

Synthesis of Silica Hybrid Nanoparticles and the Effect of Their Addition on the Hardness of the Dental Nanocomposites

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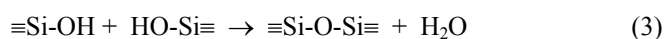
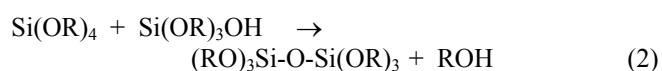
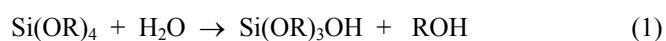
Abstract— The objective of this study is to investigate the effect of silica hybrid nanoparticles on the hardness of the dental nanocomposites. The silica hybrid nanoparticles were synthesized by sol-gel method. The powders were modified with 3-methacryloxy-propyltrimethoxy silane (γ -MPS) either by co-condensation method or one-pot method. The silanized silica were then mixed with a mixture of bisglycidyl methacrylate (BisGMA), triethylene glycol methacrylate (TEGDMA), camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) to form dental nanocomposites. The hardness of the nanocomposites were determined using vickers hardness. The results shown that hardness of the dental composites using silica hybrid nanoparticles synthesized via one-pot method was higher compared to the synthesized via co-condensation method. Transmission Electron Microscope (TEM), and Fourier Transform Infrared Spectroscopy (FTIR) were used for characterization.

Keywords— sol-gel; modified nanosilica; dental nanocomposites; hardness

I. INTRODUCTION

Recently, hybrid composites for tooth restoration have been widely used instead of amalgam. The composites have good aesthetics and make up for the weak points of amalgam such as toxicity from mercury content, corrosion and low adhesive property.

The inorganic filler such as silica has been used as filler in fabrication of hybrid dental composite to improve shrinkage and enhance the strength. Sol-gel process is a common method for silica synthesis. The process involves simultaneous hydrolysis and polycondensation reaction of silicon alkoxide. Different morphology of silica can be produced by sol-gel process by careful controlling parameters such as pH, water ratio and alkoxide ratio. The general reaction lead to the formation of silica particles can be written as [1]:



For synthesizing hybrid composite, modification of silica surface with silane coupling agent will enhance compatibility of filler with polymeric matrix due to their unique bifunctional structure with one end capable of reacting with the silanol groups of silica surface and the other end compatible with the polymer. This will increase the hardness and strength of the dental composites [2].

Most of the literature used post-modification method (grafting) for modification of silica [3,4]. However, the post-modification is time and energy consuming and the use of organic solvent. Another method, co-condensation method is also used. This technique can produce a more homogeneous incorporation of inorganic functional group to the interior and exterior of the bulk of silica particle [5].

This work focused on the synthesis of silica nanoparticles with size ranging from 10-100 nm by sol-gel method by carefully controlled the amount of ammonia as catalyst (or pH). Their surfaces were modified with 3-(trimethoxysilyl) propyl methacrylate (γ -MPS), coupling agents, via a new technique known as one pot, and compared to the co-condensation method. The effect of addition of unmodified and modified silica hybrid nanoparticles on the hardness of the dental hybrid nanocomposites was investigated.

II. MATERIAL AND METHOD

A. Reagents

Tetraethoxysilane (TEOS, 99%, Fluka), absolute ethanol (EtOH, 99.8%, System), 3-(trimethoxysilyl)propyl methacrylate (γ -MPS, 98%, Aldrich) ammonia (NH_3 , 25%, Merck), BisGMA, TEGMA, camphorquinon (CQ, 97%, Aldrich), dimethylaminoethyl methacrylate (DMAEMA, Merck).

B. Standard Procedure

A quantity of 7.76 mL of TEOS were dissolved in 38.8 mL of ethanol under low frequency ultrasound (Branson, Model 3510, 42kHz) at room temperature for 10 minutes. Then, 0.846 mL of distilled water with feed rate 0.2 mL/min were dropped into the mixture. After 2 hours, 2.5 mL of ammonia (Method 1) were dropped into the reaction mixture with feed rate 0.1 mL/min. Three different sizes of silica nanoparticles were produced by three different amount of ammonia. For Method 2 and 3, 5 mL and 10 mL ammonia were dropped. The gelled samples were washed with ethanol and distilled water (three times) and were centrifuged (4000 rpm, 7 min) to remove the unreacted and excess catalyst. The samples were dried under vacuum for overnight in a freeze dryer (Thermo ModulyoD). Finally, the samples were calcined at 600 °C for 2h.

