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Strong and super tough: Layered ceramic-polymer composites with bio-inspired morphology

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Abstract

Bio-inspired layered ceramic-polymer composites with high strength and toughness were prepared from sintered aluminum oxide ceramic sheets and cationically curing epoxy resins toughened with poly(ϵ -caprolactone) (PCL). The architecture of the composite is inspired by nacre but is arranged on a larger scale. Ceramic sheets with a nominal thickness of 250 μm were assembled into composite plates by adhesive layers with a nominal thickness of 20 μm . Before the manufacturing of the composites, the stress-strain properties of the polymer component were tailored by the variation in the PCL content between 0 and 39 wt%. For composites with 4 and 15 ceramic layers, the bending strengths achieved 327 MPa and 376 MPa, which are higher than that of pure ceramic sheets. Moreover, composites with 15 ceramic layers show a 16 times higher toughness compared to that of the pure ceramic sheets. The results indicate that the toughness of the layered composites increases significantly with the number of layers. Inspired by the geometrical ratio of the natural sheet composite nacre, we have achieved a similar strength but a 2 times higher toughness than nacre by only adding up to 6 vol% of the polymer.

KEYWORDS

cationically curing epoxy resins, composites, layered ceramics, mechanical properties, strength, toughness

1 | INTRODUCTION

Nature knows numerous ceramic-organic/polymer composite materials with superior mechanical properties. Main examples are bone, dentine, nacre or deep-sea glass sponge where the properties are mainly determined by the synergy of the material's morphology and composition. Thus, the damage tolerant behavior and the high fracture toughness originate from a number of mechanisms.¹⁻⁶ Among others, a significant toughness has been achieved by a layered or brick-structured architecture. Many natural composite materials are made up of hard mineral and weak organic components, which are organized in continued layers or segmented structures. The unique nanostructure of nacre,

for example, is mainly composed of an aragonite phase (~95 vol%) in the form of aragonite polygonal sheets of approximately 8 μm in diameter and 400-500 nm in thickness. The sheets are arranged in layers and are bound together by a much thinner biopolymer film of ~20 nm thickness.^{5,7} In such composites, a collection of microcracks naturally becomes deflected along the brittle bricks or layers, which allows for the dissipation of energy in the multicracks.⁸ However, the enormous difference in the component stiffness is one of the most important factors for high damage tolerance and fracture toughness of natural and man-made composite materials.^{9,10}

Following a bio-inspired design, ceramics received high attention in recent years as the base material for modern

biomimetic composites, which usually show a lower strength but superior fracture toughness in comparison with its brittle components.^{2,11-14} For improved toughness, the avoidance of catastrophic failure behavior is required and crack propagation through the entire material must be hindered. Brittle fracture can be avoided by a smart materials design, where soft and hard phases are distinct in size and geometry.¹⁵ For example, the fracture toughness of monolithic ceramics has been successfully enhanced by incorporating a secondary phase in form of coatings, fibers, whiskers, platelets, or particles.¹⁶⁻¹⁹ Pure ceramic bodies with a layered structure and improved damage tolerance are also known from the literature.^{20,21} These man-made composites either contain alternating highly dense and highly porous ceramic layers or have been formed from dense ceramic layers separated by weak interfaces, for example, made of carbon, boron nitride, zirconium oxide or monazite.²²⁻²⁹ The main mechanisms for increasing the fracture toughness are based on crack deflection and crack branching into the weaker composite component. By selective adjustment of the residual stresses, the mechanical properties could also be affected considerably.^{30,31} Nevertheless, due to the pure ceramic nature of such composites, all fracture processes on the micro- and macroscopic scale are brittle. Despite improvements in toughness, work of fracture, and R-curve behavior, no mechanisms regarding quasi-ductile macroscopic behavior have been realized to date.

In particular, many new nacre-like composites with excellent mechanical properties have been reported quite recently.³²⁻³⁹ The failure of human-designed bio-inspired composites based on ceramics and polymers can be divided into 2 stages. Initially, during the first stage, at a subcritical load, there is no crack propagation. The material remains undamaged, except from possible microcrack formation and non-elastic deformation of the soft component. The limit of this subcritical loading can be increased by the presence of a soft component with sufficient flexibility, amount, and adhesion to the ceramic material.^{10,40} The soft component leads to a stress distribution within the entire composite, avoiding stress peaks in the brittle and hard component. Such a reinforcement mechanism is mainly responsible for an increase in the composite load bearing capacity. During the second stage, a main crack starts to grow, derived from twisted microcracks, which are dissipated according to the composite microstructure design. The main crack can be further diverted or branched into the polymer or at the ceramic-polymer boundary.³⁸ Such mechanisms become more pronounced with additional composite layers. The growth of the main crack causes usually a load drop or a nonlinearity of the macroscopic load-displacement behavior. Generally, this nonlinear behavior is referred to as “pseudo-plastic” because its

physical background is not a grain shift or a displacement recombination, as in metal. The failure in the brittle components and consequent stress redistribution originate from the interplay with the soft component.

