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Effect of pH of Suspension and Mechanical Treatment on Nanosized Zirconia Dispersion

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ABSTRACT

Understanding zirconia 3YSZ powder dispersion is crucial in achieving colloidal stability in order to produce high-strength and translucent structures required for dental applications. In this work, pH adjustment (pH 1–11) and mechanical treatment (ball milling, ultrasonic treatment, and centrifugation) were employed to remove agglomeration. As-received zirconia 3YSZ powder was characterized by transmission electron microscopy, Brunauer–Emmett–Teller method, and laser light scattering technique to identify the primary particle size and to verify the presence of powder agglomeration. Particle dispersion of nanosized zirconia 3YSZ in aqueous suspension at various pH and different mechanical treatments were investigated by measuring the particle size distribution and zeta potential. The particle size of zirconia powder after adjustment to pH 2 was found to decrease (195 nm) compared with that of the as-received powder (388 nm), thus indicating the occurrence of powder de-agglomeration. A higher zeta potential value was also observed at pH 2. The isoelectric point of the suspension was at pH 10.7, where agglomeration was found to occur. This result is in good agreement with the average particle size result, in which larger particle sizes were observed at pH

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10 to 11. In addition, ball milling was found to be an effective method to remove weak agglomeration given that small particle sizes measuring 164 nm were produced, whereas ultrasonic and centrifugation treatments worsened the powder dispersion. Zirconia suspension at pH 2 and prepared via ball milling was well-dispersed and suitable for further consolidation process.

Keywords: *Zirconia 3YSZ, Colloidal processing, pH Suspension, Colloidal stability, Ball milling.*

Introduction

Nanosized zirconia with a large specific surface area can be highly beneficial to the mechanical performance of dental materials. The use of fine powder reduces sintering temperature during materials processing, hence allowing the formation of fine grain sizes. The fine grains will then improve the mechanical properties and translucency of the zirconia structure [1][2]. However, challenging issues were encountered during the use of nanosized powders in product development. The initial powder had the tendency to agglomerate, resulting in the depreciation of the mechanical performance of the end-product.

Wet forming method is an effective technique implemented to overcome the strong tendency of the powder toward agglomeration [3]. This technique intentionally manipulates interparticle interaction in the suspension in order to disperse the individual particles and achieve suspension stability. This technique, named colloidal processing, can basically be initiated via the addition of certain reagents, dispersants, or via mechanical actions such as ball milling, ultrasonic treatment, or centrifugation [3,4].

Two main forces are present in oxide ceramics (for example, alumina, zirconia, etc.) while in suspending medium, namely attractive van der Waals and repulsive electrostatic forces [3]. This interparticle force can be controlled by adjusting the pH of the suspension through the addition of an acidic or basic reagent that changes the surface charge of the particle. The surface charge modification will generate a potential from the electrical double layer that can be measured via zeta potential value. When a high zeta potential value is detected, the electrostatic repulsion generated is maximized and particle separation occurs [5].

Controlling the pH of the suspension will introduce the isoelectric point (IEP), which is defined as the pH value of a suspension at which the net electric charge of the particles is equal to zero [6]. At this point, the particles adhere to each other to form an agglomeration due to the weak repulsive forces. Therefore, the pH adjustment technique that aims to create a surface charge to induce a repulsive force should avoid the pH value closest to the IEP.

Powder dispersion can also be achieved via dispersant addition (usually polyelectrolyte) into the suspension to form steric or electrosteric stabilization [7]. This method needs an appropriate dispersant at optimum quantity under a particular pH suspension condition [7,8]. However, a study that did not apply this technique successfully eliminated agglomeration and noticed that the addition of a dispersant deteriorated powder dispersion [9]. The alteration of surface charge by pH adjustment may break the hard agglomeration into individual particles or small agglomerates only. Previous studies demonstrated that nanosized ceramics that have strong agglomerates are not easily separated [9,10]. They suggest the application of mechanical treatment, such as ball milling, ultrasonic treatment, and centrifugation attrition milling, to assist particle separation of weak agglomerates that may remain in the suspension [4,10,11].

However, most of the previous studies tend to investigate the effect of pH adjustment together with dispersant addition (polyelectrolyte) only to define the powder dispersion. Studies on the effect of mechanical treatment are not yet fully established and this limited information has driven the authors to investigate the effect of pH suspension adjustment along with different mechanical treatments towards powder dispersion.

