Preparation of high strength zirconia by epoxy gel-casting using hydantion epoxy resin as a gelling agent

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Abstract

In this paper, a water soluble hydantion epoxy resin (ER) was employed to prepare zirconia green bodies with high mechanical strength via epoxy gel-casting (EGC) for dental applications. The rheological properties and gelation behaviors of the suspensions, and the microstructure and mechanical strength of zirconia were systematically studied. The results revealed that solid loadings of up to 52.0 vol-% could be achieved with the addition of 0.8 wt-% dispersant. When the concentration of ER in the 52.0 vol-% suspensions increased from 10.0 to 25.0 wt-%, the mechanical strength of the resulting green bodies was enhanced from 40.96 ± 5.20 to 51.22 ± 12.01 MPa. A rough sketch of a pre-sintered zirconia crown was soft-machined from the green body consolidated from a 52.0 vol-% suspension containing 10.0 wt-% ER. The sintered body had a high mechanical strength of 942.77 ± 95.61 MPa.

Keywords: Zirconia; Epoxy gel-casting; Hydantion epoxy resin; High strength; Dental applications

1.1 Introduction

Zirconia with 3 mol %mol% yttria (3Y-TZP) shows excellent mechanical properties and is widely used to fabricate crowns and fixed partial dentures [1,2]. Restorations of 3Y-TZP blanks in prosthetic dentistry included soft machining of green bodies and hard machining of sintered bodies [3]. Hard machining led to stress-induced formation of monoclinic phase (m-) zirconia and surface microcracking at very low loads [4], resulting in low reliability and high level of degradation, which were detrimental to long-term performance even when the high mechanical strength appeared as an advantage [5]. In the contrast, soft machining of pre-sintered bodies was more desirable for restorations due to avoiding sandblasting, sharp indentation and grinding which caused the formation of m-zirconia and surface flaws [6–9]. Zirconia green bodies with high mechanical strength offered great advantages for soft machining of complex structures, especially for the high aspect ratio structure which attracted increased attention in prosthetic dentistry [10]. So, preparation of zirconia green bodies with high mechanical strength and controlling the final surface finishing were critical for dental applications [11].

EGC based on colloidal processing was one of the most attractive wet forming methods [12–17]. It offered the ability to fabricate homogenous green bodies with low addition of organic additives. The mechanical strength of green body was mainly determined by the gelling agent. Zhao et al. reported that 42.0 vol-% zirconia suspension containing 13.0 wt-% phenolic resin yielded a green body with mechanical strength of 9 MPa [18]. Liu et al. demonstrated the density of zirconia green body was up to 2.85 g/cm^3 fabricated by 45.0 vol-% zirconia suspension containing 30.0 wt-% resin [11]. However, the mechanical strength of zirconia green body was still quite low for soft machining of complex structures for dental applications. Tan et al. investigated the gel tape-casting of 3Y-TZP using acrylamide (AM) [19], however, the mechanical strength was unknown. Though AM was one of the most used gelling agent due to its ability to deliver high mechanical strength, i.e. 37.11 ± 1.67 MPa of Al_2O_3 green body [20], it encountered great difficulties in wide range of applications due to the neurotoxicity of monomer [21]. Non-toxic gelling agents were developed and the ER attracted great attentions [22–25]. This water-soluble gelling agent could be processed in air due to the polymerization was nucleophilic addition reaction. It also avoided the surface flaking of green body. Our previous works demonstrated that Al_2O_3 green bodies consolidated by EGC exhibited a mechanical strength of 43.4 MPa [26]. EGC also ensured the integrity of PZT pillar arrays with fine scales and high aspect ratio [27]. Inspired by these results, we expect that EGC process can be also used to prepare green bodies with high mechanical strength for dental applications.

The preparation of well deflocculated suspensions with solid loadings > 50.0 vol% is important in the EGC process. Due to the attraction of van der Waals forces, powders had the tendency to agglomerate in suspension [28], which could be reduced by the addition of appropriate dispersant to induce the electrostatic and steric repulsion. Meanwhile, the solid loading and concentration of gelling agent were critical to the rheological properties of suspensions and mechanical strength of green and sintered bodies. So, the aim of this research was to systematically study the effects of these parameters to enable obtaining green bodies with high mechanical strength for dental applications. The results indicated that EGC of 52.0 vol% suspensions with 10.0 wt% ER could result in homogenous green bodies with the mechanical strength of 40.96 ± 5.20 MPa, which were high enough for soft machining. A pre-sintered zirconia crown was successfully machined. The sintered body also showed reasonable high mechanical strength of 942.77 ± 95.61 MPa.

