

## Investigations on the production and forming of thermoplastic ceramic green tapes

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**Keywords:** Ceramic Tapes, Hydroforming, Hot Gas Forming, Ceramic Forming

**Abstract.** Technical ceramics such as alumina with its temperature stability, high mechanical stiffness, and good dielectric strength at low density, meet the requirements for highly resilient components for promising markets of high-performance electronics and the electrification of mobility. Ceramic components are usually manufactured using powder technology processes since forming of sintered ceramics is not possible due to the lack of plasticity. In this work, we use hydroforming to shape thermoplastic ceramic green tapes prior to sintering to add a third dimension to flat substrates. We developed alumina feedstocks based on a polyamide binder system that were extruded to 1 mm thick tapes, hydroformed, debinded and sintered. Depending on the binder composition, forming temperatures of 45-60 °C were sufficient, whereby precise temperature control was crucial for success. As a result, components with forming depths of up to 5 mm were produced without defects. This process offers the potential to revolutionize this market segment, not only in terms of geometric design freedom and low material waste, but also in terms of profitability of mass production.

### Introduction

Technical ceramics are typically produced using powder technology. Starting from fine powder, a so-called green body is formed using various manufacturing processes like pressing, casting, extrusion, and injection molding [1]. Which process is most suited depends on the dimensions, complexity and number of parts to be manufactured. The fragile green body is then sintered at 1400-2000 °C depending on the ceramic material. During this heat treatment, the part densifies without melting due to material transport processes and the final polycrystalline microstructure is formed. Depending on green density and final density, the body shrinks by 45-60 vol.% [1].

The covalent or ionic bonding type of ceramics prevents dislocation movement. For example, alumina shows linear elastic behavior with fracture strains in the range of 0.1 % [2]. This makes it impossible to use typical metal forming processes on sintered ceramic parts, so that the shape has to be created prior to sintering in green state. While pressing/green machining and injection molding are state of the art for 3D-components, tape casting is used for planar products [3]. As semi-finished product, ceramic tapes are used in microelectronics as substrates on which electrical circuits or sensors are printed. Such tapes can be stacked in multilayer technology and cofired to form a 3D-structured multifunctional component [4]. Due to the drying process in the production of green tapes, the tape thickness is limited [5] and many tapes have to be laminated for 3D-components [6], which also means material waste through cut-outs. When aiming for light-weight-



constructions, processing of green tapes like stamping and folding has been developed [7, 8, 9]. These processes are only possible because the green tapes contain a certain amount of polymer, which allows the tapes to be formed. Schwarzer et.al. [10, 11] have developed a water-based green tape that can be formed by deep drawing. The binder components act as plasticizer, and in this case, the dimensional relaxation had to be controlled by carefully controlled humidity. One challenge in powder technology in general is the production of a homogeneous green body with the same distance between the particles to ensure isotropic shrinkage. During the tape casting process particles might orient due to shear forces which leads to differing shrinkages in lateral and z-direction and can already be observed during debinding [12,13]. The shaping of green tapes can also influence the particle spacing as stretching in the shaping zone can lead to particle movement.

In this work, the authors chose an alternative approach using thermoplastics as binder to allow for better formability in green state. The reversible solid-viscous transition is temperature-controlled and shall be used during forming, so that less relaxation for improved dimensional stability was expected. Thermoforming is a well-established process in plastics [14] and has also been carried out for particle-filled systems such as PLA/PBS + calcium carbonate or PE, PP + talc [15,16]. While the filler content in these cases is usually in the range of 10-30 vol. %, for ceramic processing solids loadings of 50-60 vol.% are required which is known from ceramic injection molding [17]. In forming thermoplastics, vacuum forming is well established, whereby a suction effect is created by under pressure and the heated plastic plate is drawn into a cavity [14]. However, due to the higher thickness and stiffness of the ceramic green tapes, this process seems not suitable. In this work, the sheet metal forming process hydroforming [18] is adapted to shaping the green tapes. The conventional approach uses cold tools and a water-oil emulsion as forming medium. However, for thermoplastic forming, the tool is heated above glass transition temperature of the polymer and the tape is pushed to the tool walls by the pressurized gas media (nitrogen or argon). In this way, the flat ceramic green tapes are shaped into a 3D-structure that enables complex geometries, which can currently only be produced with great effort. Potentially, the proposed process is suitable for serial production.