Experimental Details

Materials and characterization

The raw material used in this experiment was 3 mol% yttria-stabilized zirconia (3YSZ) powder supplied from Inframat Advanced Materials, USA. The morphology and particle size of the as-received powder were characterized by transmission electron microscopy (Philip, TEM CM12) and laser light scattering technique (Zetasizer Nano ZS, Malvern), respectively. The Brunauer–Emmett–Teller (BET) technique via N_2 gas adsorption (micromeritics ASAP 2020) was used to examine the specific surface area of the as-received powder.

Suspension preparation

Aqueous zirconia 3YSZ suspension was prepared with 10 vol% solid loading using distilled water as a colloidal medium. The pH of the zirconia suspension was adjusted to pH = 1–11 using HNO_3 and NaOH. The suspensions were magnetically stirred for 45 min. The zeta potential value and particle size of each suspension were examined to identify the most homogenous suspension with well-dispersed zirconia particles.

Three different mechanical treatments (ball milling, ultrasonic treatment, and centrifugation) were performed to de-agglomerate the optimized suspensions with specific pH values. These mechanical processes were performed to separate or break the powder aggregates that might be present in the suspension. The first batch of zirconia suspension was milled in a Fritsch Pulverisette-6 planetary ball mill. Milling was performed in a zirconia jar with 10-mm-diameter zirconia balls as grinding media and at a rotational speed of 200 rpm for 1 h. The ball-to-powder ratio was 1:1.

The second batch of zirconia suspension was subjected to ultrasonication using an ultrasonic instrument (Ultrasonik 28X). The suspension was prepared in a beaker. The beaker was then immersed in distilled water in an ultrasonic bath. The ultrasonic treatment was conducted at a frequency of 50 Hz for 15 min at room temperature.

The other batch of zirconia suspension was centrifuged using a centrifuge machine (Kubota 2100). The suspension was prepared in a vial, which was then placed vertically in the centrifuge chamber. The suspension was centrifuged at 4,000 rpm for 15 min.

Particle size and zeta potential measurement

Laser light scattering technique was performed on a suspension that was diluted into approximately 0.1 wt% zirconia 3YSZ powder. The measurement was carried out by a particle size analyzer instrument as mentioned earlier. This instrument was also used to measure the zeta potential value of the same suspension at various pH. Zeta potential measurement is mainly employed to identify the dispersion behaviour of the powder in the suspension.

Results and Discussion

Materials characterization

The average particle size of the as-received zirconia 3YSZ powder observed by transmission electron microscopy (TEM) was 30 nm with homogenous spherical shapes (Figure 1). Highly agglomerated nanopowders can be observed as a result of van der Waals forces attraction [3]. The average particle size detected via light scattering technique was found to be 388 nm (Figure 2). The difference in sizes as generated by these two different techniques confirmed that agglomerates were present in the as-received fine powder. The specific surface area of the as-received powder was approximately 32 m^2/g, as measured by nitrogen adsorption via BET analysis. Rafferty et al. [12] stated that powders with larger surface areas produce undesirable agglomeration but contribute positively to the sintering process by causing the driving force for diffusion to be increased.

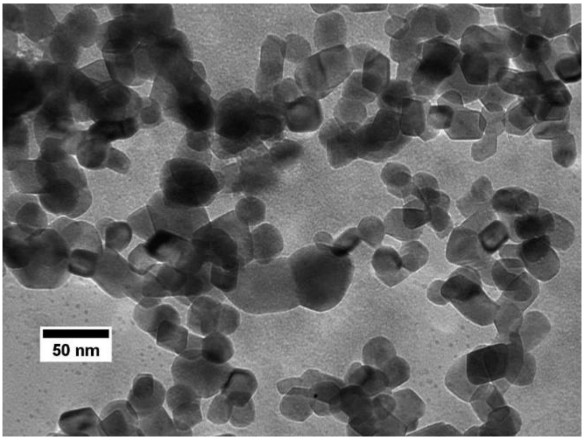

Figure 1 TEM image of as-received zirconia 3YSZ powder.

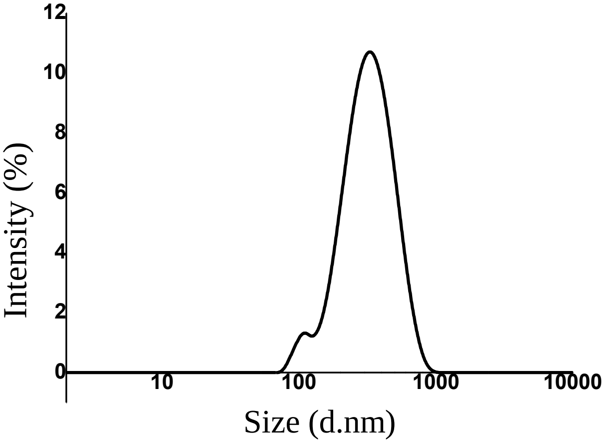

Figure 2 Average particle size of zirconia 3YSZ powder.