2.2 Experimental procedure

2.1.2.1 Materials

Zirconia with 3 mol %mol% yttria (3Y-TZP, Guangdong Orient Zirconic Ind Sci & Tech Co., Ltd.) was used as colloidal phase. The average particle size was 0.3 μm. Ammonium polyacrylate (NH_4PAA, HydroDisper A168, Shenzhen Highrun Chemical Industry Co. Ltd., China) with an average molecular weight of 1500 was utilized as the dispersant. Deionized water was used as the solvent. ER (MHR070, Meihua Chemicals Co., China) was used as the gelling agent and 3, 3′-Ddiaminodi-propylamine (DPTA, Tokyo Chemical Industry Co. Ltd., Japan) was added as the hardener. 1-octanl (Reagent grade, Shanghai Chemical Reagent Co., China) was used as the de-foaming agent.

2.2.2.2 Preparation of suspensions and EGC

The premixed solutions were prepared by adding an appreciated amount of ER and dispersant A168 in deionized water. The 3Y-TZP powders were then added into the premixed solutions to prepare suspensions from 46.0 to 52.0 vol% in a total volume of 20 ml. The degree of dispersion was promoted by dispersant and later ER. Different amount of dispersants were added in order to select the optimal content. To generate well-dispersed and stable suspensions, all slurries with 1–2 drops of 1-octanl were milled for 24 h in 100 rpm at room temperature (~25 °C), using 10 mm diameter, high-purity zirconia balls as the milling media. The ratio of zirconia balls to YSZ powders was 1.2–:1 in weight. 1-octanl helped the de-airing of the suspensions. After that, 0.25 mol/eq DPTA based on the ER concentration were added into suspensions to induce the crosslinking of gelling agent. Then, the suspensions were poured into the mold immediately. The drying process was carried out in different successive steps: at ambient environment for 48 h, then at 40 °C for 12 h and 80 °C for 4 h. Zirconia green bodies were sintered at a heating rate of 1 °C /min to 500 °C and hold for 2 h, then at a heating rate of 5 °C/min to 1550 °C and hold for 1 h. The sintered samples were cooled naturally inside the furnace to room temperature.

2.3.2.3 Characterizations

The rheological properties of suspensions were measured by the rheometer (AR2000 EX, TA Instruments, USA) with a diameter of 40 mm parallel plate. Steady state flow and time scan model were employed. The suspensions were pre-sheared at a shear rate of 100 s^{-1} for 1 min and a pause of 30 s, followed by the apparent viscosity testing with a steady increase of shear rate from 0.1 to 800 s^{-1}. The gelation behaviors of suspensions were monitored by measuring the apparent viscosities at the constant shear rate of 0.1 s^{-1} as a function of time. All measurements were carried out at 25 °C, using silicone oil as the trap solvent to reduce the evaporation. The mechanical strength of green and sintered bodies was measured by the three-point bending test, using the electronic universal testing machine (KD11-2, Shenzhen Kaiqiangli Technology Co. Ltd., China). The size of tested samples was 35 × 4 × 3 mm^3 and all tests were carried out with a span of 30.0 mm and crosshead speed of 0.5 mm/min. The green body was soft machined by soft milling machine (Cerec3, Dentsply Sirona, USA). The microstructures of green and sintered bodies were observed by scanning electron microscopy (NOVA NANOSEM 230).

3.3 Results and discussion

3.1.3.1 Rheological behaviors

Fig. 1 illustrates the effects of dispersant concentration on the apparent viscosity of 50.0 vol% suspensions containing 15.0 wt% ER as a function of shear rate. All the suspensions show high apparent viscosities at the zero shear-viscosity and pronounced shear thinning behaviors with increasing the shear rate. The apparent viscosities approach to a constant value at very high shear rate, which is due to the perturbation of concentrated suspension structure under shearing [29]. At the zero shear-viscosity, thermal motion dominates over shear force, and the structure is close to the equilibrium structure at rest. As the shear rate increases, the shear force affects the structure more than thermal motion and induces the shear thinning behavior. At the very high shear rate, the shear forces totally dominate the structure, then the plateaus of apparent viscosities are resistant to flow of suspension with the hydrodynamically controlled structure. This rheological behavior is beneficial to EGC as the shear thinning behavior guarantees the easily pouring of suspension into the mold, while the high apparent viscosities at the zero shear-viscosity help to avoid the settlements of particles.

