Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 269–275
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Process chain development for the realization of zirconia microparts using composite reaction molding

T. Hanemann [a,b,*], K. Honnef [b]

[a] Research Center Karlsruhe, Institute for Materials Research, PO-Box 3640, D-76021 Karlsruhe, Germany
[b] Albert-Ludwigs-University Freiburg, Department of Microsystem Engineering, Georges-Köhler-Allee 102, D-79110 Freiburg, Germany

Received 30 August 2007; received in revised form 14 September 2007; accepted 7 October 2007

Abstract

Composite reaction molding as rapid prototyping technique using polymer-based reactive resins and suitable inorganic fillers enables the realization of ceramic parts carrying a microstructured surface relief. In this paper the development of the whole process chain starting with feedstock preparation and characterization, molding and thermal postprocessing like debinding and sintering will be described for the fabrication of dense zirconia parts. Especially the rheological behaviour as function of the binder composition and solid load is discussed intensely. Specific feedstock parameters like critical filler load and flow activation energy are derived from the measured flow properties using empirical descriptions normally applied for feedstock systems established in powder injection molding.

Keywords: A. Injection molding; B. Composites; D. ZrO_2; Rheology

1. Introduction

In the last decade microstructured components made of different ceramic materials have become more and more important for applications. Structural ceramics like alumina or zirconia show outstanding thermomechanical and chemical resistivity properties, e.g. usable in microreaction technology, while electroceramics like PZT or $BaTiO_3$ possess excellent application potentials as actuators or dielectric material in microelectronics [1–4]. With respect to economical device fabrication, suitable replication techniques have to be selected and investigated. For the realization of dense and warp-free ceramic parts the whole process chain:

(1) ceramic filler conditioning,
(2) feedstock preparation using mixer-kneader or extrusion techniques,
(3) replication via powder injection molding,
(4) debinding, and
(5) sintering

has to be optimized.

Until now different variants of micropowder injection molding were developed using wax or thermoplastic-based binder compositions [5–8]. Almost all fundamental aspects of macroscopic powder injection molding are covered in an excellent book published by German in 1990 [9]. Quite recently the evaluation of process characteristics or the correlation of process parameters and resulting part properties has become of particular importance [10,11]. A rapid prototyping of ceramic parts is possible using a new variant of microinjection molding, microcomposite reaction molding applying curable polymer-based reactive resins as binder material [12,13]. Independent of the applied powder injection molding variant the development and the resulting properties of the feedstock are crucial for the replication quality and the thermomechanical properties of the final ceramic part. Of particular importance are the solid filler load, the feedstock homogeneity, the rheological behaviour and the sensitivity of the viscosity to temperature changes. Especially the latter ones are relevant for a successful mold filling. Hence a comprehensive characterization of the feedstock's flow behaviour is essential during new feedstock development. In general the knowledge about two feedstock

---

* Corresponding author at: Research Center Karlsruhe, Institute for Materials Research, PO-Box 3640, D-76021 Karlsruhe, Germany.
Tel.: +49 7247 82 2585; fax: +49 7247 82 2905.
E-mail addresses: thomas.hanemann@imf.fzk.de, hanemann@imtek.de (T. Hanemann).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.10.005

flow quantities is important, that is the critical filler load and the flow activation energy [9]. The first one can be estimated from the viscosity change with solid load using various empirical models established in the past. Einstein was the first to describe the change of the viscosity with load (volume content Φ) for diluted solutions or dispersions introducing a coefficient k_E, which is 2.5 for hard particle spheres, and the relative viscosity (composite viscosity η_{comp} divided by the binder viscosity η_{binder}) (1) [14]. Since then a large number of different model descriptions have been developed for a correlation of the composite's relative viscosity with filler load. The empirical approaches developed by Krieger–Dougherty (2), Quemada (3), Eilers (4), Mooney (5) Chong (6) or by Zhang and Evans (7) among others are often used [15–20]. Especially the latter one derived from the description of polypropylene–alumina-feedstock for usage in ceramic injection molding can be applied quite successfully [20]. The second item, the sensitivity of the composite viscosity to temperature changes, can be estimated in a small temperature range using the Andrade–Eyring equation, which follows a typical Arrhenius-type description (8) [9,21]. η_1 and η_2 are the apparent viscosities at the two different temperatures T_1 and T_2, R is the universal gas constant and ΔE_a is the flow activation energy, which depends mainly on the composition of the investigated system. Unlike gaseous materials the viscosity drops with increasing temperature. A pronounced sensitivity of the viscosity to temperature changes corresponds with large ΔE_a values, i.e. a temperature increase allows a significant viscosity reduction enabling an improved mold filling during injection [9]. The flow activation energy depends strongly on a large number of intra- and intermolecular interactions like molecular entanglement or van-der-Waals' forces as well as on the interaction between binder and dispersed particles. Typical thermoplastic binders consisting of polyethylene with stearic acid as additive show values around 32 kJ/mole [9]:

$$\text{Einstein}: \quad \eta_{rel} = \frac{\eta_{comp}}{\eta_{binder}} = 1 + k_E\Phi \tag{1}$$

$$\text{Krieger–Dougherty}: \quad \eta_{rel} = \left(1 - \frac{\Phi}{\Phi_{max}}\right)^{-k_E\Phi_{max}} \tag{2}$$

$$\text{Quemada}: \quad \eta_{rel} = \left(1 - \frac{\Phi}{\Phi_{max}}\right)^{-2} \tag{3}$$

$$\text{Eilers}: \quad \eta_{rel} = \left(1 + \frac{1.25\Phi\Phi_{max}}{\Phi_{max} - \Phi}\right)^{2} \tag{4}$$

$$\text{Mooney}: \quad \eta_{rel} = \exp\left(\frac{2.5\Phi\Phi_{max}}{\Phi_{max} - \Phi}\right) \tag{5}$$

$$\text{Chong}: \quad \eta_{rel} = \left(\frac{\Phi_{max} - 0.25\Phi}{\Phi_{max} - \Phi}\right)^{2} \tag{6}$$

Zhang and Evans :

$$\eta_{rel} = \left(\frac{\Phi_{max} - C\Phi}{\Phi_{max} - \Phi}\right)^{2} \text{with} C \text{ as free constant} \tag{7}$$

Table 1
Composition of the used unsaturated polyester resin

Resin abbreviation	Polymer content (wt%)	Styrene content (wt%)
UPM2	52	48
UPM3	39	61

Table 2
Measured zirconia particle properties

ZrO_2-type	TZ-3YS-E
Specific surface area (m^2/g)	5.8
Density (g/cm^3)	6.05
Measured particle sizes (μm)	
d_{10}	0.10
d_{50}	0.45
d_{90}	0.75

$$\text{Andrade–Eyring} \quad \ln\frac{\eta_1(T_1)}{\eta_2(T_2)} = \frac{\Delta E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8}$$

In the following the zirconia containing feedstock development for microcomposite reaction molding applying two different binder compositions, the influence of the solid load on the flow behaviour, the estimation of the critical filler load and the flow activation energy, and the resulting impact on replication and thermal postprocessing will be discussed.

2. Experimental

The viscosity of a commercially available unsaturated polyester resin with an initial polymer content around 65 wt%, solved in styrene as reactive thinner (Roth GmbH), was further reduced by the addition of styrene (Table 1). The chemical composition of the polyester resin is unknown and cannot be obtained from the vendor, own investigations using gel permeation chromatography delivers an average molecular weight around 1700 g/mole and a symmetric molecular mass distribution [22]. The glass transition temperature of the polymerised resin is around 89 °C [23]. The zirconia filler (Tosoh 3YSE, Table 2) was coated with a polyethylene-glycol-alkyl-ether dispersant (Brij92, Sigma–Aldrich) for improved feedstock quality. All mixtures were processed using a laboratory dissolver stirrer (IKA Eurostar power control-visc) for 30 min at 1000 rpm under ambient conditions; trapped air was removed via ultrasonic energy. All viscosity measurements were performed at three different temperatures (20, 40, 60 °C) in the shear rate range between 1 and 100 1/s using a cone and plate rheometer (CVO50, Bohlin). The experimental uncertainty of the obtained data is in the range of ±5%. The debinding and sintering experiments were performed in different chamber furnaces under ambient atmosphere (Carbolite). The Vickers hardness was measured using a Paar-Physica MHT10 microhardness testing equipment.

