

Influence of pressure-assisted polymerization on the microstructure and strength of polymer-infiltrated ceramics

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1 Introduction

Compared to conventional materials, composites have the potential to tailor the mechanical performance by offering a combination of properties in two phases. Ceramics and polymers are highly suitable for the construction of composites with an optimized mechanical behavior, due to their different material properties. While ceramic materials show excellent mechanical, biomechanical, tribological and high temperature properties, polymers are an example of materials with higher ductility and low elastic modulus. The classic approach to combine these two materials is to imbed ceramic particles in a polymer matrix. Due to the filling with ceramic particles, the strength, the elastic properties and the tribological resistance rise[1-4]. Adding the facts that the manufacturing costs are low and both materials are biocompatible, it is no surprise that polymer ceramic composites are in frequent use for dental restorations[5].

A further improvement of the material properties was found using this structural approach: By the use of two self-interpenetrating networks, the weak point of common polymer ceramic composites, unbounded ceramic particle, can be prevented. Through the replacement of loose ceramic particles in the polymer matrix by a stable ceramic matrix, higher strength, higher elastic modulus, higher toughness and better wear resistance are possible[6-9]. Higher fracture toughness, higher crack resistance and higher mechanical properties in general have been reported on similar structured polymer ceramic composites used for tissue engineering[10,11].

This interpenetrating microstructure can be reached by infiltrating a liquid monomer in a porous ceramic network. Similar to classic polymer ceramic composites, the ceramic surface is modified with an adhesion promoter to improve the interface strength between the organic polymer and the inorganic ceramic phase[12]. After the porous ceramic is completely filled with monomer, the crosslinking of the monomer is started by a thermal activation step. The challenging part of this manufacturing method is the unavoidable volume shrinkage during polymerization. A polymerization shrinkage of 8.8 % for UDMA and 14.4 % for TEGDMA was measured elsewhere[13]. Due to the polymerization within the capillaries of the porous ceramic, in which monomer supply is limited, the polymerization shrinkage generates pores (defects) in the microstructure. Furthermore this leads to an interfacial boundary loss between polymer and ceramic.

The aim of this work was to prove, that pressure during polymerization as well as a reduced polymerization speed can reduce the occurring polymerization shrinkage, which leads to a reduced appearance of defects in the microstructure of Polymer Infiltrated Ceramics (PICs). Similar materials with interpenetrating microstructure

such as metal matrix composites show improved fracture toughness. Hence, the fracture toughness, the R-curve behavior and the crack path through the microstructure of PICs were investigated additionally.

2 Materials and Methods

To characterize the used materials, the preforms as well as the organic components were tested. The aluminum oxide preforms (Al_2O_3) (15x20x12 mm) were provided by CeramTec GmbH, Germany. To quantify the relevant properties, two different methods were used. With the Brunauer-Emmet-Teller-Method (BET), the surface area of the preforms were determined. Mercury porosimetry was used to quantify the porosity of the preforms.

A mixture of two monomers was used to infiltrate the preforms. Triethylenglycolmethacrylat (TEGDMA) and Urethanedimethacrylate (UDMA) were mixed in a 1:1 (mol) ratio. Additionally, 0.3 % of a common heat sensitive polymerization starter (Dibenzoylperoxid) was added. Due to the consistence of two monomers, the cured material is named co-polymers.

To compare the strength of the primary materials with the PICs, the strength of the co-polymers and the unfilled preforms were measured. Whereas the preforms could be tested with the biaxial test which was also used for the PICs, the strength of the co-polymers was measured with tensile tests. The specimen geometry was chosen according to the standard EN 10002-1. To manufacture the specimens, the monomer mixture was casted in an open mold (of the specimens shape) and polymerized subsequently. To polymerize the specimens, the mold was stored in an oven at 100 °C for 5 hours. The tensile tests were made at ambient conditions with a loading rate of 10 $\mu\text{m/s}$. The strain was measured with an extensometer directly on the specimens.