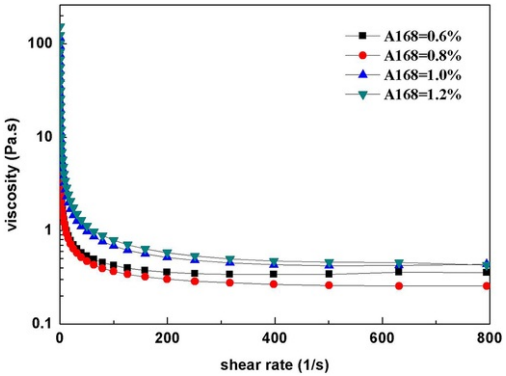

Fig. 1 Apparent viscosities of 50.0 vol% suspensions containing 15.0 wt% ER and different dispersant amount as a function of shear rate.

alt-text: Fig. 1

The suspension containing 0.8 wt% NH_4PAA has the minimum apparent viscosity of 0.3700 Pa s at the characteristic shear rate of 100 s^{-1}, which indicates the best colloidal stability and the optimal dispersant concentration. NH_4PAA is one of the cation polyelectrolytes with linear backbone. It contains one carboxylic acid group per monomer unit. The NH_4PAA becomes negatively charged under the experimental conditions while the zirconia particle is positively charged. Thus, NH_4PAA is easily adsorbed into particle surfaces and the suspension is dispersed by electrosteric force [25]. At the concentration of 0.6 wt%, an insufficient amount of NH_4PAA leads to incomplete adsorption on particle surfaces [30], resulting in the inadequate interparticle repulsive forces and high apparent viscosity. By contrast, an excessive amount of dispersant also increases the apparent viscosity due to the depletion flocculation [31]. As the amount of NH_4PAA is higher, the free ionic PAA would exist in the liquid medium, which may cause inter-locking of PAA polymer chain and bridge the particles [31].

Fig. 2 illustrates the effects of solid loading on the apparent viscosity of suspensions containing 10.0 wt% ER and 0.8 wt% dispersant as a function of shear rate. Except for the 54.0 vol% suspension, all the suspensions show shear thinning behaviors at low shear rate and approach to constant values at high shear rate, which could be explained by the mentioned theory. As the solid loading increases from 48.0 to 52.0 vol%, the apparent viscosities of suspensions increase from 0.3665 to 0.4467 Pa s at the characteristic shear rate of 100 s^{-1}. However, the 54.0 vol% suspension shows an unsteady flow, which is attributed to the damage of layered structures. As the solid loading increases, the distance between particles reduces and the particle interactions are enhanced, leading to high flocculation and unstable flow. This kind of flow behavior is not desirable for EGC process.

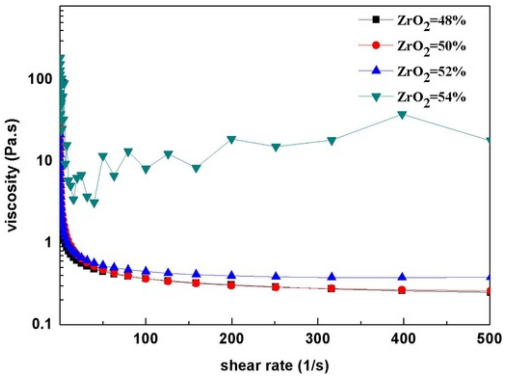

Fig. 2 Apparent viscosities of suspensions containing 10.0 wt% ER and different solid loading as a function of shear rate.

alt-text: Fig. 2

Fig. 3 illustrates the effects of ER concentration on the apparent viscosity of 52.0 vol% suspensions containing 0.8 wt% dispersant as a function of shear rate. All the suspensions show pronounced shear thinning behaviors at low shear rate and approach to constant values at high shear rate, which is similar with the rheological behaviors shown in Fig. 1 and could be explained using the same theory. With the increase of ER concentration from 10.0 to 25.0 wt%, the apparent viscosities of suspensions increase from 0.4467 to 0.7820 Pa s at the characteristic shear rate of 100 s^{-1}. However, even with the highest concentration of 25.0 wt% ER, the apparent viscosity of 52.0 vol% suspension is still lower than 1.0000 Pa s at the shear rate of 100 s^{-1} [12], indicating a good fluidity for EGC

process.

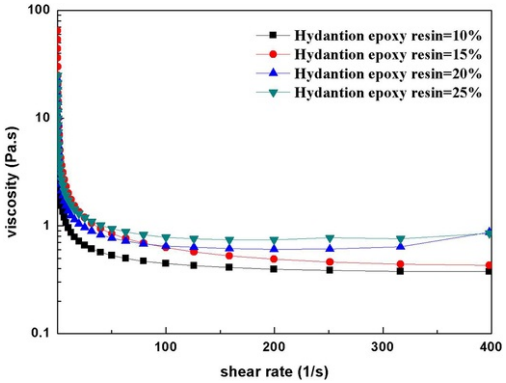

Fig. 3 Apparent viscosities of 52.0 vol.% suspensions containing 0.8 wt.% dispersant and different ER concentration as a function of shear rate.

alt-text: Fig. 3

~~3.2.~~3.2 Gelation progress

Fig. 4 illustrates the effects of ER concentration on the gelation behaviors of 52.0 vol. % suspensions containing 0.8 wt.% dispersant. DPTA with 0.25 mol/eq is added into the suspensions to induce the crosslinking reaction of gelling agent at 25~~.~~ °C. As can be seen, the apparent viscosities of suspensions remain constant values for a long period, then increase sharply at the inflection points. The period of constant apparent viscosity is called as idle time, which indicates the operation time for EGC process. Although the time required for the apparent viscosity to reach the value of 1000 Pa.s decreased from 550.3 to 249.5 s as the content of ER increased from 10.0 to 25.0 wt.%, the handling time for EGC is still enough.