3. Results and discussion

3.1. Binder composition and solid load influence on the feedstock viscosity

Two opposite effects on the binder viscosity can be achieved by dilution with reactive solvent and with solid load increase: The addition of styrene to the commercial unsaturated polyester resin lowers the viscosity significantly; following the two concentrations described in Table 1 a viscosity drop at a shear rate of 100 1/s from 0.032 down to 0.011 Pa s at a measuring temperature of 60 °C can be observed (Fig. 1). Despite some noisy scattering at shear rates below 10 1/s an almost Newtonian flow occurs. The viscosity difference is retained in composites with a zirconia load around 36 vol% (UPM2-based composite: 1.47 Pa s, UPM3-based composite: 0.44 Pa s) (Fig. 1), both composites show a pseudoplastic flow behaviour (Fig. 1). A similar behaviour was observed for unsaturated polyester-based composites filled with micro- or nanosized silica or alumina [24,25]. The influence of the zirconia load on the resulting composite viscosity for the two different binder systems is shown in Figs. 2 and 3 for all investigated temperatures, exemplarily sketched for a shear rate of 100 1/s. As expected with increasing temperature the viscosity drops to smaller values. In the case of the UPM2-based binder a smooth viscosity increase with load up to a zirconia content of around 25 vol%, under consideration of the logarithmic viscosity scale, can be seen. Large loads can only be measured at higher temperatures due to experimental reasons (exceeding viscosities values, sticking, gap emptying); the composite with 30 vol% shows a disproportionate viscosity increase, especially at the lowest measuring temperature of 20 °C. The dilution with styrene enables larger loads targeting a certain viscosity value, demonstrated at the UPM3-based composites in Fig. 3. A viscosity around 1 Pa s is reached using a composite with a load around 43 vol%, measurable at all investigated temperatures; hence the disproportionate viscosity increase at lower temperatures can be suppressed. A further load increase up to 50 vol% causes a significant viscosity increase, only measurable at 60 °C. With respect to a large solid load for improved sinter density and complete mold filling during injection avoiding voids the usage of UPM3-based feedstocks is recommendable.

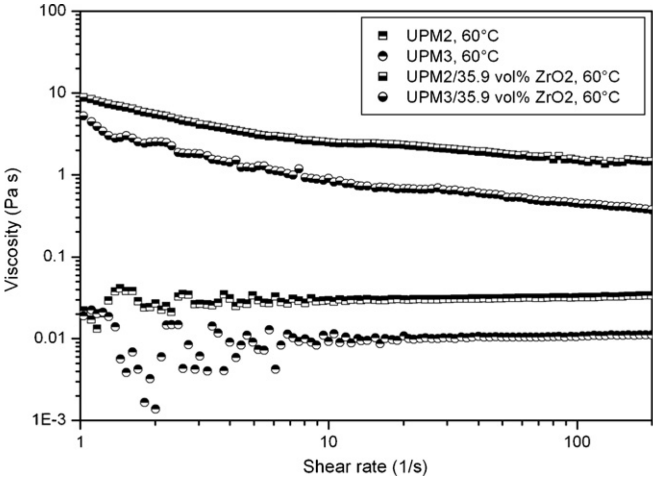

Fig. 1. Viscosities of UPM2 and UPM3 and composites containing 35.9 vol% (75 wt%) zirconia.

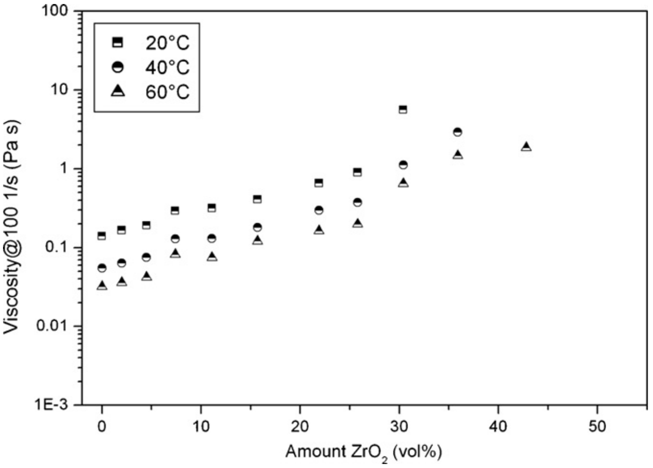

Fig. 2. Zirconia load-dependent viscosity in UPM2-based composites.