Particle size distribution and zeta potential value

Zirconia powder suspension at pH 2 produces the smallest mean particle size of approximately 195 nm (Figure 3). Upon dispersion in distilled water suspension of pH 2, ion adsorption with either H^+ or OH^- ions occurs on the large zirconia particle surface. The ion adsorption creates a high surface charge density on the particle surface that generates a strong repulsive electric double layer force. This ion adsorption eventually stabilizes the interparticle forces between the individual particles and break the agglomeration. Meanwhile, the particle size increased with increasing pH values of 3 to 11, with maximum particle size appearing at pH 11. This finding indicates that powder agglomeration was present in the suspension. In this state, H_2O molecules bridged the particle adsorbed by OH^- ion with another particle surface charge of OH^- ion via hydrogen bond and developed large agglomerates. This phenomenon occurs when the pH value is increased due to the presence of a large number of O and H atoms at basic pH values [10].

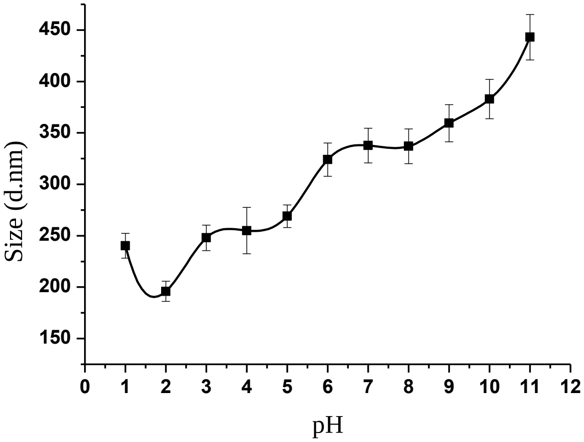

Figure 3 Particle size distribution of zirconia 3YSZ suspension at various pH.

Zeta potential value of zirconia powder in suspension at various pH values is shown in Figure 4. The IEP of the studied zirconia powder is approximately pH 10.7. The higher the zeta potential value, the stronger the repulsive force performed by the diffuse layer around the particle. Meaning that the better the dispersion of particles in the suspension. Zeta potential values of zirconia powder decrease when approaching the IEP and indicate a low or almost zero particle charge at that point. Consequently, flocculation occurs and entraps water molecules, resulting in agglomeration and unstable suspension [6]. This phenomenon was observed during the experiment, where the suspension became highly viscous and coagulated between pH values of 10 to 11.

The zeta potential value of the suspension was found to be highest at pH 2, indicating the occurrence of the highest level of particle dispersion. The result was consistent to the lowest average particle size gained from the laser light scattering technique. This available evidence demonstrates a fair agreement with previous studies that show that high zeta potential which is located far from the IEP separates the particles from each other [6]. Meanwhile, according to Hanifi et al. [10], a higher amount of acid and base are required to alter the pH and achieve suspension stability when the surface area is higher. However, the increase in ionic strength of the suspension via pH adjustment under acidic (in this study; pH 1) and basic (in this study; pH 10 -11) conditions will eventually compress the thickness of the electric double layer and weaken the repulsive force. This behaviour, caused by the excessive surface charge packing density possessed by the particle, causes the double layers around the particles to overlap with one another. This circumstance will narrow the distance between the individual particle repulsive forces, thus inducing the agglomeration of particles.

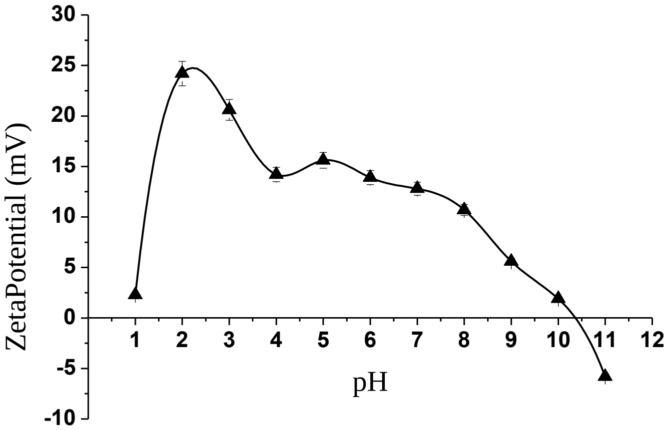

Figure 4 Zeta potential value of zirconia 3YSZ suspension at various pH values.