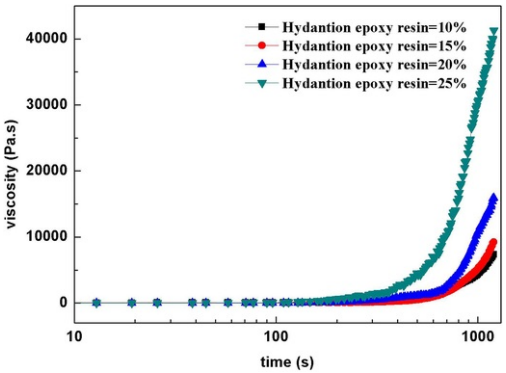

Fig. 4 Apparent viscosities of 52.0 vol.% suspensions containing 0.8 wt.% dispersant and different ER concentration as a function of gelation time at 25 °C.

alt-text: Fig. 4

Fig. 5 illustrates the effects of solid loading on the gelation behaviors of suspensions containing 25.0 wt.% ER and 0.8 wt.% dispersant. The gelling agent is crosslinked with 0.25 mol/eq DPTA at 25 °C. Although the time required for the apparent viscosity to reach the value of 1000 Pa.s decreased from 588.6 to 249.5 s as the solid loading increased from 48.0 to 52.0 vol.%, the handling time for EGC is still enough.

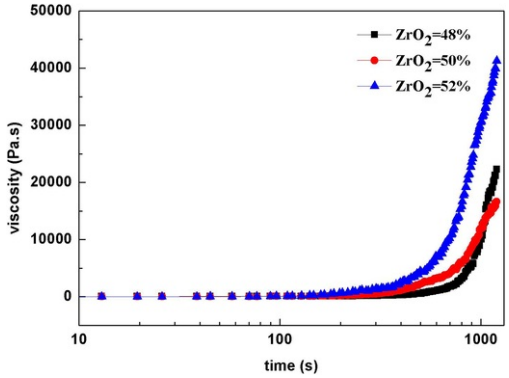

Fig. 5 Apparent viscosities of suspensions containing 25.0 wt-% ER and different solid loading as a function of gelation time at 25 °C.

alt-text: Fig. 5

~~3.3.~~3.3 Characterization of the green bodies

Fig. 6 illustrates the effects of solid loading on the densities and mechanical strength of green bodies consolidated from suspension containing 15.0 wt-% ER and 0.8 wt-% dispersant. With solid loading increasing from 48.0 to 52.0 vol-%, the mechanical green strength changed from12.97 ± 4.21 MPa to 41.47 ± 8.90 MPa, while green density was improved from 3.347 ± 0.090 g/cm^3 to 3.537 ± 0.160 g/cm^3. When the solid loading is up to 52.0 vol-%, the mechanical strength is high enough for soft machining of crowns and fixed partial dentures.

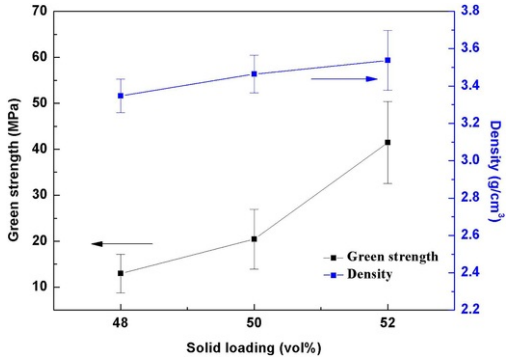

Fig. 6 The densities and mechanical strength of green bodies consolidated from suspension containing 15.0 wt-% ER and 0.8 wt-% dispersant as a function of solid loading. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alt-text: Fig. 6

Fig. 7 illustrates the effects of ER concentration on the mechanical strength and densities of green bodies consolidated from the 52.0 vol-% suspensions containing 0.8 wt-% dispersant. With ER concentration increasing from 10.0 to 25.0 wt-%, the mechanical green strength changed from 40.96 ± 5.20 MPa to 51.22 ± 12.01 MPa, while green density was improved from 3.476 ± 0.121 g/cm^3 to 3.604 ± 0.201 g/cm^3. The mechanical strength of green body is mainly provided by the gelling agent. With the increase of ER contents, more compact and higher level of crosslinking networks are formed in the green bodies, resulting in higher mechanical strength and density [30]. The green body has a significant high mechanical strength even with a low level of addition, i.e. 10.0 wt-%. The results show great advantages for soft machining of fine structures with high aspect ratio and complex shape for dental applications.

