Thin high-strength zirconia tapes with extreme flexibility

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\section{ABSTRACT}
The yttria stabilized zirconia ceramics (Y-TZP) are known for their high fracture toughness and high strength. Due to their excellent mechanical properties, the thin zirconia tapes can possess extraordinary behavior – extreme flexibility. In the present work, we introduce an adaptation of gel-tape casting method for the preparation of thin, high-strength zirconia tapes from water-based suspensions. Fine ceramic powder with a particle size of around 100 nm was used. The negative effect of sodium ions on the strength and toughness of sintered ceramic samples was revealed and explained. Ceramic tapes with a thickness of 190 μm with as-sintered surfaces reached a characteristic biaxial strength of 1805 MPa. The huge elastic deformation of ceramic tapes was demonstrated in a 3-point bend test, and a bending radius of 25 mm for a 75 μm thick tape was reached.

\section{INTRODUCTION}

Thin self-supporting ceramic tapes with the thickness in the range from tens to hundreds of microns are used in many industrial applications (ceramic barrier layers [1–4], sensors [5–7], and flexible substrates [8,9]). Due to the subtle thickness of ceramic tapes, it is possible to reach an unusually high strength of ceramic tapes and even their substantial elastic deformations [8,9]. The yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) are a material known for its outstanding mechanical properties. The high strength of Y-TZP mainly depends on the stress-induced transformation of the metastable high-temperature tetragonal (t) polymorph into the stable monoclinic (m) polymorph [10,11]. Cracks propagating in Y-TZP can induce a t-m transformation of the tetragonal matrix, and the volume expansion associated with the t-m transformation effectively hinders crack propagation in the sample volume [11]. Moreover, ferroelastic domain switching was found to be another contributor to the toughening mechanism in TZP [12]. Tetragonal zirconia stabilized with 3 mol\% Y\textsubscript{2}O\textsubscript{3} (3Y-TZP) has become the most used zirconia ceramic because it exhibits the best combination of toughness and strength (typically 5–6 MPa m\textsuperscript{1/2} and more than 1 GPa) [13–15]. Low Young’s modulus, high fracture toughness and corresponding high strength make the 3Y-TZP ceramic a suitable material for the preparation of extremely flexible ceramic tapes [5,16] with applications in electronics as chemically, thermally, and mechanically resistant substrates. Although no large elastic deformation of ceramic products can commonly be observed, theoretical calculations show that a relatively high flexibility of thin ceramic sheets can be obtained [17]. To demonstrate the flexibility of ceramic tapes, we can calculate the radius of maximal curvature for the 3Y-TZP sheet [17]. In the case of pure bending, the maximum radius of curvature, \( r \), can be determined according to the simple equation:

\[ r = \frac{E y}{\sigma^2} \]  

where \( y \) is the distance from the neutral axis to the outer fiber of the sheet in tension, \( E \) is Young’s modulus, and \( \sigma \) is the flexural strength. For a ceramic tape with a thickness of 200 μm, the maximal radius of curvature is 20 mm (considering a tetragonal zirconia ceramic with \( E = 200 \) GPa and \( \sigma = 1000 \) MPa). The flexibility of the tape can be further increased by reducing the tape thickness. Extreme flexibility (and strength) can be obtained just and only in fully dense, homogeneous ceramics. The microstructural requirements put extremely high demands on the processing method for ceramic tapes. For thin tapes with thicknesses from tens to hundreds of micrometers, the tape casting method (sometimes referred to as the doctor blade technique) is often used [18–20]. The tape casting of submicrometre- and, preferably, nanometer-sized ceramic powders, which are necessary for obtaining high-strength (thus highly flexible) thin sheets, brings many difficulties [20]. The main problem of standard tape casting systems based on dissolved
long-chained polymers or dispersed polymer micro-
particles (latexes) is the high viscosity of the binder
system resulting in a low solid loading of suspensions
with submicrometre – or even nanometer-sized parti-
cles [21]. Massive particle rearrangement during drying
and binder removal of low-concentrated suspensions
hinders a regular packing of fine ceramic particles in
the tape. Non-uniform particle packing in the tapes
after binder removal does not allow obtaining fully
dense and defect-free zirconia tapes necessary for
high strength and flexibility [22]. Only a few papers
have reported on an investigation into zirconia tapes
that exhibited properties suitable for high flexibility.
Unfortunately, the ability to deform elastically to
a large extent was not proved and the processing
details were not revealed [23,24].

