Karlsruhe Institute of Technology

Development of partially water soluble binder system for ceramic powder Injection moulding

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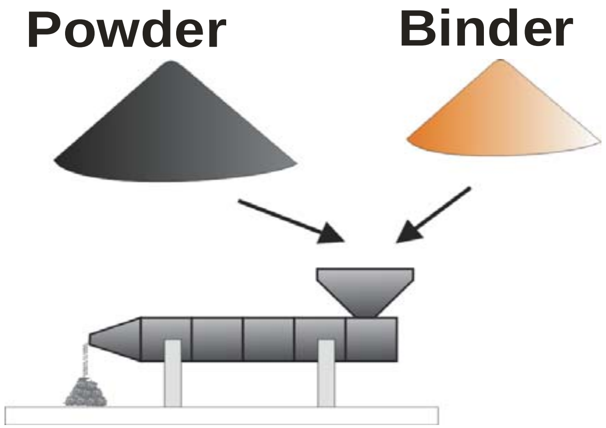
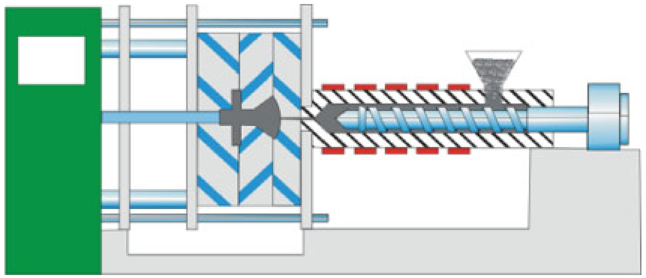
Outline

1. Process chain Micro Powder Injection Molding
2. Feedstock requirements
3. Compounding of established feedstock systems
4. Process chain of new developed feedstock system
    1. Reactive compounding
    2. Melt viscosity
    3. Injection molding
    4. Debinding and sintering
5. Conclusion and outlook

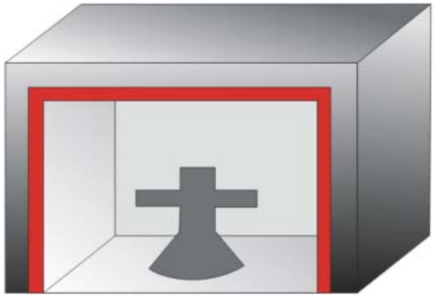
Process chain Micro-PIM

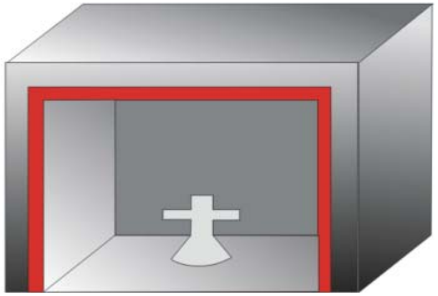
Preparation of feedstock → **Powder injection molding**





Debinding → **Sintering**





www.mikrospritzgiessen.de

Advantages of Micro-PIM

- Exploits established plastic micro replication technology for the realization of ceramic and metal microparts
- Enables multi-component fabrication
- Huge potential for automation
- Low cost fabrication method for ceramic and metallic microparts
- Technology close to industry

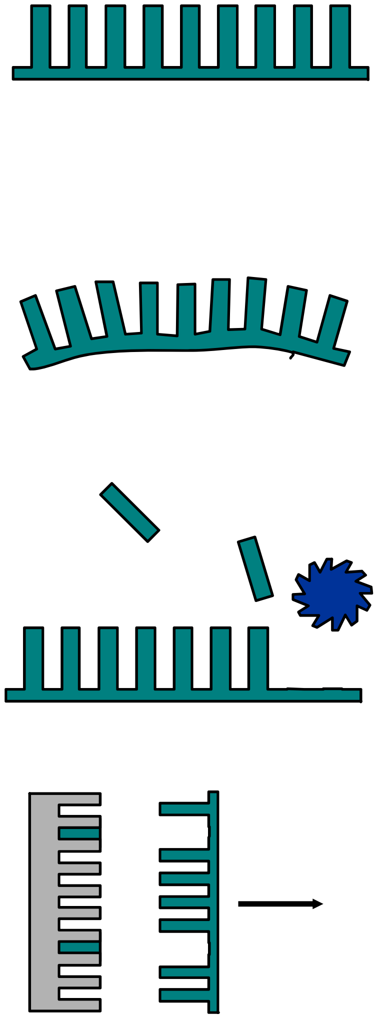
- **But: moulding is only a part of a complex process chain**

