolapix CE64 η_a (mPa s)	Dolapix ET85 η_a (mPa s)	Sokrat 32A η_a (mPa s)
TZ-3Y	(71.3 wt.% solids)	66	-	1308
TZ-3YE	(71.3 wt.% solids)	106	-	1770
TZ-3Y20A	(62.5 wt.% solids)	35	3386	(not flowing)

viscosity can attain very high (sometimes even unmeasurably high) values, see figure 3.

The optimum content of deflocculant can be determined from the dependence of the apparent viscosity on the deflocculant content (the deflocculation curve) and corresponds to a minimum of apparent viscosity. For suspensions with 71.3 wt.% solids content deflocculated by CE64 the deflocculation curves are shown on figure 4.

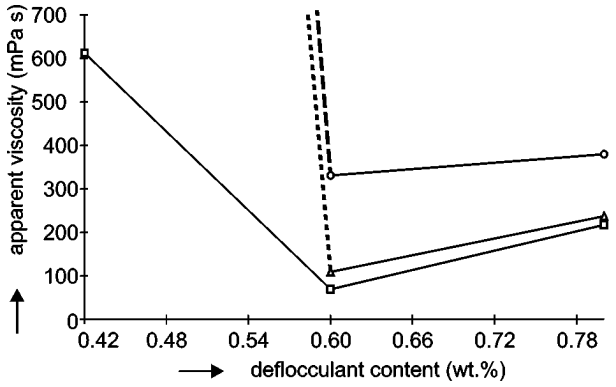

Figure 4. Deflocculation curves of suspensions with 71.3 wt.% solids content of the powder types TZ-3Y, TZ-3YE and TZ--3Y20A, respectively.
□ – TZ-3Y, Δ – TZ-3YE, ○ – TZ-3Y20A

determined optimum deflocculant content of 0.6 wt.% (CE64) has been chosen for all suspensions.

According to this detailed view of the measured flow curves the rheological flow behavior of all these suspensions can be characterized as that of a time-dependent non-Newtonian liquid with positive thixotropy. Since suspensions with 71.3 wt.% of the powder TZ-3Y20A are inappropriate for slip casting (due to the high viscosity and the wide hysteresis loop)

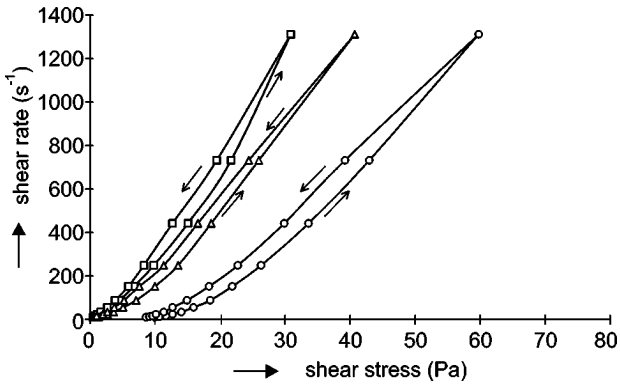

Figure 5. Flow curves of suspensions with 71.3 wt.% solids content of the powder types TZ-3Y, TZ-3YE and TZ-3Y20A, respectively, with 0.6 wt.% of Dolapix CE64.
□ – TZ-3Y, Δ – TZ-3YE, ○ – TZ-3Y20A

Table 4 lists the optimum contents of deflocculant and the corresponding apparent viscosity values for suspensions with the respective powder types.

In order to compare the rheological character of suspensions with the different powder types (figure 5), a constant solids content of 71.3 wt.% and the

Table 4. Optimum content of deflocculant for 71.3 wt.% suspensions with the powder types TZ-3Y, TZ-3YE and TZ--3Y20A.

	TZ-3Y	TZ-3YE	TZ-3Y20A
Optimum deflocculant content (wt.%)	0.6	0.6	0.6
Apparent viscosity at optimum deflocculant content (mPa s)	66	106	329

the rheological behavior of these suspensions has additionally been measured at solids contents of 65 wt.% and 62.5 wt.% (table 5).

The reduction of the solids content in these suspensions changed the flow curve to almost Newtonian and reduced the hysteresis loop considerably.

In subsequent measurements the suspension containing powder type TZ-3Y20A has been prepared with 65 wt.% (the optimum deflocculant content for this case was again determined to be about 0.6 wt.% CE64, see figure 6).

Table 5. Apparent viscosity h_a of the suspension with powder type TZ-3Y20A in dependence of the solids content.