Recently, new tape casting methods based on gel
casting principles have been introduced [25–27]. These
methods can be advantageously used for tape casting
of ceramic suspensions with nano-sized particles.
Stastny et al. [9] have developed a gel-tape casting
method that uses a binder system based on epoxy
monomers of low molecular weight dissolved in
water. The low initial viscosity of the binder system
allows high solid loadings even with nanoparticle pow-
ders. The monomers in the slurry polymerize after
casting and create a polymer network that gives the
tapes handling strength. The slurry could be polymer-
ized in air atmosphere at room or elevated tempera-
tures. The strength of the wet tapes allowed the gelled
tape to be peeled off from the carrier; the gelled tapes
were moved into a drying chamber without any visible
damage. This gel-tape casting process was successfully
used to prepare high-strength [9] and transparent thin
alumina tapes [28].

In the present work, we adopted and tailored this
approach to the preparation of thin high strength,
flexible zirconia substrates. The aim of the present
study was to develop a process for the preparation of
zirconia tapes, investigate the microstructure and
strength of sintered tapes, and prove the flexibility of
the tapes prepared.

2. Materials and methods

2.1. Preparation of ceramic tapes

Zirconia tapes were prepared using fine zirconia pow-
der (HWYA-N-1S, Guangdong Huawang Zirconium
Materials, China) with a specific surface area of
15.6 m² g⁻¹. The tape casting process was based on
a previously published method of epoxy-based gel
casting [29], and on gel-tape casting processes [9,30].
The optimal solid loading of zirconia powder was 31
vol. %. The powders were dispersed in a mixture of
deonized water, epoxy resin – ethylene glycol diglyci-
dyl ether (Quetol 651, Electron Microscopy Sciences,
USA), abbreviated to EGDGE, and a dispersant. Two
types of dispersant were used in this study. The sodium
salt of polyacrylic acid (Sigma-Aldrich Chemie,
Germany) with a molecular weight of 2100 g mol⁻¹,
referred to as Na-PAA, and the commercially available
Dolapix PC75 (Zschimmer&Schwarz, Germany), abbre-
viated to PC 75, were used as dispersants. Dolapix PC
75 is a solution of alkali-free salt of polyacrylic acid.
These dispersants had previously been found to be
effective dispersants for alumina and zirconia nano-
powders [30,31]. The optimal dispersant dosage
found by rheological measurement was 0.35 wt% of
Na-PAA and 1.5 wt% of Dolapix PC75. The overall
composition of the ceramic suspensions can be found
in Table 1.

The dispersion of ceramic particles in the liquid
medium was enhanced by ball milling. Zirconia balls
with a diameter of 1 mm were used as the milling
medium. The suspensions were milled for 24 h in
a plastic bottle. After the milling, the suspensions
were degassed for 15 minutes under a pressure of
9.10³ Pa. Before tape casting, dipropylentriamine
(Sigma-Aldrich, Steinheim, Germany), abbreviated
to DPTA, was added to the suspensions as a hardener.
The ratio of EGDGE: DPTA was kept stoichiometric or
higher in the case of suspensions with an extra addi-
tion of EGDGE (Table 1). The suspensions were thor-
oughly mixed for 120 s to disperse the hardener
homogenously. The suspensions with the dispersed
hardener were cast on float glass. Before casting, the
glass surface was thoroughly cleaned in a mixture of
ethanol and hydrochloric acid (C₂H₅OH: HCl = 1:1 in wt
%). The cleaning procedure made the surface of the
glass wettable and therefore suitable for the casting of
water-based suspensions. A tape casting machine
(MSK-AFA-II-VC, MTI, USA) with a double doctor blade
setup was used. Both blade gaps were set to 300 μm or
150 μm. The casting speed was 9 mm s⁻¹. The cast
tapes were covered with a polypropylene lid that
maintained a moisture-saturated atmosphere during
the curing. The cured tapes were peeled off from the
glass carrier and dried in a climate chamber at
a temperature of 20°C and a relative humidity of 98%
for 24 h. After 24 h, the tapes were taken out of the
climate chamber and dried under laboratory condi-
tions for 24 h. The tapes were heat-treated in two
steps. In the first step, the tapes were heated up to
900°C (or 700°C) to burnout all organic components.
The heating rate was set to 2°C min⁻¹. The samples