To improve the adhesion between inorganic and organic components, an adhesion promoter was used[14]. To reach a proper adhesion between ceramic and polymer, the preforms were modified with Methacyloxypropyltrimethoxysilane (MPS) before the monomer was infiltrated. The surface modification with MPS was carried out with the high-flow-infiltration-method to guarantee an equal coating of MPS on the ceramic surface. The details of the surface modification method are described elsewhere[15]. Using this method, the complete preform surface is coated with a sufficient amount of MPS. Before the monomer mixture was infiltrated, the preforms were dried at 100 °C and a pressure of 200 Pa for 12 hours.

The infiltration of the preforms was achieved with a dip-coating process. The driving forces to infiltrate the preforms are the capillary forces. To reach a complete monomer infiltration without trapped gases, the constantly stirred monomer mixture and the preforms were stored in an infiltration chamber at a pressure of 200 Pa. To

lower the viscosity of the monomer mixture, the temperature of the chamber was raised to 40 °C. After a complete gas removal of the monomer and the preforms (approx. 12 h), the preforms were half submerged in the monomer mixture for 3 h. After the dwell time, the capillary forces lead to completely monomer soaked preforms. Due to the capillary forces, monomer appeared on the top-plane of the preforms. Afterwards, the specimens were totally submerged inside the monomer mixture and the pressure was raised to atmospheric pressure. After a second dwell time of approx. 1 h, the completely filled preforms were removed and vacuum packed with a sufficient amount of monomer in a commercial polymer wrap. Surrounded by the monomer mixture and protected in the hermetically closed polymer wrap, the specimens were polymerized in the pressure chamber.

The conversion from monomer to polymer is started due to the thermic decay process of the polymerization starter. The details of the activation process and the polymerization are described elsewhere[16]. To activate the polymerization process, the infiltrated preforms were heated up to a temperature of 100 °C. Depending on the heating rate, the polymerization started between 60 °C and 80 °C. Due to the applied temperature of 100 °C for at least 2 h, a high conversion rate was expected. To investigate the influence of the heat treatment on the mechanical properties and the microstructure of PICs, two different heating rates were used. The fast and slow heating rates were performed at 2 K/min and 0.1 K/min, respectively. The influence of pressure during polymerization on strength and microstructure was examined using the pressure levels 0 MPa, 100 MPa, 200 MPa and 280 MPa. Since the pressure chamber was designed for a maximum pressure of 300 MPa, the process pressure was adjusted to slightly under the construction limit. Due to the rising temperature and the simultaneously occurring volume dilatation inside the pressure chamber, the testing machine was driven in the force controlled mode during the polymerization process. Nevertheless, stick-slip effects of the used O-ring sealing occurred. To avoid sudden pressure drops, controlled cross head drives were performed to adjust the pressure inside the chamber to the defined level. After the polymerization process, the specimens were removed from the pressure chamber, cut in discs and the surfaces of all specimens were polished with the same procedure. To measure the materials strength, the 3-balls on 1-ball test (from now on called biaxial-test), was used. This test method is widely used to investigate the strength of brittle materials and was studied intensively by other researchers[17-19] (Fig. 1).

3 steel balls (1.3505, (100Cr6)) were positioned at an angle of 120° with a 5 mm distance from the center. The fourth ball to apply the force is positioned at the center over the specimen. To calculate the fracture strength σ_{\max} , formula 1 which was developed by Börger et al.[19] was used.

$$\sigma_{max} = f \cdot \frac{F}{t^2} \quad (1)$$

Where F is the applied force, t the thickness of the plate and f a dimensionless factor that depends on the specimens geometry and the Poisson's ratio. Due to the high ratio of Al_2O_3 in PICs, a Poisson's ratio related to the Poisson's ratio of Al_2O_3 was approximated (0.25)[20]. A detailed description of the f is given elsewhere[19]. Börger et al. used round discs. Due to the cuboid preforms, the available discs had a rectangle shape. However, to calculate fracture strength an equivalent radius r' was used (formula 2).

$$r' = \sqrt{\frac{A}{\pi}} \quad (2)$$

The equivalent radius r' was calculated using the specimens plain A and π .