Solids content (wt.%)	62.5	65	71.3
η_a at 0.6% CE64 (mPa s)	35	119	329

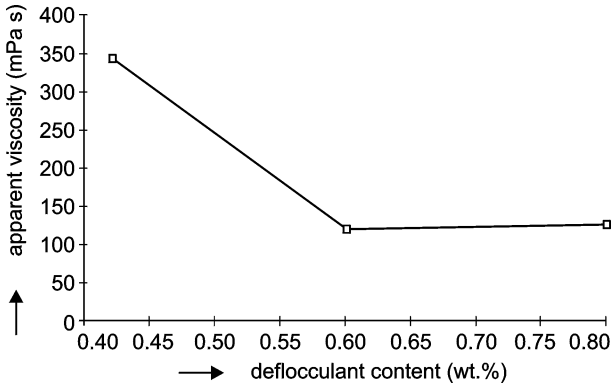

Figure 6. Deflocculation curve of the suspension with 65 wt.% TZ-3Y20A.
□ – TZ-3Y20A (65 wt.% solids)

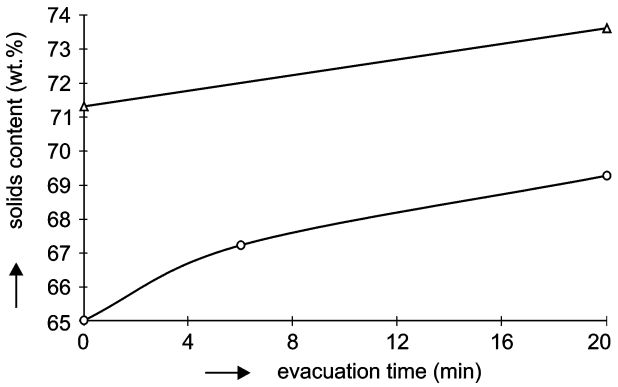

Figure 7. Dependence of the solids content on the evacuation time of a suspension with powder type TZ-3Y20A.
Δ – TZ-3YE, ○ – TZ-3Y20A

Influence of the evacuation time

For suspensions containing powder type TZ--3Y20A a significant dependence of the apparent viscosity and the solids content on the evacuation time has been found, see figure 7 and table 6.

It has been found e.g. that the solids content in a suspension with the powder type TZ-3YE increased from 71.3 wt.% to 73.6 wt.% after two evacuation periods of 10 min each.

From these results it can be concluded that with the evacuation of air there is at the same time an increased evaporation of water from the suspension, and the resulting concentration changes are not negligible, since their effect on the viscosity of the suspensions is significant.

Table 6. Apparent viscosities h_a for different evacuation times (suspensions containing initially 65 wt.% of powder type TZ-3Y20A).

Evacuation time (min)	0	6	20
Solids content (wt.%)	65	67.2	69.3
Apparent viscosity (mPa s)	78	102	120

Properties of the suspensions prepared by ball-milling of the dispersed powders

In this series of experiments the powders TZ-3YE and TZ-3Y20A were ball-milled for 1 h in dry state in an agate mortar in order to test the possiblity of mechanically dispersing the relatively hard agglomerates.

The particle size distribution of the ball-milled powders was measured by low-angle laser light scattering (LALLS) on the Analysette 22 (Fritsch GmbH, Idar-Oberstein / Germany). Table 7 summarizes some of the parameters of the ball-milled and the as-received powders, respectively.

Also for suspensions with the ball-milled powders deflocculation curves were measured and compared with those of the suspensions with the as-received powders (figures 8 and 9).

From the figures shown it is evident that for both powder types (TZ-3YE and TZ-3Y20A) the optimum deflocculant addition remained 0.6 wt.% even after ball-milling. The suspensions of the ball-milled powders showed a significant reduction in apparent viscosity although the specific surface area (as measured by LALLS) has increased during milling (see table 8). From these results it can be concluded that ball-milling caused mainly a deagglomeration of agglomerates, which absorbed water in the suspensions containing as-received (unmilled) powders and thus effectively immobilized a certain amount of water in the unmilled suspensions.

Table 7. Numerical characteristics of the particle size distribution of the as-received and the ball-milled powders, respectively.