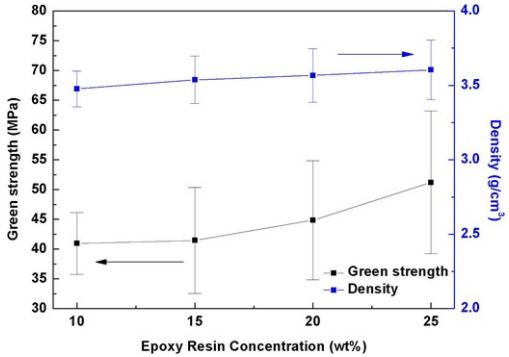

Fig. 7 The densities and mechanical strength of green bodies consolidated from the 52.0 vol-% suspensions containing 0.8 wt-% dispersant as a function of ER concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alt-text: Fig. 7

Fig. 8 shows the fracture surface of green body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER and 0.8 wt-% dispersant. As seen from Fig. 8A, the ER is packed around the particles and responsible for the high mechanical strength. There are no obvious defects in the structure and the particles show a uniform size distribution, as shown in Fig. 8B.

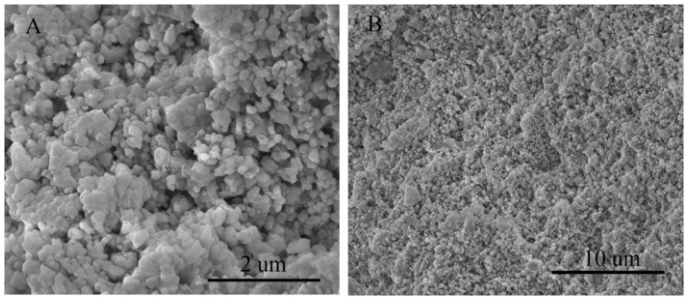

Fig. 8 SEM images of green body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER and 0.8 wt-% dispersant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alt-text: Fig. 8

~~3.4.~~3.4 Soft machining of the green body

Fig. 9 exhibits a rough sketch of zirconia crown by soft machining green body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER. Fig. 9A shows the top side of crown while Fig. 9B is taken from the back side. As can be seen, the green body has an enough mechanical strength for soft machining. The structure keeps good shape during the machining process and the surface is quite smooth without cracks and flaws.

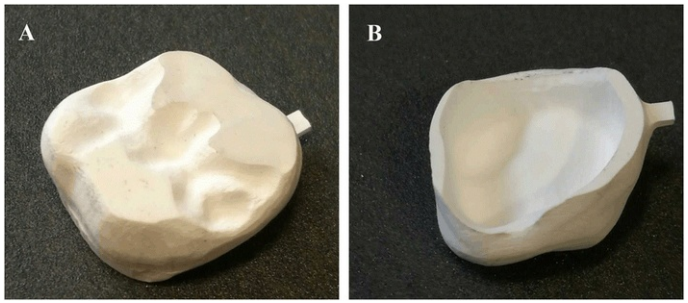

Fig. 9 Rough sketch of zirconia crown by soft machining of green body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER and 0.8 wt-% dispersant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

alt-text: Fig. 9

~~3.5.~~3.5 Characterization of the sintered bodies

The XRD pattern of sintered body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER is shown in Fig. 10. As can be seen, the main phase of sintered body is tetragonal. There exists a few amount of monoclinic zirconia, which could be attributed to the phase transition from tetragonal to monoclinic during the sintering process. Further researches will carry on the optimization of sintering process to improve the content of tetragonal phase.

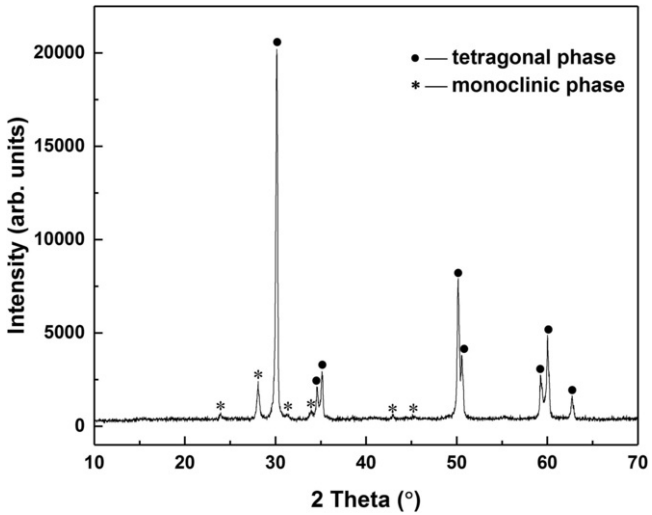

Fig. 10 XRD of sintered body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER and 0.8 wt-% dispersant.

alt-text: Fig. 10

After sintering at 1550 °C for 2 h, the zirconia body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER gains a homogenous and dense microstructure, shown in Fig. 11. There are no obvious pores, agglomerations and defects in the microstructure. The average grain size is around 0.5 μm and has a narrow size distribution, which is desirable for dental applications [32].