The aim of this first work is to evaluate the feasibility of this process for forming ceramic green tapes in order to enable easy-to-process 2D semi-finished products into 3D-components.

**Process chain for manufacturing 3D-shell components**

For this study the alumina powder CT1200SG (Almatis) was used. It has irregular shaped primary particles with a mean particle size of 1.7 μm, its specific surface is 3.1 m<sup>2</sup>/g. The binder system bases on polyamide, waxes and surfactants. It was supplied in various compositions, which vary in polyamide-wax ratio and additions of modifiers. The exact composition is confidential. They are denoted with A20, A22, A26, A38, and A44, and were delivered by the company Inmatec Technologies, Rheinbach, Germany.

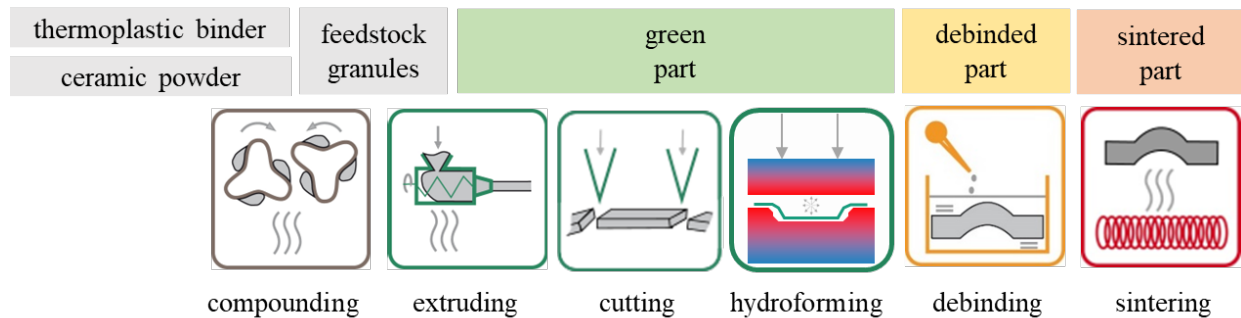


Figure 1: Process route for hydroforming of ceramics.

The production process is shown in Fig. 1. First, powder and binder were mixed and kneaded at 150°C to form a homogeneous feedstock in which particle agglomerates are broken and particles are coated by a polymer layer. The solid loading was 57 vol.%. This compounding step was carried out in three passes using a twin screw extruder KETSE 20/40 (Brabender, Germany). The feedstock was extruded at 150 °C through a 3.5 mm round die and granulated by cutting. The granulates enabled a continuous feed into the extruder and a homogenous mass flow during tape extrusion. Tapes were extruded using the same device equipped with a slot die with a width of 150 mm and a thickness of 1.0 mm. The endless tapes were cut to sheets of a size of 150 mm x 150 mm and placed into the hydroforming tool. The forming process is discussed in detail in the following section Hydroforming of Green Tapes. After shaping the green part, the samples were debinded and sintered. Debinding was a two-step procedure starting with extraction debinding in acetone for 48 h (MDU-30, Debatec) where 72 % of the binder was extracted. The remaining polymer was decomposed by thermal treatment in air at temperatures of up to 600 °C. Sintering was performed with a heating rate of 3 K/min up to a temperature of 1650 °C and then kept at that temperature for 2 h. Shrinkage of the tapes was measured using samples cut to a size of 20 mm x 40 mm. They were aligned in parallel, perpendicular, and in 45 ° to extrusion direction.