As shown by Quinn et al.[21], load point friction, eccentric loading, twisted specimens and improper alignment of the specimens are serious sources of error using 4-point-bending-tests. With the used experimental setup, eccentric loading and twisted specimens do not influence the measurement due to the concentrated contact on three balls. To avoid an improper alignment, a positioning device was used. As shown by Börger et al.[22], load point friction, buckling of the specimens and the size of the bearing balls can also be neglected by using the described experimental setup. Hence, the selected experimental setup to measure the strength of PICs shows several advantages compared to the 4-point-bending-test. The force was applied with a loading rate of 15 N/s, to ensure a measurement of the inert strength value.

To measure the fracture toughness, the standardized SEVNB-Method was used. All the PICs used for the investigation of the fracture toughness were polymerized with a pressure of 300 MPa and a slow heating rate. The insertion of the V-notch was realized with a razor blade and diamond paste (1 μm), to generate a sharp notch. After the notch was produced in the bars, the specimens were tested in a 4-point-bending setup to measure the residual strength. The fracture toughness (K_{IC}) was calculated using formula 3.

$$K_{IC} = \frac{F}{B * \sqrt{W}} * \frac{S_2 - S_1}{W} * \frac{3 * \sqrt{c}}{2 * (1 - c)^{1.5}} * I \quad (3)$$

Beside the force F , the geometric data B (specimen width), W (specimen height), I (stress intensity form factor) and c (deepness of the V-notch) are needed to calculate the fracture toughness. Detail for the calculation of the

stress intensity form factor, the experimental setup and the generation of the V-notch are described in the standard DIN CEN/TS 14425-5.

It is well known, that the radius of the inserted V-notch influences the measured fracture toughness significantly. With an increasing notch radius increased fracture toughness can be calculated misleadingly. Earlier analysis regarding the influence of the notch radii on fracture toughness for dense sintered ceramics showed that notch radii over 20 μm lead to an enhanced fracture toughness[23,24]. The radii generated in the tested PIC specimens are below the mentioned value.

To study the R-curve behavior and the strengthening mechanisms in PICs, a testing machine with in-situ monitoring of the crack propagation was used (Exakt 6000EA). To study the R-curve behavior, the load of the V-notched PIC bars was manually raised until crack growth was detected. As soon as crack growth appeared, the load of the specimens was reduced. To calculate the crack resistance (K_{IR}), formula 3 was used. To consider the crack length in the calculation of the K_{IR} , the actual crack length was entered as c . The actual crack length was measured with the in-situ monitoring of the testing machine.

3 Results

The results of the material characterization of the primary materials are listed in Table 1.

The used preforms are optimized to enable a fast infiltration process. The preforms offer a tree-like pore structure with big and small pores analog to the vascular system inside the human body. Hence, two different mean pore radii were measured using mercury porosimetry. The measured surface area is important to select the amount of MPS. To interpret the strength of PICs, the ceramic to polymer ratio is essential. For this reason, the porosity of the preforms was investigated. Comparing the filler to matrix ratio of common polymer ceramic composites for dental applications, the ceramic ratio of the manufactured PICs is lower[25]. The fracture strengths of the primary materials are needed to evaluate the strength of the manufactured PICs. Due to the high porosity of the preforms, the polymer strength is higher than the preform strength. The measure fracture strain is comparable with the fracture strain of other methacrylate polymers[26].

The results of the mechanical tests are presented in Fig. 2. The Weibull parameter σ_0 and Weibull modulus m as well as the process parameters and the annotation of Fig. 2 are listed in Table 2. The PICs polymerized with a heating rate of 2 K/min are diagramed with squares and the PICs polymerized with a heating rate of 0.1 K/min are diagramed with circles.

As shown in Fig. 2 and Table 2, PICs show a significant increase of strength. All PICs show a doubled or respectively tripled characteristic strength σ_0 compared to the unfilled preforms. Furthermore, a higher process pressure during polymerization leads to higher strength of PICs. The Weibull modulus m characterizes the strength distribution in a material. The Weibull modulus m of the unfilled preforms is comparable with the Weibull modulus m of PICs polymerized at ambient pressure. In case of an increased pressure during polymerization, the Weibull moduli m of PICs increased measurably (an exception is batch nr. 6).