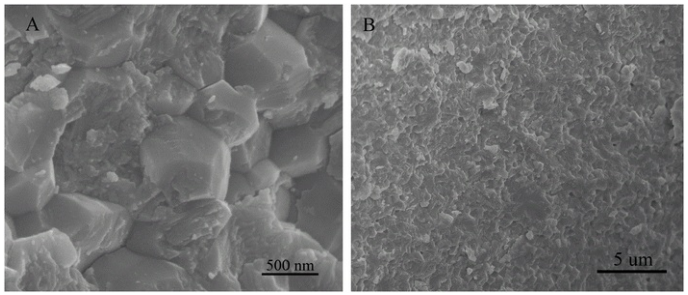

Fig. 11 SEM images of sintered body consolidated from the 52.0 vol-% suspension containing 10.0 wt-% ER and 0.8 wt-% dispersant.

alt-text: Fig. 11

Fig. 12 illustrates the effects of ER concentration on the mechanical strength and densities of sintered zirconia consolidated from the 52.0 vol-% suspension containing 0.8 wt-% dispersant. As the ER concentration increases from 10.0 to 25.0 wt-% in green bodies, the mechanical strength of sintered zirconia reduces from 942.77 ± 95.61 MPa to 551.64 ± 49.89 MPa, with the densities reduce from 6.0445 ± 0.030 g/cm^3 to 5.9967 ± 0.018 g/cm^3. This phenomenon could be attributed to the defects and flaws in the microstructure. As the ER concentration increases, more pores and flaws are created in the sintered body during the binder removal process, resulting in the lower strength and density. The mechanical strength in the range of 800–1000 MPa is suitable for zirconia dental crowns and fixed partial dentures [4]. So, the appropriate amount of ER for sintered zirconia is 10.0 wt-%.

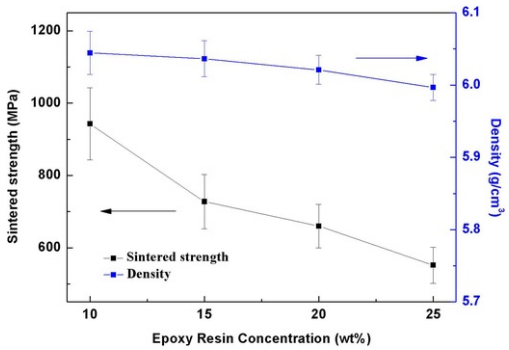

Fig. 12 The densities and mechanical strength of sintered zirconia consolidated from the 52.0 vol~~.~~% suspension containing 0.8 wt~~.~~% dispersant as a function of ER concentration.

alt-text: Fig. 12

4.4 Conclusion

In summary, we have employed ER to fabricate zirconia green body with high mechanical strength via EGC for dental applications. A high solid loading of 52.0 vol~~.~~% was achievable with 0.8 wt~~.~~% dispersant. When the 52.0 vol~~.~~% suspension contains 25.0 wt~~.~~% ER, the suspension had a low apparent viscosity of 0.7820 Pa~~.~~s at the characteristic shear rate of 100 s^{-1} and the idle time of gelation was 249.5 s, which was long enough for EGC process. When the ER concentration increased from 10.0 to 25.0 wt~~.~~% in the 52.0 vol~~.~~% suspensions, the mechanical strength of green bodies increased from 40.96 ± 5.20 MPa to 51.22 ± 12.01 MPa, with the densities improved from 3.476 ± 0.121 g/cm^3 to 3.604 ± 0.201 g/cm^3. However, even with a low addition of 10.0 wt~~.~~% ER, the fabricated green body had strong mechanical strength for soft machining and the pre-sintered zirconia crown was successfully machined. After sintering at 1550 °C for 2~~ hours~~h, dense sintered body with the mechanical strength of 942.77~~.~~ ± 95.61 MPa and an average grain size of 0.5 μm was obtained.

Acknowledgements

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References

[1] M. Kern and ~~S. M.~~S.M. Wegner, Bonding to zirconia ceramic: adhesion methods and their durability, *Dent. Mater.* **14**, 1998, 64–71.

