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Influence of dispersant, storage time and temperature on the rheological properties of zirconia–paraffin feedstocks for LPIM

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Abstract

The dependence of the rheological properties of zirconia–paraffin feedstocks for low-pressure injection moulding (LPIM) on binder composition, storage time and temperature was investigated. Feedstocks with varying amounts of dispersant were fabricated to work out the required quantity for a monolayer of dispersant molecules on zirconia particles. Experimental results revealed that a shear rate dependent characteristic of the viscosity against the amount of dispersant exists. The observations were compared with calculated values according to an adsorption model, which overestimated the required quantity of dispersant to form a monolayer. Feedstocks stored at elevated temperature for several days exhibited a time-dependent decrease of the yield stress and viscosity, which is supposed to be caused by physical or chemical interactions among zirconia and the dispersant. Increasing working temperature and decreasing solids loading were found to significantly decrease the yield stress as well as the viscosity. Flow activation energies and flow indices were calculated and compared with literature. This study shows that the dispersant used in this investigation has a remarkable influence especially on the time-dependent flow behaviour of zirconia–paraffin feedstocks that affects further processing and reproducibility.

Keywords: Injection moulding; Plasticity; Rheology; ZrO_2; Low-pressure injection moulding

1. Introduction

Microsystems technology (MST) covers the fabrication of components in the micrometre or millimetre scale. Typically, silicon, plastics and some selected metals are used for the production of microcomponents. Regarding their particularly good mechanical, chemical, thermal, tribological and other special physical properties, the interest in design and manufacturing of ceramic microcomponents is increasing.[1,2] Usually, ceramic components are fabricated by casting, pressing or plastic shaping methods, e.g. injection moulding.[3] However, some of these techniques are not appropriate for microcomponents. For instance, defect-free fabrication of complex shaped ceramic or metal microparts by pressing is limited and not appropriate for MST.[4] In contrary, accurate and flaw-free components are possible by using plastic shaping techniques, especially powder injection moulding (PIM), i.e. ceramic injection moulding (CIM). Due to low tooling costs, simple moulds and good flowability of low-viscosity feedstocks mostly consisting of paraffin and dispersants (surfactants) as the binder component, low-pressure injection moulding (LPIM), which is sometimes also referred as hot moulding, is predestined for the fabrication of prototypes and small series production of ceramic and metal microcomponents.[1,5,6]

In this study, the behaviour of zirconia–paraffin feedstocks used for LPIM of ceramic microcomponents was investigated. The main focus of this paper lies on the influence of dispersant concentration, storage time and working temperature on the rheological properties. Due to the low weight, merely a small amount of feedstock is necessary for microcomponents. For the running of a LPIM machine, however, a suspension volume far above this amount has to be produced. As a result, feedstocks of proper amount have to be prepared and stored for a certain time until used up completely. Even if initial flow properties can be regained by redispersing the feedstock after a short storage time,[7] the long-term stability of zirconia–paraffin feedstocks with varying amounts of dispersant has not been studied yet. Usually the feedstocks have to be stored at elevated

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temperatures, as after a solidification of the feedstock a reliable redispersing cannot be guaranteed within the LPIM machine. In this span of time a change in rheological properties like viscosity or yield point of the suspensions may occur that would affect further processing and reproducibility. The influence of working temperature on the rheological behaviour of zirconia–paraffin feedstocks is also crucial. In order to detect the sensitivity of the process on temperature variations, the viscosity and yield stress of different feedstocks were quantified below and above the standard working temperature, thus, to enable the evaluation the flow activation energy of feedstocks with varying compositions.

As a rule of thumb, the particle size of the powder should be at least about one order of magnitude smaller than the minimum internal dimension of the microcomponent in order to obtain fairly isotropic behaviour.[8,9] Thus, submicron or nano-powders have to be used to reproduce details down to micrometre range. Colloidal processing techniques[10] have to be exploited to stabilize and to homogenize small particles in a dispersing medium. For instance, adsorption of carboxylic acids like stearic or oleic acid on zirconia enables the coupling of ZrO_2 particles to the unpolar paraffin matrix, causes a decrease of attractive interparticle forces and, thus, enables well homogenized feedstocks with higher solids loadings compared to surfactant-free suspensions. Therefore, in feedstock development special attention must be paid to the influence of dispersants on the rheology due to the fact that the binder composition and, thus, the flow behaviour may also have a remarkable effect on the properties of the green and sintered microcomponents.[11–14]

In this regard, Hypermer LP1 (formerly Hypermer KD4) is an interesting dispersant, as previous studies showed that densities higher than 99.5% of the theoretical density of sintered microcomponents could be achieved by using this dispersant for TZ-3YS-E zirconia–paraffin feedstocks.[11,12] With other commercial dispersant systems such high sintered densities could not be achieved, which indicates that Hypermer LP1 results in a better microstructural homogeneity. The high sintered density, low porosity, low surface roughness and, as a result, the exceptional high strength of as-fired microcomponents fabricated via LPIM of zirconia–paraffin feedstocks illustrate the advanced feedstock quality, when Hypermer LP1 is used as dispersant.

2. Experimental

In this study, feedstocks were prepared containing commercial zirconia powder with 3 mol% Y_2O_3 (TZ-3YS-E, Tosoh, Japan) with an average particle size of 0.39 μm, monomodal particle size distribution, virtually spherical particle shape and a specific surface area of 6.6 m^2/g. The binder formulation is based on paraffin (TerHell Paraffin 6403, Schümann Sasol, Germany) with a setting point of 64.5 °C and a commercial dispersant (Hypermer LP1, Croda, UK). Before homogenization, the powder was dried at 300 °C for 2 h and was kept at 120 °C prior to adding to the molten binder. A laboratory vacuum dissolver (Dispermat, VMA-Getzmann, Germany) was used for plastification and homogenization of the powder-binder mixture at 90 °C. The rheological properties of the feedstocks were analyzed with a rotational rheometer (MCR 300, Anton-Paar, Austria) by using a plate–plate measuring system (PP25, gap between plates: 0.5 mm). The yield stress was obtained by shear stress-controlled measurements and the viscosity was determined at shear rates of 10 s^{-1} and 100 s^{-1} as reference values.