Furthermore, the influence of the adhesive properties on the mechanical behavior of the composites is pivotal and is hence investigated in this study. The damage tolerant behavior and the nonbrittle failure of man-made composites are also enabled, among other mechanisms, by the significant difference in the deformability of its constituents, namely, a ceramic and a polymer. Moreover, a good ceramic-polymer adhesion is needed to ensure the structural integrity of the composite. Most adhesives with a combination of high strength and high toughness have a heterogeneous morphology due to polymer segregation during curing or because they are nanocomposites.⁴¹⁻⁴³ For this study, cationically curing epoxy resins were selected as adhesives because their properties and morphology can be changed in a wide range by a very controlled variation in the composition.⁴⁴ This variation is mainly carried out by the addition of polyols, which are polymeric alcohols with more than 1 alcohol group. These alcohols are integrated into the epoxy network by a chain transfer reaction called an “activated monomer mechanism”.⁴⁵ If water is present, then it is integrated into the polymer network by the same mechanism.⁴⁶ If crystalline polyols such as the ones based on poly(tetrahydrofuran),⁴⁷ poly(ϵ -caprolactone) (PCL)⁴⁸⁻⁵³ or other polyesters^{54,55} are applied, then a pronounced toughening can be achieved. The obtained polymers exhibit a high elongation at break combined with high failure strength and a high glass transition temperature. When these polymers are in this combination, they are superior to other polymers. Therefore, the selection of adhesives for multilayered ceramic-polymer composites presented in this study is based on the above-mentioned publications and is discussed later in detail.

Layered composites with high fracture toughness, such as nacre and spicules of deep-sea glass sponges feature a multiscale structure with several hierarchical levels and a high number of layers. The phenomena, which is reasonable for the mechanical performance are very complex and can originate from different length scales.^{3,6} However, to examine the crack deflection mechanisms linked to the properties of the polymer and the number of layers we performed experiments with bio-inspired artificial composites having only a few ceramic layers. The macroscopic behavior was then evaluated in terms of bending strength and toughness.

The toughness, defined as the area under the experimental stress-strain curve, is a sample-size-independent parameter widely used for biological materials. This property can be interpreted as how much mechanical energy per volume can be loaded onto a material before it fails.³ Materials

such as monolithic ceramics are very strong but fail at a low strain and are consequently brittle (i.e., not tough). Similarly, materials with a very high strain to fracture and low strength are also not tough. So, a tough material must be both strong and ductile (in the sense of high strain to fracture). Therefore, the toughness as a commonly used independent parameter was used for comparison reasons in this study and not the work of fracture.

2 | MATERIALS AND METHODS

2.1 | Preparation of the adhesives and the polymer samples for the tensile tests

The thermoinitiator benzyl tetrahydrothiophenium hexafluoroantimonate was prepared according to the literature.⁵⁶ One wt% (0.6 mol%) of this initiator was dissolved in cycloaliphatic diepoxide 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (Omnilane OC1005, IGM resins, Krefeld, Germany). The polymeric diol PCL with a mean molecular weight of 400 g/mol (CapaTM 2043, Perstorp UK Ltd., Warrington Cheshire, United Kingdom) was dissolved in the monomer initiator mixture in different amounts at 65°C. Samples with 0, 15, 23, 31, and 39 wt% PCL (named P0, P15, P23, P31, P39) were prepared. The sample assignment is shown in Table 1.

For the determination of the polymer's mechanical properties, resin plates were prepared in aluminum molds with dimensions measuring 290 mm × 120 mm × 4 mm, which were precoated with the release agent Acmosan 82-6007 (Acmos Chemie KG, Bremen, Germany) and preheated to 75°C. All samples were polymerized by heating from 90°C to 145°C within 5 hours. Afterward, they were jet cut to the sizes required for the following mechanical tests.

2.2 | Preparation of the composites and the pure ceramic samples for the bending tests

Four- and 15-layered composites were prepared from 250- μ m-thick ceramic sheets joined together by epoxy

resin layers with an approximately 20 μ m thickness. Sintered aluminum oxide sheets (KERAFOL, Keramische Folien GmbH, Eschenbach, Germany) with dimensions of 60 mm × 40 mm × 0.250 mm were applied. Before the bonding, the ceramic sheets were treated for 2 minutes with a solution of 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane (ECHTMO) (5% in isopropanol) and dried afterward for 30 minutes at 80°C. To maintain the correct thickness of the adhesive layers, 0.001 wt% glass microbeads with a nominal diameter of 21 μ m (Wolff Glaskugeln GmbH, Mainz, Germany) were added to the adhesives. Five different sets of 4-layered composites were produced from epoxy resin with a 0-39 wt% PCL content. In addition, 1 set of 15-layered composites having a 31 wt% PCL content was prepared (see Table 1). The 31 wt% PCL composition exhibited the highest strength and breaking strain values and was therefore chosen as the adhesive to fabricate the composite. All composites were prepared layer by layer in an aluminum mold and polymerized according to the neat polymers.

The mechanical properties of the ceramic sheets and the ceramic-polymer composites were evaluated by a 3PB test. Pure ceramic samples with dimensions of 6 mm × 2.5 mm × 0.25 mm (length × width × thickness) were prepared from the ceramic sheets using a diamond wire saw machine. Rectangular beams with dimensions of 6 mm × 2.5 mm × 1.06 mm and 18 mm × 4.5 mm × 3.85 mm for 4-layered and 15-layered composites, respectively, were cut from the composite plates by the same saw machine. The specimen thickness is given by the total thickness of the composite plate. Representative composite samples after the mechanical test are presented in Figure 1.

2.3 | Mechanical tests

Tensile tests of the polymer samples were performed in accordance with standard DIN EN ISO 527-2 shape 1BA at 24°C ± 1°C at a testing rate of 1 mm/min.⁵⁷ A Zwick-Z050 (Zwick GmbH, Germany) testing machine with 10 kN load cell was used. The tensile strength, strain at break, and deformation energy (toughness) were determined from the measurements. Each type of sample was evaluated by the testing of 8 identical specimens.