[2] ~~P. F.~~P.F. Manicone, ~~I. P.~~I.P. Rossi and L. Raffaelli, An overview of zirconia ceramics: basic properties and clinical applications, *J. Dent.* **35**, 2007, 819–826.

[3] F. Filser, P. Kocher and ~~L. J.~~L.J. Gauckler, Net-shaping of ceramic components by direct ceramic machining, ~~*Assembly Autom.*~~*Assem. Autom.* **23**, 2003, 382–390.

[4] M. Guazzato, M. Albakry, ~~S. P.~~S.P. Ringer and ~~M. V.~~M.V. Swain, Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics, *Dent. Mater.* **20**, 2004, 449–456.

[5] H. Huang, Machining characteristics and surface integrity of yttria stabilized tetragonal zirconia in high speed deep grinding, ~~*Mater. Sci. Eng. A: Struct.*~~*Mater. Sci. Eng. A* **345**, 2003, 155–163.

[6] ~~S. Y.~~S.Y. Liu and I.W. Chen, Fatigue of yttria-stabilized zirconia. I. Fatigue damage, fracture origins, and lifetime prediction, *J. Am. Ceram. Soc.* **74**, 1991, 1197–1205.

[7] Y. Zhang and B. Lawn, Fatigue sensitivity of Y-TZP to microscale sharp-contact flaws, ~~*J. Biomed. Mater. Res: Appl. Biomater.*~~*J Biomed Mater Res B Appl Biomater* **72B**, 2005, 388–392.

[8] Y. Zhang, A. Pajares and B.R. Lawn, Fatigue and damage tolerance of Y-TZP ceramics in layered biomechanical systems, ~~*J. Biomed. Mater. Res. B: Appl. Biomater.*~~*J Biomed Mater Res B Appl Biomater* **71B**, 2004, 166–171.

[9] Y. Zhang, ~~B. R.~~B.R. Lawn, ~~E. D.~~E.D. Rekow and ~~V. P.~~V.P. Thompson, Effect of sandblasting on the long-term performance of dental ceramics, ~~*J. Biomed. Mater. Res. B: Appl. Biomater.*~~*J Biomed Mater Res B Appl Biomater* **71B**, 2004, 381–386.

[10] R. Xie, ~~K. C.~~K.C. Zhou, ~~X. P.~~X.P. Gan and D. Zhang, Effects of ~~E~~epoxy ~~R~~resin on ~~G~~gelcasting ~~P~~process and ~~M~~mechanical ~~P~~properties of ~~A~~alumina ~~C~~ceramics, *J. Am. Ceram. Soc.* **96**, 2013, 1107–1112.

[11] G. Liu, ~~M. M.~~M.M. Attallah, Y. Jiang and ~~T. W.~~T.W. Button, Rheological characterization and shape control in gel-casting of nano-sized zirconia powders, *Ceram. Int.* **40 (**, 2014, 14405–14412.

[12] A. Kaushal, S.M. Olhero, B. Singh and C. Bhardwaj, 3D multiscale controlled micropatterning of lead-free piezoelectric electroceramics via Eepoxy Ggel Ccasting and lift-off, ~~J. Europ. Ceram. Soc.~~J. Eur. Ceram. Soc. **37**, 2017, 3079–3087.

[13] ~~S. M.~~S.M. Olhero, E. Lopes and ~~J. M. F.~~J.M.F. Ferreira, Fabrication of ceramic microneedles-~~T~~the role of specific interactions between processing additives and the surface of oxide particles in Eepoxy Ggel Ccasting, ~~J. Europ. Ceram. Soc.~~J. Eur. Ceram. Soc. **36**, 2016, 4131–4140.

[14] A. Kaushal, ~~S. M.~~S.M. Olhero, P. Antunes and A. Ramalho, Structural, mechanical and dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$-The benefits of a colloidal processing approach, *Mater. Res. Bull.* **50** (2), 2014, 329–336.

[15] ~~S. M.~~S.M. Olhero, A. Kaushal, P. Antunes and ~~J. M. F.~~J.M.F. Ferreira, Microfabrication of high aspect ratio BST pillar arrays by epoxy gel casting from aqueous suspensions with added water soluble epoxy resin, *Mater. Res. Bull.* **60**, 2014, 830–837.

[16] ~~S. M.~~S.M. Olhero, ~~L. G.~~L.G. Gancedo, ~~T. W.~~T.W. Button and ~~F. J.~~F.J. Alves, Innovative fabrication of PZT pillar arrays by a colloidal approach, ~~J. Eur. Cer. Soc.~~J. Eur. Ceram. Soc. **32**, 2012, 1067–1075.