### Characterization of green tapes

The thermomechanical behavior of the green tapes was tested by two methods: DMA (dynamic mechanical analysis) and tensile testing at elevated temperatures. In the green state, the feedstock behaves like a filled polymer instead of a ceramic, as the particles are dispersed in a polymer matrix. In DMA, the visco-elastic behavior is characterized by oscillating rheological measurements. Polymers have elastic and viscous components in their mechanical response, which can be described by the complex dynamic modulus  $G$ , where  $G'$  is the storage modulus and  $G''$  is the loss modulus. The amplitudes of stress  $\sigma_0$  and strain  $\epsilon_0$  have a phase shift  $\delta$  (loss factor  $\tan \delta$ ) between them. (Eq. 1-3)

$$G = G' + iG'' \quad (1)$$

$$G' = \frac{\sigma_0}{\epsilon_0} \cos \delta \quad (2)$$

$$G'' = \frac{\sigma_0}{\epsilon_0} \sin \delta \quad (3)$$

For the oscillating rheological measurements, rectangular, solid specimens were cut in extrusion direction with a size of 55 mm x 10 mm x 1 mm. The specimens were mounted on a SRF (solid rectangular fixture) sample holder of a rheometer MCR302 by Anton Paar. A sinusoidal force was applied in torsion on the specimen and the response was measured. Prior to temperature dependent measurements an amplitude sweep was carried out between 0.001% and 1% to determine the linear-visco-elastic region. The amplitude was set to 0.01 %. The oscillation measurements were carried out with 1 Hz in a temperature range of 20-100 °C with a heating rate of 2 K/min. Two specimens were tested per sample and the results were in good agreement. These parameters comply with ASTM standard D7028-07.

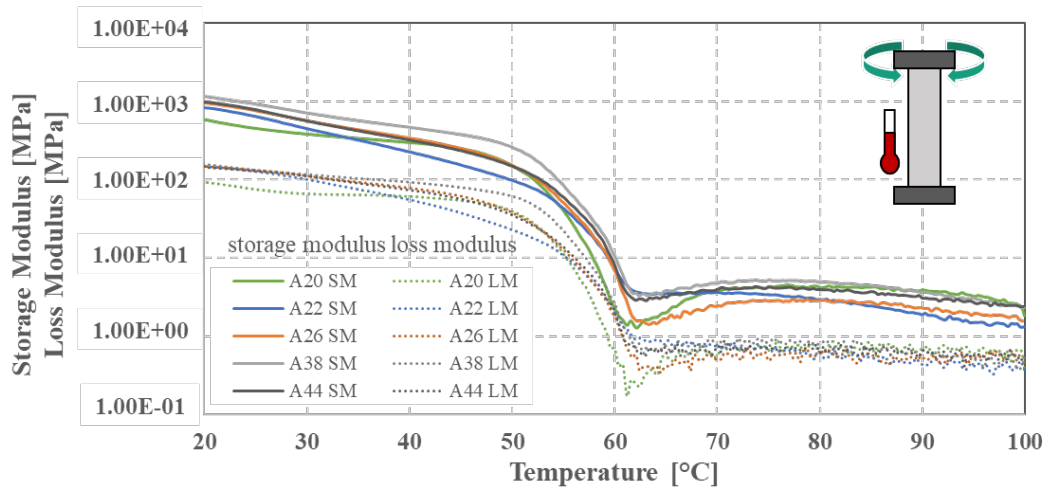


Figure 2: Storage (SM) and loss modulus (LM) of green tapes measured in oscillating rheometry.

Fig. 2 shows storage and loss moduli for all samples. They have similar behavior since they base on the same binder system. In the low temperature region, both moduli are high. The stored elastic energy, that leads to relaxation after stresses are removed, is one magnitude higher than the loss energy which is consumed by molecule movement and friction and leads to viscous flow. The tapes appear as a solid but flexible body. At higher temperatures both moduli have dropped down by almost two magnitudes which marks the transition to a polymer melt and marks also the glass-transition temperature of polyamide. The transition area between 45 °C and 60 °C is the proposed process window for the following hydroforming experiments.