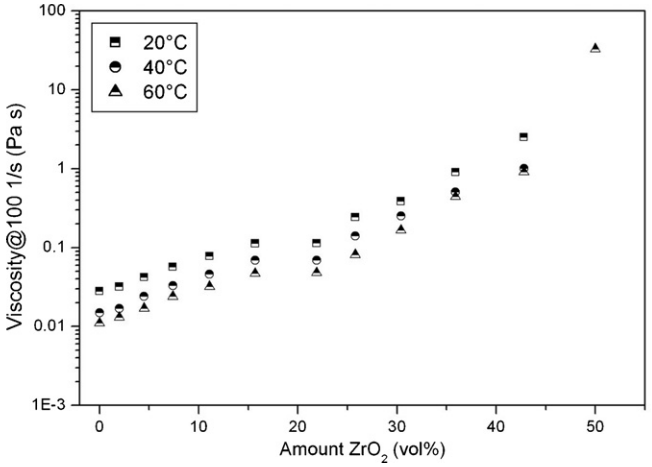

Fig. 3. Zirconia load-dependent viscosity in UPM3-based composites.

3.2. Estimation of the critical filler load

As used in ceramic injection molding applying thermoplastic binder systems [9], the knowledge about the critical filler load is crucial for feedstock development. The applicability of different semiempirical models developed for the estimation of the critical filler load on new feedstock systems avoids time consuming and cost intensive investigations on the maximum accessible load. The applicability of these models on binders consisting of unsaturated polyester resins was proved in previous experiments [24–26]. In the following the transferability to diluted binders with zirconia load was examined. Table 3 lists for the UPM2-zirconia-feedstocks the critical load Φ_{max} and the related fit stability index R^2 applying different established empirical models as described earlier. With exception of the Krieger–Dougherty model, all approaches

Table 3
Estimated critical filler load and stability index at different temperatures applying different empirical models describing the relative viscosity of UPM2/zirconia-composites

	Critical filler load $\Phi_{\max}$ (and related fit stability index R^2)		
	20 °C	40 °C	60 °C
Krieger–Dougherty	0.28 (0.77)	0.27 (0.67)	0.44 (0.54)
Quemada	0.36 (0.97)	0.42 (0.98)	0.49 (0.69)
Chong	0.35 (0.99)	0.40 (0.96)	0.48 (0.63)
Eilers	0.33 (1.00)	0.39 (0.92)	0.47 (0.59)
Mooney	0.38 (1.00)	0.46 (0.99)	0.58 (0.62)
Zhang–Evans	0.33 (1.00)	0.45 (0.99)	0.80 (0.93)

describe the experimental data quite well especially at lower temperatures depicted from the R^2 values close to 1. At 60 °C only the Zhang–Evans model originally developed for a thermoplastic–ceramic-feedstock delivers an acceptable fit stability index, but the resulting value for the critical filler load seems to be too large. Averaging all calculated values the following $\Phi_{\max}$-values for the different temperatures can be estimated: 20 °C: 0.34; 40 °C: 0.40; 60 °C: 0.54. These calculated data are in good agreement with experimental data and seem to be realistic. The quality of the fit can be improved with an increasing number of experimental values like in the UPM3-based feedstock systems. Table 4 lists the values for the critical filler load and the related fit stability index. Again the Krieger–Dougherty model does not give any practicable results; at 20 °C all other models can be used. Especially the Zhang–Evans approach delivers at all investigated temperatures an outstanding description of the experimental data. As mentioned earlier the viscosity of the composite containing 50 vol% can only be measured at 60 °C, therefore the fit stability index is quite excellent.

3.3. Estimation of the flow activation energy

The dependence of the feedstock viscosity with temperature at constant load can be described using the Andrade–Eyring Eq. (8). Within a small temperature interval far beyond any phase transition or rearrangement phenomena the flow activation energy ΔE_a can be calculated. Typical values for low molecular weight waxes are in the range between 4.4 kJ/mole (paraffine) and 19 kJ/mole (polyethylene wax). A polypropylene melt show larger values up to 32 kJ/mole [9]. Fig. 4 shows for all investigated feedstock systems the flow activation energy change relative to the pure binders (9). The flow activation energies of the two different resins are 10 kJ/mole (UPM2) and 5–7 kJ/mole) (UPM3):

$$\Delta\Delta E_a = \Delta E_{a,\text{comp}} - \Delta E_{a,\text{binder}} \quad (9)$$

Table 4
Estimated critical filler load and stability index at different temperatures applying different empirical models describing the relative viscosity of UPM3/zirconia-composites