	TZ-3YE (as-received)	TZ-3YE (ball-milled)	TZ-3Y20A (as-received)	TZ-3Y20A (ball-milled)
Arithmetic mean diameter (μm)	9.4	0.33	3.61	1.817
Harmonic mean diameter (μm)	2.323	0.264	0.787	0.603
Mode x_M (μm)	13.7	0.15	0.94	0.813
Median x_{50} (μm)	9.9	0.28	1.08	0.785
Specific surface area with respect to volume (μm^{-1})	2.58	22.74	7.62	9.94

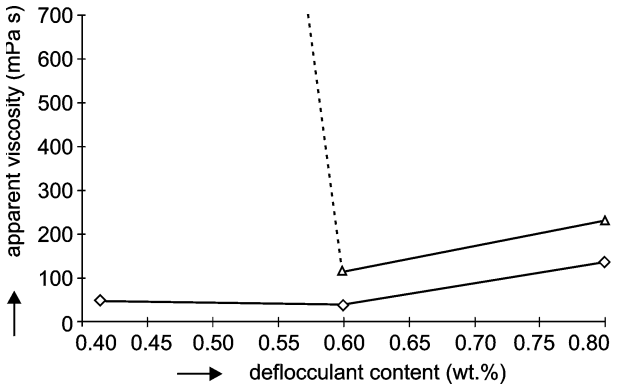

Figure 8. Deflocculation curves of suspensions with 71.3 wt.% solids content of the powder type TZ-3YE as-received and ball--milled, respectively.
Δ – TZ-3YE (as-received), ◊ – TZ-3YE (ball-milled)

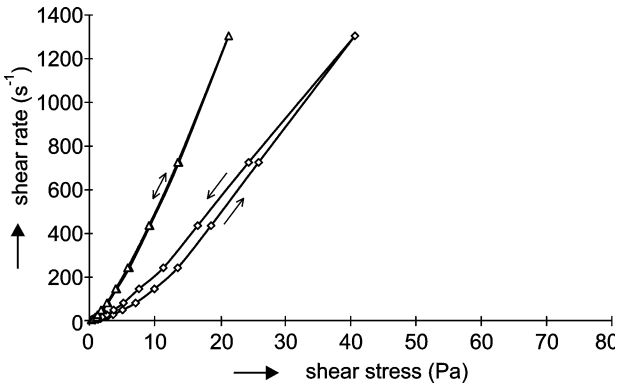

Figure 10. Flow curves of a suspension with 71.3 wt.% solids content of the powder type TZ-3YE (as-received and ball-milled, respectively), with 0.6 wt.% of Dolapix CE64.
Δ – TZ-3YE (as-received), ◊ – TZ-3YE (ball-milled)

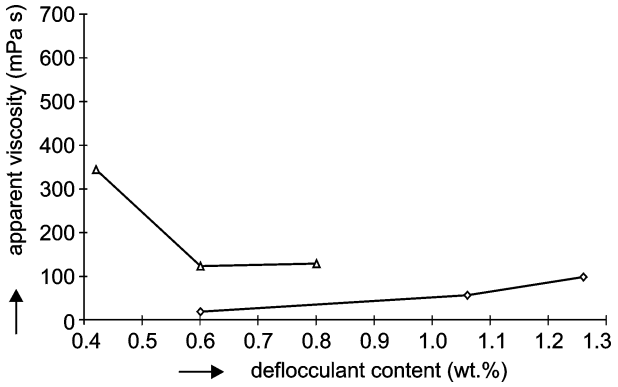

Figure 9. Deflocculation curves of suspensions with 65 wt.% solids content of the powder type TZ-3Y20A (as-received and ball-milled, respectively).
Δ – TZ-3Y20A (as-received), ◊ – TZ-3Y20A (ball-milled)

The rheological character of the suspensions of both powders TZ-3YE is shown on figure 10.

From this figure it follows that the suspension of the ball-milled powder TZ-3YE is a time-independent liquid, with a flow behavior close to Newtonian (slightly pseudoplastic). This is the desirable flow behavior for the intended forming technology. Similarly, the 65 wt.% suspension of the ball-milled powder TZ-3Y20A showed more or less Newtonian behavior in contrast to the thixotropic character of the suspension with the as-received powder.

Stability of the suspensions

For the suspensions of as-received and ball-milled powders their temporal stability was investigated after time intervals of 1h, 2h and 24 h.

The stability of the suspension was determined as follows: Immediately after the preparation of the suspension the dependence $D(t)$ was measured (i.e. at the time instant $t = 0$ h). After this first measurement the suspension was left in a rest state in the rotational viscometer for 1 h and then it was measured again (second measurement). The same was done after 2 h (third measurement). During the second measurement of the suspension (i.e. that after 1 h) the suspension was intensively mixed at high shear rates and thus the flow curve obtained from the third measurement after 2 h (for which the history of the suspension was essentially the same as for the second measurement) can be considered as a means to check the reproduciblity of the results (under the assumption that there is no degradation of the deflocculant properties during this short period of time).