Feedstock requirements - general

- Huge solid of at least 45 vol% (ceramic) or 60 vol% (metal)
- average particle size should be smaller than a 10th of the smallest structural detail
- low viscosity @ moderate temperatures
- simple and reproducible compounding
- no phase separation under large shear stress
- good mold filling behavior
- high green stability
- simple debinding and sintering

Feedstock requirements - micro

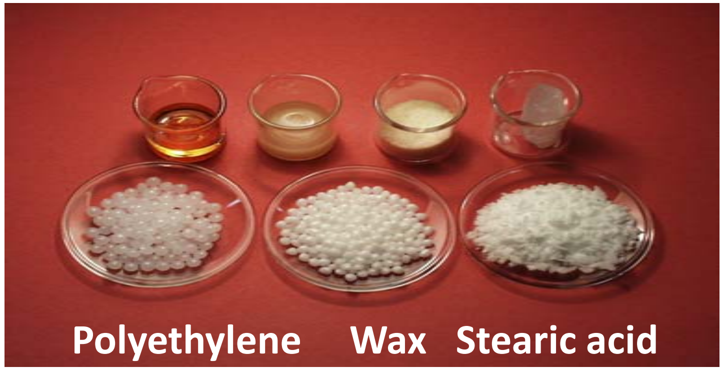
- Microsized parts often possess complex and fragile structures
- structural aspect ratio can be higher than one
- high structural homogeneity required
- near-net-shape structure necessary, mechanical postprocessing almost impossible
- defect-free demolding

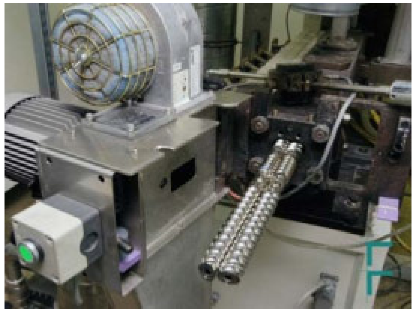


Compounding of established feedstock systems

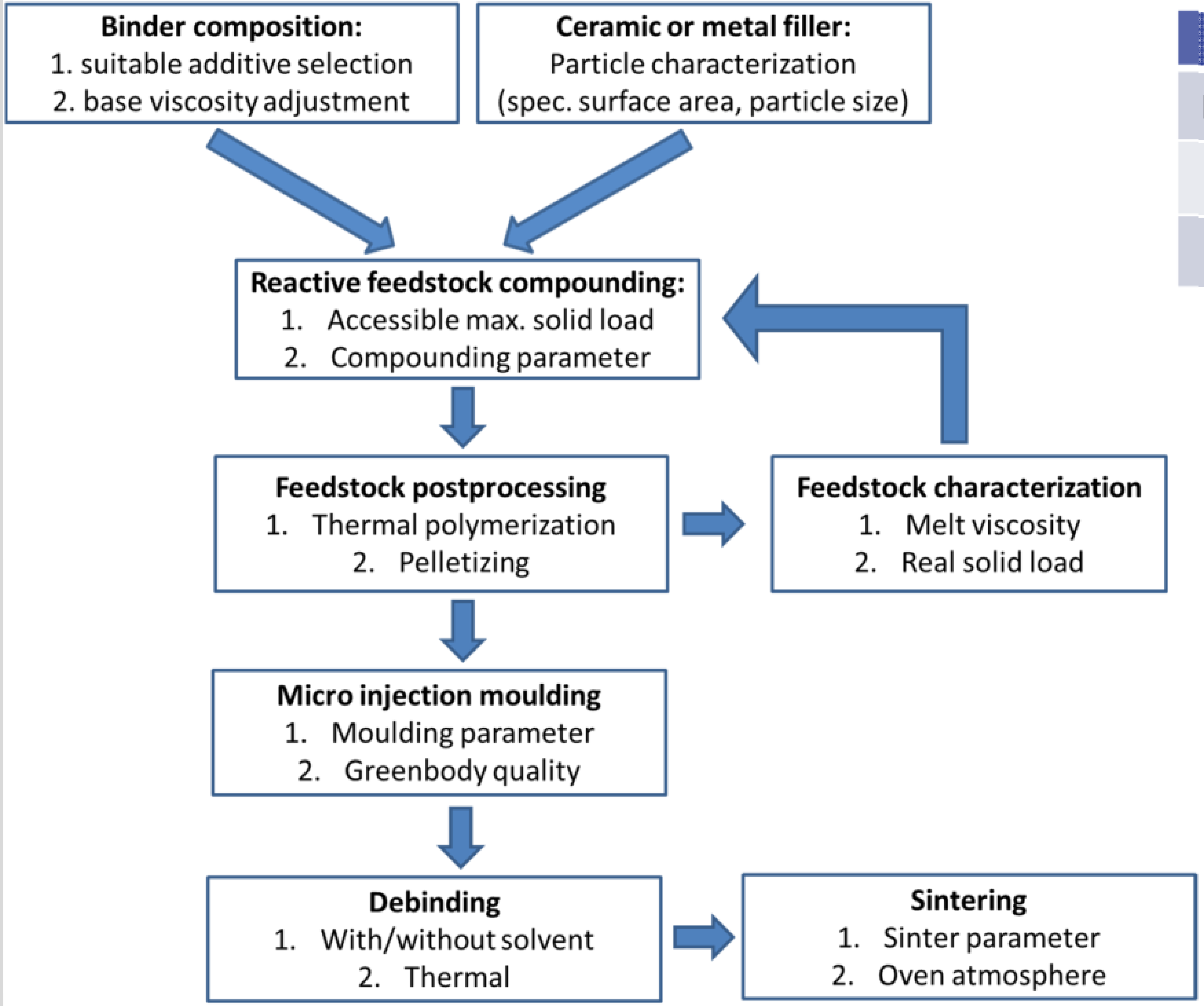
Binder system	PE/Wax
Partial solubility	n-hexane
ceramic	ZrO_2 (bimodal), Al_2O_3, Si_3N_4, $BaTiO_3$, ATN
metal	17-4PH, 316L, Cu, Au, W, W-La_2O_3, WC-Co