Tensile tests inspired by DIN EN ISO 527-1 were carried out on a Zwick Z020 using a strain gauge-based load cell. The test set-up including details about the shape and size of the samples is shown in Fig. 3. A total of 60 tests were performed. Hot air flow was used from one side of the specimens to heat them up and to control the temperature, which was measured using an infrared camera. The representative thermal image in Fig. 3 (d) demonstrates the homogeneity of the temperature, which was checked for both sides of the specimen in pre-tests. The specimen was a shoulder bar (Fig. 3 (b)) with a testing length shortened to 20 mm. This deviation from the standard specimen geometry was made to ensure a more even heat distribution. Based on the results of the DMA measurements, 40 °C, 50 °C and 60 °C were defined as test temperatures. The elongation of the tensile specimen is determined via the crosshead extension. The test speed was 1.0 mm/min.

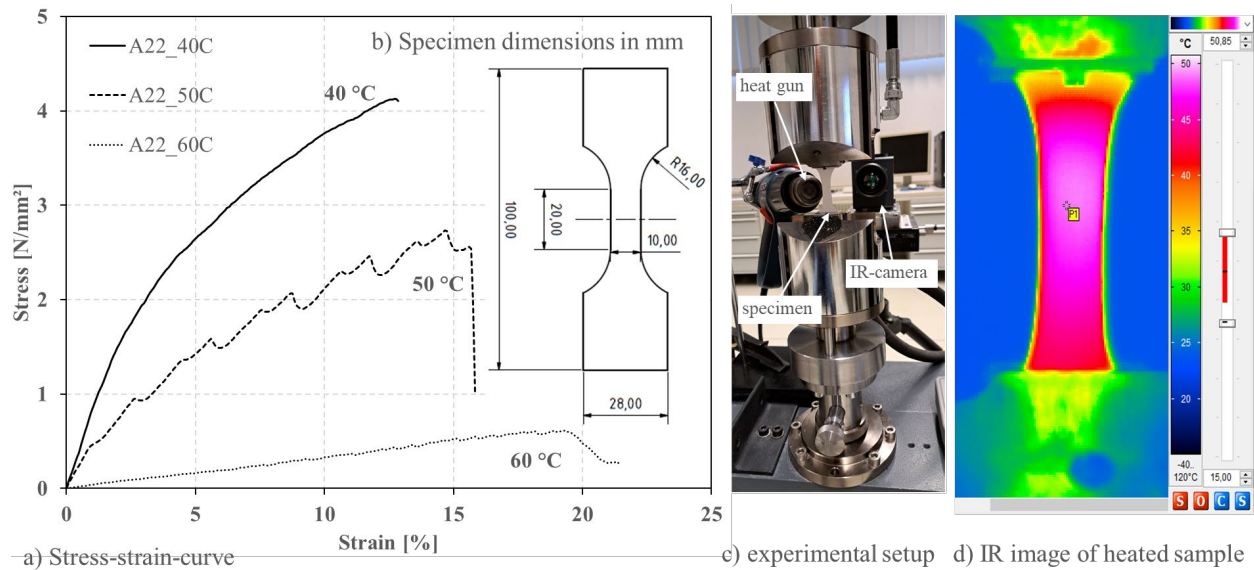


Figure 3: Tensile tests for ceramic green tape (a) stress-strain-curve for sample A22, (b) specimen geometry, (c) experimental setup, (d) heat distribution of heated sample