To assess the influence of the amount of surfactant, processing temperature and storage time on the rheological properties of the feedstocks, the solids loading was kept constant at 50 vol%, whereas the amount of the surfactant varied from 1.6 mg/m^2 to 3.2 mg/m^2 (mg surfactant per m^2 surface of powder, Table 1). According to an adsorption model of dispersant molecules the required amount for a monolayer of dispersant molecules per square meter powder was estimated and compared to the experimental observations. Temperature-dependent measurements were conducted from 70 °C to 130 °C, whereas standard measurements were carried out at a processing temperature of 90 °C. The flow behaviour of freshly prepared feedstocks and suspensions stored at 80 °C (beaker covered by a petri dish to exclude possible vaporization of binder components) for 1, 2 and 7 days and stored at room temperature (set suspensions) for at least 50 days, respectively, was determined to evaluate the influence of storage time on the rheology. Measurements of feedstocks aged at 80 °C and room temperature were conducted after homogenization for 5–10 min. Additionally, suspensions with 45.0 and 47.5 vol% were prepared to evaluate the effect of solids loading on viscosity and yield stress. To ensure reproducibility of the generated rheological data, each measurement was performed generally three times.

3. Results and discussion

3.1. Influence of surfactant amount β_{surf}

The yield point represents the rigidity of the particle networks resulting in a certain shear stress (yield stress), which is needed to overcome and to induce flow in the suspension.[7] Thus, the yield stress prevents sedimentation and phase separation in the suspension. The influence of the amount of dispersant on viscosity and yield stress is considerable. In Fig. 1 representative

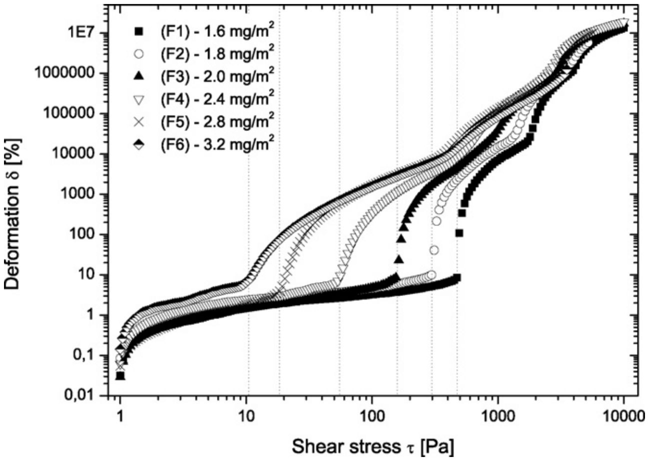

Fig. 1. Representative deformation curves illustrating the dependence of the yield stress on the amount of dispersant of freshly prepared zirconia–paraffin feedstock at 90 °C.

Table 1
Composition and abbreviations of the investigated feedstocks.

Feedstock	Solids loading Φ [vol%]	Paraffin [vol%]	Dispersant [vol%]	Resulting surfactant content [mg/m^2]
F1	50.0	46.6	3.4	1.6
F2	50.0	46.1	3.9	1.8
F3	50.0	45.7	4.3	2.0
F4	50.0	44.9	5.1	2.4
F5	50.0	44.0	6.0	2.8
F6	50.0	43.1	6.9	3.2
F7	47.5	48.4	4.1	2.0
F8	45.0	51.1	3.9	2.0

deformation curves of freshly prepared feedstocks with varying amounts of dispersant, constant working temperature and constant solids loading are illustrated. The interpretation of the yield point from the deformation curves presented in Fig. 1 is defined as the shear stress, where δ varies 5% from the regression line of the input data. With increasing surfactant content the yield point is decreasing remarkably, which can also be seen in Fig. 2, where the yield point is plotted against the surfactant content. Similar behaviour is mentioned in the literature.[15,16] This observation can be explained by the fact that attractive interparticle forces among zirconia particles are lowered by dispersant molecules.[17] Carboxylic fatty acids like stearic and oleic acid merely result in semisteric stabilization,[18] as the chain length of these molecules is limited to approx 4 nm.[19] Johnson and Morrison[20] propose that a particle separation of greater than 10 nm is required for true steric stabilization of micrometer-size particles, which is not the case for C-18 fatty acids like stearic and oleic acid. For the commercial dispersant Hypermer LP1 used in this study it is assumed that the chain length of the carboxylic acid is greater than 10 nm according to the information of the manufacturer that a relatively high molecular weight gives a steric stabilization barrier some 2–4 times thicker than conventional fatty acid based dispersants. However, no further information regarding the chemical structure of the surfactant is available. According to Moloney et al.[19] Hypermer LP1 (formerly Hypermer KD4) is identical to the dispersant Solsperse 3000 (Lubrizol, formerly Zeneca, UK), which consists of a pentamer made up of one stearic acid unit and four units of 12-hydroxystearic acid ($C_{90}H_{172}O_{10}$) yielding a molecular weight of 1414 g/mol. Indeed, physical properties like density, viscosity, flash point and colour of both dispersants are identical at first glance. Pursuant to available information we suppose that Hypermer LP1 offers steric and not merely semisteric stabilization. A strong adsorption of the dispersant onto the hydroxylic zirconia particle surface is the basic requirement for steric (or semisteric) stabilization regardless of the chain length. Different adsorption mechanisms can be postulated, whereas hydrogen bonding is seen as the most likely mechanism in this case. According to Zürcher and Graule[18] an additional stabilization contribution to the steric barrier is expected due to the modification of the Hamaker constant that results in a reduction of the attractive interparticle forces.