| Table 1. Composition of the suspensions. |
|------------------------------------------|
| Suspension | ZrO₂ | H₂O | EGDGE | DPTA | Na-PAA | PC75 |
|------------|------|-----|-------|------|--------|------|
| Na-PAA     | 73.07 | 21.34 | 4.10 | 1.23 | 0.26   | -    |
| PC 75      | 72.85 | 20.85 | 4.00 | 1.21 | 0.26   | -    |
| PC 75 + extra epoxy | 72.13 | 20.60 | 5.00 | 1.19 | 0.08   | -    |
were placed between two porous ceramic plates during this step. The plates improved the flatness of the ceramic tapes while the porous structure enabled better removal of gaseous products. The second step consisted in sintering the pre-sintered tapes for 2 h at selected sintering temperatures. The pre-sintered tapes were sintered between sapphire plates to keep the samples flat during sintering. The heating rate was set to 5°C.min⁻¹ to 780°C and then slowed down to 2°C.min⁻¹ until a sintering temperature of 1450°C or 1550°C was reached.

2.2. Evaluation methods

Particle size distribution in the suspensions was determined using a laser diffraction particle size analyzer (LA-960, Horiba, Japan) on water-diluted suspensions after the milling. The suspensions were diluted with pH-adjusted deionized water (pH = 8.5). The rheological behavior of the ceramic suspensions was examined in the steady shear mode. A rotational rheometer (HAKE MARS II, Thermo Scientific, Germany) equipped with a double-gap cylinder sensor system was used. Suspensions without the addition of hardener (DPTA) were used for the measurement in the steady shear mode. The curing process in the suspensions was monitored by small-strain oscillatory shear measurement, using the same rheometer equipped with a parallel plate sensor system. The pore size distribution in samples after binder removal was investigated via mercury intrusion porosimetry (PoreMaster 60, Quantachrome, USA). The linear shrinkage during heat treatment was calculated by measuring sample dimensions after drying and after final sintering. The microstructures of the sintered samples were visualized using a scanning electron microscope – SEM (Vierios 460 I, ThermoFisher Scientific, Czech Republic). The mean grain size was calculated by the linear intercept method (ASTM E1382 – 97(2015)). The values were measured on at least four SEM micrographs of polished and thermally etched microstructure (at least 400 grains in total). Confidence intervals were calculated using the individual values of the measured grains. The mean grain size was multiplied by a factor of 1.56 to yield the true grain size [32]. Normalized histograms of the grain size were calculated using the individual intercept lengths corrected by the 1.56 factor. Relative densities of the sintered tapes were measured by the Archimedes double weighting method in water. The theoretical density 6.08 g.cm⁻³ for tetragonal zirconia was used. To analyze the phase composition of sintered samples, an X-ray diffraction analysis (XRD) was performed in the Bragg-Bratano configuration (Rigaku SmartLab 3 kW, Rigaku, Japan) using Cu Kα radiation. Diffraction patterns in the range (2θ) from 10° to 90° were recorded. The quantification of monoclinic zirconia content was performed using the Rietveld refinement (tetragonal zirconia ICSD code 79,197, monoclinic zirconia ICSD code 89,426, cubic zirconia ICSD code 89,429). The PDXL2 software (PDXL 2.8.3.0 version, Rigaku, Japan) was used for the Rietveld refinement. The biaxial strength was measured in the ball-on-3-balls setup. The samples were of a rectangular shape (4 mm x 3 mm) with a mean thickness of 190 μm. The exact thickness of each individual sample was measured and used for the calculation of the biaxial strength. The biaxial strength was calculated according to the equation:

\[ \sigma_{BB} = f \frac{F}{t^2} \]