All bending tests were carried out under displacement control with crosshead displacement rate of 1 mm/min on a spindle testing machine Zwick 005 (Zwick GmbH, Germany) with 5 kN and 50 N load cells. The pure ceramic samples and the samples of the 4-layered composites, denominated as CP0, CP15, CP23, CP31, and CP39 according to the type of adhesive used (Table 1), were tested by loading in a 3PB test with a 4-mm support span.

TABLE 1 Composition and denomination of the adhesives and the prepared composites

PCL (wt%) in epoxy resin	Polymer abbreviation	Composite (4-layers)	Composite (15-layers)
0	P0	CP0	-
15	P15	CP15	-
23	P23	CP23	-
31	P31	CP31	CP31L15
39	P39	CP39	-

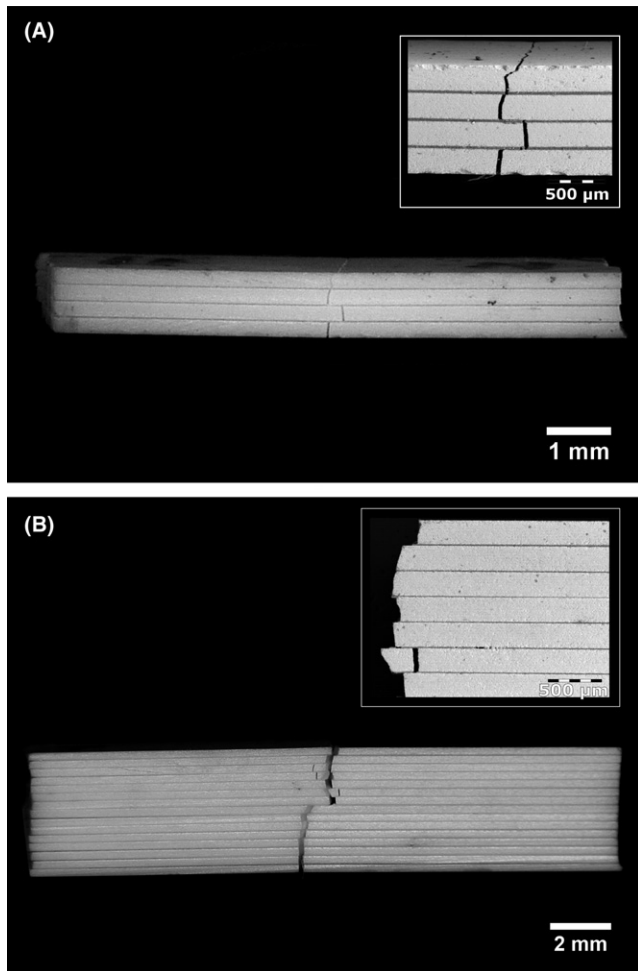


FIGURE 1 Composite specimen consisting of Al_2O_3 -ceramic sheets and polymer after mechanical testing: A, 4-layered composite; and B, 15-layered composite

For proper statistical relevance, 40 pure ceramic samples were examined. For each composite, 27-30 identical specimens were tested. A statistical evaluation of the bending strength was performed according to the Weibull analysis.⁵⁸ In addition, the Kolmogorov-Smirnov fit of goodness test (KS-test)^{59,60} was carried out.

Due to the small support span, the bending of the samples could not be measured directly during the test. Therefore, the cross-head displacement was recorded, which includes both the bending of the tested specimen and a displacement caused by the compliance of the experimental setup. A correction in the load cross-head displacement curves for each tested sample was then performed by a reference measurement of the system stiffness using a very stiff monolithic ceramic sample with a thickness of 20 mm and a width of 10 mm.

The properties of the composite with 15 ceramic layers denominated as CP31L15 (see Table 1) were evaluated in 3PB tests with a support span of 16 mm. Tests on 6 identical specimens were performed.

3 | RESULTS AND DISCUSSION

3.1 | Adhesive selection

The aim of this study is to improve the toughness of ceramic-based materials by the preparation of composites with a layered architecture. This improvement was carried out by adhesively bonding ceramic sheets forming a stack of 4 or 15 ceramic layers. For this purpose, the adhesive between the ceramic layers should have appropriate combination of strength and elasticity. In addition, the glass transition temperature (T_g) should be well above room temperature to maintain the high strength and stiffness at the highest temperature. From previous examinations, it was known that the properties of the cationically curing epoxy resins can be varied in a wide range by only moderate changes in the composition. Particularly, the addition of polyester polyols leads to improved strength and elasticity without strongly reducing the glass transition temperature compared to the pure epoxy resin. Therefore, this class of adhesives was selected. To select a proper starting point for the composition variation, literature data^{48-55,61,62} on the tensile strength and elongation at break and the glass transition temperature were evaluated and collected in Figure 2. This figure shows that the adhesive represented by the large triangle \blacktriangledown (PCL400 [23 wt%]) has a tensile strength of 58 MPa, an elongation at break of 3.7% and a T_g of 125°C. These results seem to be a good compromise among the 3 properties. Therefore, this adhesive was selected as the base, and the amount of PCL was varied for the examinations carried out here to improve the property profile for the preparation of the layered ceramic composites. In addition, the data for the pure epoxy resin are represented by the large black cube \blacksquare (ECC), showing that this polymer has a higher T_g but lower tensile strength and elongation at break. Moreover, the properties of 2 commercial adhesives are integrated and represented by open triangles Δ . These adhesives have similar properties compared to the selected one but do not allow the possibility of varying the composition systematically because the composition is unknown. The fact that most commercial epoxy-based adhesives cured by polyaddition makes the additional systematic variation in the composition more difficult: The components need to have a distinct relation in contrast to the selected system that is cured by cationic polymerization.