The binder components are semicrystalline polymers. Since the ceramic particles act as crystallization nuclei, it is assumed that the polymer matrix is mostly crystalline with molecules coiled and folded. At the lowest temperature considered (40 °C) the recorded stress strain behavior features a linear rise of the curve indicating linear elastic deformation followed by a non-linear curve section typically indicating plastic flow. In this section of the curve, molecules unfold and are stretched until finally fracture occurs at approximately 12 % strain. At the highest considered temperature (60 °C), which is within the range of the glass transition temperatures of polyamides, the mobility of the polymer chains is considerably higher and crystalline structures gradually dissolve. Consequently, the stresses necessary to achieve a defined elongation are significantly lower and the strain at fracture is higher compared to the material behavior at 40 °C. The intermediate temperature of 50 °C marks a transitional state in which stress build-ups and releases alternate. On molecular scale, crystalline areas unfold when a certain yield stress is reached followed by the next build-up. This behavior is represented in the curve via a wavy shape. Generally, the tensile tests have confirmed the process window identified via DMA (45 - 60 °C).

### Hydroforming of green tapes

Based on the results of the characterization of the thermoplastic ceramic green tapes and especially considering the identified process window, the hydroforming process and the corresponding hydroforming tool was designed. As shown in Fig. 4 (a) the forming tool consists of an upper and lower half, which include two heated segments. The latter clamp and heat up the green tapes. The tools are made of an aluminum alloy for better heat transfer. The lower half of the tool has a heated cavity in which the green tape is formed. The upper half of the tool is flat and has an opening through which the forming medium (nitrogen) is injected. The ceramic green tape is formed into the cavity by building up an internal pressure of 2.0 - 3.5 MPa. When the forming process is complete, the tool is opened. The part is cooled by compressed air to retain its shape and removed. However, as with other forming processes at elevated temperatures, temperature control throughout the process is a critical aspect.

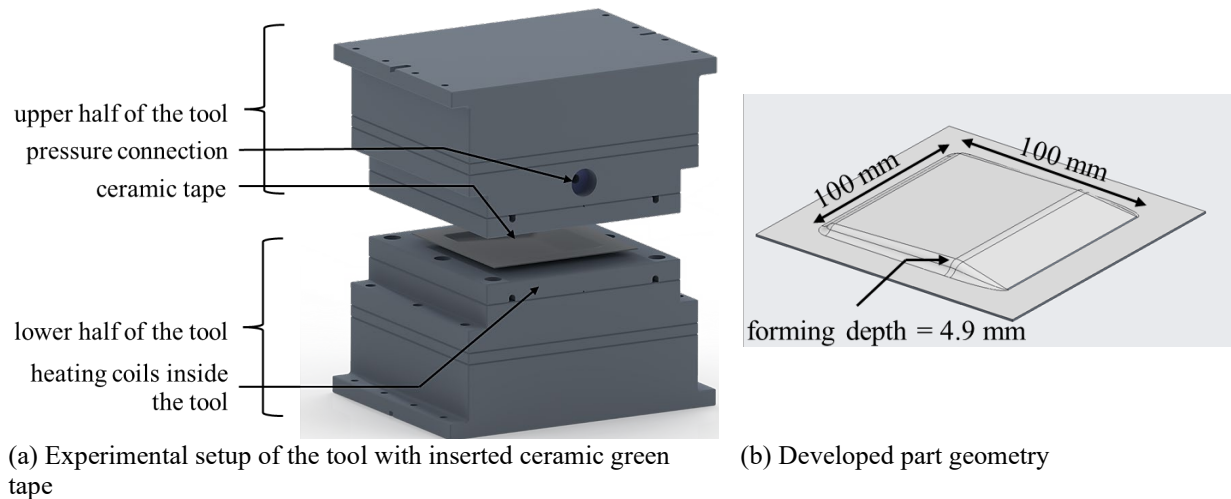
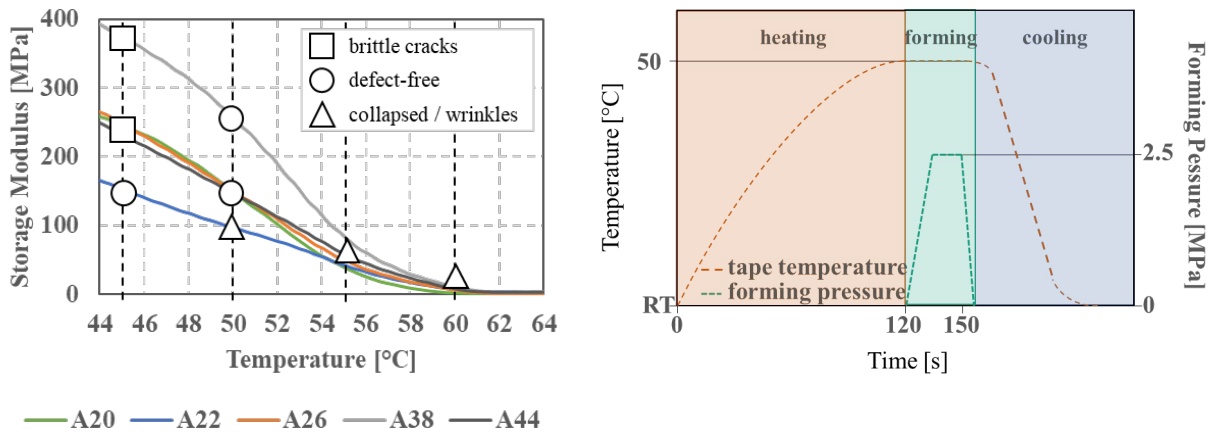