- Torque recording kneader, extruder, shear-rolls
- Compounding temperature: 125-180°C
- Viscosity: 100-500 Pa s





Process chain of new feedstock system



Binder composition:
1. suitable additive selection
2. base viscosity adjustment

Ceramic or metal filler:
Particle characterization
(spec. surface area, particle size)

Reactive feedstock compounding:
1. Accessible max. solid load
2. Compounding parameter

Feedstock postprocessing
1. Thermal polymerization
2. Pelletizing

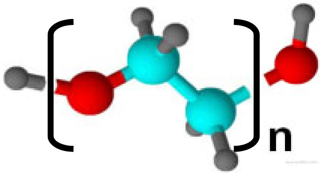
Feedstock characterization
1. Melt viscosity
2. Real solid load

Micro injection moulding
1. Moulding parameter
2. Greenbody quality

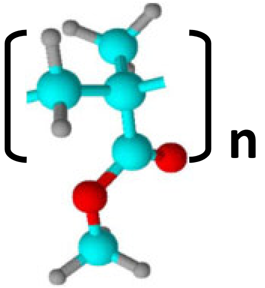
Debinding
1. With/without solvent
2. Thermal

Sintering
1. Sinter parameter
2. Oven atmosphere

Binder system	PMMA/PEG
Partial solubility	**water**
ceramic	ZrO_2
metal	17-4PH

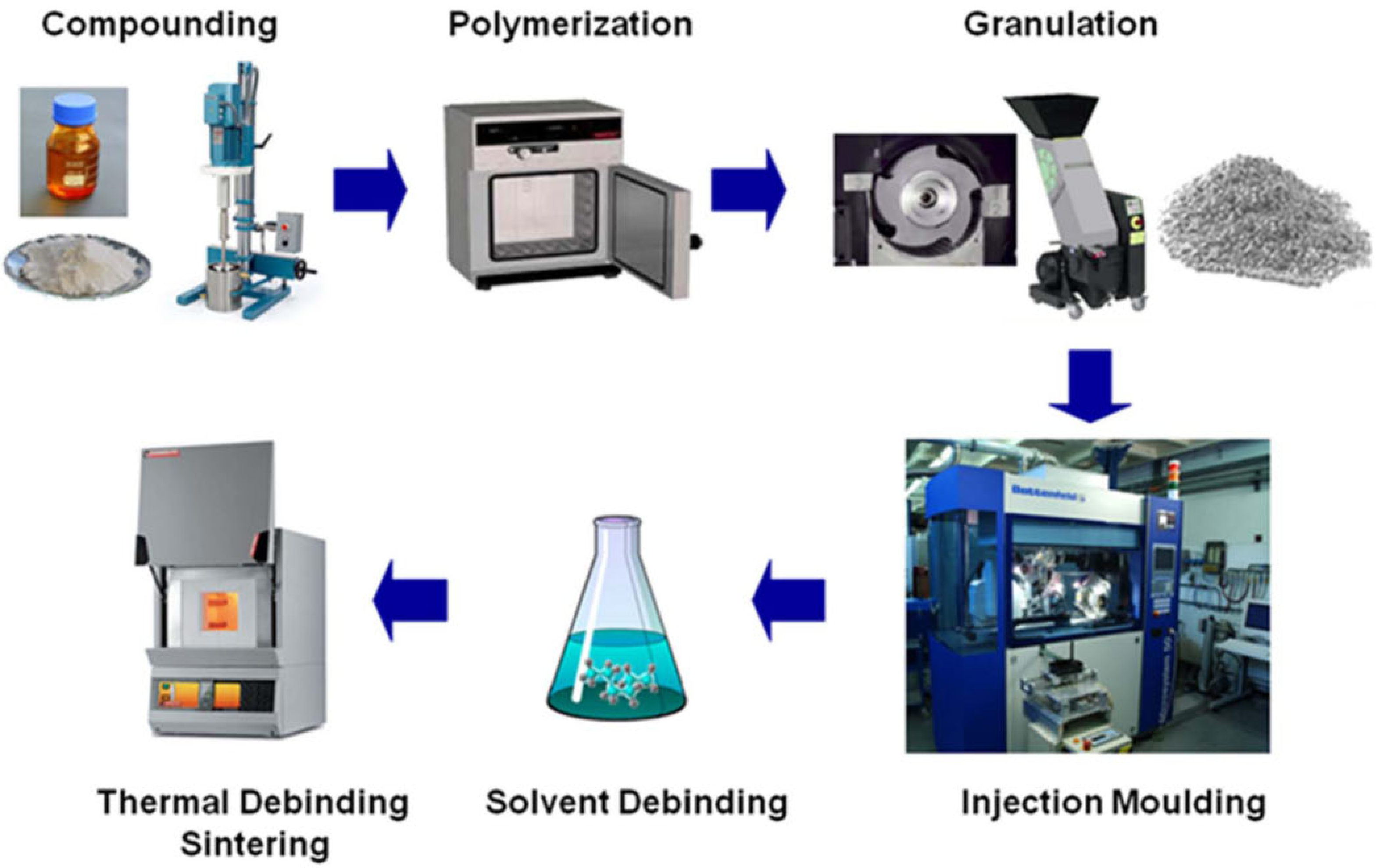


Polyethylenglycol (PEG)



Polymethylmethacrylat (PMMA)