In Fig. 3 the dependency of the viscosity of freshly prepared feedstocks on the surfactant content at different shear rates is shown. For shear rates at 10 s^{-1} the viscosity is decreasing exponentially between 1.6 mg/m^2 and 2.8 mg/m^2 comparable to the yield point behaviour in Fig. 2 and increases slightly from 41.1 Pa s to 45.5 Pa s at 3.2 mg/m^2. In contrary, a minimum of viscosity for 100 s^{-1} and 1000 s^{-1} was found at 2.4 mg/m^2 with 11.0 Pa s and 2.5 Pa s, respectively. Two effects are supposed to cause such an increase in viscosity after passing through a minimum. On the one hand, entanglement of the non-polar chains of

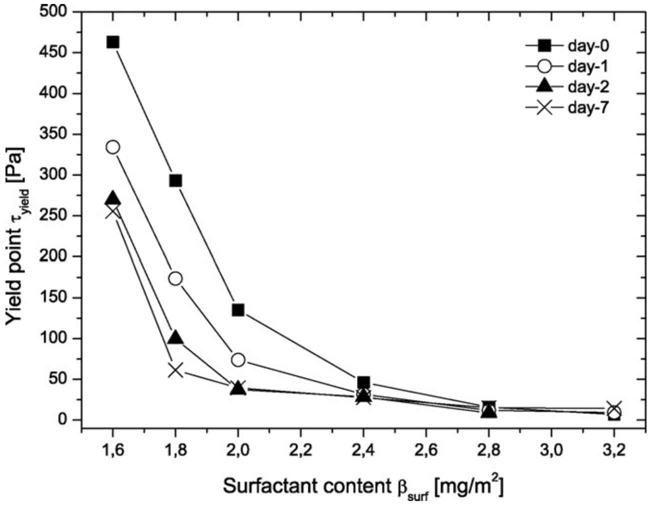

Fig. 2. An increase in surfactant content results in a decrease of the yield point; by storing the suspensions at 80 °C a remarkable decrease of the yield point can be observed.

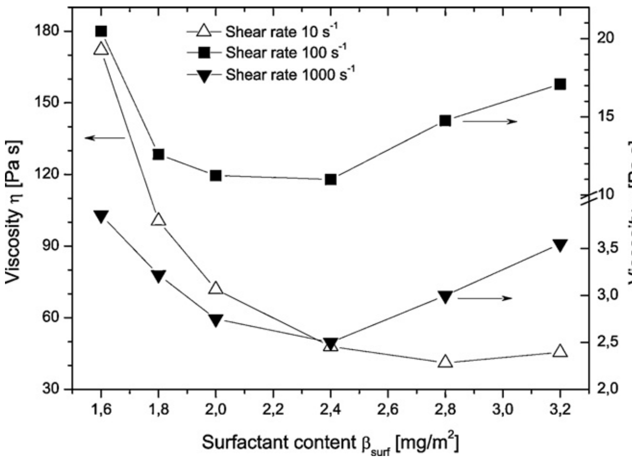

Fig. 3. Viscosity of LPIM feedstocks versus surfactant content β_{surf} for different shear rates (10–1000 s^{-1}).

the dispersant molecules may occur at high shear rates (>10 s^{-1}) for surplus amount of surfactant resulting in increased viscosity. On the other hand crosslinking of polar ends of the surfactant molecules may occur, which also would increase the viscosity.[21] Similar behaviour was reported in literature.[18,19] Shear rates much higher than 10 s^{-1} have to be expected for moulding by applying a significant injection pressure, e.g. by using a LPIM machine.[22] For rapid prototyping processes, where the feedstock is moulded manually into soft silicone moulds, shear rates below 1000 s^{-1} have to be expected.

Another drawback of excess dispersant is that a thicker adsorbed surfactant layer is not necessarily better and can limit the maximum amount of solids that can be incorporated in the suspension, as the adsorbed surfactant molecules contribute to the effective volume fraction in the feedstock.[3,19] Tseng et al.[15] and Liu[23] reported that the amount of dispersant required for a monolayer stearic acid and 12-hydroxystearic acid on ZrO_2 particles was found to be 1.5 $\mathrm{mg/m^2}$ and 1.6 $\mathrm{mg/m^2}$, respectively. Assuming that carboxylic acid molecules follow patterns similar to Langmuir adsorption isotherms, adsorb perpendicular and single (without crosslinking of the polar ends) onto the surface of zirconia particles[24,25] only via hydrogen bonding[26] of one polar end per molecule, the amount of surfactant required for a monolayer of dispersant molecules on ideally spherical ZrO_2 particles can be calculated according to an adsorption model[27] as follows:

$$m_{\mathrm{disp}} = \frac{24 m_{\mathrm{p}} M_{\mathrm{disp}}}{\pi d_{\mathrm{p}} N_{\mathrm{A}} d_{\mathrm{disp}}^{2} \varphi_{\mathrm{p}}} \qquad (1)$$

where m_{p} is the mass of the powder, M_{disp} the molecular weight of the dispersant, d_{p} the average particle size of the powder, d_{disp} the diameter of the polar end of the dispersant and ρ_{p} the density of the powder. The molecular weight and diameter of the polar end of the dispersant used in this study was assumed as 1414 g/mol[18] and 5.10×10^{-10} m,[27] respectively. As presented later, the required amount of the surfactant necessary for a monolayer on ideally spherical zirconia particles was calculated as 4.5 $\mathrm{mg/m^2}$, which is not in agreement with experimental observations. Experimentally, the amount for a monolayer of dispersant molecules can be evaluated either by determination of the adsorption isotherm of the zirconia powder with varying amounts of dispersant[15,23] or by determination of the optimum rheology of the feedstock,[19] i.e. a low viscosity, presumed that a dispersing medium with lower viscosity than the surfactant is used, which is given in this study (for paraffin and dispersant the viscosities were measured as 5.13 mPa s and 140.8 mPa s at 100 s^{-1} and 90 °C, respectively). In this study the viscosity minimum for 100 s^{-1} and 1000 s^{-1} was found at 2.4 $\mathrm{mg/m^2}$ (Fig. 3). This is in agreement with the study of Zürcher and Graule,[18] who investigated the influence of Solsperse 3000 on the rheological properties of zirconia–kerosene suspensions, where a minimum in the suspension viscosity was found at 2.3 $\mathrm{mg/m^2}$ for 100 s^{-1} with similar powder. In contrast, Moloney et al.[19] reported that zirconia–kerosene suspensions with similar materials as used in[18] exhibit a minimum of viscosity at 1.5 $\mathrm{mg/m^2}$.