3.2 | Adhesives composition and properties

The adhesives consist of the cycloaliphatic diepoxide 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate and different amounts of the polymeric diol PCL (mean molecular weight 400 g/mol, 1,4-butane diol as starting

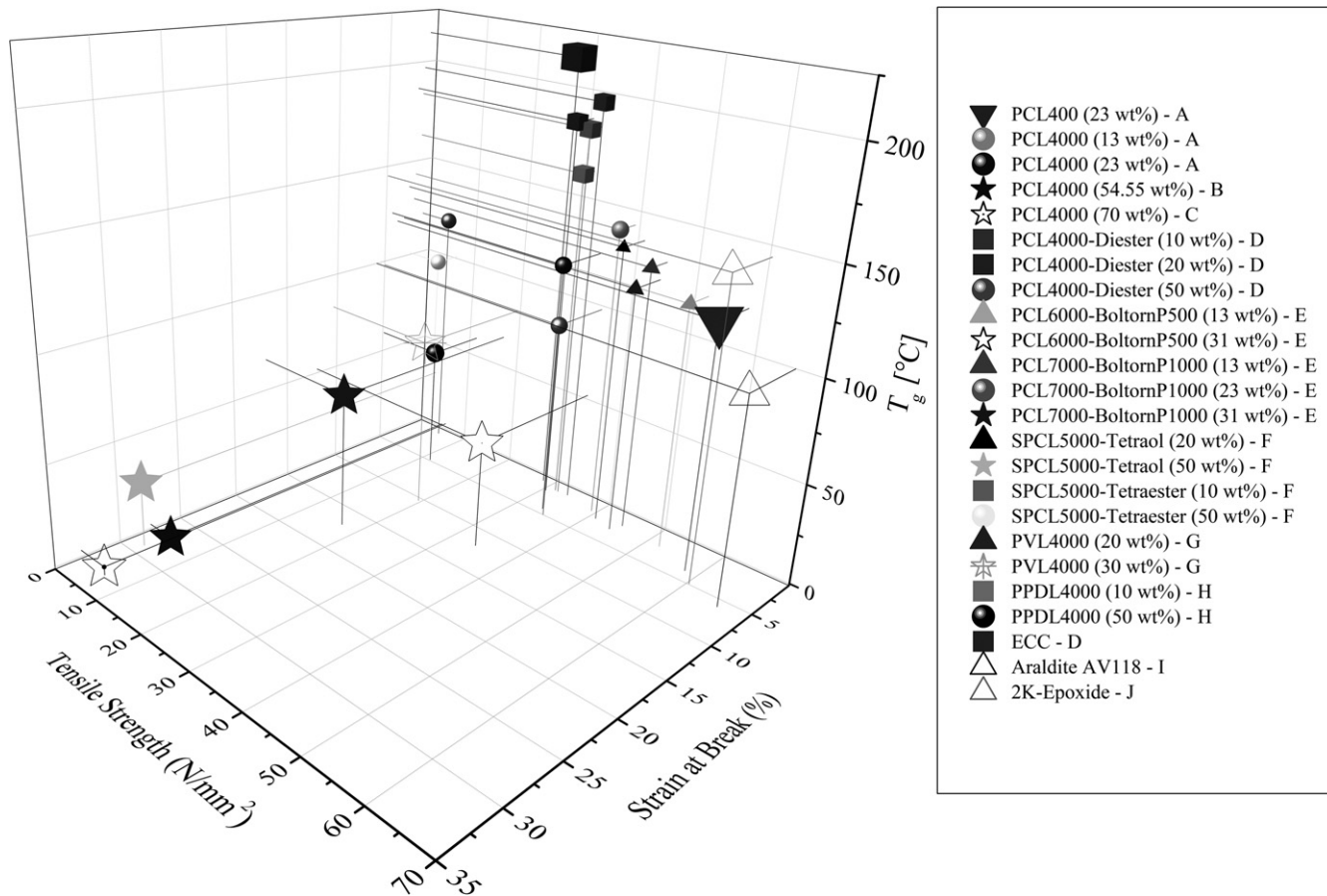


FIGURE 2 Tensile strength, strain at break and T_g of the epoxide compositions known from literature. Most materials are based on cationically cured epoxides modified with polyesters. The composition selected for further variation is represented by the large triangle ▼, the base resin by a large cube ■ and the 2 commercial adhesives by open triangles Δ. For details on the composition and other properties, the literature should be consulted. The lettering of the points is associated with the literature: A,⁴⁸ B,⁴⁹ C,⁵³ D,⁵¹ E,⁵⁰ F,⁵² G,⁵⁵ H,⁵⁴ I,⁶¹ and J⁶²

alcohol) according to the selection discussed in the previous section. Cationic curing was initiated thermally by benzyl tetrahydrothiophenium hexafluoroantimonate. Starting with the amount of 23 wt% PCL from the literature,⁴⁸ to vary the mechanical properties of the adhesives, 0, 15, 31, and 39 wt% contents were also used.