C. Modification of nanosilica via co-condensation and one-pot method

Silica nanoparticles were prepared under same conditions as standard procedure but in co-condensation method, a quantity of 2 mL of γ -MPS as coupling agent were added together with TEOS and ethanol. In one-pot method, γ -MPS were added at the end of the synthesis procedure. Then, the samples were calcined at 110 °C for 2h. Experimental conditions for the preparation of silica nanoparticles were tabulated in Table 1.

TABLE I
COMPOSITION FOR THE PREPARATION OF MODIFIED SILICA NANOPARTICLES

Reagent/molL ⁻¹	Method 1	Method 2	Method 3
[TEOS]	0.64	0.64	0.64
[H ₂ O] / [TEOS] + [γ -MPS]	0.1	0.1	0.1
[NH ₃]	0.6	1.2	2.4

E. Characterizations of silica nanoparticles

Transmission electron microscopy (TEM) images were taken using a Philips CM 12. FTIR spectra were recorded using a Perkin Elmer Spectrum 100. The diameters of 100 particles were measured for the average particles size and the standard deviation using AnalySis 2.11 image analyzer software.

F. Preparation of dental hybrid nanocomposites

The Bis-GMA as a base monomer was mixed with TEGMA (50:50 wt/wt). Then, the photoinitiator system CQ and DMAEMA (1%wt) were added to the mixture. Then,

three sizes of filler, silica were mixed with the resin by hand spatulation. Finally, the paste of dental nanocomposites were molded and light cured for hardness testing using vickers hardness VM50.

III. RESULT AND DISCUSSION

A. Characterization of silica nanoparticles

Figure 1 shows the TEM images of silica nanoparticles prepared by using three different amount of ammonia before and after modification via co-condensation and one-pot method. The morphology of the particles were spherical nanosize with low aggregation. Figure 2 shows particle size distribution of the unmodified and modified silica. The average particle size for unmodified silica were 19.6 ± 3.3 nm, 27.6 ± 2.3 nm and 64.6 ± 8.2 nm for 0.6 molL⁻¹, 1.2 molL⁻¹ and 2.4 molL⁻¹ concentration of ammonia, respectively. For modified silica via co-condensation method, the average particle size were 18.6 ± 5.6 nm, 31.8 ± 4.6 nm and 68.0 ± 6.5 nm. The average particle size for modified silica via one-pot method were 25.16 ± 6.1 nm, 32.09 ± 5.6 nm and 62.13 ± 8.0 nm (Table 2). The results agreed with those reported by Kim et al. [6], the particles size increased by increasing amounts of the catalysts (ammonia). The ammonia increased the rate of hydrolysis and also condensation reaction, which induces the growth of the particles. After modification, there were slightly increased particle sizes but not on particle distribution.

TABLE II

EFFECT OF ADDITION OF AMMONIA, MODIFICATION VIA CO-CONDENSATION AND ONE POT ON PARTICLE SIZE OF NONOSILICA

Ammonia (molL ⁻¹)	Average particle size (nm)		
	Unmodified SiO ₂	SiO ₂ -MPS co-condensation	SiO ₂ -MPS one-pot
0.6	19.6 ± 3.3	18.6 ± 5.6	25.16 ± 6.1
1.2	27.6 ± 2.3	31.8 ± 4.7	32.09 ± 5.6
2.4	64.6 ± 8.2	68.0 ± 6.5	62.13 ± 8.0

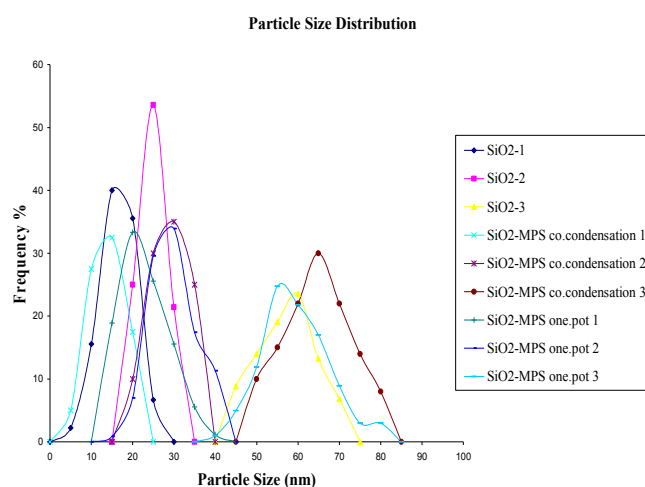


Fig.2 Particle size distribution of nanosilica with different amount of ammonia, after co-condensation and one pot modification.