[17] L. Garcíagancedo, ~~S. M.~~S.M. Olhero, ~~F. J.~~F.J. Alves and ~~J. M. F.~~J.M.F. Ferreira, Application of gel-casting to the fabrication of 1-3 piezoelectric ceramic-polymer composites for high-frequency ultrasound devices, *J. Micromech. Microeng.* **22**, 2012, 125001–125008.

[18] ~~H. P.~~H.P. Zhao, ~~C. S.~~C.S. Ye and ~~Z. T.~~Z.T. Fan, A simple and effective method for gel casting of zirconia green bodies using phenolic resin as a binder, *J. Eur. Ceram. Soc.* **34**, 2014, 1457–1463.

[19] Q. Tan, Z. Zhang, Z. Tang, S. Luo and K. Fang, Rheological properties of nanometer tetragonal polycrystal zirconia slurries for aqueous gel tape casting process, ~~Mater. Lett.~~Mater. Lett. **57**, 2003, 2375–2381.

[20] J. Ma, Z. Xie, H. Miao, Y. Huang, Y. Cheng and W. Yang, Gel casting of Aalumina Cceramics in the Mmixed Aacrylamide and Ppolyacrylamide Ssystems, *J. Eur. Ceram. Soc.* **23**, 2003, 2273–2279.

[21] K. Prabhakaran, S. Ananthakumar and C. Pavithran, Gel casting of alumina using boehmite as a binder, *J. Eur. Ceram. Soc.* **19**, 1999, 2875–2881.

[22] ~~O. O.~~O.O. Omatete, ~~M. A.~~M.A. Janney and ~~R. A.~~R.A. Strehlow, Gel casting-a new ceramic forming process, *Am. Ceram. Soc. Bull.* **70**, 1991, 1641.

[23] ~~A. C.~~A.C. Yong, ~~O. O.~~O.O. Omatete, ~~M. A.~~M.A. Janney and ~~P. A.~~P.A. Menchhofer, Gel casting of alumina, *J. Am. Ceram. Soc.* **74**, 1991, 612–618.

[24] ~~J. S.~~J.S. Ha, Effect of atmosphere type on gel casting behavior of Al_2O_3 and evaluation of green strength, ~~Ceram.Int.~~Ceram. Int. **26**, 2000, 251–254.

[25] Y. Jiang, ~~C. E. M.~~C.E.M. Demore, C. Meggs, C. Dunare, T. Stevenson and J. Bamber, Micro-moulded randomised piezocomposites for high frequency ultrasound imaging, ~~Ultrason. Symp.~~IEEE Ultrason. Symp. **10**, 2012, 1–4.

[26] R. Xie, X.D. Zhang, Y. Zhang, ~~K. C.~~K.C. Zhou and ~~T. W.~~T.W. Button, Gel casting of alumina ceramics with improved green strength, *Ceram. Int.* **38**, 2012, 6923–6926.

[27] R. Xie, C. Liu, Y. Zhao, P. Jin, ~~K. C.~~K.C. Zhou and D. Zhang, Gelation behavior and mechanical properties of gelcast lead zirconatetitanate ceramics, *J. Eur. Ceram. Soc.* **35**, 2015, 2051–2056.

[28] ~~R. G.~~R.G. Horn, Surface Fforces and ~~T~~their Aaction in Cceramic Mmaterials, *J. Am. Ceram. Soc.* **73**, 2010, 1117–1135.

[29] ~~C. G. M.~~C.G.M. Kruif, The rheology of colloidal dispersions in relation to their Mmicrostructure, In: ~~J. P.~~J.P. Hulin, ~~A. M.~~A.M. Cazabat, E. Guyon and F. Carmona, (Eds.), *Hydrodynamics of dDispersed mMedia, Amsterdam, The Netherlands,* 1990, 79–85.

[30] ~~S. L.~~S.L. Morissette and ~~J. A.~~J.A. Lewis, Chemorheology of Aaqueous-Bbased Aalumina-Ppoly (Vvinyl Aalcohol) Ggelcasting Ssuspensions, *J. Am. Ceram. Soc.* **82**, 1999, 521–528.

[31] B. Chen, Z. Zhang, J. Zhang, M. Dong and D. Jiang, Aqueous gel-casting of hydroxyapatite, ~~Mater. Sci. Eng.: A~~Mater. Sci. Eng. A **435**, 2006, 198–203.

[32] I. Denry and ~~J. R.~~J.R. Kelly, State of the art of zirconia for dental application, *Dent. Mater.* **24**, 2008, 299–307.

Highlights

- The hydantion epoxy resin was employed to prepare zirconia green body with high mechanical strength for dental application.
- The mechanical strength of zirconia green body was reach to 51.22 ± 12.01 MPa.
- Pre-sintered zirconia crown was soft-machined and the sintered body had a high mechanical strength of 942.77 ± 95.61 MPa.

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