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Rheological characteristics of zirconia slurries for gel-casting of a fixed partial denture (FPD) framework

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This study identifies the conditions for preparation of stable submicrometer zirconia slurries with a high solids content for the production of aqueous gel-casting fixed partial denture (FPD) framework with improved rheological properties. The effects of the powder and dispersant on the rheological properties were investigated. The results indicated that a polyelectrolyte dispersant had a significant effect on the surface charge of the zirconia powder and the rheological behavior of the suspension. In the optimal range for each factor, a low viscosity was achieved for a slurry of high solids loading. The optimal content of the dispersant is about 0.15 wt.%, based on zirconia. The rheological character of high solids slurries approximates non-Newtonian flow, with a 'shear-thinning' character changes as the shear rate is increased. The viscosity of the 80 wt.% powder slurry with 0.15 wt.% polyelectrolyte (based on the powder) was less than 3 Pa s^{-1} at a shear rate of 191 s^{-1}. Under these optimal conditions, a slurry met the demands of an aqueous-gel-casting process.

Key words: rheology, submicrometer tetragonal polycrystalline zirconia, polyelectrolyte dispersant, aqueous gel-casting process, fixed partial denture, framework.

Introduction

All-ceramic dental restorations are attractive to the dental community because they provide higher strength, higher abrasion resistance, better biocompatibility, and better aesthetics compared with metal and resin restorations [1-3]. On the other hand, the applications of all-ceramic crowns and bridges have been limited by their brittle behavior, long processing time, and poor machining performance [4-8]. A new method has recently been developed for making all-ceramic dental composites, glass-infiltration processing (In-ceram) [9, 10]. The alumina-glass composites obtained by this method have a low shrinkage, exceptional mechanical properties, and a homogeneous microstructure [4-8, 11]. Moreover, glass-infiltrated luminous-core restorations were made by combining the successfully Celay CAD/CAM system and In-ceram technology. In-ceram zirconia is the only product with 33% cerium stabilized zirconia. To date, no glass infiltration has occurred in pure zirconia-core restorations. Yttrium stabilized tetragonal zirconia (Y-TZP) is gaining recognition as a candidate material in dentistry due to its good mechanical properties [2]. It is currently used as a core material in full-ceramic dental restorations. Its superior mechanical properties compared to other dental ceramics are due to the transformation toughening mechanism, similar to that exploited in quenched steel [12]. Y-TZP has optimized physical properties and exhibits higher fracture toughness and fracture strength than alumina ceramic. However, a large volume change can becaused by the phase transformation of zirconia when cooling down from a high temperature after sintering, which makes the dimensions of the sintered body unstable. In this paper, a submicrometer-sized zirconia powder with a bimodal grain size was used to prepare the slurry for gel-casting of the fixed partial denture cores and frameworks, in which the larger grains assumed the responsibility for the dimensional stability and the smaller grains gave the most transformation toughening.

Compared to slip casting, gel-casting enables fabrication of complex-shaped green bodies with a high green strength and low binder content (< 5%) based on the in situ polymerization of an organic monomer binder. The advantages of gel-casting have received a great deal of attention in many research fields. Most gel castings use more than 15% binder content, such as monomer acrylamide which is neural toxin and is unsuitable for hand fabrication by technicians[13]. Here, gelatin, a natural non-toxic macromolecular polymer with a freezing temperature below 40 °C, was chosen as the gel system cross linking agent.

All-ceramic systems have the goal of reducing the number of defects to improve the strength and fracture toughness. Microstructure, composition, and processing have been reported to be the controlling factors in the development of the desired mechanical properties [14, 15].

This study focuses on identifying the optimal conditions

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for the preparation of stable slips with high solids contents for the production of aqueous gel-casting FPD frameworks and on correlating the slurry properties to the final FPD framework properties. The rheological behavior of slips prepared according to an optimum dispersant content was investigated based on zeta potential tests which achieved the best pH coverage for the dispersion.

Experimental Procedure

Materials

The submicrometer zirconium powder was supplied by the Sansai Company, Jiangsu province, PRC. The powder had a mean particle size of 400 nm and a specific surface area of 3.575 m^2g^{-1} (measured by the X-ray centrifugal sedimentation method, BI-XDC, Brookhaven Instrument Corporation, USA). The results are shown in Fig. 1. The characteristics of the powder were qualitatively and semi-quantitatively analyzed by X-ray Fluorescence (Axios-advanced, PANalytical, Neterland) and are summarized in Table 1. Gelatin with a chemical reagent purity (supplied by Shanghai Chemical Company, China), was used as the organic monomer. This study used the widely accepted commercially available polyelectrolyte dispersant ammonium polymethacrylate (Darvan C-N, RT Vanderbilt Co. Norwalk. CT. USA).