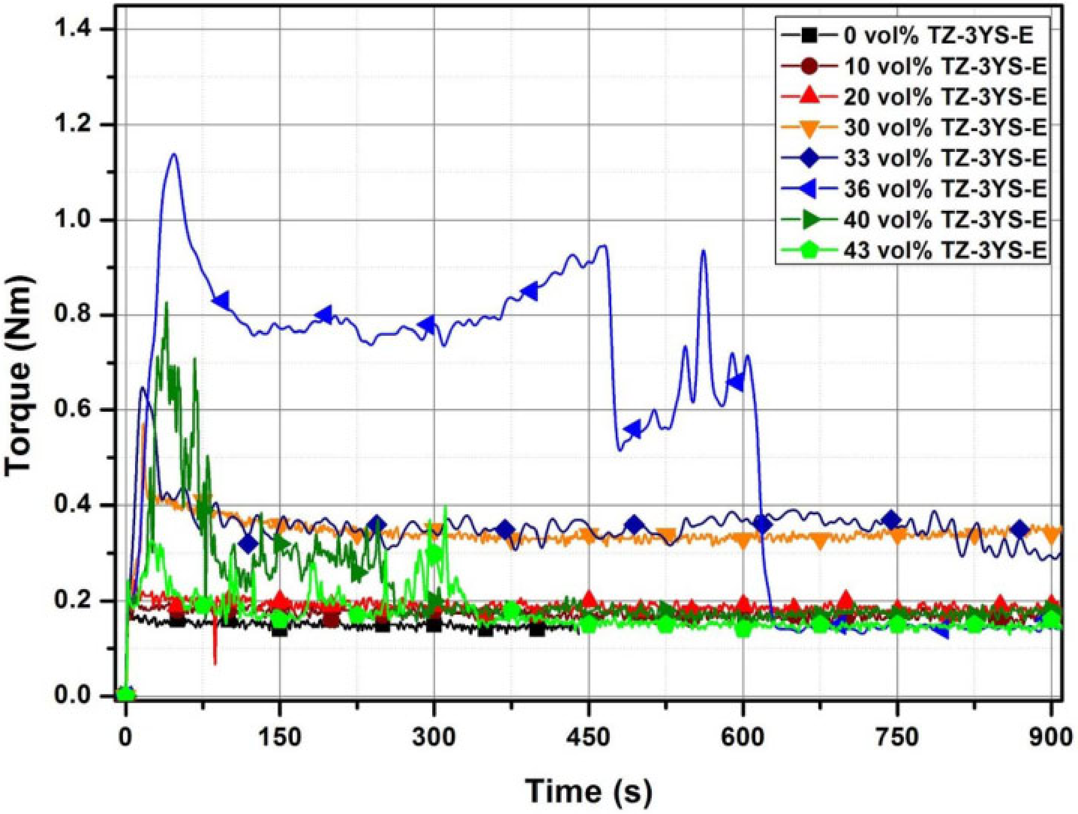
Modified process chain

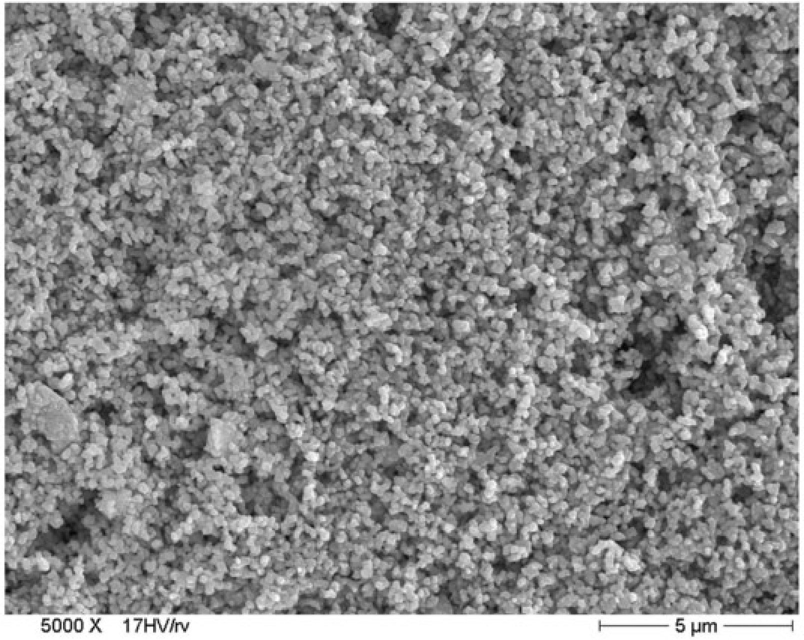


Reactive compounding

- MMA/PMMA reactive resin/phenanthrene as plastizizer
- PEG300 as water soluble component
- Polyethyleneglycolalkylether (Brij92/93) as surfactant
    - concentration 8.8 mg/m² filler surface area
- Microsized ZrO_2 (Tosoh TZ-3YS-E)
    - Average particle size: 0.45 µm
    - Specific surface area: 6.6 m²/g
    - Sinter density: 6.05 g/cm³
- Torque controlled dissolver (VMA: Getzmann AE03-C1)
- Compounding parameters
    - 25°C
    - 1000 rpm
    - 15 min
- Maximum measured torque < 1.2 Nm