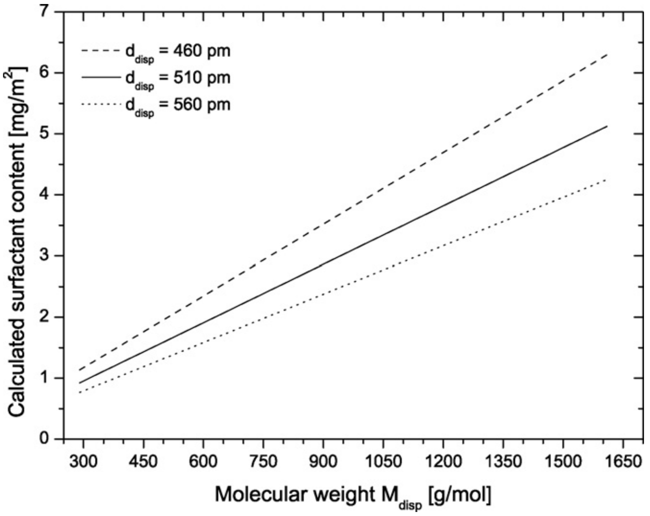

Fig. 4. Calculated amount of surfactant according to the adsorption model in dependency of molecular weight and diameter of the polar ends of the surfactant molecules.

Comparing the results obtained by the adsorption model according to Eq. (1) with the experimental observations, a significant disagreement for the required amount for a monolayer of surfactant molecules was found. The influence of the molecular weight of the dispersant, M_{disp}, and the diameter of the polar end of the dispersant, d_{disp}, on the amount of surfactant for full covered zirconia particles, m_{disp}, was analyzed exploiting Eq. (1). The results of the calculations are illustrated in Fig. 4. With increasing molecular weight the amount of surfactant increases linearly as expected. Considering d_{disp}, it is also obvious that less molecules can adsorb onto the particle surface, when the diameter of the polar end of the dispersant would increase. Presuming the molecular weight of Hypermer LP1 is 1414 g/mol and each molecule adsorbs single (without crosslinking onto the surface of zirconia particles) via hydrogen bonding of one polar end per molecule with $d_{\mathrm{disp}} = 510$ pm, the required surfactant amount for a monolayer coverage on zirconia was calculated as 4.5 $\mathrm{mg/m^2}$, contrary to the experimentally obtained value of 2.4 $\mathrm{mg/m^2}$. This overestimation is thought to be caused by the ideal presumptions made in the adsorption model. Influence of side-fed functional groups, e.g. of 12-hydroxystearic acid molecules, multiple adsorption of one dispersant molecule and parallel adsorption onto the particle surface (instead perpendicular) are not covered by the model. Therefore, a higher calculated amount of surfactant at ideal conditions, as presented in Fig. 4, is obvious. According to the model, full coverage at 2.4 $\mathrm{mg/m^2}$ is achieved for $d_{\mathrm{disp}} = 700$ pm, which is not in agreement with the value given for stearic acid (510 pm).[27] However, the tendency to higher d_{disp} values to achieve the observed value of 2.4 $\mathrm{mg/m^2}$ implies that the influence of side-fed functional groups, multiple and parallel adsorption is not negligible, when predicting the monolayer coverage of ceramic particles by dispersants using the proposed model.

In Fig. 5 typical flow curves of the zirconia–paraffin feedstocks are illustrated. The linearity in the logarithmic viscosity-shear rate plot indicates that the suspensions follow

Table 2
Calculated flow activation energies, flow indexes and resulting correlation coefficients R^2 of investigated LPIM feedstocks (shear rate 100 s^{-1}, temperature range 70–130 °C).

Feedstock	$\lvert E_a \rvert$ [kJ/mol]	Flow index	R^2 $\lvert E_a \rvert$	R^2 flow index
F1	41.4	0.07	0.97	0.99
F2	38.5	0.14	0.96	0.99
F3	33.4	0.25	0.98	0.99
F4	28.4	0.34	0.99	0.98
F5	25.8	0.55	0.99	0.98
F6	21.9	0.56	0.99	0.99
F7	28.8	0.23	0.99	0.99
F8	27.9	0.21	0.99	0.99
Dispersant (*D*)	34.5	–	0.99	–
Mixture of *D* and *P* (equ. to 2.0 mg/m^2)	21.1	–	0.99	–
Paraffin (*P*)	18.2	–	0.99	–

a power law according to Ostwald and de Waele[28]:

$$\eta = k\dot{\gamma}^{(n-1)} \tag{2}$$

where η stands for the viscosity, $\dot{\gamma}$ for the shear rate and n for the flow index. There are different mathematical models describing the flow behaviour of paraffin-based ceramic feedstocks properly, such as Bingham or Casson, which are often used in literature.[16,17,29–33] Flow indices n were calculated by fitting the data in Fig. 5 according to Eq. (2). Shear rate range between 10 s^{-1} and 1000 s^{-1} was selected, as the power law generates accurate values only in middle range shear rates.[29] In general, Newtonian behaviour is observed for $n = 1$, pseudoplastical (shear thinning) behaviour for $n < 1$ and dilatant (shear thickening) behaviour for $n > 1$. In this study flow indices between 0.07 and 0.56 with correlation coefficients higher than 0.98 were calculated depending on the amount of dispersant (Table 2). Thus, the feedstocks exhibit pseudoplastical behaviour, also reported elsewhere.[34] A linear correlation was found between the flow index and the surfactant content between 1.6 mg/m^2 and 2.8 mg/m^2 (Fig. 6). With increasing amount of dispersant the flow index is also increasing and the suspensions approximate to Newtonian behaviour. For higher amount of surfactant (3.2 mg/m^2) the flow index reaches a plateau, which is in agreement with literature.[19] In summary, it can be concluded that with increasing surfactant content the flow indices of the feedstocks also increase enhancing the mouldability of LPIM feedstocks. However, feedstock development for LPIM requires a compromise between the mouldability (low viscosity and yield stress, high flowability) and the resistance to deformation during thermal debinding (high viscosity and yield stress, low flowability).