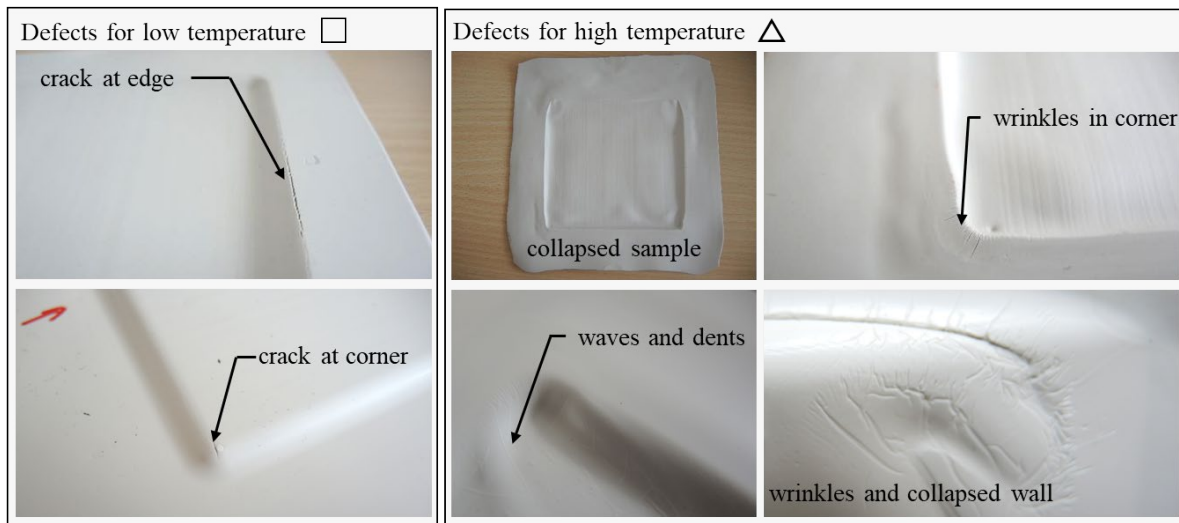
Figure 4: Developed experimental setup (a) and part geometry (b) for hydroforming trials.