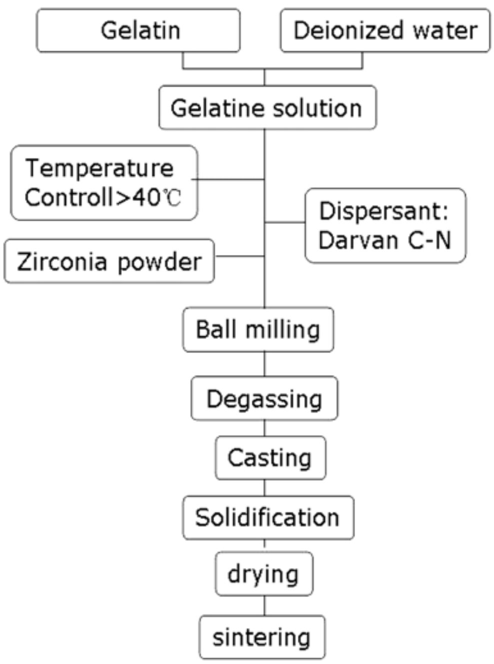

Fig. 1. Flow chart of the aqueous gel-casting process.

Table 1. Components of the zirconia powder

Analyte	Mg	Al	Ni	Y	Zr	Hf	Cl
Compound formula	MgO	Al_2O_3	NiO	Y_2O_3	ZrO_2	HfO_2	Cl
Measured (kcps)	2.754	6.532	0.640	336.460	1654.798	23.406	0.376
Used (kcps)	1.094	6.663	0.643	338.091	1681.457	23.494	0.379
Concentration (wt. %)	0.114	0.370	0.037	4.646	92.688	2.102	0.043

Procedure

The premixed solutions were prepared with zirconia powder and distilled water. With the ultimate goal of determining the optimum conditions to stabilize slurries with high solids contents, slurries with a 70 wt.% percent solids content using gelatin solutions as the solvent were treated by ball-milling with agates grinding media and a carnelian jar for 24 h after the addition of the dispersant. The 70 wt.% percent concentration was selected for the reason that it was the highest solids loading of water without the dispersant having better fluidity, a higher solids loading would become thicker and the dispersant would embody the notably dispersing effect. The optimal slurries were used to make the green body by aqueous gel-casting. A flow chart of the aqueous gel-casting process is shown in Fig. 1.

Measurement and analysis

The zeta potentials of the diluted zirconia suspensions (about 0.01 wt.% solids) were calculated from the electrophoretic mobility measured using a Zeta Plus Analyzer (ZetaPlus, Brookhaven, USA). Hydrochloric acid and sodium hydroxide solutions were used to adjust the pH value, and the zeta potential was determined as a function of pH. The particle size distribution of the powder was measured by the X-ray centrifugal sedimentation method (BI-XDC, Brookhaven Instrument Corporation, USA). Steady shear measurements of the viscosity were conducted at various shear rates with a stress-controlled rheometer (SR5, Rheometric Scientic Inc., Piscataway, NJ). The measurements were performed within a shear rate range of 1-1000 s^{-1} at a constant temperature of 25 °C. A JSM-6700F field emission scanning electron microscope was used to observe the microstructure of the green body.

Results and Discussion

Particle size distribution

The particle size distribution of the submicrometer sized tetragonal polycrystalline zirconia powder is shown in Fig. 2. From the particle size distribution measurements it was found that the powder exhibited a bimodal size distribution with a mean specific surface area of 3.575 m^2/g. Less agglomeration and smaller particle diameter could be noted in the dispersed powder (Fig. 3) compared with the undispersed (Fig. 2); 22% of the dispersed powder diameter was below 0.55 μm and 60% was about 4.34 μm, as desired to retain dimensional stability. Although the prevailing trend in ceramic processing is the development of very fine particles to enhance sintering rates as well as to reduce the size scale to enable mixing uniformity in powder blends, the combination of high solids loading and small particles leads to an increase in viscosity because

