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SYNTHESIS AND CHARACTERIZATION OF MULLITE-ZIRCONIA NANO PARTICLES BY SOL-GEL METHOD AS FILLER OF DENTAL COMPOSITE

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KEYWORDS

Mullite
Zirconia
Nano particles
Sol-gel
Dental composite

ABSTRACT

Background. *Currently, researchers are working on the development of dental composite fillers that are composed of a combination of two or more inorganic materials.* ***Objective.*** *The study aims to synthesis mullite-zirconia using the sol-gel method and observe the influence of zirconia on the particle characteristics of the filler including the size of the diameter, distribution and charge of the filler.* ***Methods.*** *The design of this study is descriptive explorative. The study consisted of four sample groups: 100% mullite (M); 85% Muliite - 15% zirconia (MZ15); 80% Mullite - 20% circonia(MZ20); 75% mullites - 25% zirconía (MZ25). The mullite-zirconia filler synthesis was initiated by mixing the hydrolyzed-precursor after hydrolysis stage then were dried for 6 hours at 100 °C. The ZrO_2 was mixed with the Mullite according to the prescribed ratio. The sample was then characterized using Particle size analysis and Zeta potential (HORIBA)* ***Result.*** *The results showed that the mullite-zirconia particle sizes decrease as the amount of zirconia added after the hydrolysis phase increases. Sample M, MZ15 and MZ20 showed polydisperse particle distribution while MZ25 showed monodispersed particle distribution. Mullite and mullite-zirconia particle loads in the range of 10-30 mV. This shows that the stability of the particle is incipient* ***Conclusion.*** *Nano-sized mullite-zirconia particles were successfully synthesized using sol-gel methods. Increased zirconium in the mullite-zirconia ratio decreased the diameter of the particle and particle load and resulted in a more homogeneous particle distribution*

INTRODUCTION

Dental composites provide several advantages, such as better aesthetic qualities and conservative behaviour toward the tooth structure because of its adhesive mechanism, which eliminates the need for extensive tooth preparation.[1,2] The two primary components of dental composites are inorganic filler and organic resin, which serves as the matrix. Multifunctional monomers and initiators are combined to create organic resins, whereas inorganic fillers come in a variety of sizes (from nanometers to micrometers), forms, and purposes.[3-5]

Despite the greater mechanical and physical qualities of the modern dental composites compared to classic composites, their average lifespan is slightly less than ten years,

necessitating expert intervention thereafter. Consequently, to address the issues, researchers have introduced many advancements in dental resin composites with the aim of enhancing the characteristics of dental composite materials.[2,6,7] The fillers in dentistry have undergone substantial improvements and modifications, particularly in terms of size reduction, form enhancement (including platelike, rods, and nanoparticles), functionalisation, and the potential to be bioactive. These upgrades of dental composite have been made to meet the specific requirements of dentists.[5,8]

The early dental composite known as macrofill composites were filled with large particles ranging in size from 10 to 50 μm, resulting in limited polishability and aesthetics. Subsequently, there has been a growing trend towards reducing the physical size of particles.[9-11] The industry traditionally use procedures that include high synthesis temperatures and extensive grinding times to produce smaller particle of fillers. These processes also demand significant amounts of water and HCl, making them environmentally unfriendly. The sol-gel process is appealing due to its low energy consumption, as it allows for nano-sized filler synthesis to be conducted at low temperatures.[1,8,12]

Borosilicate glasses, quartz, Al_2O_3, and zirconia belong to the conventional filler particles, available in different sizes and forms.[13-15] Currently, researchers are working on the development of fillers that are composed of a combination of two or more inorganic materials, such as alumina-silica, aluminium-zirconia, fluoroaluminasilica, and so on.[16,17] Variations in the ratio of each component are known to result in changes in the properties of the filler.[12,13,18] The study aims to synthesis mullite-zirconia using the sol-gel method and observe the influence of zirconia on the particle characteristics of the filler including the size of the diameter, distribution and charge of the filler. Particle size analysis (PSA) and Zeta potential tests are employed to determine the size and electrical charge of nanoparticles.