The stress-strain curves from tensile tests on the epoxy/PCL resins are shown in Figure 3. The mean curves from 7 or 8 identical samples are represented by solid lines and the standard deviation is represented by 2 dashed lines. The deviation is very small, especially for resins with a zero or a low PCL amount, but it increases for resins with a higher PCL amount, which have a pronounced strain at a constant stress. The addition of 15 or 23 wt% PCL increases the tensile strength, decreases the elastic modulus and results in a higher elongation at break when compared to the pure epoxy resin (P0) (Table 2). The stress-strain curves become nonlinear when 31 or 39 wt% PCL is added. The samples with a higher PCL amount also demonstrate a considerable elongation at a relatively constant load. On the other

hand, the maximum load and the stiffness decrease with an increasing PCL amount. In other words, PCL toughens the epoxy resin. This toughening is due to a reduced cross-linking density but is especially due to the formation of a heterogeneous morphology that was discussed previously.⁴⁸⁻⁵³

3.3 | Properties of the ceramic sheets

For calculating the stress σ and the strain ε in the 3PB tests, the well-known formulas according to the Euler-Bernoulli bending theory were used:

$$\sigma = \frac{3FL}{2bd^2} \quad (1)$$

$$\varepsilon = \frac{6Dd}{L^2} \quad (2)$$

where F is the load force (N), L represents the support span (mm), b is the sample width (mm), d is the sample

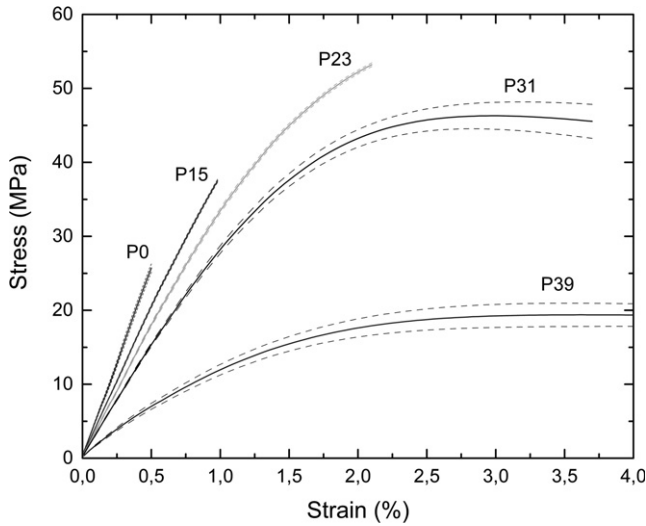


FIGURE 3 Stress-strain curves for polymers with different PCL amounts; the mean values of 7 or 8 specimen are shown by a continuous line and the standard deviations by 2 dashed lines. For the assignment of the composition and samples see Table 1

thickness (mm), and D represents the bending at the middle point (mm).

Using the maximal load force and according Equations 1 and 2, an average strength of 324 MPa with a standard deviation of 74 MPa was calculated for the pure ceramic sheets. An elastic modulus of 300 GPa together with the obtained bending strength led to a 0.18 MJ/m³ toughness.

In addition, due to the brittle failure of the pure ceramic sheets, the Weibull method for statistical data analysis according to DIN EN 843-5 was used. The strength distribution was described by the 2-parametric cumulative distribution function: $F(\sigma) = 1 - \exp(-(\sigma/\sigma_0)^m)$ (Figure 4). The characteristic strength of $\sigma_0 = 355$ MPa and Weibull modulus of $m = 5$ were calculated. The applicability of the Weibull method was confirmed by the KS-test, which provides a high significance level of $\alpha = .94$. This level means that if one decided to reject the null hypothesis that the Weibull statistic is correct, then the individual would be wrong with a probability of 94%.

The mechanical properties of the pure ceramic sheets in relation to the composites' properties are discussed in sections 3.4 and 3.5.

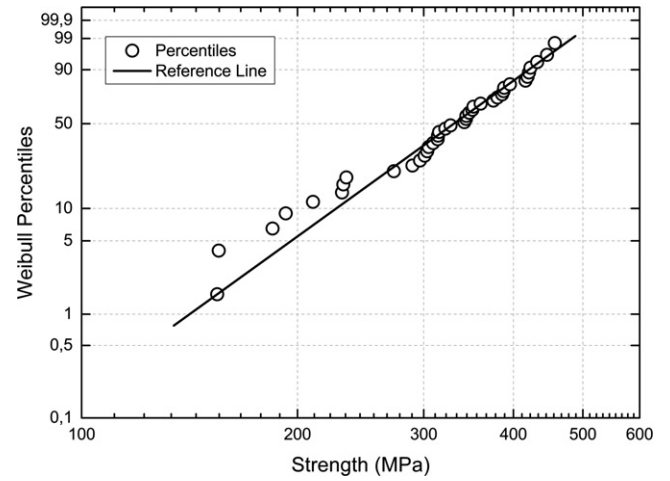


FIGURE 4 Weibull plot of the failure probability vs bending strength of 40 ceramic specimens with thicknesses of 250 μm . Experimental values are presented by circles, and the line is determined according to the Maximum-likelihood method for the Weibull cumulative distribution function, $F(\sigma) = 1 - \exp(-(\sigma/\sigma_0)^m)$, where the obtained values are the characteristic strength ($\sigma_0 = 355$ MPa) and the Weibull modulus ($m = 5$)

3.4 | Properties of the ceramic-polymer layered composites

For calculating the stress and the strain in 3PB tests on the ceramic-polymer composites, the same Equations 1 and 2 according to the Euler-Bernoulli bending theory were used. It is clear that these formulas are valid only for isotropic homogenous materials and are not related to real stresses and strains in layered composites. However, it is common practice when one refers to a composite material as a respective reference homogenous material, which will be broken with the same force and deflection in similar experiments as the composites. Therefore, we used these formulas to calculate the stress-strains curves and to compare our composites with other homogenous and composite materials in terms of strength and toughness.