Reactive compounding - zirconia load sweep

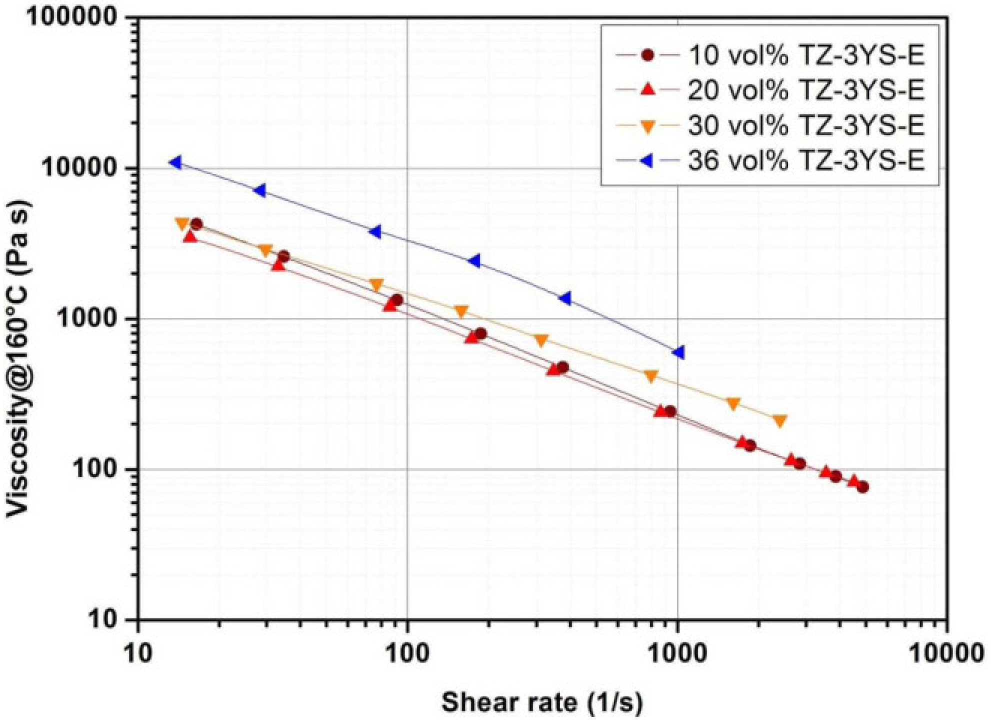


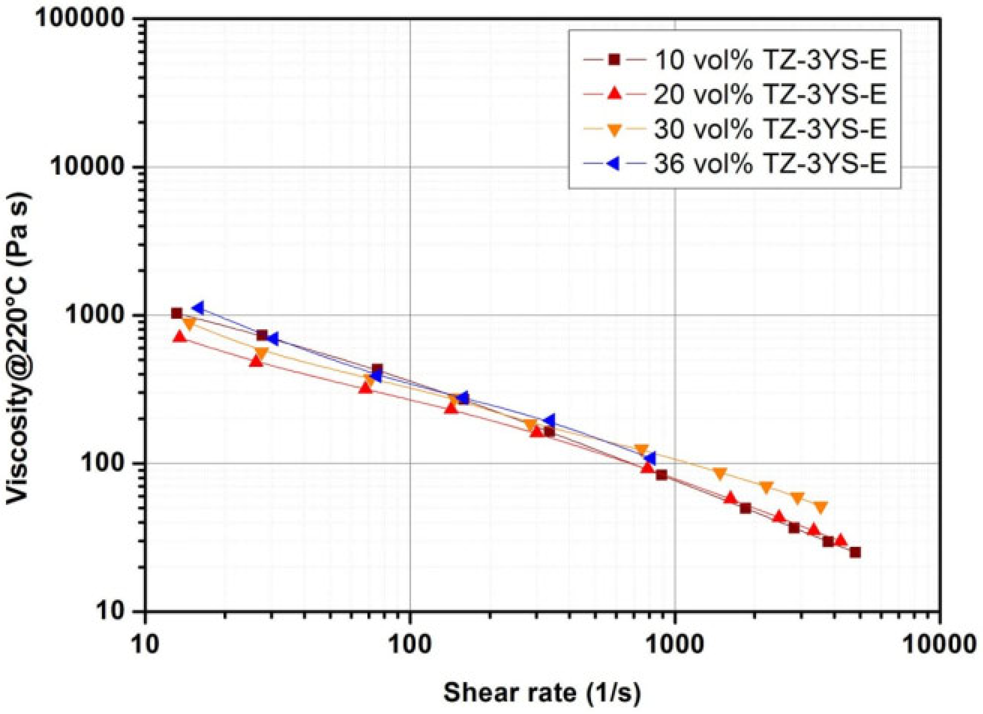


Submicron-sized ZrO_2

- Stable torque up to a zirconia load of only 33 vol%
- At higher solid loadings
  - pronounced evaporation of MMA due to evolved shear heat
  - insuffcent wetting of the dissolver blade