3.2. *Influence of storage time t_s*

A time dependency of viscosity and yield point on storage time (stored at 80 °C) of freshly prepared feedstocks was found. According to the literature[35] an increase of viscosity and yield point was expected with time as no powder pretreatment like chemisorption of the surfactant onto the zirconia particles was applied to stabilize the powder against humidity or desorption of the merely physically adsorbed dispersant molecules. In contrary, a remarkable decrease of the yield point was observed (Fig. 2). In the first 2 days of storage the yield point decreased gradually and remained almost constant after 2

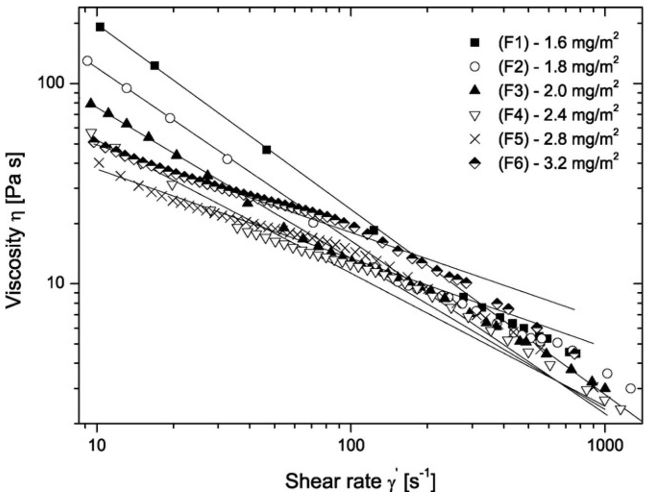

Fig. 5. Flow curves of zirconia–paraffin feedstocks (10–1000 s^{-1}) with different amounts of surfactant.

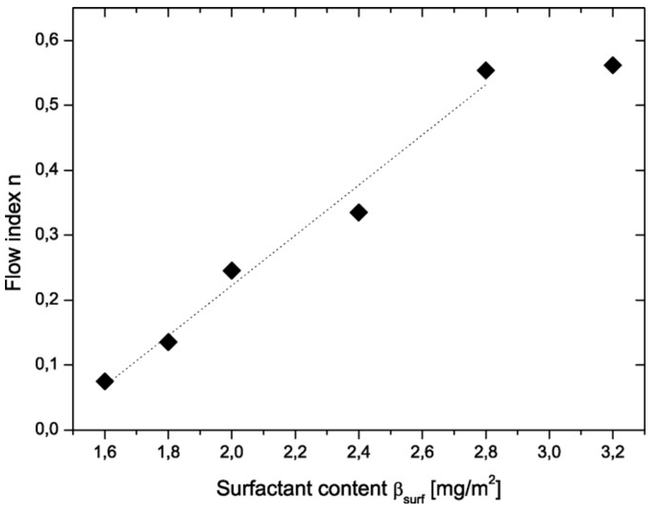

Fig. 6. Linear correlation was found between the flow index calculated according to Eq. (2) and the surfactant content; enhanced mouldability is implied by an increasing flow index.

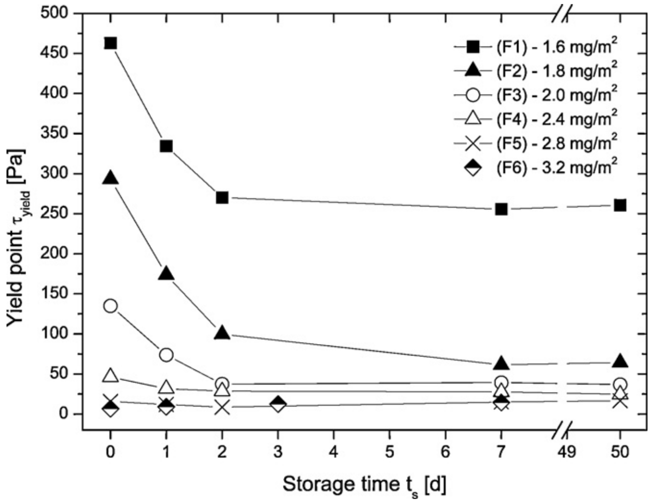

Fig. 7. Yield point of LPIM feedstocks versus storage time t_s.

days (Fig. 7). This observation implies that chemical or physical effects occur within the feedstock as a function of time. Even, remelting of the feedstocks after aging of at least 50 days at room temperature caused no difference in the yield point (Fig. 7), which is in agreement with a recent study by Dakskobler and Kosmac.[7] Regarding the viscosity, a comparable behaviour could be observed, as shown in Fig. 8 that depicts the behaviour for the shear rate $10\,s^{-1}$. In the first 2 days a gradual decrease of the viscosity takes place, and for longer storage time the viscosity values stay almost at a constant level for the feedstocks with higher surfactant amount (F3, F4 and F5) similar to the yield point behaviour in Fig. 7. In contrast, the viscosity of F2 increases significantly after remelting of the aged and set suspension and for the feedstock with the lowest amount of surfactant (F1) the viscosity is already remarkably increased after 7 days.

In general, a decrease of the yield point is caused, when attractive interparticle forces among the ceramic particles are reduced, for instance by adding a surfactant to the system, where the polar end of the surfactant molecules adhere onto the particle surface and the non-polar chains remain in the non-polar binder yielding dispersion and flowability of the feedstock. In this study the attractive interparticle forces are reduced as a function of time. Two reasons are considered to have caused such an effect, in particular, (a) physical processes like degradation of the binder components or some rearrangement of dispersant molecules, or (b) chemical interaction among zirconia and paraffin, zirconia and dispersant, or paraffin and dispersant. It is supposed that a physical or chemical interaction among zirconia and dispersant takes place. Adding small amounts of dispersant (few drops) to the re-melted feedstocks F1 after at least 50 days significantly reduced the viscosity from 29.1 Pa s to 6.4 Pa s at a shear rate of $100\,s^{-1}$. No change in viscosity was observed for a mixture of dispersant and paraffin (equivalent to the composition F3) after storage at 80 °C for 7 days. Besides, the viscosity of the pure binder components showed no change at same conditions. But a change in viscosity and yield point takes place with feedstocks merely consisting of zirconia and paraffin. To study the influence of the dispersant on viscosity, yield point, solids loading and homogenization, feedstocks without surfactant were produced and analyzed. A critical solids loading of approximately 22 vol% was found at 90 °C for feedstocks merely consisting of zirconia and paraffin. The critical solids loading corresponds to the composition where all particles are in close contact due to the predominance of attractive interparticle forces and the relative viscosity tends to infinite. Depending on the processing type and degree of homogenization higher solids loadings of feedstocks without surfactant up to 40 vol% can be possible, e.g. by using a kneader for plastification.[36] It was not possible to produce homogenized suspensions without agglomerates and high solids loadings due to the poor wettability of the polar surface of zirconia particles by non-polar paraffin. Moreover, the inhomogeneous feedstock with phase separation of powder and binder made it difficult to obtain reproducible values for viscosity and yield stress. Nevertheless, a remarkable time dependency of the flow behaviour was found for the feedstock without dispersant. After storage at 80 °C for 1 day the yield stress increased dramatically and the viscosity ($100\,s^{-1}$) increased from 5–10 Pa s up to 30–40 Pa s. The flow behaviour after 2 days could not be determined as the suspension flocculated after gentle stirring. Therefore, we suppose that either physical processes like rearrangement of dispersant molecules or some chemical reactions among zirconia and surfactant occur causing the observed time dependency, i.e. the decrease of the yield point and viscosity.