where \( \sigma_{BB} \) is the biaxial strength (MPa), \( F \) is the fracture force (N), and \( t \) is the thickness of the sample (mm). The dimensionless factor \( f \) depends on the loading configuration and sample geometry. In our work, the factor \( f \) was calculated for every specimen tested and the value of \( f \) was in the range of 2.2–2.3. The hardened steel balls with a diameter of 2.38 mm (supporting diameter of about 2.75 mm) were used for a ball-on-3-balls biaxial bending loading of rectangular tape samples [33,34]. The geometrical factor \( f \) for thin tape samples was calculated from a 3D numerical model using the FEM software Abaqus/CAE6.13 (Dassault Systemes Simulia Corp., Providence, RI, USA). For the simulation, the rectangular samples and the balls were modeled using 3D deformable elements of the C3D8R type [35]. The loading speed was set to 0.5 mm.min⁻¹. The tape samples were tested as sintered, i.e. the surface of the samples was neither ground nor polished. The parameters of the Weibull strength distribution were calculated numerically, using the maximum likelihood method, in accordance with the EN 843–5 Standard. The fracture toughness of prepared materials was measured using the standard SEVN8 method on rectangular bars [EN ISO 23,146] extracted from discs. The discs (30 mm in diameter, 5 mm in thickness) were gelcast from the suspensions stabilized with Na-PAA and PC 75 with extra epoxy. Drying of the discs was slowed down compared to tapes and the heating rate was set to 0.8°C/min to prevent the cracking of discs due to non-uniform binder removal and shrinkage. The discs were sintered using the same schedule as in the case of the tapes. The bars were cut from the discs, ground and polished to a final cross-section of 3 mm x 2.4 mm. The straight V-shape notch with a nominal depth of 0.7 mm was cut into the specimen using an Exact notching device (Exakt, Germany), where a razor blade and diamond paste are used to produce a sharp-tip V-notch. The 3-point bending configuration with a span of 16 mm and a roller diameter of 5 mm was used for loading via the Instron universal testing system (8862, Instron, USA). The fracture toughness data of both materials
were statistically analyzed using Gaussian distribution to reveal differences. The flexibility of the sintered zirconia tapes was tested in the 3-point bending configuration (8862, Instron, USA). The ceramic tapes with a thickness of 70–140 μm and with a width of 7 mm were tested. The span of the supports was 30 mm and 50 mm and the diameter of the rollers was 10 mm. The cross-head speed was set to 10 mm/min and the force-deflection courses were recorded. The test was carried out using a Nikon D750 camera (Nikon, Japan) using the Camera Control Pro software. The maximal deflection was derived from the force-deflection curves.

3. Results and discussion

3.1. Characterization of ceramic suspensions

The suspensions stabilized with Na-PAA had a smaller particle size than the suspensions stabilized with the PC 75 dispersant. The median particle size in the case of the suspensions stabilized with Na-PAA was 108 nm (d_{90} = 126 nm), whereas the suspensions stabilized with PC 75 were characterized by a median particle size of 121 nm (d_{90} = 143 nm). The particle size distributions are shown in Figure 1. Similar to our previous research [30], the particle dispersion was narrower in the case of the dispersant based on sodium salt of polyacrylic acid (Na-PAA) when compared to the dispersant based on ammonium salt of polyacrylic acid (PC 75). We assume that the main difference can be found in the molecular weight of the dispersants and the different dissociation properties in water environment. Even though the better results in terms of particle size distribution were found in the systems stabilized with Na-PAA, we used both the suspension stabilized with Na-PAA and the suspension stabilized with PC 75 for further preparation of the ceramic tapes. The main reason can be derived from our previous research on tape casting of high-strength alumina [30], where the traces of alkali from the dispersant caused changes in the structure and properties of the sintered tapes. The results of rheological measurement in the steady shear mode are shown in Figure 2. The suspensions stabilized with Na-PAA had the lowest viscosity of all the tested systems. With a solid loading of 31 vol% the suspension stabilized with Na-PAA reached viscosities below 0.03 Pa.s in the whole range of the measurement (1–1000 s^{-1}). The suspensions with the same solid loading of 31 vol% stabilized with PC 75 with and without an extra addition of EGDGE exhibited higher viscosity. The viscosities were in the range of 0.05 Pa.s – 0.06 Pa.s at shear rates of around 30 s^{-1}, which roughly corresponded to the shear rate during tape casting with a doctor blade gap of 300 μm and a casting speed of 9 mm.s^{-1}. Moreover, the suspensions stabilized with PC 75 exhibited a more prominent shear thinning behavior. The effect of dispersants on the curing behavior of the suspensions was investigated in the oscillatory mode. The evolution of complex viscosity described the curing kinetics of the system (Figure 3).