Melt viscosity - zirconia load sweep

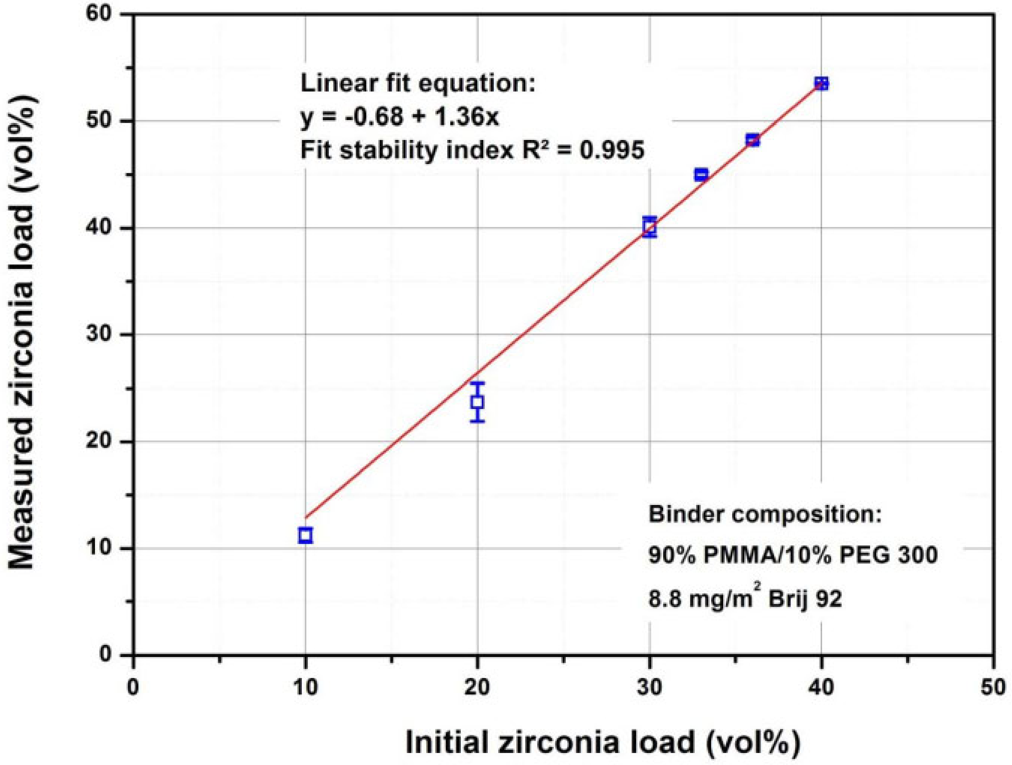




- Melt viscosity increases with zirconia load
- Melt viscosity drops with increasing temperature
- Stable feedstocks up to 36 vol%

Solid load to small for powder injection moulding

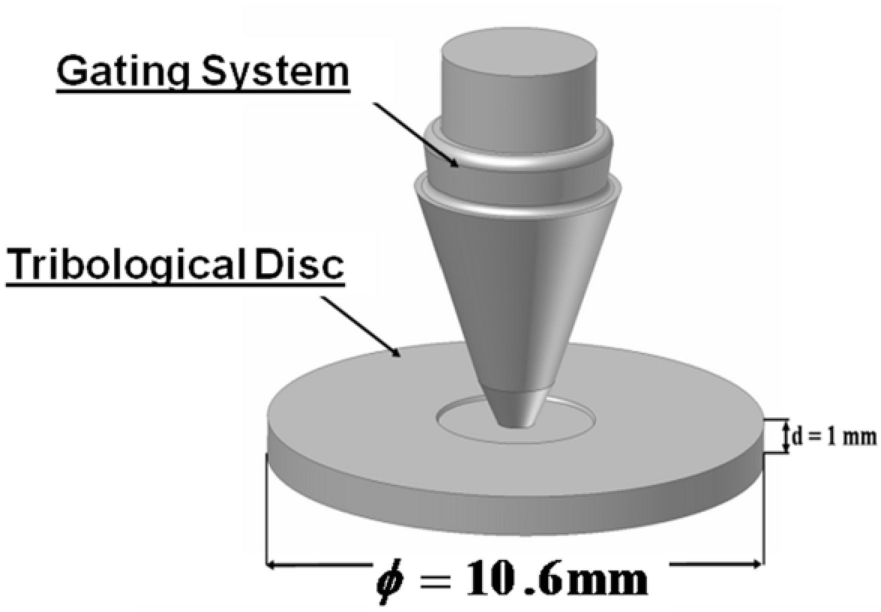
Measurement of the effective zirconia load by combustion experiments



- Observed MMA-loss during reactive compounding
- Effective zirconia load significantly higher
  - Initial 36 vol% means effective 48 vol%