It is unlikely that carboxylic groups at the polar end of the dispersant molecules react with the O–H group on the powder surface during storage at relatively low temperatures (80 °C). Such a chemisorption would lead to the formation of one H_2O molecule per dispersant molecule[18] and, due to its hygroscopic nature, even a small amount of water would increase the viscosity of the suspension remarkably, as the zirconia tends to interact with water rather than with carboxylic groups, similar to alumina, which would cause the release of the fatty acid.[21] A physical process like rearrangement of surfactant molecules seems to be more likely. According to literature,[18] we suppose that the Hypermer LP1 molecules possess molecule chains with side-fed functional groups (12-hydroxystearic acid). Induced by

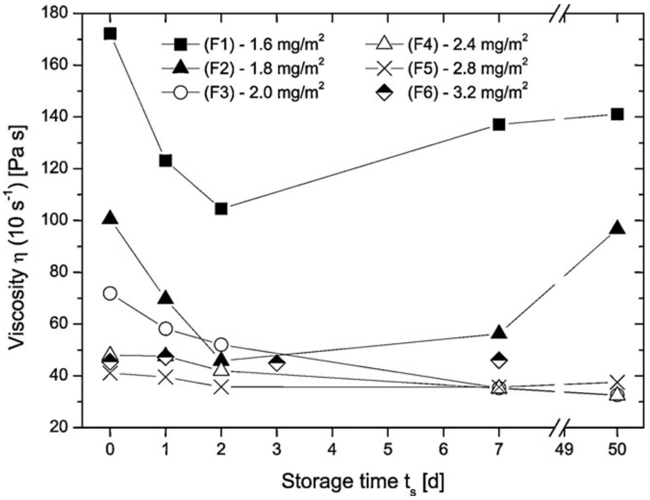

Fig. 8. Viscosity of LPIM feedstocks (at $10\,s^{-1}$) versus storage time t_s.

the storing temperature it is possible that the adsorbed molecules undergo some rearrangement with time and cause a significant decrease in viscosity and yield stress of the feedstocks with low amounts of dispersant (<2.4 mg/m^2), where the powder particles are covered only partially by the surfactant molecules. It is supposed that an equilibrium condition of the dispersant concentration exists among already physically adsorbed dispersant molecules (static state) and not yet adsorbed molecules (mobile state), e.g. micelles. This equilibrium might be affected by storing the feedstocks at elevated temperature that causes a shift of the equilibrium to an energetic more favourable static state and, thus, results in the observed time dependency of the rheological properties. In contrary, for the feedstocks F4, F5 and F6 with sufficient amount of Hypermer LP1 ($\geq$2.4 mg/m^2) no characteristic time dependency of the viscosity or yield point was observed, as the particles are fully covered with surfactant and, thus, fully stabilized due to the steric barrier induced by the dispersant molecules. However, the devolution of the viscosity versus time (Fig. 8) was not similar to that of the yield point (Fig. 7) for the feedstocks with the lowest amount of surfactant (F1 and F2). This observation is supposed to arise from the fact that yield stress and viscosity represent different aspects of the flow behaviour. The yield point describes the transition from static to dynamic state (required stress to overcome rigidity and interaction of the particle network), whereas the viscosity describes the dynamic state of flow behaviour. Therefore, it is not compulsory that time-dependent physical processes like rearrangement of dispersant molecules result in similar behaviour in the static as well as in the dynamic state of the flow behaviour. It is possible that the physical process in question causes an increase of viscosity in the dynamic state, e.g. due to entanglement of non-polar chains and side-fed functional groups of dispersant molecules, while the grade of steric stabilization and, consequently the yield point, is maintained. Nevertheless, it can be concluded that the surfactant used in this study has an exceedingly important time-dependent influence on the flow behaviour of paraffin-based zirconia feedstocks.

3.3. *Influence of temperature*

With increasing temperature the yield point as well as the viscosity of the zirconia–paraffin feedstocks decreases. In Fig. 9 the temperature dependency of the yield point with varying amounts of dispersant is illustrated. The higher the surfactant content the less pronounced is the decrease of the yield point with increasing temperature, which is a result of the decline of attractive interparticle forces with increasing amount of dispersant (Fig. 2). It is interesting to see that a high surfactant content can reduce the yield point by approximately one order of magnitude from 804.3 Pa (F1) down to 75.5 Pa (F5) at a working temperature of 70 °C fairly above the setting point of the paraffin (64.5 °C). Equally, the viscosity at 100 s^{-1} decreases from 30.6 Pa s (F1) to 19.0 Pa s (F4) and at 10 s^{-1} η decreases from 211.0 Pa s (F1) to 59.6 Pa s (F6). This leads to the conclusion that the working temperature can be adjusted depending on the composition and can be lowered for feedstocks with higher amounts of dispersant. It should be mentioned, however, that higher surfactant contents result in low yield points and, therefore, may have a considerable drawback, as the moulded green parts require a sufficient yield point to prevent deformation during thermal debinding.