The experimental data were fitted and analyzed by the Hill equation [36]:

\[
|\eta^*(\omega)| = |\eta^*(\infty)| \left(\frac{t^n}{t^n + \theta^2}\right)
\]

where \(\eta^*(\infty)\) is the final value of the complex viscosity of the gel, \(\theta\) is the half-gelation time for which \(|\eta^*(\theta)| = |\eta^*(\infty)|/2\), and \(n\) is a coefficient relative to the slope of the tangent at the half-gelation time \(\theta\). Based on the analysis of the model fitted to the data points

![Figure 1. Particle size distribution measured in ceramic suspensions after ball milling.](image-url)
we could determine the processing time (i.e. the idle time before the polymerization onset), the final (equilibrium) value of complex viscosity (its absolute value), and the total curing (polymerization) time (Table 2).

The processing time was defined as a period between the addition of the hardener and the time point where the complex viscosity reached a value of 1000 Pa.s.

The system stabilized with Na-PAA was characterized by the shortest processing time of 68 min while the equilibrium value of complex viscosity reached 71 kPa.s with a curing time of around 2.5 h. The stabilization of the suspensions with PC 75 resulted in a prolonged processing time of 80 min and significantly lower values of the final complex viscosity 24 kPa.s. A similar effect of ammonium polyacrylate salt

Figure 2. Flow curves of the ball-milled zirconia suspensions with a solid loading of 31 vol% The gray area represents the range of shear rates corresponding with the shear rates during tape casting.

Figure 3. Time dependence of complex viscosity during polymerization of ceramic suspensions. The curves represent the fit of the Hill model to the datasets and its extrapolation.

Table 2. Parameters of the polymerization process derived from the Hill model.

| Epoxy solution         | Processing time (min) | Equilibrium viscosity (kPa.s) | Polymerization time (min) |
|------------------------|-----------------------|-------------------------------|---------------------------|
| Na-PAA                 | 68                    | 71                            | 142                       |
| PC 75                  | 80                    | 24                            | 120                       |
| PC 75 + extra epoxy    | 83                    | 78                            | 185                       |
on the curing behavior of the suspensions has been described in our previous work [30]. This inconvenient effect of the ammonium-based dispersant could be overcome by an overdosage of the epoxy resin with the respect to the stoichiometric ratio of EGDGE:DPTA. In our case, based on previous results [30], an extra addition of 25 wt% of epoxy resin (EGDGE) substituted the disabled epoxy groups. As a result, a final complex viscosity of 78 kPa.s was reached. The curing time was in this case around 3 h. The handling strength of a wet tape was qualitatively improved in comparison with tapes prepared with a stoichiometric amount of EGDGE, where the strength of a wet tape allowed neither safe peel-off from the glass carrier nor tape transfer to the drying chamber.

3.2. Drying and heat treatment of the tapes

No problems associated with drying cracks were found. Unfortunately, during the drying period the tapes did not remain flat and warping of the tapes occurred. The warpage was reduced during the debinding step. The binders were successfully removed at 900°C and no cracking during debinding occurred. The pore size distributions in the tapes after drying and debinding are shown in Figure 4.

Contrary to the better particle size distribution in the suspensions stabilized with Na-PAA, the green bodies (Figure 4a) and bodies after debinding (Figure 4b, c) prepared with Na-PAA were characterized by larger pores than the bodies prepared with PC75. Moreover, a pore-opening effect in Na-PAA bodies was observed when comparing the pore size distributions in the Na-PAA bodies heated to 700°C and 900°C (Figure 4b, c).

The pore coarsening at the beginning of the sintering is related to the inhomogeneous distribution of ceramic particles in the green body. The PC 75 samples did not show any pore size coarsening and, therefore, we assumed a better particle packing of the PC 75 samples. The final flattening of the samples occurred during sintering between sapphire plates. Due to their fine structure, the tapes (Figure 5) were deformed by creep during sintering and perfectly flat samples were obtained.