	Critical filler load $\Phi_{\max}$ (and related fit stability index R^2)		
	20 °C	40 °C	60 °C
Krieger–Dougherty	0.33 (0.59)	0.33 (0.44)	–
Quemada	0.48 (0.95)	0.49 (0.88)	0.51 (1.00)
Chong	0.47 (0.93	0.47 (0.84)	0.51 (1.00)
Eilers	0.46 (0.91)	0.46 (0.80)	0.51 (1.00)
Mooney	0.56 (0.93)	0.57 (0.83)	0.54 (1.00)
Zhang–Evans	0.55 (1.00)	0.63 (0.99)	0.52 (1.00)

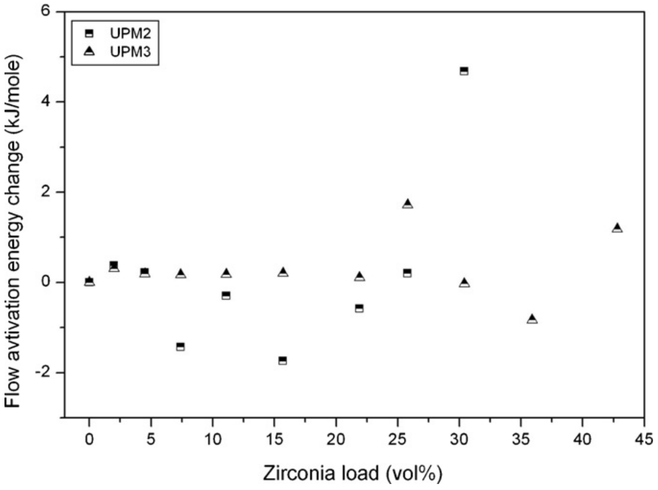

Fig. 4. Relative flow activation energy change with zirconia load.

Besides some scattering at low zirconia load which is due to the consideration of only three measured temperatures, two basic statements can be depicted from Fig. 4. First, with approaching the critical filler load the flow activation energy increases, which is in agreement with literature and previous results describing thermoplastic as well as unsaturated polyester resin binders [9,22,24–26]. Second, especially at larger loads, the use of the dispersant reduces the numerical value of the flow activation energy. This phenomenon can be explained by the improved coupling of the filler to the hydrophobic polymer matrix and has been observed earlier in case of surface-treated alumina [22] or silica [24] as well as by the addition of amphiphilic ethylene-vinyl-acetate (EVA) to aluminum silicate–polyethylene wax-composites [27].

3.4. Micromolding

The replication process was established using a composite reaction molding equipment, which was originally invented for a rapid prototyping of microstructured polymer parts using photocurable reactive resins like acrylates or unsaturated polyesters [12]. By exploiting the huge evolution of heat a thermal curing of the feedstock systems can be realized using suitable thermal initiators like organic peroxides, here dilauroylperoxide (DLP). Prior to injection the feedstock has to be degassed avoiding voids in the replicated part.

The micromolding process consists of four basic steps [12]:

(1) mold closing and evacuation of the mold insert cavities,
(2) feedstock injection (maximum injection pressure 20 bar),

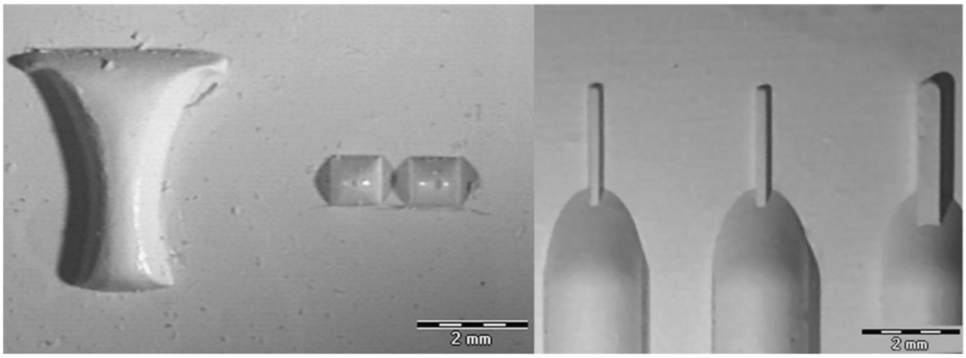

Fig. 5. Greenbodies of replicated free form test structure (left, sample 10 05 07) and microbending bars on substrate (right, sample 18 06 07).

(3) feedstock solidification, and
(4) solid greenbody demolding.