→ **Solid load sufficient for powder injection moulding**

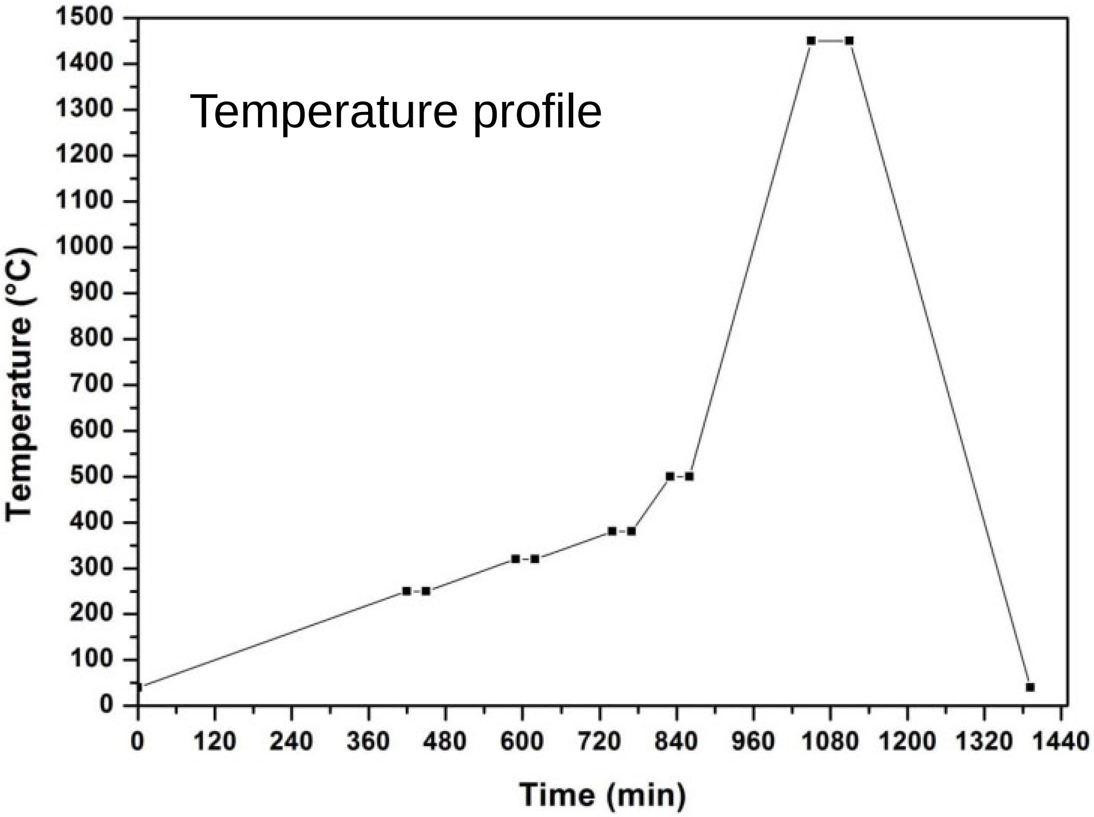
Injection Moulding of test specimen



- Feedstock with (initial 33 vol%), effective 45 vol% zirconia processed
- Isothermal process control
- Green density 3.45 g/cm³ (57 % theoretical density of zirconia)

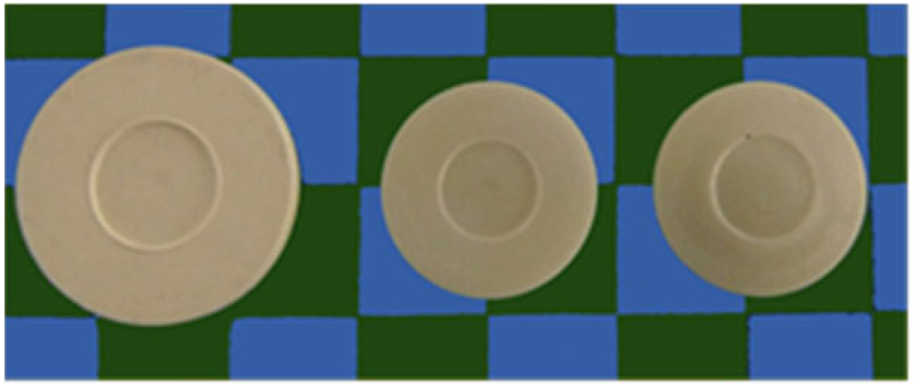
Debinding and sintering

- Two strategies:
    - Solvent (water) assisted (deionized water, 8 h, 25°C) plus thermal debinding
    - Direct thermal debinding
- Sintering

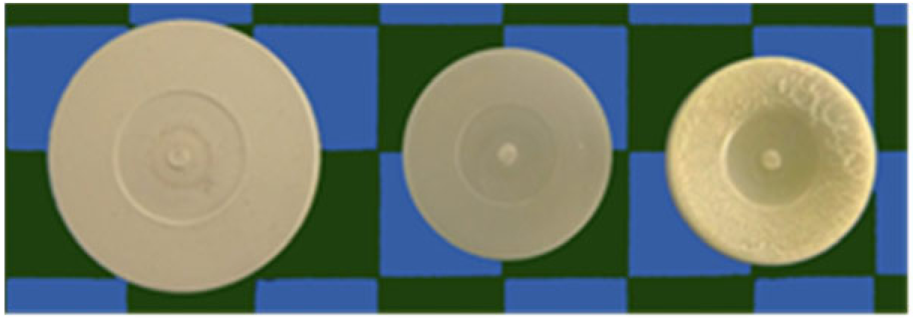


Debinding and sintering

Debinding strategy	Density (g/cm³)	Theoretical density (%)
Solvent plus thermal debinding	**5.98**	**98.1 ± 1.1**
Thermal debinding	**6.05**	**98.9 ± 0.2**



Free space
faced side



Solid substrate
faced side

Greenbody

Solvent/
thermal debinding

Thermal debinding

- Sinter densities almost identical
- Improved quality by using combined debinding

Conclusion and Outlook

- Successful use of environmental-friendly binder system was shown
- Waiving of solvent-assisted debinding possible
- Importance of interface chemistry
- Huge ceramic densities possible

- Replication of “real“ microsized parts
- Further extension to metal injection moulding

Acknowledgement

- Lisa Merklein for reactive compounding
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DFG Deutsche Forschungsgemeinschaft

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4µ association Ceramics Interest Group