METHODS

The design of this study is descriptive explorative. The precursor of the mullite-zirconia fillers consists of Aluminium Nitrate Nonahydrate ($Al(NO_3)_3$); Merck, CAS number: 7784-27-2. Zirconium Chloride (ZrCl4); Merck, Cas number: 10026-11-6. Tetraethyl Orthosilicate (TeOS); Merck (CAS) number: 78-10-4. The study consisted of four sample groups: 100% mullite (M); 85% Muliite - 15% zirconia (MZ15); 80% Mullite - 20% circonia(MZ20); 75% mullites - 25% zirconía (MZ25).

The mullite filler synthesis procedure was initiated by dissolving the TeOS precursor into the ethanol solvent and then stirring over the magnetic stirrer for 30 minutes. The pH of the solution was adjusted with 1 N CH_3COOH with heating to 45ºC. $Al(NO_3)_3$ was added and stirred for 30 min. Aquadest was added little

by little to accelerate hydrolysis. The samples were then dried up in the oven at 60 °C to start the gelation stage for 2 hours. Increase in the temperature to 100 °C for 6 hours then the mullite powder was acquired. In the mullite-zirconia samples, the hydrolysis of zirconia was synthesized separately using the $ZrCl_4$ and aquadest that were mixed over the magnetic stirrer for 30 minutes. Zirconia was then mixed with mullite prior to gelation stage then dried in the furnace at 60°C for 2 hours. The samples were continuously dried for 6 hours at 100 °C. The ZrO2 was mixed with the Mullite according to the prescribed ratio. The sample was then characterized using Particle size analysis and Zeta potential (HORIBA).

RESULTS

Table 1 shows that the mullite sample produces the largest particle size among all groups of 219 nm. The mullite-zirconia particle sizes decrease as the amount of zirconia added after the hydrolysis phase increases. The smallest size is shown by the MZ25 sample of 121.8 nm. Standard deviation values of each sample group are included in the table.

Table 1. Average particle size and standard deviation of mullite-zirconia particles.

No	Sample	Average size (nm)	Standard Deviation (nm)
1	M	219.0	100.1
2	MZ15	191.0	97.8
3	MZ20	142.9	102.7
4	MZ25	121.8	70.6

Figure 1 shows that the mullite sample produces a polydisperse peak (more than 1 peak) which means that the particle distribution is not homogeneous. The mullite sample shows two peaks, a smaller peak in the area of < 100 nm diameter and a larger peak at the area > 100 nm. The MZ15 and MZ20 sample show a similar picture, but the peak height in the region < 100nm increases as the number of zirconium increases. Meanwhile, the MZ-20 sample displays a monodispersed peak (1 peak), which is visible in an area of about 100nm.

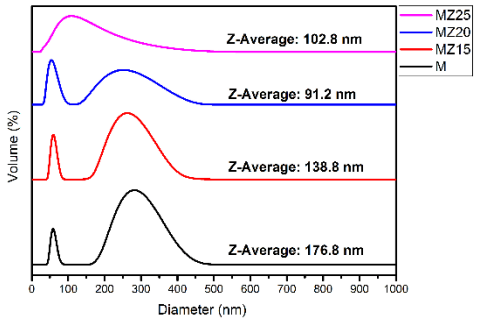

Figure 1. Disperse graphic of the particle distribution of the mullite and mullite-zirconia samples

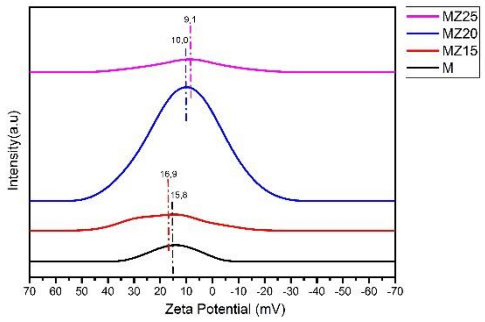

Figure 2. zeta potential values of the filler particles mullite and mullite-zirkonia.

Figure 2 shows Mullite and mullite-zirconia particle loads in the range of 10-30 mV. This shows that the stability of the particle is incipient. The increase in the amount of

zirconium causes the charge value to be closer to 0 mV.