DLP starts to decompose around 60 °C, therefore the replication process has to be performed at elevated temperatures. The molding temperature of 60 °C in the cavity can be achieved just by irradiation with the lamp source due to the huge amount of emitted infrared radiation. In contrast to pure reactive resin solidification, which occurs with a rate of 1 mm/min irradiation time using photo induced polymerisation, the composite curing takes between 20 and 30 min depending on the sample thickness due to the relative slow thermal curing process. The used mold inserts were fabricated either by laser micromachining (3D free form microstructure) by or micromilling (bending bars) [28].

Fig. 5 (left side) shows a molded greenbody replica of a free form microstructure. The used feedstock material consisted of 42.8 vol% zirconia dispersed in UPM2. Due to the large solid load, which causes a pronounced viscosity, trapped air bubbles in the feedstock and consequently voids in the greenbody occur. Therefore a reduced sinter density can be expected. A reduction of the solid load down to 36 vol% improves the feedstock degassing due to the reduced viscosity and enables a better mold filling especially for finer structures like microbending bars shown in Fig. 5 (right side). As a drawback a reduced sinter density as well as a pronounced crack formation may occur. As recommended in Section 3.1, the use of highly filled UPM3 should allow a good filling as well as a warp-free sintered ZrO_2 part. Unfortunately UPM3-based composites with 42.8 vol% zirconia load cannot be demolded due to a pronounced sticking to the steel mold insert. The sticking does not occur in case of brass mold inserts.

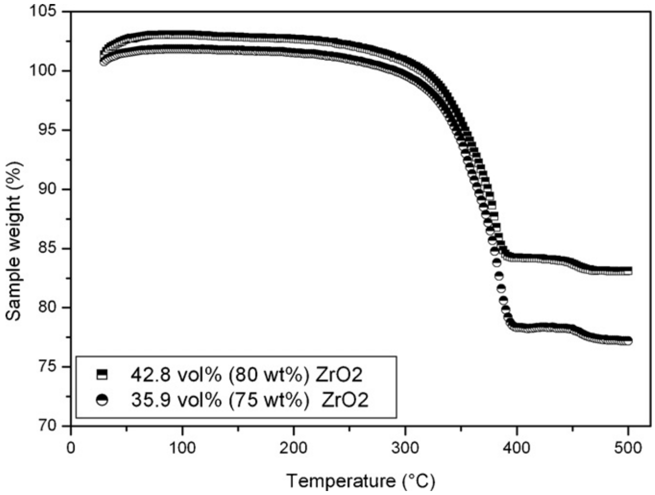

Fig. 6. Thermogravimetric investigations of UPM3-based ZrO_2 composites.

3.5. Debinding and sintering

As a prerequisite for a successful debinding and sintering the thermal decomposition behaviour has to be evaluated via thermogravimetry (TGA). In contrast to earlier investigations using unsaturated polyester, filled with alumina or zirconia [12,13], a surface modified zirconia, treated with a polyethylenglycole-based dispersant, was used. Fig. 6 shows the TGA traces of two feedstock containing 35.9 (75 wt%) and 42.8 vol% (80 wt%) surface modified zirconia in the temperature range from 30 °C up to 500 °C. There is no remarkable weight loss up to 300 °C, then a first significant decomposition step of the binder occurs, which is finished around 380 °C. After a small interval with constant weight a second small binder decomposition accompanied by a weight loss around 2 wt% can be observed. The different solid load can be identified by the remaining weight plateau, which is around 77 and 83 wt%. The larger values in comparison to the initial solid content can be explained by the slight loss of styrene during feedstock formation. The given decomposition behaviour is almost identical to the one found for the alumina containing

Table 5
Change of the greenbody and sintered specimen characteristics with solid load

Item	Sample 18 06 07	Sample 10 05 07
Solid load (vol%)	35.9	42.8
Average green density (%)	47.5	52.5
Average sinter density (%)	95.4	98.1
Best sinter density (%)	96.5	99.1
Vickers hardness	1710HV0.4	1670HV0.4
Linear shrinkage (%)	24.8 (part density 95.7%)	21.3 (part density 96.8%)