The stability of the suspension with regard to the deflocculant was tested by measuring a last flow curve after a rest time 24 h (fourth measurement), after the suspension had been intensively mixed by a glass rod before starting the measurement. The apparent viscosity after a rest time of 24 h was then compared with the

Table 8. Apparent viscosities h_a of suspensions prepared with the as-received and the ball-milled powders, respectively (with 0.6 wt.% CE64).

	TZ-3YE (71.3 wt.% solids)	TZ-3Y20A (65 wt.% solids)
η_a of suspension with as-received powders (mPa s)	106	119
η_a of suspension with ball-milled powders (mPa s)	43	14

viscosity at t = 0 h (i.e. immediately after the preparation of the suspension). According to literature references a suspension can be denoted as stable if the new value of apparent viscosity does not deviate from the original one by more than 10-20 % [10, 11].

The dependence of the apparent viscosity on time is shown on figure 11 and the corresponding values are listed in table 9. As before, the suspension with powder TZ-3YE contained 71.3 wt.% of solids and the suspension of powder TZ-3Y20A 65 wt.%.

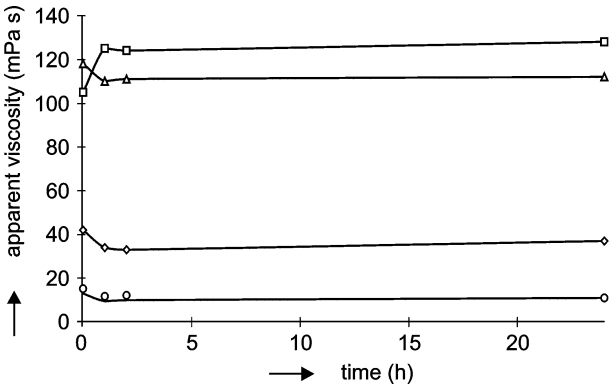

Figure 11. Dependence of the viscosity of suspensions with powder types TZ-3YE and TZ-3Y20A (as-received and ball--milled, respectively) on time.
□ – TZ-3YE (as-received), ◊ – TZ-3YE (ball-milled)
Δ – TZ-3Y20A (as-received), ○ – TZ-3Y20A (ball-milled)

From the above temporal stability results it is evident that the suspension with the as-received powder TZ-3YE shows an increase of viscosity by approx. 20 % (19 % after 1 h, 18 % after 2 h and 22 % after 24 h), while for the suspension with the ball-milled powder TZ-3YE there is a decrease of viscosity by approx. 20 % (19 % after 1 h and 21 % after 2 h), which is reduced, but still visible, after 24 h (12 %). The increase of viscosity in the first case can probably be explained by the existence of agglomerates, which cause a certain delay of water absorption. Suspensions prepared with powder type TZ-3Y20A exhibited a moderate decrease of viscosity for as-received as well as for ball-milled powders (by approx. 10 % in both cases).

CONCLUSIONS

For aqueous suspensions prepared with the three commercial zirconia powders TZ-3Y (< 0.1 wt.% Al_2O_3), TZ-3YE (0.253 wt.% Al_2O_3) and TZ-3Y20A (20.73 wt.% Al_2O_3) produced and supplied by TOSOH Corporation (Japan) the deflocculant Dolapix CE64 by Zschimmer & Schwartz (Germany) has turned out to be the most appropriate deflocculant. Its chemistry is based on organic acids. The optimal deflocculant content was found to be approx. 0.6 wt.% for all suspensions investigated. The rheological character of suspensions with a solids content of 71.3 wt.% (for suspensions with optimal deflocculant content) is time-dependent non-Newtonian (with positive thixotropy) for all three powder types TZ-3Y, TZ-3YE and TZ-3Y20A, but for the latter the hysteresis loop was significantly larger and the apparent viscosity significantly higher than for the first two (with the same solids concent).

The experiments clearly showed the influence of the solids content on the rheological character of the suspensions. Reducing the solids content in the suspension causes a significant decrease of apparent viscosity (cf. table 5) but also a sensible reduction of the degree of time-dependence (thixotropy).

It has been found that evacuation during the preparation of the suspension leads to a significant decrease of water content in comparison to the non-evacuated suspension, i.e. to an increase of the solids content and the viscosity of the suspension. By evacuating the suspension 2×10 min during the preparation the solids content increased from 65 wt.% to 69.3 wt.% and its viscosity from 78 mPa s to 120 mPa s for suspensions with the powder type TZ--3Y20A and from 71.3 wt.% to 73.6 wt.% for suspensions with the powder type TZ-3YE. Changes in the solids content with this order of magnitude have therefore to be accounted for when an evacuation step is included in the preparation of the suspensions.