DISCUSSION

Table 1 displays the particle diameter measurements obtained through the utilization of the Dynamic Light Scattering (DLS) technique. DLS, or Dynamic Light Scattering, is a widely used technology for measuring the size of particles. It works by analyzing the changes in light scattered by particles in a suspension due to their random motion, known as Brownian motion. This allows for the determination of the distribution of the hydrodynamic size of the particles. DLS quantifies the extent of particle diffusion in response to increasing concentration and/or for particles of lower size.[19,20]

The results show that the size of the Mullite-zirconia particles decreases as the amount of zirconia increases. This is supposed to be due to the inhibition of the growth of mullite particles at the stage of condensation and aging.[21,22] Figure 3. assumes the process of hydrolysis and condensation that occurs in the precursors TEOS and $Al(NO_3)_3$. TEOS is protoned by ethanol and acetic acid to form a silanol compound by producing ethyl acetate as a by-product. At this stage the precursor-precursor undergoes a hydrolysis reaction triggered by the presence of H^+ of the CH_3COOH catalyst. This reaction is said to be hydrolysed due to hydroxyl ions then binding to metal atoms namely Si and Al. The hydrolyse reaction will be followed by a condensation reaction in which silanol undergos a temporary polymerization process, $Al(OH)(H_2O)^{3+}$ undergoing an olation process. At the condensation stage, compounds with polyfunctions (the number of bonds that a compound can form) more than two, such as $Si(OH)_4$ and $Al(OH)_3$, can merge through cross bonds to form three-dimensional structures. The free hydroxyl group in alumina is supposed to be the growth nucleus. Zirconium ions are supposedly forming hydrogen bonds in the growth core thus inhibiting the growth of mullite particles.[21-24]

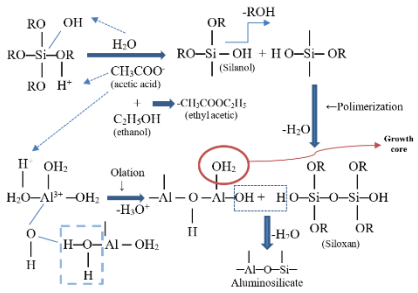

Figure 3. Hydrolysis reaction between silicon alcoxide (OR = OC2H5) and acid catalysts as well as cross linking reactions between silanol and aluminum on hydrophilic surfaces.

Figure 1 shows the polydisperse graph on the particles M, MZ15 and MZ20. This is supposed to be due to the lack of zirconium ions that can control the growth of mullite particle diameters. MZ20 shows more controlled and homogeneous particle diameter sizes. This result is consistent with the result seen in table 1. The peak of the graph is seen monodisperse in an area close to 100 nm. Homogeneous and smaller particle sizes are more capable of producing better

polish ability properties on dental composites.[10] These results are supported by the results of Aquiar et al showing that commercial dental composite fillers generally show monodisperse graphs. Dental composite studied in this study is a composite that has a good polish ability.[8]

Zeta potential is a characteristic displayed by particles that are suspended in a liquid. The source of surface charges changes depending on the characteristics of the particle and the medium in which it is located. The magnitude of the zeta potential provides insight into the possible stability of a system. However, a specific threshold value is required to determine the stability of a suspension containing dissimilar particles, such as dental resin composites. Under these conditions, the relative zeta potential was solely utilized to assess the colloidal stability of similar particles in the identical medium. Particles in suspension having a significant negative or positive zeta potential tend to reject one other, resulting in a reduced likelihood of particle aggregation. If the particles possess a low zeta potential or are electrically neutral, there may be insufficient forces to hinder particle aggregation.[22,25,26]

Figure 2 shows M fillers, MZ15, MZ20 and MZ25 have a positive charge. The entire sample has a charge in the 10-30 mV range which is included in the incipient stability. Load values close to zero indicate that the particles are undergoing aggregation. These results show that the increase in zirconium ions also increases the degree of aggression in the formation of mullite particles.[21] Aquiar et al research shows that commercial composite dental filler particles generally have a positive charge and potential zeta values ranging from 10-50 mV.[8] Zeta potential values are known depending on the type of filler and the ageing conditions of the particle filler.[26]

CONCLUSION

Nano-sized mullite-zirconia particles were successfully synthesized using sol-gel methods. Increased zirconium in the mollite-zirconium ratio decreased the diameter of the particle and particle load and resulted in a more homogeneous particle distribution.

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