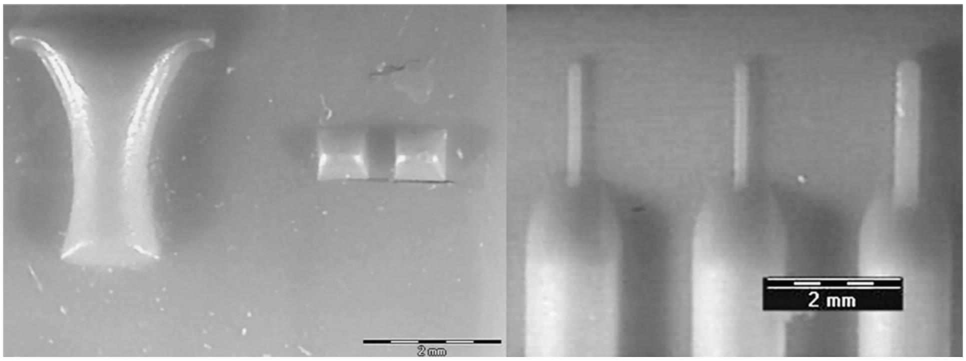

Fig. 7. Sintered free form test structure (left, sample 10 05 07) and microbending bars on substrate (right, sample 18 06 07).

polyesters [13]. Derived from the experiences obtained from polyester–alumina-composites [12,13] a combined thermal postprocessing can be used if a furnace with precise temperature control in the lower temperature range up to 500 °C is available:

(1) heating from ambient temperature up to 200 °C with 30 °C/min,
(2) holding at 200 °C for 30 min,
(3) heating from 200 °C up to 500 °C with 1 °C/min,
(4) holding at 500 °C for 120 min,
(5) heating from 500 °C up to 1550 °C with 10 °C/min,
(6) holding at 1550 °C for 6 h, and
(7) cooling down to ambient temperature with 5 °C/min.

Depending on the solid load, zirconia parts with a density up to 99% (feedstock: UPM3 with 42.8 vol% zirconia) can be obtained (Table 5). As expected, the measured green and sinter densities as well as the linear shrinkage correlate with the feedstock's solid load. Even a relative low solid load around 36 vol% allows a sinter density around 96% of the theoretical density. The Vickers hardness data are quite similar with a value around 1700HV0.4 (for comparison: 1250HV10, Tosoh Corp. data sheet). Exemplarily Fig. 7 shows the sintered microstructures of the replicated parts shown in Fig. 5.

4. Conclusion

In this work a process chain for the realization of microstructured zirconia parts has been developed. With respect to a complete mold filling and warp-free ceramic parts, loading content studies using two different unsaturated polyester resins with different viscosities as binders have been performed. The use of a binder with reduced viscosity enables the realization of feedstocks with larger solid load up to 50 vol% possessing acceptable low viscosities. Important feedstock flow properties like critical filler load and flow activation energy can be deduced from experimental data. Dense microstructured parts with high sinter densities up to 99% can be realized using composite reaction molding followed by thermal postprocessing.

Acknowledgements

TH thanks the Deutsche Forschungsgemeinschaft (DFG) for financial support within the framework of the Sonderforschungsbereich SFB 499 as well as the European Commission for the funding within the 4M-Network of Excellence.

References

[1] W. Menz, J. Mohr, O. Paul, Microsystem Technology, Wiley–VCH, Weinheim, FRG, 2001.
[2] B. Alm, R. Knitter, J. Hausselt, Development of a ceramic micro heat exchanger: design, construction and testing, Chem. Eng. Technol. 28 (2005) 1554–1560.
[3] J. Hausselt, H.-J. Ritzhaupt-Kleissl, R. Ruprecht, Ceramics in microtechnology—materials, processing, design, IMAPS/ACerS, in: Proceedings of the 1st International Conference and Exhibition on Ceramic Interconnect and Ceramic Microsystems Technologies (CICMT), 10–13 April, 2005, Baltimore, USA, pp. 211–221.
[4] A.J. Moulson, J.M. Herbert, Electroceramics, John Wiley & Sons Ltd., Chichester, UK, 2003, pp. 339–409.
[5] W. Bauer, R. Knitter, G. Bartelt, A. Emde, D. Göhring, E. Hansjosten, Replication techniques for ceramic microcomponents with high aspect ratios, Microsyst. Technol. 9 (2002) 81–86.
[6] V. Piotter, N. Holstein, K. Plewa, R. Ruprecht, J. Hausselt, Replication of micro components by different variants of injection molding, Microsyst. Technol. 10 (2004) 547–551.
[7] S. Rath, L. Merz, K. Plewa, P. Holzer, T. Gietzelt, J. Hausselt, Isolated metal and ceramic micro parts in the sub-millimeter range made by PIM, Adv. Eng. Mater. 7 (2005) 619–622.
[8] R. Zauner, Micro powder injection molding, Microelectron. Eng. 83 (2006) 1442–1444.
[9] R.G. German, Powder Injection Molding. Metal Powder Industries Federation, Princeton, 1990.
[10] B. Kasanická, M. Müller, M. Auhorn, V. Schulze, W. Bauer, T. Beck, H.J. Ritzhaupt-Kleissl, D. Löhe, Correlations between production process, states and mechanical properties of microspecimens made of zirconia, Microsyst. Technol. 12 (2006) 1133–1141.
[11] R. Heldele, M. Schulz, D. Kauzlaric, J.G. Korvink, J. Haußelt, Micro powder injection molding: process characterization and modelling, Microsyst. Technol. 12 (2006) 941–946.
[12] T. Hanemann, K. Honnef, J. Hausselt, Process chain development for the rapid prototyping of microstructured polymer, ceramic and metal parts: composite flow behaviour optimization, replication via reaction molding and thermal postprocessing, Int. J. Adv. Manuf. Technol. 33 (2007) 167–175.
[13] T. Hanemann, R. Heldele, K. Honnef, S. Rath, B. Schumacher, J. Haußelt, Properties and application of polymer-nanoparticle-composites, CFI/Ber. DKG 84 (2007) 49–54.