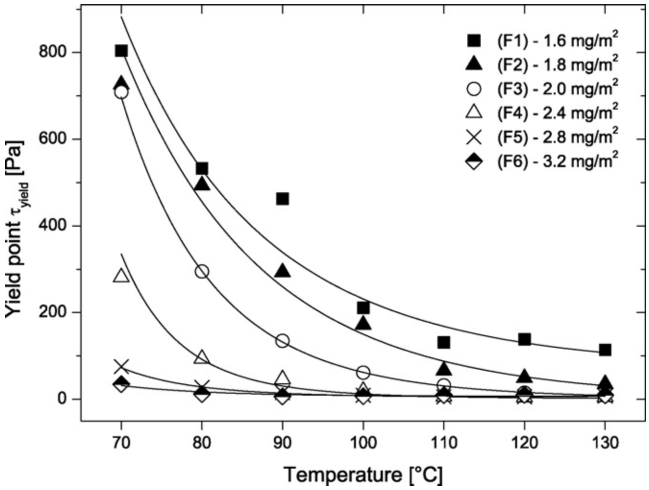

Fig. 9. With increasing working temperature the yield point is decreasing exponentially; the lower the surfactant content the more pronounced the exponential devolution of the yield point versus temperature.

The temperature dependency of the viscosity follows the Arrhenius equation:

$$\eta(T) = Ae^{-E_a/RT} \tag{3}$$

where A stands for a material specific constant (threshold value for infinite temperature), R for the gas constant and E_a for the flow activation energy, which is necessary to overcome the interaction among neighbouring molecules in the suspension (potential threshold).[29] The different thermal expansion coefficients of paraffin and powder result in a change in loading with temperature. With increasing temperature the binder expands to a larger degree and the resulting relative increase in binder volume corresponds to a decreasing solid content resulting in a lower viscosity.[37] Thus, the solids loadings of the feedstocks F1–F6 change to approximately 46 vol%, of F7 to 43 vol% and of F8 to 41 vol% at 90 °C processing temperature (compare with Table 1). Strictly speaking, the solids loadings given in Table 1 are valid for solidifed green parts and not for the feedstocks at processing temperature.

Applying natural logarithm on Eq. (3) results in a linear relation that allows the calculation of the flow activation energy, which is given by the slope in the Arrhenius diagram. The activation energy values for the feedstocks investigated in this study lie around 20 kJ/mol and 40 kJ/mol depending on the surfactant content with correlation coefficients between 0.96 and 0.99 (Table 2). In literature[23,38,39] similar values between 20 kJ/mol and 50 kJ/mol for paraffin-based zirconia feedstocks are reported, depending on particle size distribution and morphology as well as on the type and amount of applied binder components. In Fig. 10 the activation energy values for the feedstocks investigated in this study are shown graphically. It is obvious that the flow activation energy is decreasing with increasing amount of dispersant and tends to values fairly above that of the binder. Again, this is a result of the previously

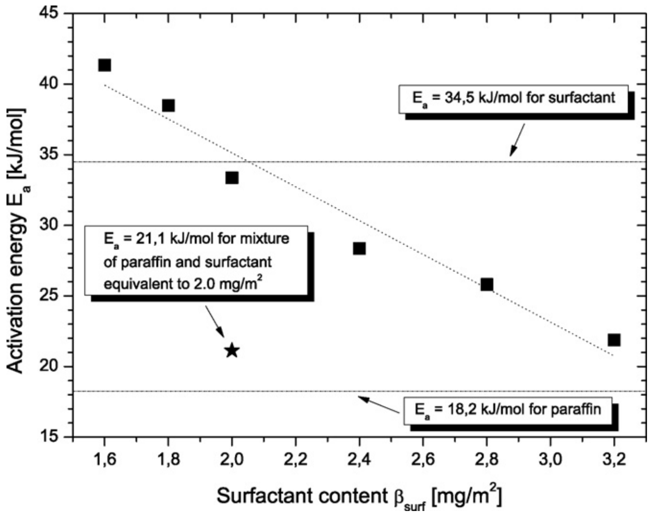

Fig. 10. The activation energy of the feedstocks ($100\,s^{-1}$) decreases with increasing surfactant content.

explained fact that dispersants enhance flowability by decreasing attractive interparticle forces, as the coupling of the zirconia particles to the hydrophobic paraffin-matrix is enhanced.[38]

Some differences in the activation energies were calculated for values generated at different shear rates. With increasing surfactant content the activation energy for the measurements at $10\,s^{-1}$ exhibit lower values than at $100\,s^{-1}$. Compared to Table 2, the activation energy values at $10\,s^{-1}$ are 31.4 kJ/mol for F3, 24.9 kJ/mol for F4, 18.4 kJ/mol for F5 and 12.2 kJ/mol for F6, respectively. This observation may be caused by the effect explained previously. For surplus amounts of surfactant either entanglement of the non-polar chains or crosslinking of polar ends of the dispersant molecules may occur causing higher viscosities at higher shear rates than for lower shear rates. German reports $|E_a| = 4.4$ kJ/mol for paraffin with $\eta = 9$ mPa s at 100 °C and a melting point of 58 °C.[37] However, in this study an activation energy of 18.2 kJ/mol (correlation coefficient 0.99) was measured for paraffin with $\eta = 4.5$ mPa s at 100 °C and a melting point of 64.5 °C. The difference may arise from the distribution of the molecular weight and the alkanes as well as from the temperature range of the measurement. The paraffin used in this study exhibits an alkane distribution of approx 65 wt% n-alkanes and 35 wt% iso-alkanes with mostly C-30 chains for n-alkanes and C-33 chains for iso-alkanes. $|E_a|$ was calculated according to Eq. (3) in the temperature range between 70 °C and 130 °C at the reference value $100\,s^{-1}$. For comparison, the activation energy of a mixture of paraffin and dispersant equivalent to a feedstock composition with 2.0 mg/m² was calculated. It is obvious that the $|E_a|$ of the paraffin is increased from 18.2 kJ/mol to 21.1 kJ/mol by adding a small amount of dispersant.

3.4. *Influence of solids loading*

In the prior chapter we described the viscosity change with temperature and also presented the flow activation energies of feedstocks with constant solids loading. Besides, the critical or maximum solids loading is important, when describing feedstocks for powder injection moulding. Previous investigations showed that the maximum solids loading for feedstocks applied in this study lie between 50 vol% and 60 vol% depending on temperature and surfactant content. It was not the aim of this investigation to analyze the critical solids loading applying various empirical models established in the past.[33,38] Merely, the dependence of viscosity and yield stress on the solids loading was determined and compared with results from literature.