In the context of the process design, the time required for the 1.0 mm thick tape to completely heat up to 60°C was determined using a thermocouple inside the green tape. It was 120 s. Consequently, the forming experiments were conducted at a certain temperature in the range of 45°C-60°C after a heating time of 120 s as shown in the process flow diagram in Fig. 5 (b). This is followed by the hydroforming process in which the clamping force is applied to seal the tape and the gaseous forming medium is introduced. After a linear pressure build-up of up to 2.5 MPa, the internal pressure is briefly retained before it is released, and the tool is opened. Cooling to ambient air is sufficient to remove the form-stable part from the tool.

Finding the right process temperature proved to be the most important task. Experiments were conducted at 45 °C, 50 °C, 55 °C, and 60 °C for the tapes with different binder systems. Fig. 5 (c) summarizes the characteristic defect patterns due to inappropriate process parameters. They can be categorized in brittle cracks at too low temperatures and collapsed structures with wrinkles at too high temperatures. These effects can be correlated to the visco-elastic behavior measured by DMA as shown in Fig.5 (a). If the storage modulus is at 100 MPa and below the strength seems too low and the samples collapse. This becomes obvious when comparing the results of A22 with A20, A26, A44 which had good results at 50 °C while A22 already collapsed. At even higher temperatures and thereby lower strength all binder compositions showed deformations. For 45 °C, all compositions, except A22, were too brittle and cracks formed at edges and corners. For sample A38, it was possible to achieve defect-free samples at 50 °C despite its high storage modulus of 250 MPa. These findings show that the temperature window for defect-free forming covers a range of approximately 5 K and is therefore extremely narrow. Both lower and higher temperatures lead to defects. While at too low temperatures the higher strength is associated with brittleness, resulting in cracks at radii transitions and corners, at too high temperatures the material tends to wrinkle and corrugate. In extreme cases the entire green tape collapses. The hydroforming tests showed that already low internal pressures were sufficient for complete forming. However, higher internal pressures could compensate for wrinkling at higher temperatures.



(a) Storage modulus of green tapes measured in DMA and defect types, detail from Fig. 3 (b) Process flow diagram for hydroforming of green tapes



(c) Characteristic defects in dependence of temperature range

Figure 2: Close-up of DMA measurements (a) in linear scale within the temperature process window. Process flow diagram for temperature and forming pressure (b). Defect types for non-optimal heating conditions (c).

Depending on the binder composition, forming temperatures between 50 °C and 55 °C have been identified to provide the best compromise of strength and formability. Green parts could be reproducibly formed in this temperature range, as shown in Fig. 6. Visual inspection and 3D coordinate measurements confirmed that the target geometry could be reached without relaxation effects or visible defects.

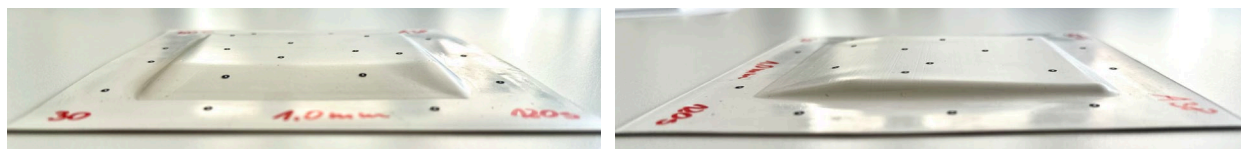


Figure 3: Images of completely formed ceramic green tapes without visible defects.

After forming, the green parts were debinded and sintered. As a result of sintering, the components shrank considerably, as shown in Fig. 7. Due to the extrusion process, the polymer chains are stretched which leads to directional shrinkage. Precisely, shrinkage parallel to the extrusion direction was 17.3%, while shrinkages at angles of 90° and 45° to the extrusion direction were 14.4% and 15.5%, respectively. These data were obtained using cut outs of a size of 20 mm x 40 mm. This effect was also visible in the produced parts, so that the dimensions differed by

almost 2 mm parallel and perpendicular to the extrusion direction. This direction-dependent shrinkage must be compensated for in the design for future ceramic components when calculating the oversize factors.