[14] A. Einstein, Eine neue Bestimmung der Moleküldimension, Ann. Physik 19 (1906) 289–306 and A. Einstein, Berichtigung zu meiner Arbeit: Eine neue Bestimmung der Moleküldimension, Ann. Physik 34 (1911) 591–592.

[15] I.M. Krieger, T.J. Dougherty, A mechanism for non-newtonian flow in suspensions of rigid spheres, Trans. Soc. Rheol. III (1959) 137–152.

[16] D. Quemada, Rheology of concentrated disperse systems and minimum energy dissipation principle. I. Viscosity-concentration relationship, Rheol. Acta 16 (1977) 82–94.

[17] J.S. Chong, E.B. Christiansen, A.D. Baer, Rheology of concentrated suspensions, J. Appl. Polym. Sci. 15 (1971) 2007–2021.

[18] M. Mooney, The viscosity of a concentrated suspension of spherical particles, J. Colloid Sci. 6 (1951) 162–170.

[19] H. Eilers, Die Viskosität von Emulsionen hochviskoser Stoffe als Funktion der Konzentration, Kolloid-Zeitschrift 97 (1941) 313–321.

[20] T. Zhang, J.R.G. Evans, Predicting the viscosity of ceramic injection moulding suspensions, J. Eur. Ceram. Soc. 5 (1989) 165–172.

[21] C.W. Macosko, Rheology: Principles, Measurements, and Application, VCH Publishers Inc., USA, 1994, pp. 100–102.

[22] T. Hanemann, Viscosity change of unsaturated polyester–alumina-composites using polyethylene glycol alkyl ether based dispersants, Compos. A: Appl. Sci. Manuf. 37 (2006) 2155–2163.

[23] T. Hanemann, J. Böhm, K. Honnef, E. Ritzhaupt-Kleissl, J. Hausselt, Polymer/phenanthrene-derivative host–guest systems: rheological, optical and thermal properties, Macromol. Mater. Eng. 292 (2007) 285–294.

[24] T. Hanemann, R. Heldele, J. Hausselt, Particle size dependent viscosity of polymer–silica-composites, in: Proceedings of the 4M 2006-2nd International Conference on Multi-Material-Micro-Manufacture (4M), Grenoble, France, September 20–22, (2006), pp. 191–194.

[25] T. Hanemann, Influence of particle properties on the viscosity of polymer–alumina-composites, Ceram Int. 34 (2008) 2099–2105.

[26] T. Hanemann, Influence of dispersants on the flow behaviour of unsaturated polyester–alumina-composites, Compos. A: Appl. Sci. Manuf. 37 (2006) 735–741.

[27] M. Attarian, E. Taheri-Nassaj, P. Davami, Effect of ethylene-vinyl acetate copolymer on the rheological behaviour of alumino-silicate/polyethylene wax suspensions, Ceram. Int. 28 (2002) 507–514.

[28] T. Hanemann, W. Pfleging, J. Haußelt, K.-H. Zum Gahr, Laser micromachining and light induced reaction injection molding as suitable process sequence for the rapid fabrication of microcomponents, Microsyst. Technol. 7 (2002) 209–214.