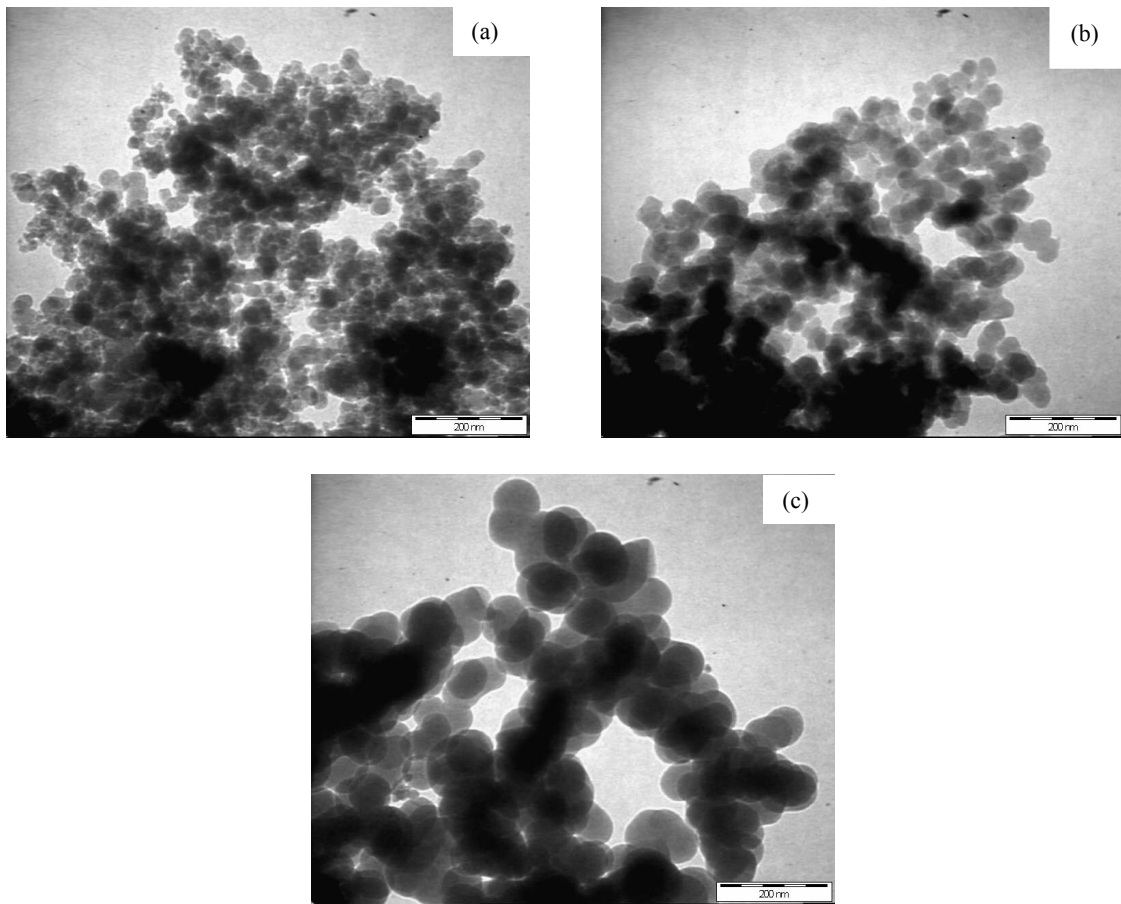


Fig. 1 TEM of unmodified silica nanoparticles in different amount of ammonia (a) 0.6 molL⁻¹ (b) 1.2 molL⁻¹ (c) 2.4 molL⁻¹

