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Synthesize and Characterization Zr-Al-Si Post Through Eggshell Membrane Strengthening with PMMA Matrix

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Abstract. Zr-Al-Si posts were successfully synthesized using biotemplate of eggshell membrane by sol-gel method and strengthening with matrix of polymethyl methacrylate (PMMA). The dental posts made were analyzed with the scanning electron microscope (SEM), three point bending and microvickers hardness tester. There are two methods used to synthesized Zr-Al-Si posts, with calcination and without calcination. The synthesized mechanism is discussed here.

Introduction

A dental post is used when the remaining coronal tooth tissue can no longer provide adequate support and retention for the restoration. Restorative dental materials that can be used to replace tooth structure include metal-ceramics, ceramics, resin-based composites, denture polymers and etc[1]. The mechanical structure of a dental post will be compared to the mechanical structure, hardness and modulus elasticity, of a dentin. The hardness of dentin are 53 – 63 HVN [2] and 65.6 HVN [3]. The elastic modulus of dentine are 5.3 – 6.1 MPa for the incisors and canine teeth [4] and 1653.7 MPa for the premolar teeth [3].

Eggshell membrane (ESM) is a unique biomaterial, which is generally considered as waste. However, it has extraordinary properties and potential to be used in various applications [5]. The mesh biopolymer structure in ESM yield an elastic modulus of 235.24 MPa [6]. Zirconia holds a unique place amongst oxide ceramics due to its excellent mechanical properties. The addition of alumina is used as a stabilizer for zirconia[7]. The esthetic properties of silica makes them the material choice for ceramic restoration [8].

Herein, we use the biomaterial eggshell membrane as the biotemplate to synthesize dental post using the ceramics of zirconia, alumina and silica through sol-gel method and strengthening with the PMMA matrix, followed by the calcine process.

Materials and Methods

Materials. All the reagents used in the experiments were analytical grade. $ZrCl_4$, $Al(NO_3)_3$, and sodium silicate were purchased from Merck. Chitosan low molecular weight and polymethyl methacrylate (PMMA, Mw 350,000) were purchased from Sigma-Aldrich.

Preparation of Eggshell Membrane. Eggshell washed thoroughly in water to remove the albumen from the eggshell membrane. The washed eggshell was immersed in 1M nitric acid solution to dissolve the $CaCO_3$ mineral to obtain the eggshell membranes. After that, the eggshell membranes were cleaned by immersing them into a 0.1M NaOH solution for 24 hours.

Preparation of Precursor Zr-Al-Si. The precursor mixture solution of $ZrCl_4$, $Al(NO_3)_3$, sodium silicate and sodium citrate buffer were made in three variations like in the **Table 1**.

Table 1. Variations of the precursor mixture solution

Solutions	M	Variations (%v)		
		1	2	3
$ZrCl_4$	0.5	40	35	25
$Al(NO_3)_3$	0.5	5	7.5	12.5
Sodium silicate	0.5	5	7.5	12.5
Sodium citrate buffer	1.75	50		

Synthesize of Zirconia-Alumina-Silica Post. There are two methods applied in synthesize the Zr-Al-Si post. The first method is using the calcination process. The eggshell membrane was dipped in 1% (m/v) chitosan solution and immersed in the precursor of Zr-Al-Si in vacuum condition for 24 hours. Then, the eggshell membrane was calcined in the temperature of 850^{o}C until it decomposed. After that, the Zr-Al-Si nanoparticle products were mixed with the 25% (m/v) fully dissolved polymethyl methacrylate (PMMA) matrix. The mixture was moled using glass mold with 1.5 cm of length and 1.5 mm of diameter. The second method is synthesizing Zr-Al-Si posts without the calcination process. After the eggshell membrane was dipped in 1% (m/v) chitosan solution and immersed in the Zr-Al-Si solution in vacuum condition for 24 hours, it is widened in a petri dish and rolled to form a post. Then, the post is dipped in chitosan solution (1% and 2% (m/v)) and immersed in the solution of PMMA matrix (8% and 10% (m/v)).

Characterization. The morphology of the Zr-Al-Si posts were analyzed using SEM (JEOL-JSM-6510LV). The mechanical properties were tested by Microvickers Hardness Tester (LECO-Japan M-400-H1/H2/H3) and Three Point Bending (TENSILON UCT-5T).

Result and Discussion.

The SEM image in **Fig.1** shows the Zr-Al-Si nanoparticle products by calcination were in an interwoven structure. The Zr-Al-Si were successfully templated in the eggshell membrane using the *sol-gel* method. **Fig.2** shows the post with calcination had an excellent cross-sectional morphology with almost no cavity on the surface. Meanwhile, the post without calcination shows its best cross-sectional morphology using 2% (m/v) chitosan and 10% (m/v) PMMA matrix, **Fig.3 (b)**.