The creep behavior and fine polished sapphire sintering plates were critical to obtaining flat tapes after sintering. A shrinkage of 31% was measured on the samples after sintering for in-plane and out-of-plane directions for the samples sintered at 1450°C. The relative densities of the samples sintered at 1450°C and 1550°C are summarized in Table 3. The samples prepared with Na-PAA reached lower sintered densities than the samples prepared with PC 75. The mean values of relative densities of the Na-PAA and PC 75 samples sintered at 1450°C were 99.19% and 99.42%, respectively. This result could be results of impaired sinterability of the zirconia ceramics with sodium traces. From the initial suspension composition, we estimated that the sintered Na-PAA samples consisted of 0.065 wt% of sodium. It has been reported in the work of Liu et al.

Figure 4. Pore size distribution of the (a) green bodies and (b) bodies after heating to 700°C (c) bodies after heating to 900°C.
that small amounts of Na$^+$ ions can effectively hinder sintering. Moreover, they showed that sodium ions in a concentration higher than 0.81 wt% improved the stability of the tetragonal phase. The stabilization effect of Na$^+$ ions was attributed to the occupation of the vacant sites in the zirconia, hindering the t − m transformation. We supposed that even lower concentrations than 0.81 wt% of Na$^+$ ions could affect the sintering behavior of zirconia ceramics. The mean values of relative density of both types of samples, Na-PAA and PC 75, sintered at 1550°C, were lower compared to samples sintered at 1450°C. For the explanation of this phenomenon, we need to look at the phase composition of the samples. The XRD analysis of the samples sintered at 1550°C revealed a (111) monoclinic peak in addition to tetragonal peaks (Figure 6a).

The (111) monoclinic peak is the most intensive diffraction peak of the monoclinic phase and its presence is considered to be a good marker of a small amount (~1 wt% in our case) of a monoclinic phase in the sample [38]. The occurrence of monoclinic phase (especially on the surface) can be attributed to the mean grain size of about 800 nm, which is close to the critical grain size for the 3Y TZP ceramics [14]. A small amount of cubic phase was also detected in samples sintered at 1550°C by a reflection of the (200)
plane of the cubic lattice (Figure 6b). Diffractions with higher intensities overlap with diffractions of the tetragonal lattice. The evolution of the cubic phase in the 3Y-TZP ceramic can be explained by Y$^{3+}$ ions segregating along the grain boundaries, as observed by Matsui et al. [39]. Unfortunately, the intensities of cubic diffractions were too low to exactly quantify and compare the amounts of cubic phase in the Na-PAA and PC 75 samples. Both additional phases, monoclinic and cubic, have a lower density than the tetragonal phase has. Because we kept the theoretical density 6.08 g.cm$^{-3}$ constant for the calculation of all the relative densities, the presence of a small amount of other phases was responsible for a slight decrease in the relative densities of samples sintered at 1550°C. Only statistically insignificant differences in the mean grain size (Table 3) as well as in the grain size distribution (Figure 7) were found to exist between the Na-PAA and PC 75 samples. Therefore, we assume that Na$^+$ ions did not significantly affect the grain growth.

### 3.3. Biaxial strength of the tapes and fracture toughness

The biaxial strength of the tested tapes is given in Table 4. The corresponding Weibull plots are shown in Figure 8.

The samples prepared with Na-PAA reached Weibull strengths of 1090 MPa and 1244 MPa for the samples sintered at 1450°C and 1550°C, respectively.

The samples prepared with PC 75 were characterized by a substantially higher strength compared to the Na-PAA samples. Weibull strengths of 1765 MPa and 1805 MPa were obtained for PC 75 samples sintered at 1450°C and 1550°C, respectively.

The Weibull moduli of all samples were statistically similar, reaching values between 6–7. Two main differences between the Na-PAA and the PC 75 samples were observed (Figure 8). The first difference was the overall strength dissimilarity between the Na-PAA and the PC 75 samples. The second difference was the smaller shift of the strength between the PC 75 samples sintered at 1450°C and 1550°C when compared to the shift of the strength observed for the Na-PAA samples sintered at the same temperatures.

The huge difference in the biaxial strength between the Na-PAA and the PC 75 samples can be attributed to the different fracture toughness of the samples. The fracture toughness of Na-PAA and PC 75 samples sintered at 1450°C is graphically compared in Figure 9. The statistically significant difference between the fracture toughness of Na-PAA and PC 75 samples can be derived from Figure 9. The mean value of $K_{IC}$ for the Na-PAA samples was 7.8 MPa.m$^{0.5}$, whereas the mean value of $K_{IC}$ for the PC 75 samples reached 12.3 MPa.m$^{0.5}$.