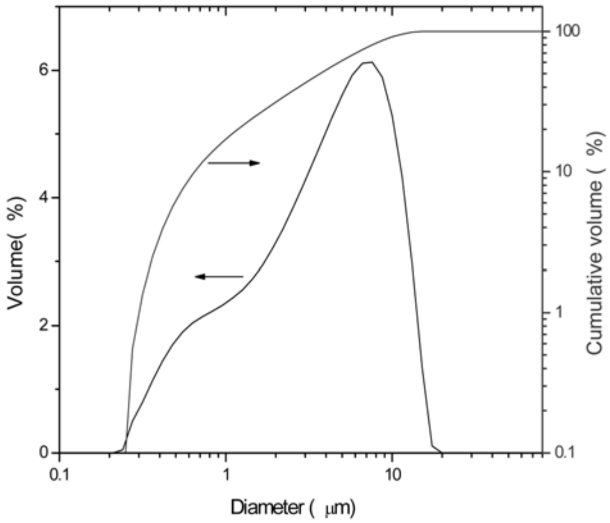

Fig. 2. Zirconia diameter.

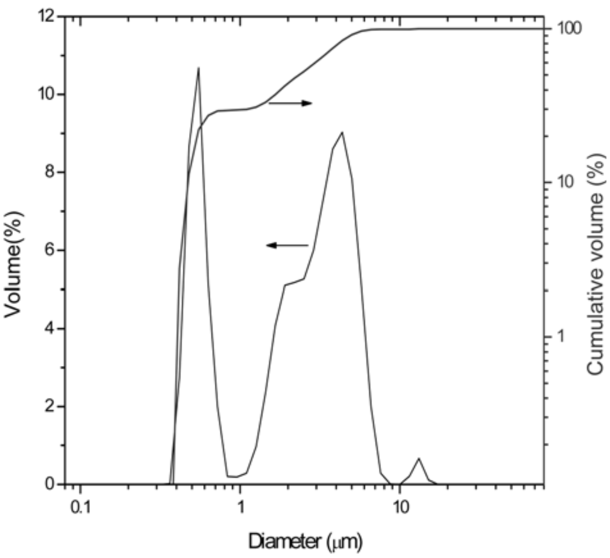

Fig. 3. Zirconia diameter distribution after dispersion via pH control.

of increased particle-particle interactions, and consequently to difficulties in the handling of a slurry [16]. We chose a submicrometer grade zirconia powder to achieve a balance between a high solids loading and a low viscosity slurry. At the same time, we achieved an ideal strength and control over the dimensional stability.

Zeta potentials

To identify the optimal pH value for stable slurries, zeta potentials of the submicrometer sized tetragonal polycrystalline zirconia powder with varying dispersant contents of 0, 0.15 and 0.3 wt.% (based on the powder) were measured. As shown in Fig. 4, the pure tetragonal polycrystalline zirconia suspension had an isoelectric point (IEP) of 5.0. A dramatic shift of the IEP occurs when the suspension is doped with a polyelectrolyte [17]. When Darvan C-N NH_4PAA (Molecular weight is 10,000-16,000) dispersant is added, the zeta potential becomes more negative and

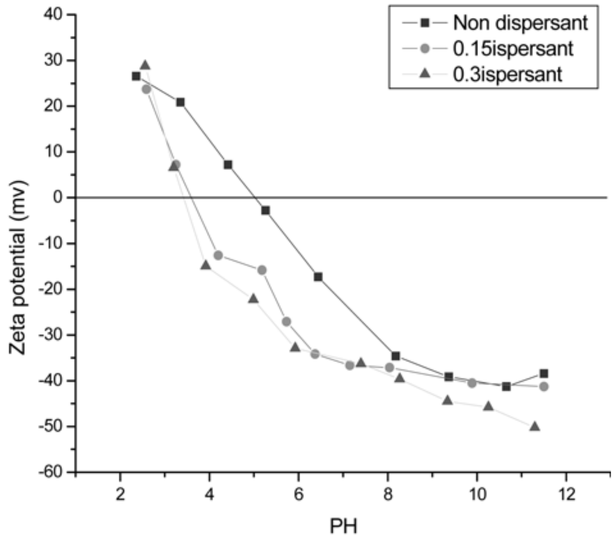

Fig. 4. Zeta potential vs. pH value dependence of zirconia powder.

the IEP is displaced towards acidic values, reaching a pH value of about 3.4. For the suspensions containing a dspersant, a relatively high zeta potential is about 40 mV at a pH value of 9-11, which is the optimal pH condition for stable dispersed slurries.