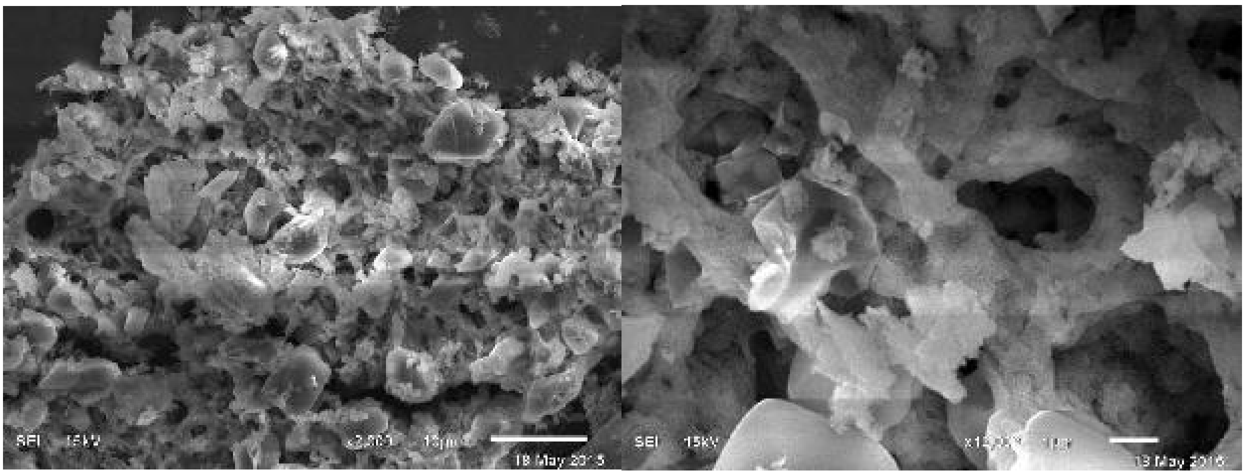

Figure 1. The Zr-Al-Si nanoparticle products through calcination templated by ESM.

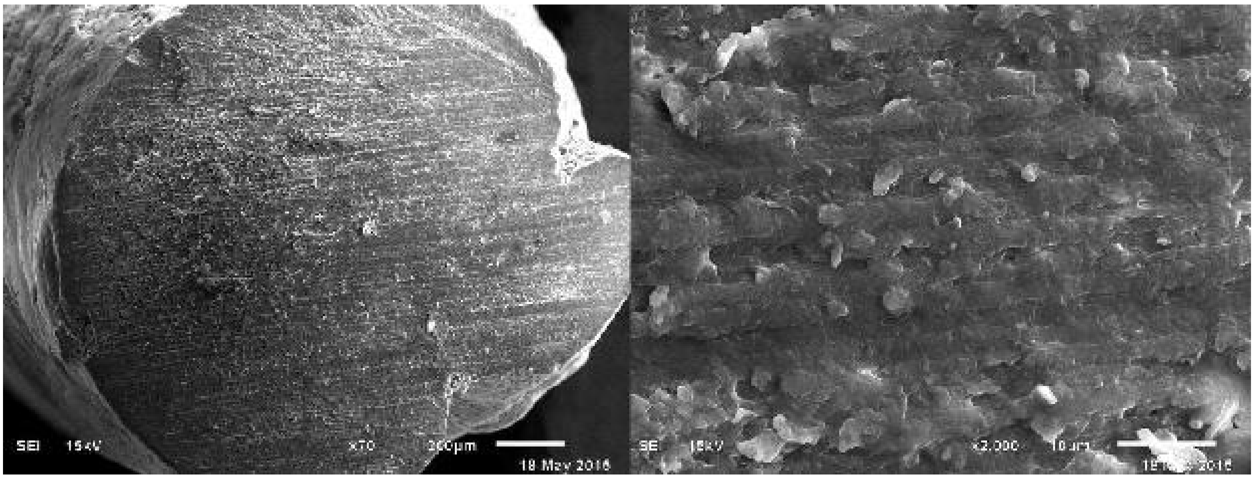

Figure 2. The Zr-Al-Si post with calcination.