With ambient conditions pressure during polymerization, the influence of the heating rate is significant. In case of pressure assistance during polymerization, no considerable impact of the heating rate was recognizable. The Weibull modulus m was not strongly affected by the heating rate. Hence, if batch nr. 6 is neglected, a tendency to slightly higher moduli is recognizable.

The influence of pressure during polymerization is also recognizable in the microstructure of PICs. For the high resolution images shown in Fig. 3, the specimens were polished before recording.

While the polymerization at ambient pressure leads to a huge amount of defects in the PICs, the polymerization with high pressure does not show visible defects. Comparing these results with the measured strength, a direct correlation between strength and microstructure is possible.

The fracture toughness of PICs and preforms were measured using the SEVNB method. The results of the tests are shown in Table 3 [27].

The fracture toughness of PICs was found to be much higher than the fracture toughness of the co-polymers and the unfilled preforms.

To investigate the R-curve behavior of PICs, V-notched 4-point bending bars were tested on a testing machine which enables a manual loading in sub- μm steps. The dependency of the fracture toughness on the crack length is shown in Fig. 4.

All tested specimens show an increasing crack resistance (K_{IR}) with an increasing crack length. The crack resistance calculated after the first visible crack growth is approx. $1.5^\circ\text{MPa}\cdot\sqrt{\text{m}}$. The graphs of all tested specimens show a comparable behavior. In addition to the measured crack resistance, an investigation of the crack path through the interpenetrating structure was determined. After crack growth occurred in the tested PICs, the opened cracks were recorded with the optical camera of the testing machine. The disadvantage of this camera is the low resolution. Due to the fact that the cracks are only visible while loading, no high resolution images of the loaded specimens can be shown. The images in Fig. 5 show some representative cracks in the PICs. To

visualize the crack in the microstructure of the tested PICs, a high resolution image of a specimen with inserted crack is shown in Fig. 5d. The test procedure of this specimen was discontinued before total failure occurred.

Due to the low resolution of the camera in the testing machine, the images in Fig. 5a to 5c were post-processed to visualize the crack. Beside the crack path through the interpenetrating structure, different strengthening effects are shown in the images. In Fig. 5a crack branching and in Fig. 5b polymer bridging and crack deflection are shown. The crack path mainly occurs along the interface, which can be seen in Fig. 5b and c. A polymer bridge was also found using a scanning electron microscope (SEM) (Fig. 5d). However, the pictured crack is not as explicit as the other images due to the fact that the specimens cannot be loaded inside the SEM. For this reason, the crack is highlighted with white arrows. Similar to the results of shown light camera, the crack propagates along the interface.

4 Discussion

Analog to similarly structured composites, a significant increase in strength was found for the manufactured PICs compared to the unfilled preforms. An over than three times higher strength was measured. Furthermore, the process pressure and the heating rate show an impact on strength. The process pressure shows a significant influence on the mechanical strength and the microstructure of PICs. A strength increase of 15 % was found comparing the characteristic strength σ_0 of the tested batches. Simultaneously, no or respectively less defects occurred using a high process pressure. The applied pressure impacts the strength and the microstructure of PICs in two different ways. The first consequence is a higher degree of conversion and crosslinking, which leads to a slightly higher polymer strength[28]. The second effect of the process pressure is a higher amount of monomer in the preforms. Due to the applied pressure, the distance between the monomer molecules is reduced significantly[29,28], which leads to a higher amount of monomer and simultaneously of polymer in the PICs. This pressure-induced raise in monomer density leads to a reduced amount of defects in the PICs. The process includes different changes in the polymerization procedure, for which reason it is explained in detail.

During the conversion from monomer to polymer, a volume reduction of approximately 10 % occurs[13]. In pure monomer, the volume reduction is characterized by isotropic shrinkage. If a permanent flow of monomer towards the polymerization centers is possible, the polymerization occurs without the generation of pores. Due to the given three-dimensional capillary structure and polymerization towards the center of the preforms, the volume reduction generates defects in form of pores inside the preforms. As a consequence of the limited

amount of monomer in the preforms and the restriction of monomer mobility due to spatial separation and the capillary forces, the polymerization shrinkage generates a huge amount of defects in PICs (Fig. 3a).