The zeta potential of suspensions with different dispersant contents at the same pH value (pH = 10) were tested, and Fig. 4 shows the change in the surface charge of zirconia particles with different volumes of addition.

Optimal rheological properties of slurries: effects of ammonium polymethacrylate

The addition of a dispersant can dramatically reduce the viscosity of slurries with very high solids contents as effective dispersant or deflocculant [18]. Dispersion of ceramic powders in a medium is achieved either by an electrostatic mechanism or a steric mechanism, or a combination of both [19-23]. The addition of a polyelectrolyte as dispersing agent helps to achieve stabilization by a combination of electrostatic and steric mechanisms. In an aqueous-based system, the additional parameter of pH can be controlled to achieve good dispersion. This becomes the unique advantage of aqueous processing, especially for ceramic-polymer composites [23-25].

A polyelectrolyte (NH_4PAA) was employed for the stabilization of slurries with 70 wt.% solids content, and it was used at concentrations of 0.1, 0.15, and 0.2 wt.% (based on the dry zirconia powder). The pH value of the slurries was adjusted between 10 with the addition of ammonium content. Fig. 5 shows the effect of the dispersant concentration on the viscosity. For every group, the flow curve deviates from a Newtonian behavior, its viscosity becomes lower as the shear rate is increased, which is known as shear-thinning in rheology [26]. Besides, it is found that the viscosity of slurry decreases with increase in dispersant dosage, and an optimum value of the dispersant dosage was discovered. It is noteworthy that the daaition of excess

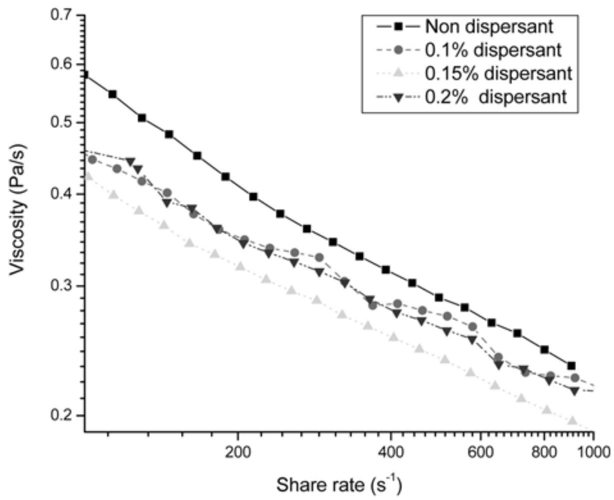

Fig. 5. Effect of NH_4PAA content on the suspension viscosity.

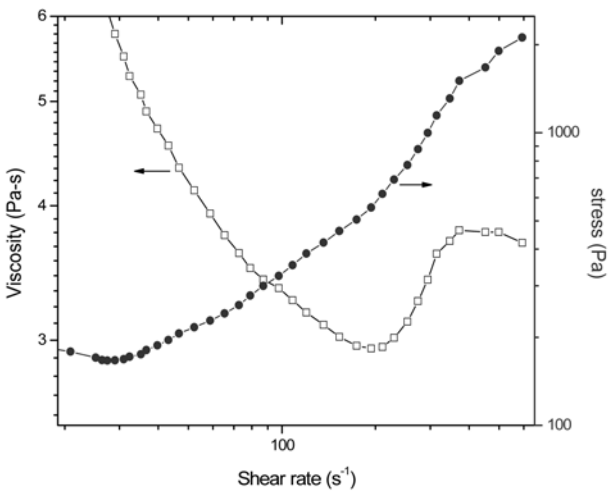

Fig. 6. The rheological curve of the highest solids loading slurries.

dispersant btings out an increase in the particle interaction and promotes the total destabilization of ceramic particles.

Particle-particle interactions are known to be strongly influenced by the deflocculant concentration. When an excess of a polyelectrolyte is not adsorbed by the particles, phenomena such as depletion or bridging of deflocculant chains can occur and lead to the flocculation of particles [21]. Flocculation by depletion arises when the non-adsorbed molecules of the polyelectrolyte are excluded from the interparticle gaps, resulting in an osmotic pressure difference that promotes coagulation. On the other hand, the free polyelectrolyte molecules in solution can be adsorbed partially on two particles at the same time, resulting in flocculation by a bridging mechanism. Since the solids content of a slurry with 0.15% dispersant content is the same as that with 0.2% dispersant content, the greater destabilization observed in the latter slurry can be explained in terms of the above-mentioned flocculation mechanism based on an insufficient adsorption of the excess deflocculant. With different dispersant contents for the 70 wt.% solids loading, the 0.15% dispersant addition gave the best flow curve.