Adjusting the pH of the zirconia suspension to achieve a well-dispersed powder and suspension stability has been proven to be an effective technique to break the agglomeration naturally possessed by nanosized powders. In this study, the pH 2 adjustment has managed to reduce the average particle size from 388 nm to 195 nm only. Mechanical treatment has to be conducted further to break the soft agglomerates that may remain even after the pH adjustment. Figure 5 shows the average particle size of zirconia powder after being treated by different mechanical actions. Performing ball milling procedure on the zirconia suspension under pH 2 caused the removal of weak agglomerates and reduced the particle size to 164 nm. This result was consistent with the findings obtained by Pradhan et al. [4] where ball milling treatment reduces the particle size of powder agglomerates. Meanwhile, particle size yield from ultrasonic treatment and centrifugation was 220 nm and 396 nm, respectively, where the particle sizes obtained were larger compared with that after pH 2 adjustment.

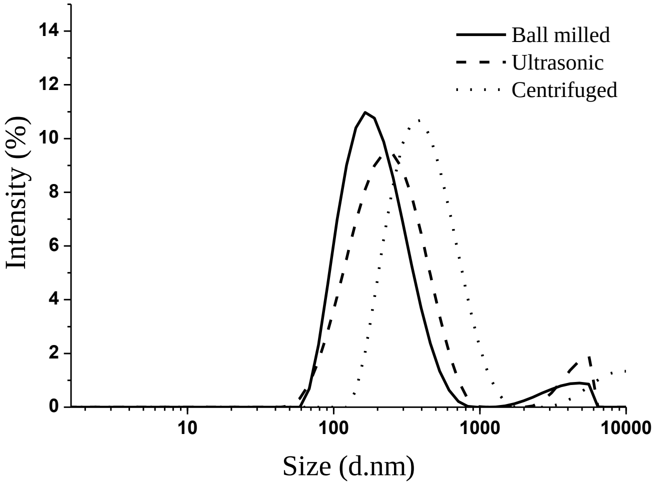

Figure 5 Particle size distribution of zirconia 3YSZ powder after different mechanical treatments.

The ball milling process effectively broke up powder agglomerates and reduced the particle size of the zirconia powder. The powder agglomerates were broken up when they physically collided with the grinding balls. The broken particles were dispersed in the prepared suspension with the addition of the optimal amount of dispersant. The prepared suspension was stabilized at the appropriate pH. However, previous studies have shown that the elimination of agglomerates by mechanical action may be unsuitable under certain parameters or conditions and may possibly introduce additional problems [5,9].

By contrast, ultrasonic treatment did not considerably improve the dispersion of zirconia particles. The introduction of ultrasonic waves to the zirconia suspension generated microbubbles, which then collapsed and created shock waves that broke up the aggregated powder. However, ultrasonication can only break up powder aggregates of a certain size within a certain period. Prolonging the duration of ultrasonic treatment may cause a thermal effect that increases the steam pressure of the microbubbles [5]. The microbubbles thus become difficult to collapse and prevent the production of shock waves that disperse the particles. The Brownian motion of the particles is also induced. The dispersed particles then re-aggregate because of the thermal effect caused by ultrasonication.

Centrifugation adversely affected colloidal stability and was unsuitable for de-agglomeration because most of the powder became accumulated at the bottom of the vial. Centrifugation, however, enabled the separation of fine particle from the hard agglomerates. The high rotational speed during centrifugation kinetically drove the remaining agglomerates deposited and left the fine particles suspended. This phenomenon will reduce the powder loading of the suspension because the agglomerated powder in the suspension is not preferred for consolidation.

Conclusions

The effects of pH and mechanical treatment on the dispersion behavior of nanosized zirconia 3YSZ powder were studied. In all cases, the presence of nanosized zirconia 3YSZ agglomerates in this study adversely affects powder dispersion and colloidal stability of the ceramic suspension. Surface charge manipulation via pH adjustment found that pH 2 was the optimum pH for powder de-agglomeration. Ball milling was found to be an efficient and simple technique to remove soft agglomerates and preserve suspension stability. Further research work is needed to improve nanosized powder dispersion via both ultrasonic and centrifugation treatments.

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