Representative stress-strain curves of the 3PB tests for the pure ceramic sheets and for different composite sets CP0, CP15, CP23, CP31, CP39, and CP31L15 with their polymer components of 0%, 15%, 23%, 31%, and 39% of PCL content are presented in Figure 5. All tested materials

TABLE 2 Polymer properties for different PCL amounts determined from the stress-strain curves

Adhesive	P0	P15	P23	P31	P39
Elastic modulus (GPa)	5.1 \pm 0.1	4.1 \pm 0.06	3.6 \pm 0.05	3.1 \pm 0.05	1.3 \pm 0.1
Strength (MPa)	30 \pm 2.7	54 \pm 7.3	57 \pm 1.7	46 \pm 1.8	23 \pm 1.8
Elongation at break (%)	0.6 \pm 0.1	1.6 \pm 0.3	3.0 \pm 0.4	4.9 \pm 1.4	26 \pm 4.3
Toughness (MJ/m ³)	0.09 \pm 0.02	0.5 \pm 0.1	1.2 \pm 0.2	1.8 \pm 0.6	5.2 \pm 1.1

show almost linear stress-strain behavior until ultimate failure. Moreover, the broken specimens show almost straight crack propagation with some crack deflection at the polymer layers.

The slight nonlinearity in the composite curves close to failure is probably due to the nonlinear deformation of the polymer at a higher shear stress (Figure 3). In addition, due to the softer components between the ceramic layers, the composites have much lower elastic moduli and feature higher elongation values at break in comparison to those of the pure ceramic sheets. By combining these features, a much higher toughness for this composite can be expected. Table 3 summarizes the calculated strength and toughness of the pure ceramic sheets and the composites. The results show that CP15 provides the best combination of bending strength and toughness for 4-layered composites. On the other hand, the composite with 15 ceramic layers (CP31L15) showed almost a 2 times higher toughness and more than a 20% higher strength than CP15. From Figure 5 and Table 3 one can see that elastic modulus for the 4-layered and 15-layered composites are in the same range, but the 15-layered composite has a higher strength and strain to fracture, which provides double the toughness in comparison with CP15 and a 16 times higher toughness than that of pure ceramic sheets. It is expected, that the values determined in this study are not the limit for these composites. It is well-known that natural composites combining brittle and soft components with a large number of layers show more pronounced nonlinear behavior and a large strain to fracture. Using similar technology and creating more layers, one can obtain ceramic-polymer

composites with a higher strength and much higher toughness while maintaining a similar elastic modulus of approximately 30 GPa.

3.5 | Statistical failure stress distribution

A statistical analysis of the composite strength was carried out with a KS-test to verify the goodness of fit of the Weibull statistics (and so the Weibull hypothesis) (see Table 4). The statistical data for CP31L15 were not analyzed, as in the other sets, because there are not enough samples in this set. The KS-test is based on the comparison of experimental cumulative distribution function and fitted function. The CP0 set of experiments was taken as an example with a low significance level, $\alpha = .35$. Figure 6 shows a significant difference between the Weibull statistics and experiment.

In Figure 6B, for the CP0 distribution lower strength values have a much lower probability than does the in corresponding Weibull statistics, based on the maximum likelihood. This is preferable for applications because it means that there is a much smaller chance compared with the calculated Weibull distribution that the material will fail at lower strengths. Moreover, even if this statistic follows the Weibull distribution, then the Weibull modulus m is 2 times higher than for pure ceramic sheets, which also means less deviation and a lower probability for failure at a lower strength.

The experimental results presented in Figure 4, Figure 6, and Table 4 indicate less scatter in the strength of the composites compared to the pure ceramics sheets. However, due to the small size of the tested samples, the effect of measurement uncertainties on the strength distribution may become significant. It has been demonstrated by Monte Carlo simulation technique that the influence of the measurement uncertainties on the characteristic strength is relatively small but on the other hand, an underestimation of the Weibull modulus becomes very possible for small samples.⁶³

According to stress-strain curve for some CP39 samples, it was found that after reaching the failure stress, the stress drops down to a lower value, then increases, and then again drops down 4 times. This finding means that for such a soft polymer, the composites can be broken layer by layer. Therefore, considering the maximum stress, the failure statistics should be similar to the statistics of the bottom ceramic layer. These statistics are confirmed by the significance level, which are much closer to .94 for pure ceramic and .93 for CP39; therefore, Weibull statistics work very well for these cases. For the other composites (CP0, CP15, CP23, CP31), especially for CP0, the low significance level leads to the conclusion that Weibull statistic do not apply very well (Table 4). Therefore, for the

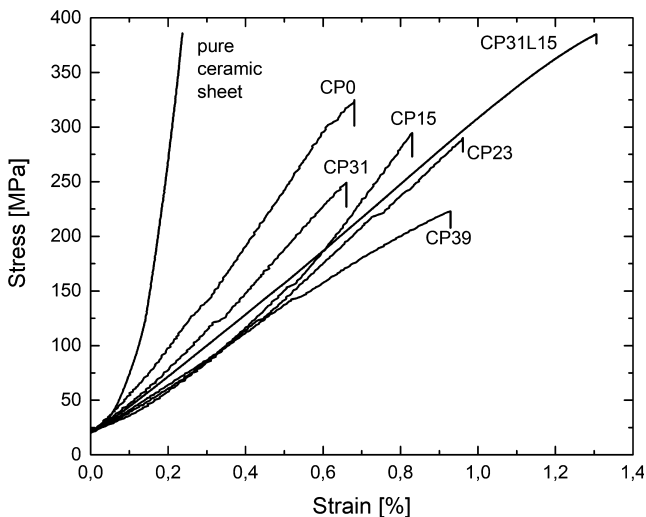


FIGURE 5 Representative stress vs strain curves of the 3PB tests with ceramic-polymer layered composites (see Table 1 for sample composition and denomination). The CP0 set consists of 27 samples, CP15-29 samples, CP23-29 samples, CP31-30 samples, CP39-28 samples, and CP31L15-6 samples