In the case of high pressure during polymerization, the shrinkage-induced defects are immediately filled up with liquid monomer. Due to the applied isostatic pressure the uncured monomer is pressed inside the occurring defects. With this technique, the so far impossible monomer flow towards the polymerization center inside the preforms is possible. Comparing the results of the microstructural analysis (Fig. 3), a significant reduction of defects can be seen with a high pressure during polymerization. Using a pressure of 100 MPa, a reduced defect density was found. With process pressures larger than 200 MPa no defects occurred inside the PIC structure.

Compared to the unfilled preforms, the Weibull moduli m of the PICs polymerized without pressure are similar. In the case of high pressure polymerization, the Weibull moduli m increase with an increasing pressure. As an exception, batch nr. 6 shows a reduced Weibull modulus. This was probably because of a 40 % reduced amount of specimens and premature failure of one tested specimen (Fig. 2). Thus, the polymer filling leads to a compensation of the biggest defects and a more equal distribution of defects.

In pressure-less polymerization tests, the reduction of the heating rate had positive effects on the mechanical strength. In contrast, the variation in the heating rate at a high process pressure, did not affect the strength significantly. Two causes were encountered for this behavior. The first one is enhanced crosslinking in case of a polymerization at reduced heating rates[30], which increases the polymer strength. The second one is again related to the mobility of the monomer molecules during polymerization[30,31]. It is commonly known that a reduced heating rate leads to a delayed polymerization start, which means that the polymerization takes place at higher temperatures. Additionally, a reduced heating rate leads to a slower polymerization. A higher temperature during polymerization combined with a reduced conversion speed increase the mobility of the monomer molecules drastically. To describe the impact of the changed polymerization speed and the changed monomer mobility in the case of a polymerization without pressure, the different polymerization conditions are characterized as follows:

1. Due to the fast heating rate and the low heat conductivity of the monomer the polymerization starts at the outermost layer of the monomer that surrounds the preforms. The raised and continued heat flow leads to a directed polymerization towards the center of the preforms. After the outermost layer of the monomer that surrounds the infiltrated preforms is polymerized, the subsequent polymerization shrinkage generates a negative pressure which leads to a monomer flow from the center out of the preforms.

2. At slow heating rates, the temperatures inside the monomer and the preform are nearly equal. Therefore, the polymerization starts at many randomly distributed points in and around the preform without a directed polymerization. The combination of the dislocated polymerization start and the higher monomer mobility can lead to a filling of generated defects in the preforms.

In the case of pressure polymerization, the monomer flow is dominated by the expanding monomer, for which reason the heating rate does not have a strong influence.

The fracture toughness yielded a mean value of $2.3 \text{ MPa}\cdot\sqrt{\text{m}}$. Compared with the fracture toughness of pure copolymers and the fracture toughness of the unfilled preforms, the increase of fracture toughness is significant. This raise is an effect of the polymer filling, the interpenetrating microstructure and their resulting strengthening mechanisms. Crack growth in PICs is only possible, when the maximum stress in the stress field around the crack tip is higher than the adhesion between ceramic and polymer, the strength of the ceramic or the strength of the polymer. Due to the interpenetrating matrix structure cracks need to cross all phases. However, a preferred crack growth along the interface between the ceramic and polymer was observed (Fig. 5c,d). Therefore, the adhesion between ceramic and polymer has a direct effect on crack growth. The high resolution microstructure analysis confirms a preferred crack growth along the interface (Fig. 5d). In a previous research, an interface adhesion of approx. 18 MPa was found in pull-off tests with polished surface[32]. Comparing the measured polymer and preform strength (Table 1) with the interface adhesion, the preferred crack growth along the interface correlates with the measured strength and respectively adhesion values. The advantages of the interpenetrating microstructure becomes obvious when the fracture toughness of PICs is compared with the fracture toughness of common polymer ceramic composites ($K_{IC} = 1.5 - 1.9 \text{ MPa}\cdot\sqrt{\text{m}}$ [33,34]). Nevertheless, the fracture toughness of dense aluminum oxide (approx. $3.7 \text{ MPa}\cdot\sqrt{\text{m}}$)[24] could not be reached.