The rheology of suspensions is greatly affected by the solids loading of submicrometer sized zirconia powder. High solids loading was pursued to achieve less sintering shrinkage which is better for core margin adaption, at the same time, the suspension for handcrafting does not need very high fluidity, so this experiment did not test the viscosity with different solid contents.

For every group, the flow curve deviates from a Newtonian behavior, its viscosity becomes lower as the shear rate is increased, which is known as shear-thinning in rheology. These results indicate that solids content exerts a distinct effect on the rheology of high loading slurries.

At the highest solids loading of 52.7 vol.%, the powder dominates the great part of suspension, which gradually shifts to a non-Newtonian fluid. As shown in Fig. 6, its viscosity decreases initially, which is consistent with the shear-thinning charcter in Fig. 5; then hoiks, evincing the reinforced van der Waals attractive potential within a short particle separation distance. From another point of view, the frequency of particle interaction with each other increases for the higher solid loading slurry. The results indicate that solids content exerts distinctly effect on rheology of high loading slurries.

Fortunately, the slurry viscosities of the higher solids concentrations (52.7 vol.%) are still less than 3 Pa s^{-1} at a shear rate of 191 s^{-1}. This means that the slurry meets the demand of an aqueous-gel-casting process.

The property of the green body

For a high performance green body produced by an aqueous-gel-casting process, the optimal conditions of the zirconia powder slurry are a pH value of 10 and a 0.15 wt.% dispersant content (based on the powder) with an 52.7 vol.% submicrometer sized tetragonal polycrystalline zirconia powder. According to the flow chart shown in Fig. 1, the slurry was used to form a green body by the aqueous-gel-casting process. The flexural strength of the $3 \times 4 \times 36$ mm^3 green body was 7.36(± 0.14) MPa, which is enough

Fig. 7. Picture of the core of the FPD.

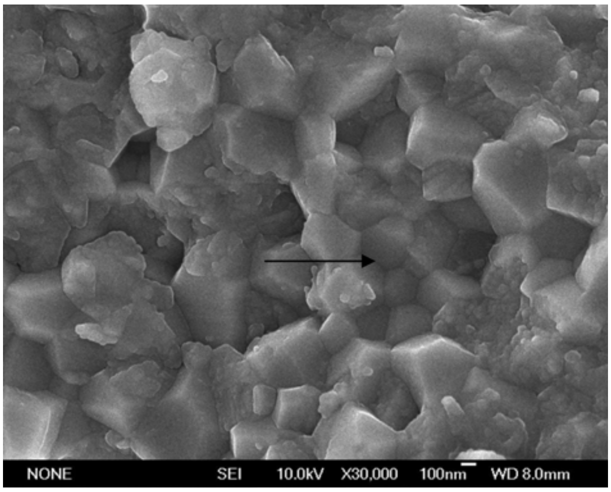

Fig. 8. SEM micrograph of the sintered green body.

for simple machining and finishing. Fig. 7 shows a general picture of an all-ceramic fixed partial denture framework molded manually by using 50 vol. % solid slurry and Fig. 8 shows a SEM image of the microscopic morphology. As shown in Fig. 8, a homogenous structure was observed without large agglomerates and voids. These results validate the credibility of the optimal slurry conditions. As shown in Fig. 7 and Fig. 8, the general picture and SEM of the FPD framework (after being sintered) made by gel-casting, the structure demonstrated the feasibility and stability of the slurry in the optimal conditions. While the uniform and dense structure took up a majority of the body, pores were also found, as indicated by the arrow in Fig. 8, which is consistent with the foaming tendency of gelatin.

The sintering properties and mechanical properties after sintering will be investigated in future work.

Conclusions

Through the addition of a polyelectrolyte and regulation of the pH, the zeta potential was maximized and gave the submicron sized zirconia powder a bimodal diameter distribution. From rheological tests, the optimal dispersant addition was indicated to be 0.15 wt.%. An up to 52.7 vol.% solids loading slurry with a low viscosity was created. A FPD framework was shaped with a 50 vol.% slurry by hand, and SEM observations showed a uniform and dense structure which verified that gel-casting of a high solids loading slurry is a suitable mathod for making dental frameworks.

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