TABLE 3 Properties of ceramic-polymer layered composites and pure ceramic determined from the 3PB tests

	CP0	CP15	CP23	CP31	CP39	CP31L15	Pure ceramic
Strength (MPa)	327 ± 35	300 ± 37	288 ± 36	249 ± 32	219 ± 32	376 ± 28	324 ± 74
Toughness (MJ/m ³)	1.27 ± 0.32	1.61 ± 0.37	1.20 ± 0.29	1.13 ± 0.29	0.85 ± 0.18	2.90 ± 0.58	0.18 ± 0.08

TABLE 4 Weibull parameters σ_0 and m and the significance level α (close to 1 means that it is close to the Weibull statistics) calculated by the KS-test for the pure ceramic sheets and layered composites CP0, CP15, CP23, CP31, and CP39

	Ceramic sheets	CP0	CP15	CP23	CP31	CP39
σ_0 (MPa)	355	343	315	304	263	232
m	5.0	9.6	10.0	9.5	8.3	8.1
α	.94	.35	.70	.53	.60	.93

statistical strength evaluation of these layered composites, one should consider the real mechanisms of crack growth.

3.6 | Comparison with other ceramic composites

Due to the small number of ceramic layers and thin polymer layers, the sets of 4-layered composites feature rather pure elastic behavior, whereas toughness and resilience (elastic part of toughness) are equivalent. Therefore, it was found that it is sufficient to have only a few ceramic layers to obtain excellent toughness, which was found to be up to 10 times higher than that for a pure ceramic sheet. In Figure 7, the composites developed in this study are compared in terms of toughness and bending strength with the pure ceramic sheets and with similar composite materials from literature sources. For toughness estimations, the surface area under the stress-strain curve was considered. Stresses and strains are calculated using formulas derived for a uniform material (Euler-Bernoulli formulas, see Eqs. 1 and 2), so the composite materials may be compared with each other and with other materials in similar experiments.

Here, it should be mentioned that in many studies where materials are used for comparison, the authors prefer to the use the work of fracture $W = \Gamma/S$ (J/m²) instead of toughness T (J/m³), where Γ (J) is the strain energy accumulated in a sample during experiment and S (m²) is the cross-section of the sample failure surface. The strain energy is usually calculated by determining the area under the load-displacement curve and dividing it by the area of the fracture surface. Considering samples with the same cross-sectional area and different lengths, it is obvious that the work of fracture will grow proportionally to the support span in

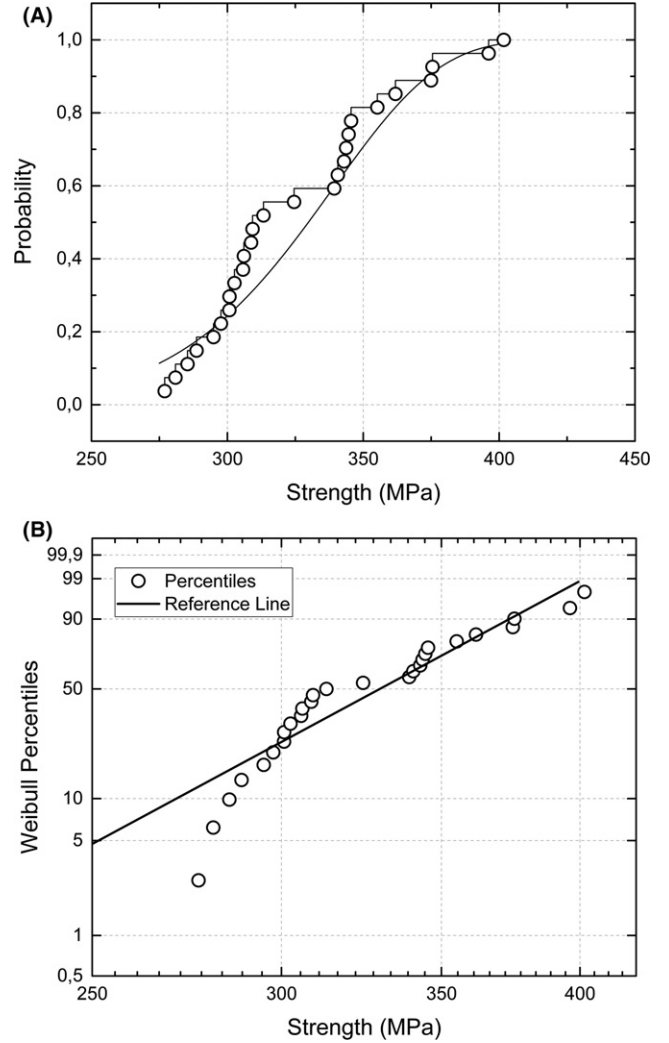


FIGURE 6 Experimental cumulative distribution function and Weibull cumulative distribution function, with fitted Weibull parameters for CP0 according to the maximum likelihood: A, Illustration of the KS-test. The largest difference in the probability allows the calculation of the significance level; and B, Weibull plot: the experimental points are shown by circles and the continuous line is the fitted Weibull distribution

the bending test or sample length in the tensile test. Consequently, the work of fracture calculated in this way is dependent on the size. Moreover, it is not known which part of the strain energy will be spent on crack growth and which part will be later released as kinetic energy out of the elastic term of the accumulated strain energy. In contrast, the toughness is a material parameter, which is surely