Beside higher fracture toughness a strong R-curve behavior was found. This means that the crack resistance (K_{IR}) increases with increasing crack length. Rising R-curve behavior is especially in brittle materials a required effect due to its contribution to defect tolerance. While the initial K_{IR} -values were measured at approx. $1.5 \text{ MPa}\cdot\sqrt{\text{m}}$ at crack length $c = \text{V-notch}$, the K_{IR} raised to values as high as $4.5 \text{ MPa}\cdot\sqrt{\text{m}}$ at $c = 2.2 \text{ mm}$. This means that crack growth in PICs is hindered by different strengthening mechanisms[35]. In the tested PICs, the strengthening is attributed to crack branching, crack deflection and polymer bridges (Fig. 5).

However, since the R-curve behavior in unfilled preforms as well as monolithic ceramic is significantly smaller, the strongest contribution to the R-curve behavior of PICs is attributed to polymer bridges. Polymer bridges hinder the crack opening and simultaneously reduce the stress at the crack tip[36,37,11]. The observed polymer

bridges occurred in areas with large polymer ranges (Fig. 5b and d). In areas with small polymer ranges the polymer strain is restricted to a view μm due to low volume. It is assumed that a large number of small polymer bridges occur directly behind the crack tip. However, these small polymer bridges could not be found due to the insufficient resolution of the camera used. With a mean failure strain of 6.8 % (Table 1) for the used co-polymers, visualizable polymer bridges are only possible in large polymer ranges.

The R-curve of composites usually shows a plateau after the initial increase of crack resistance. Shah et al.[38] relates the occurrence of the plateau to the state where the forming and breaking of polymer bridges are generated at a similar rate. This behavior was not found in the present analysis. It is assumed, that the tested crack length was not long enough to form a plateau. Longer crack lengths were not possible due to the used specimen size.

Other strengthening effects typical for ceramic polymer composites are crack branching (Fig. 5a) and crack deflection[39]. Crack branches generate several stress concentration centers, which leads to a reduced stress at the main crack[20]. Crack deflection has been identified as the main strengthening mechanism in common composites with a high filler to matrix ratio[40]. In contrast to common composites where crack deflection is mainly caused by large ceramic particles, crack deflection in PICs mainly occurred along big polymer ranges (Fig. 5c). Both phenomena are effective strengthening mechanisms and lead to strong R-curve behavior in PICs.

5 Conclusion

The process parameters, pressure and heating rate show, a strong influence on the strength and microstructure of PICs. An optimized, defect-free microstructure was obtained with a process pressure of 300 MPa. In addition to strength, an increase of the Weibull moduli m was achieved with an increasing of the process pressure. This behavior implies, that a more even defect distribution is generated with a pressure assisted polymerization. The influence of the heating rate on strength is only significant at ambient pressure, due to interactions between the two process parameters. Among an improved mechanical strength, an increased fracture toughness compared to the porous preforms was established for PICs. Furthermore, a distinct R-curve behavior was observed. The rising fracture toughness with an increasing crack length is caused by strengthening mechanisms like crack deflection, crack branching and polymer bridges. The crack path through the interpenetrating structure mainly occurs along the interface between ceramic and polymer.

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7 References

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Figures

Fig. 1: Experimental setup of the biaxial test

Fig. 2: Weibull distribution of the tested PICs; ■ 0 MPa, 2 K/min, ● 0 MPa, 0.1 K/min, ■ 100 MPa, 2 K/min, ● 100 MPa, 0.1 K/min, ■ 200 MPa, 2 K/min, ■ 200 MPa, 0.1 K/min, ■ 300 MPa, 2 K/min, ● 300 MPa, 0.1 K/min, ▲ Unfilled preform

Fig. 3: Microstructure analysis of the manufactured PICs (fast heating); a) Manufactured under atmospheric pressure b) Manufactured with 100 MPa, c) Manufactured with 200 MPa, d) Manufactured with 300 MPa

Fig. 4: R-curve behavior of PICs

Fig. 5: Cracks in PICs; a) crack branching, b) polymer bridging and crack deflection, c) preferred crack path along the interface, d) high resolution image of a polymer bridge. The contrast and the brightness of the images 5a), 5b) and 5c) in the area of the cracks were intensified.