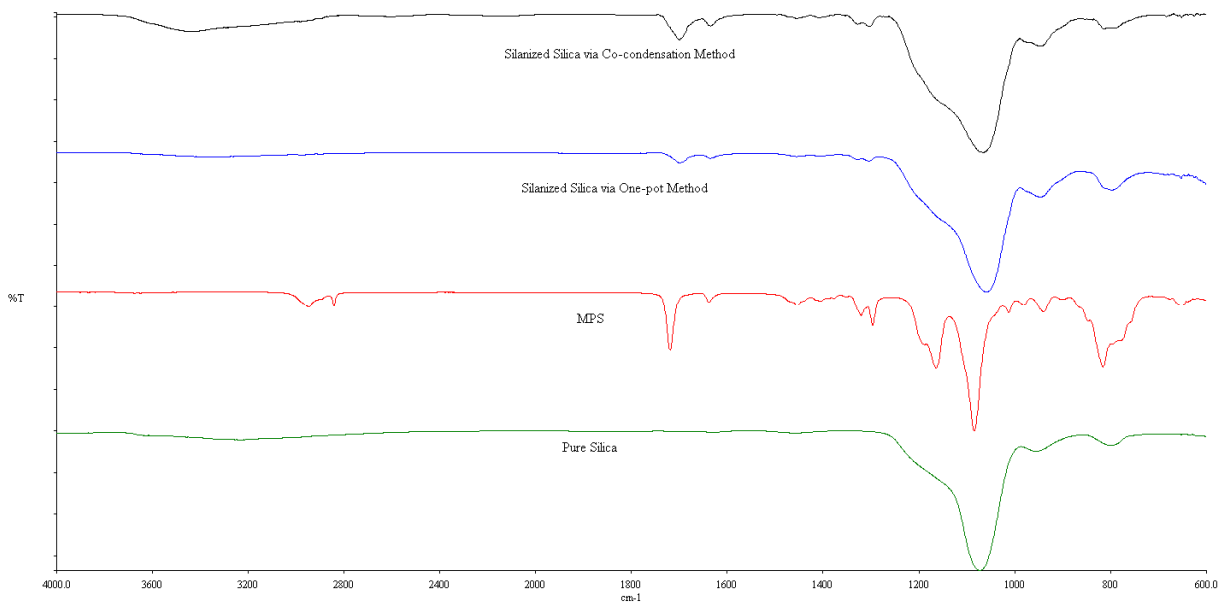


Fig.3 FTIR spectra of pure silica, γ -MPS and modified silica

Figure 3 shows the functional group in the modified silica nanoparticles compared to the pure silica and γ -MPS using FTIR. The spectra show that the bands at 1720, 1700, 1635, 1320 and 1300 cm^{-1} were indicating the presence of γ -MPS on the surface of the silica. The bands at 1720 cm^{-1} is due to the free carbonyl (C=O) and the peak at 1700 cm^{-1} is carbonyl groups which form hydrogen bonds with the silica or adjacent silane hydroxyls. The absorption bands at 1630 and 1320 cm^{-1} are due to the stretching vibration of the C=C bond in MPS and Si-CH₂, respectively. The bands at 1062 and 940 cm^{-1} correspond to the asymmetric stretching and bending of silanol groups (Si-OH) on the silica surface. Intensive bands at 1200 -1100 cm^{-1} represent the asymmetric stretching and bending of siloxane groups (Si-O-Si) [7, 8].

B. Hardness of the dental nanocomposites.

Table 3 shows that the filler loads of dental nanocomposites were increased with addition of coupling agent, γ -MPS. The filler load for unmodified silica maximum at ~ 50% compared to the modified silica, which can go up to ~ 60%. From the results show that the hardness value of dental nanocomposites were increased by increasing the filler load. The hardness value of dental nanocomposite for modified silica via one-pot method were slightly increased compared with modified silica via co-condensation method. This due to the homogeneous distribution of the filler in one-pot method.

TABLE III
HARDNESS VALUE OF DENTAL NANOCOMPOSITES USING UNMODIFIED AND MODIFIED NANOSILICA

Dental hybrid nanocomposites Type of Silica	% Filler Loading	HV1kgf (mean±SD)
Unmodified Silica	40%	24.7 ± 2.6
Modified silica via co-condensation method	40%	17.7 ± 4.7
	50%	34.7 ± 10.4
	60%	36.5 ± 7.5
Modified silica via one-pot method	40%	24.5 ± 2.6
	50%	39.6 ± 10.7
	60%	42.4 ± 9.3

IV. CONCLUSIONS

A stable modified nanosilica has been synthesized by using a co-condensation and one-pot method. Ammonia influences the particle size of the nanosilica. With increasing the concentration of ammonia, the particle size of the silica was increased. The hardness values of modified nanosilica were increased compared to the modified nanosilica.

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