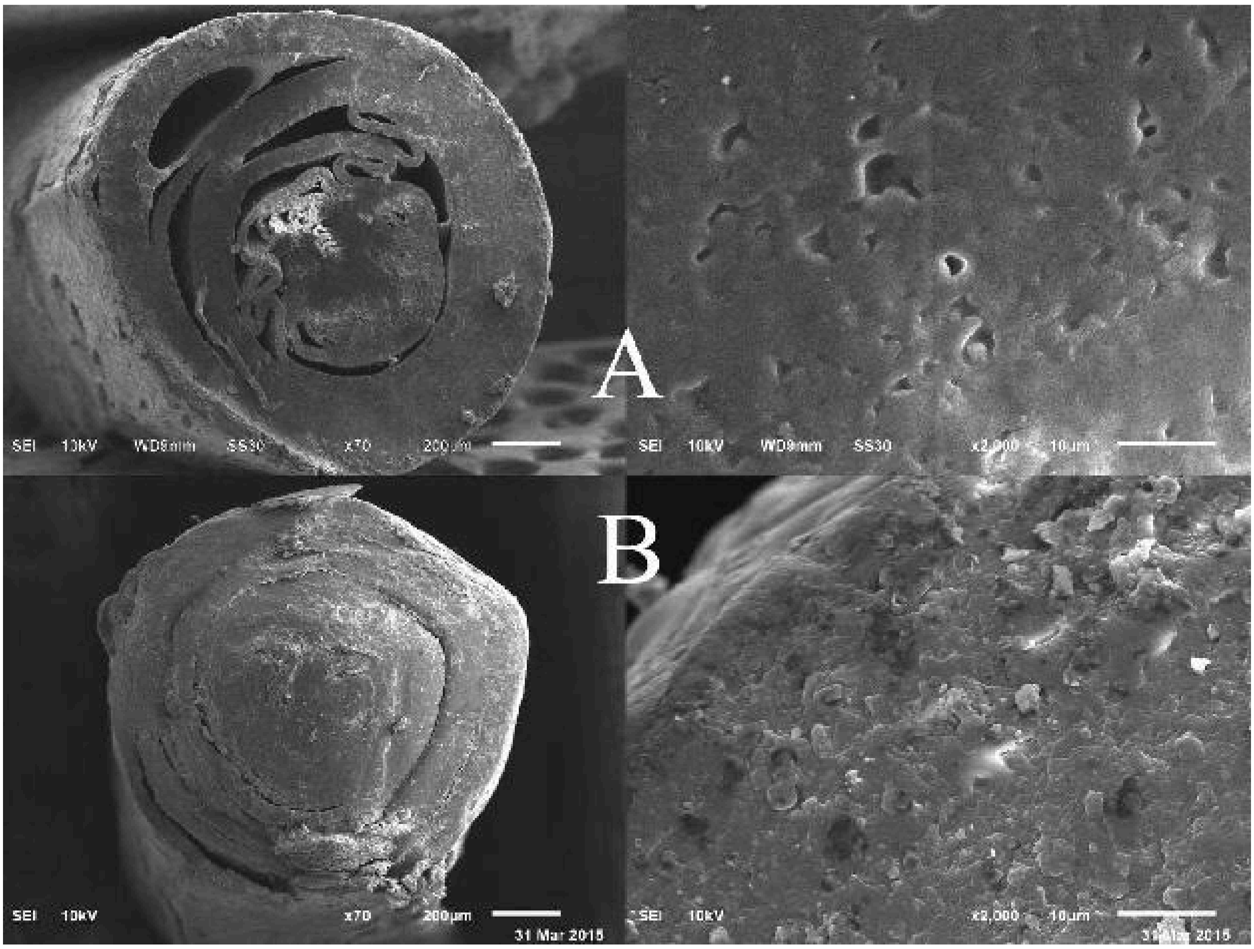

Figure 3(a). The Zr-Al-Si post without calcination using 1% chitosan and 8% PMMA matrix.
(b). The Zr-Al-Si post without calcination using 2% chitosan and 10% PMMA matrix.

In the post without calcination, the use of chitosan increase the bonding interaction between the biotemplate of eggshell membrane and the PMMA matrix. The viscosity of PMMA matrix in synthesizing the posts without calcination also bring affect to the cross-sectional morphology. High viscosity of PMMA matrix makes it difficult to enter the pores of the eggshell membrane template. But if the viscosity is too low, it will create pores and cavities in the cross-sectional of the post without calcination.

Table 2. The mechanical properties of the Zr-Al-Si post with and without calcination

Variations	Zr-Al-Si post with calcination		Zr-Al-Si post without calcination	
	Elastic modulus (MPa)	Hardness (HVN)	Elastic Modulus (MPa)	Hardness (HVN)
1	414.14	1.7	793.19	2.15
2	379.18	1.525	193.96	2.53
3	367.70	1.9	296.81	2.15

From the mechanical properties test, the post with and without calcination shows the best in the variations with the most zirconia inside. The post without calcination shows a better mechanical properties than the post with calcination, **Table 2**. The higher elastic modulus in the post without calcination happens because the post contains the biotemplate of eggshell membrane inside, while the eggshell membrane in the post with calcination has decomposed. However, the hardness of both posts have not met the standard yet, which has to be resemble with the dentin hardness, 53 – 63 HVN [2] dan 65,6 HVN [3]. For the elastic modulus both posts have reach the standard for incisors and canine teeth, 5,3 – 6,1 MPa [4], but not for the premolar teeth, 1653,7 MPa [3].

Summary

The Zr-Al-Si posts have been successfully synthesized using sol-gel method through the biotemplate of eggshell membrane. The posts synthesized without calcination process showed better mechanical properties than the posts with calcination. The best result of the elastic modulus shown by the post with and without calcination are 414.14 MPa and 793.19 MPa. The average hardness from both posts with and without calcination are 1.7 HVN and 2.27 HVN.

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