The rheological character of the peptized suspensions prepared from the as-received powders did

Table 9. Apparent viscosities η_a of suspensions prepared with as-received and ball-milled powders, respectively, in dependence of time.

TZ-3YE (71.3 wt.% solids; 0.6 wt.% CE64)				
Time (h)	0	1	2	24
η_a of suspensions with as-received powder (mPa s)	106	126	125	129
η_a of suspensions with ball-milled powder (mPa s)	43	35	34	38
TZ-3Y20A (65% solids.; 0.6 wt.% CE64)				
η_a of suspensions with as-received powder (mPa s)	119	111	112	113
η_a of suspensions with ball-milled powder (mPa s)	14	10.5	11	12

not fulfil one of the basic requirements (even if the deflocculant content was optimal), since these suspensions exhibited time-dependent behavior.

By mechanical dispersion of the agglomerates, i.e. by ball-milling the powders TZ-3YE and TZ-3Y20A for 1 h the desired rheological character could be attained. The suspension of the ball-milled powder TZ-3YE (with 71.3 wt.% solids) with an optimal deflocculant content exhibits time-independent pseudoplastic character and the suspension of the ball-milled powder TZ-3Y20A (with 65 wt. solids) becomes a time-independent Newtonian liquid.

By ball-milling (and thus also increasing the specific surface area of the powders as revealed by LALLS) the optimum deflocculant content remains unchanged, and only the apparent viscosity of these ball-milled powders was clearly reduced. At first sight this finding might seem paradoxical and moreover it is in contrast to findings obtained for other powders such as the alumina powder types by SUMITOMO CHEMICAL Corp. (Japan) studied in [12], where it has been found that the optimum content of deflocculant as well as the viscosity increases in proportion to the specific surface area of the powder in the suspension. Those formerly studied alumina powders, however, were absolutely free of agglomerates, while the zirconia powders studied in the present work (TOSOH Corp., Japan) clearly contain agglomerates which can take up water from the system. This part of bound water is thus effectively immobilized and is not at disposal in the inter-agglomerate space of the suspension to facilitate flow. Mechanical dispersion by ball-milling significantly improved the rheological properties of these suspensions, which became time-independent (i.e. non-thixotropic) and approached Newtonian flow behavior.

The temporal stability of the suspensions of the as-received and the ball-milled powders TZ-3YE and TZ-3Y20A was determined by flow curve measurements after 1 h, 2 h and 24 h. Only the suspension with powder type TZ-3YE exhibited an increase in viscosity with time. The suspensions of ball-milled TZ-3YE as well as of powder TZ-3Y20A (both as-received and ball-milled) all exhibit a decrease in viscosity. All suspensions thus prepared can be termed stable because the deviation from the original viscosities lies within the admissible tolerance of ± 20 %.

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STABILIZACE BIOKERAMICKÝCH SUSPENZÍ PRÁŠKŮ ZrO_2 S PŘÍMĚSÍ Al_2O_3

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Bylo sledováno reologické chování suspenzí připravených z komerčních prášků ZrO_2-Al_2O_3 fy TOSOH CORPORATION (obsah Al_2O_3 u TZ-3Y je <0.1 hmotn.%., u TZ-3YE 0.253 hmotn.% a u TZ-3Y20A 20.73 hmotn.%) pro vytváření litím. Měření reologických vlastností probíhalo na rotačním viskozimetru a stanovení rozdělení velikosti částic metodou LALLS.

Ze sledovaných bezalkalických ztekutiv Dolapix CE64, Dolapix ET85 a Sokrat 32A bylo vybráno jako nejúčinnější ztekutivo Dolapix CE64 s optimálním přídavkem 0.6 hmotn.%. Reologický charakter peptizovaných suspenzí připravených z původních prášků jejichž původní koncentrace pevné fáze byla 65 % a 71.3 hmotn.% však nesplňoval požadované vlastnosti, kdy se suspenze reologicky chovaly tixotropně. Dispergací prášků mletím, kdy se rozdružily přítomné aglomeráty částic, se výrazně zlepšily vlastnosti suspenzí, které získaly reologický charakter blízký newtonskému. U těchto suspenzí došlo rovněž i ke zlepšení časové stálosti, která byla sledována po dobu 24 h. Dále bylo zjištěno, že při přípravě vzorku vakuováním suspenze, dochází k úbytku její vlhkosti a tím ke zvyšování viskozity. U prášku TZ-3YE obsah pevné fáze vzrostl během vakuování z 71.3 hmotn.% na 73.6 hmotn.%, u prášku TZ-3Y20A ze 65 hmotn.% na 69.3 hmotn.%.