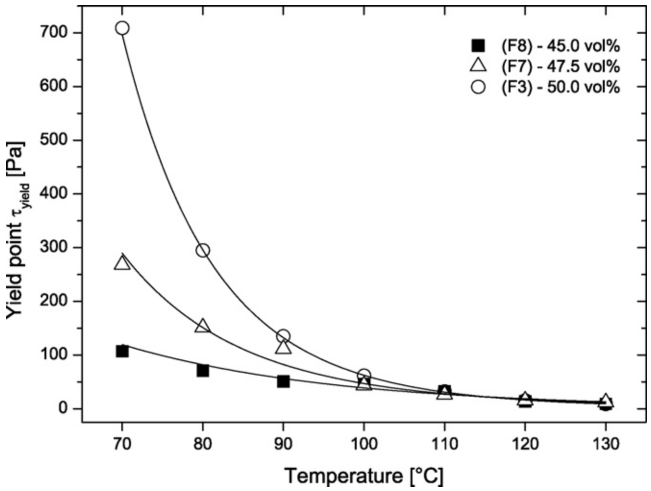

Fig. 11. Solids loading significantly affect the yield point of LPIM feedstocks: with decreasing solids loading the yield point decreases remarkably.

Feedstocks F7 and F8 with 47.5 vol% and 45 vol% solids loading and a reference surfactant amount of 2.0 mg/m² as used in feedstock F3 (50 vol%, 2.0 mg/m²) were fabricated. As expected, the decline of the yield point with increasing temperature is less distinctive for lower solids loadings (Fig. 11), which is in conformity with other studies.[7,17] For instance, the yield point decreases from 709.2 Pa (50 vol%) to 268.4 Pa (47.5 vol%) and to 107.0 Pa (45 vol.%) at 70 °C working temperature. The viscosity behaves analogically, e.g., η decreases from 21.03 Pa s (50 vol%) to 10.4 Pa s (47.5 vol%) and 5.3 Pa s (45 vol%) for a shear rate of $100\,s^{-1}$ at 70 °C. As a result, the working temperature can be adjusted depending on the solids loading and can be chosen lower for feedstocks with lower solids loadings. However, a reduced solids loading will result in an increased sintering shrinkage, which usually is not desirable.

4. Conclusions

(1) The influence of the dispersant on the overall flow behaviour of zirconia–paraffin feedstocks was found to be very crucial. An increasing amount of dispersant caused a significant decrease of both yield point and viscosity of the zirconia–paraffin-based feedstocks. For low shear rates ($10\,s^{-1}$) the viscosity of the feedstocks decreased gradually, whereas for high shear rates ($100\,s^{-1}$ and $1000\,s^{-1}$) an increase of viscosity for feedstocks with surplus amount of surfactant was observed due to (a) entanglement of the non-polar chains of the dispersant molecules, or to (b) crosslinking of polar ends of the surfactant molecules. By applying an adsorption model for the calculation of the

required amount for full coverage of the zirconia particles by dispersant molecules a value of 4.5 mg/m^2 surfactant per square meter powder was estimated that is significantly higher than the experimental observations exploiting rheological measurements, which yielded 2.4 mg/m^2 as the optimum amount of surfactant resulting in a minimum of viscosity at high shear rates (100 s^{-1} and 1000 s^{-1}). The difference is thought to be caused by the ideal presumptions made in the adsorption model. A linear correlation among surfactant content and flow indexes of the shear thinning feedstocks with yield point was found. With increasing surfactant content the flow indexes of the feedstocks also increased, which enables a better mouldability of zirconia–paraffin feedstocks for LPIM.

(2) With increasing storage time at elevated temperature (80 °C) the yield point and viscosity of the feedstocks with low amounts of dispersant (<2.4 mg/m^2) remarkably decreased in the first 2 days. It is supposed that (a) physical processes like rearrangement of dispersant molecules, or (b) chemical interactions between zirconia and dispersant caused this effect. We assume that the adsorbed dispersant molecules possess molecule chains with side-fed functional groups and, thus, undergo some rearrangement with time at elevated temperature resulting in a decrease in viscosity and yield stress of the feedstocks with low amounts of dispersant, where the powder particles are covered only partially by the surfactant molecules. It is supposed that an equilibrium condition of the dispersant concentration exists among already physically adsorbed dispersant molecules (static state) and not yet adsorbed molecules (mobile state), e.g. micelles. This equilibrium might be affected by storing the feedstocks at elevated temperature that causes a shift of the equilibrium to an energetic more favourable static state and, thus, results in the observed time dependency of the rheological properties. No characteristic time dependency of the viscosity or yield point was observed for feedstocks with sufficient or surplus amount of dispersant ($\geq$2.4 mg/m^2), as the particles are fully covered with surfactant and, thus, fully stabilized due to the steric barrier induced by the dispersant molecules. This observation is crucial, as a change in rheological properties affects further processing and reproducibility.

(3) The temperature dependency of the viscosity of zirconia–paraffin-based feedstocks follows an exponential law. The lower the surfactant content of the feedstock is, the more pronounced is the exponential decrease of the viscosity and the yield point versus temperature. Flow activation energies between 20 kJ/mol and 40 kJ/mol for feedstocks with different surfactant amounts were calculated, which are in agreement with data from literature. Moreover, the effect of solids loading on the flow behaviour was studied. With decreasing solids loading viscosity as well as yield point is also decreased. However, feedstock development for LPIM requires a compromise between the mouldability (low viscosity and yield stress, high flowability) and the resistance to deformation during thermal debinding (high viscosity and yield stress, low flowability).

Previous studies showed that zirconia–paraffin feedstocks containing Hypermer LP1 as surfactant result in advanced feedstock quality (compared to other commercial dispersant systems), which is illustrated by high sintered density, low porosity, low surface roughness and remarkably high strength of as-fired microcomponents fabricated via LPIM. Due to the lack of verifiable information about the chemical structure of Hypermer LP1, further investigations on the mode of action of this dispersant is necessary, inter alia for an effective evaluation of its influence on the quality of mechanical properties of so fabricated ceramic microcomponents.

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