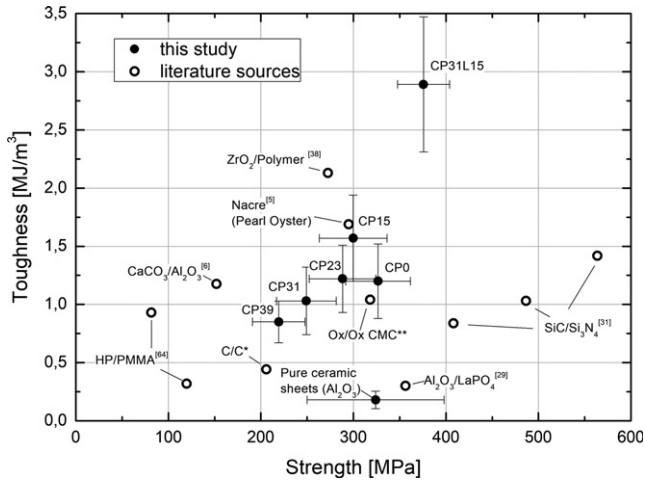


FIGURE 7 Dependence between toughness and bending strength (mean values and standard deviation) for the ceramic-polymer laminated materials from this work compared with similar materials from the literature. *Carbon-fiber reinforced carbon (SGL CARBON GmbH, Germany) tested in our laboratory. **Oxide/oxide ceramic matrix composite, Nextel 610™/(Al₂O₃+ZrO₂) (Walter E.C. Pritzkow Spezialkeramik, Germany) tested in our laboratory

independent of the sample size. This fact is also clearly visible from the relationships between the work of fracture and the fracture toughness could be easily derived. For the 3PB test, one can directly derive the formula that $T = 9W/L$ (J/m³), where L (m) is the support span. A similar formula can be derived for the tensile test $T = W/L_T$ (J/m³), where L_T (m) is the length of the specimen. For this reason, the newly developed composites are compared in Figure 7 with the composite materials from the literature in terms of the strength and toughness. Data from the literature such as stress-strain curves^{5,6} and work of fracture^{29,31,64} were used to calculate the toughness of the tested materials.

The comparisons in Figure 7 show that the 4-layered composites developed in this study feature a bending strength in the same range with those of the used ceramic sheets. However, as the PCL amount in polymer increases, the strength of the composite decreases. This result can be correlated with the increasing extensibility of the polymers, which leads to a change in the stress distribution in the load-bearing ceramic layers. On the other hand, the toughness values of the composites clearly exceed those of the pure ceramic sheets. Moreover, the 4-layered composites have a comparable or higher toughness than many artificially layered and fiber composites. From the considered materials, only the natural composite nacre and the fifty-layered ZrO₂/polymer composite have a higher toughness. At the same time, the strength of the 4-layered composites is comparable to these of fiber-reinforced ceramic composites. Moreover, the inclusion of a higher number of ceramic layers in the composites led to a much improved

mechanical performance. The 15-layered composite CP31L15 demonstrated the highest toughness and a very high strength in this class of materials. This result shows the great potential of the developed material as the number of layers is increased.

4 | CONCLUSIONS

Ceramic-polymer layered composites with high strength and toughness are presented in this study. The morphology of the composites is inspired by natural composite materials but is arranged on a larger scale using sintered Al₂O₃ sheets with a nominal thickness of 250 μm. Composites with 4 and 15 ceramic layers were prepared and examined. Cationically cured epoxy resin toughened by PCL was used as a thin adhesive layer. This polymer system was selected because their mechanical properties can be varied in a wide range without changing the composition too much. The 4-layered composite with approximately 15 wt% PCL content achieves a flexural strength of 300 MPa and a toughness of 1.6 MJ/m³, which is 10 times higher than the strength and toughness of pure ceramic sheets. By increasing the number of layers, the mechanical properties were further improved. This was shown by a 15-layered composite with polymer layers of 31 wt% PCL, a toughness of 2.9 MJ/m³ and a bending strength of 376 MPa. The elastic modulus is 28 GPa, which is almost the same as for the 4-layered composite based on the same polymer. In comparison to other composites from the literature, the 15-layered composite shows the best toughness and a very high strength. It is expected that this class of composites can show even a better performance with a further increase in the number of layers.

Weibull statistics was applied for the evaluation the strength distribution for the pure ceramic component and for the 4-layered composites. The applicability of Weibull statistics was analyzed by the KS-test method. As expected, it was found that the strength scattering of the pure ceramic sheets could be described very accurately by the Weibull statistic method. In contrast, the Weibull statistics does not satisfactorily fit the layered composites, probably due to the more complicated crack growth mechanisms. The exception is for a composite with an adhesive containing 39 wt% PCL, which is the adhesive with the lowest elastic modulus and highest elongation at break. Nevertheless, the ceramic-polymer composites feature a Weibull modulus in the range of 8-10, which is up to 2 times higher than the Weibull modulus of the pure ceramic sheets. Based on the presented results it can be stated that the presented approach offers an enormous potential for the development of new ceramic-polymer composites with improved strength and toughness.

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