According to Liu et al. [37], the sodium ions could occupy the vacant sites in the zirconia and hinder the t–m transformation. Thus, the presence of Na$^+$ ions in the structure had a detrimental effect on the fracture toughness of Na-PAA ceramics. This effect can also explain the higher sensitivity of Na-PAA samples to grain growth, causing a bigger shift between the strength of Na-PAA samples sintered at 1450°C and 1550°C. We assume that the larger grain size of the Na-PAA samples sintered at 1550°C increased the driving force to t-m transformation overcoming the stabilization effect of Na$^+$ and thus increased the strength (and fracture toughness) of Na-PAA ceramics more than in the case of PC 75 samples. On the other hand, the possible increase in fracture toughness due to grain growth in the high-strength PC 75 ceramics was offset by bigger critical defects caused by microstructural coarsening and surface t-m transformation [14,40].

The highest biaxial strength of thin unpolished zirconia tapes has been reported by Fleischhauer et al.

![Figure 7](image_url) Normalized grain size distributions represented by corrected intercept lengths measured on the Na-PAA samples and PC 75 samples sintered at (a) 1450°C and (b) 1550°C.

| Table 4. Biaxial strength of the zirconia tapes. |
|-----------------------------------------------|
| Sample | Average Strength (MPa) | Weibull Strength (MPa) | Weibull Modulus (-) | Number of Measurements (-) |
|--------|------------------------|------------------------|-------------------|-----------------------------|
| Na-PAA 1450°C | 1022 ≤1020 | 1090 ±16 | 6.59 ±1.44 | 40 |
| Na-PAA 1550°C | 1165 1244 +15 | 1461 ±1.78 | 6.24 ±1.75 | 36 |
| PC 75,450°C | 1655 1765 ±15 | 1865 ±15 | 7.25 ±1.46 | 47 |
| PC 75,550°C | 1689 1805 ±15 | 1905 ±15 | 6.19 ±1.45 | 35 |
They achieved a biaxial strength of 1634 MPa and 2162 MPa for the rough and the smooth side of a 140 µm thick tape, respectively. Masini et al. [24] have later reported a strength of 1819 MPa and 1854 MPa for the rough and the smooth side of a 90 µm thick tape, respectively. In the present investigation, the tapes were randomly oriented during strength testing and no surface roughness effect was observed. Taking into account the average of reported strength values, and with respect to the effective loaded volumes of tapes with different thicknesses [17], the tape developed in the present investigation exhibited similar or even better strength values compared with the reported studies.

The flexibility of the samples was tested in 3-point bending, using two different support spans, 50 mm and 30 mm. The sintered samples with a thickness of about 75 µm were bent until failure. The flexibility of sintered zirconia tapes is demonstrated in Figures 10 and 11. The samples tested using the 50 mm span were pushed through the support gap without any damage to the sample. It demonstrated that a bending radius of ~25 mm could be achieved. The limit in the sample flexibility was obtained at the 30 mm support span.
4. Conclusions

Thin zirconia tapes were prepared by the water-based gel-tape casting method. This processing method enabled the preparation of ceramic suspensions with a reasonably high solid loading of 31 vol% of the zirconia powder with a mean particle size of about 100 nm. A significant effect of different dispersants on the properties of sintered ceramics was observed. The sodium-based dispersant negatively affected the mechanical properties of sintered tapes. The optimized zirconia tapes with a thickness of 190 µm reached a characteristic biaxial strength of 1805 MPa. The flexibility of the tapes was demonstrated in the 3-point bending configuration with tapes of 75 µm in thickness. A maximal deflection of 10.5 mm was reached when using the 30 mm support span, whereas no fracture was obtained using the 50 mm support span. The developed gel-tape casting method represents a novel processing possibility for high-strength flexible ceramic sheets.

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Data availability Statement

The data that support the findings of this study are available from the corresponding author, P. Stastny (Premysl.Stastny@ceitec.vutbr.cz) upon reasonable request.

Disclosure of potential conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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