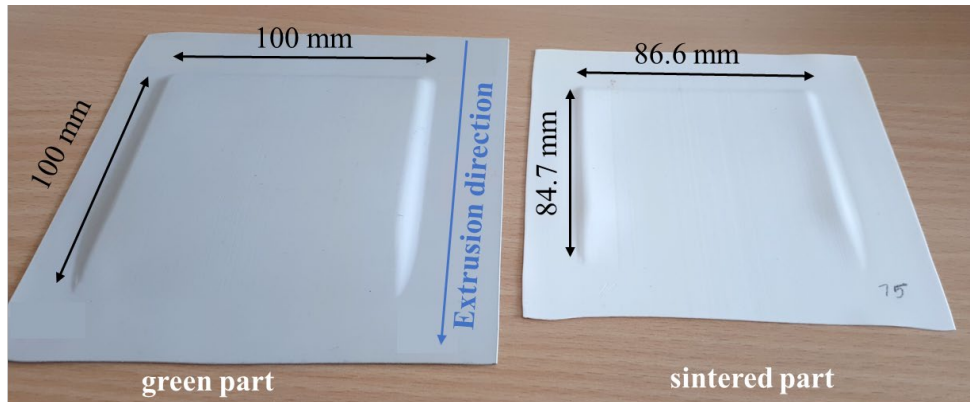


Figure 4: Green part (left) produced within the processing window and sintered part (right).

The sintering process itself also faces a number of challenges. For example, the manufactured samples tend to collapse during sintering if flat areas are unsupported which is caused by creep processes at 1650 °C sintering temperature. This can be remedied by both design adjustments and modifications during the sintering process, such as the inclusion support structures. In general, however, it has been found that no defects are introduced during the forming process that would subsequently lead to component failure during the sintering process.

### Summary

This study presents basic investigations on the production and processing of ceramic green tapes using thermoplastic binders. As part of the investigations, highly filled tapes with 57 vol.%  $\text{Al}_2\text{O}_3$  particles were extruded using polyamide-based thermoplastic binders, providing ceramic flat material for a subsequent hydroforming process. The PA binder system provides the necessary formability at elevated forming temperatures to produce complex 3D ceramic green parts. The thermoplastic properties could be utilized as part of the forming process. The temperature-controlled softening and solidification process of thermoplastics is suitable for producing dimensionally stable parts without relaxation phenomena. Subsequent process steps, in particular debinding and sintering, are well established in industry and are known from ceramic injection moulding (CIM). DMA studies and tensile tests have shown that the properties of the tapes are highly temperature dependent, which is later reflected in the temperature sensitivity during forming. Defects in the production of green parts are caused by temperatures that are either too low, resulting in increased brittleness, or too high, resulting in insufficient material stability. Even and complete heating of the part before forming and accurate temperature control is therefore essential to meet the process window.

Overall, the following key results were obtained:

- Ceramic particles in thermoplastic binders can be processed into green tapes by extrusion, which can be used as flat material in further process steps.
- Preliminary mechanical tests show that plastic strains of 12 % to 18 % are possible at elevated temperatures, which clearly demonstrates the potential for forming processes.
- The developed hydroforming process at 50°C is suitable for forming green tapes into complex shaped ceramic green parts. The temperature window is highly dependent on the binder composition and must be very precisely controlled during the process.



- Subsequent debinding and sintering processes have enabled the production of ceramic parts based on the green parts. However, the shrinkage of the parts as a result of sintering must be taken into account in the part design.

The results presented demonstrate that ceramic green tapes with thermoplastic binders can be produced by extrusion and formed into 3D-geometries by hydroforming. The process is suitable for series production and has the potential to produce temperature-stable housings or curved substrates for microelectronics.

### Acknowledgements

The research project was funded as part of the Fraunhofer-Gesellschaft's SME-oriented research program. The authors are thankful to Inmatec Technologies for supplying the thermoplastic binder.

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