

RADIOPACITY OF RESTORATIVE COMPOSITES FILLED WITH SiO₂/ZrO₂ CORE-SHELL PARTICLES

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1. Introduction

One of the most desirable properties of any dental restorative materials is radiopacity, a property that both facilitates the radiographic diagnoses adjacent to dental composites and enables a practitioner to distinguish a restorative material from caries and the surrounding tooth structure [1,2]. To render radiopacity, elements having a relatively high atomic number such as zirconium, barium, strontium or titanium, are often incorporated into SiO₂-based filler particles [3]. Although barium is considered to be the strongest radiopacifier for the filler phase of composites [4], Smith et al. found that barium ions, once leached out into the oral fluid, are not biocompatible. Moreover, severe foreign body reactions were noted in the oral soft tissue [5]. In contrast, the zirconium is biologically inert in the oral environment [6] and only slightly reduces the chemical stability of SiO₂-based fillers [3].

Recently, various studies of SiO₂-ZrO₂ hybrid fillers utilizing the sol-gel process have been observed and discussed. Most of them were focused on SiO₂-ZrO₂ mixed particles [3,7,8,9,10]. There has been little research in which a precisely controlled SiO₂/ZrO₂ core-shell structure prepared by the sol-gel process for radiopacity has been applied. Core-shell particles can be tailored according to the characteristics of the core and the shell. The mono-dispersed SiO₂ as core particles in the resin matrix, assuming that they have the proper size and a spherical shape, enhance the mechanical and optical properties. The formation of a ZrO₂ shell on silica spheres differs in terms of radiopacity depending on the nanometer scale-shell thickness. This study assesses the possibility of using SiO₂ spherical cores

coated with ZrO₂ nanoparticle as a filler to render proper radiopacity.

2. Material and Method

Radiopaque SiO₂/ZrO₂ core-shell fillers having a controlled shell thickness were obtained using a sol-gel process. Commercial silica spheres having a mean diameter of 110 nm (Sukgyung AT, Korea) were used as the core particles. To prepare the core-shell particles, SiO₂ particles (5g) were initially dispersed in a mixture solution of ethanol (99.5%) and H₂O using an ultrasonicator. To deposit a uniform ZrO₂ shell on monodispersed silica spheres, a mixture solution of zirconium(IV) butoxide (TBOZ, 80%, Aldrich, USA) and ethanol was then constantly added to the reactor for 2h, and this was followed by heating 45°C for 90min to complete the sol-gel process. The concentrations of TBOZ were adjusted at 0.015, 0.03, 0.045 and 0.1mol/l so as to control the ZrO₂ shell thickness. Finally, the solution was dried at 100°C for 24h and pulverized with a mortar and pestle. The size, morphology and shell thickness of the zirconia-coated silica particles were examined using transmission electron microscopy (JEM 2000EX, Jeol, Japan).

The visible light-cured composite specimens were fabricated by mixing 50wt% monomer mixture and 50wt% core-shell fillers. The monomer mixture consisted of 50wt% bis-GMA (Aldrich, USA), 50wt% TEGDMA (Aldrich, USA) and 0.5wt% CQ (λ=468nm, Aldrich, USA). The composite resins contained bare SiO₂ particles, and barium silicate glasses (Ba Glass, avg. dia. =1.0 μm, Schott, Germany) were used as a control, respectively. All

specimens were manufactured in the form of disks 15 mm in diameter and 1, 2 and 3 mm thick.

Each sample was placed on a phosphor plate with an aluminum step-wedge having 20 steps ranging from 1 to 20 mm as a standard to compare the radio-density. The radiographic exposure was done using an x-ray unit (MULTIX-UH, Siemens, Germany), operated for 0.5 s at 70 kV and 5 mA. The film-object distance was 50 cm. The radiographs from the phosphor plates were developed and printed on medical x-ray film 32 × 39 cm in size. The optical density of radiographic film was analyzed with a transmission densitometer (PDA-100, Konica Co., Japan). The measured value was converted in terms of the equivalent thickness of aluminum by referring to the calibration curve for the radiographic density of an aluminum step-wedge.

3. Results and Discussion

A series of SiO₂-ZrO₂ core-shell particles were prepared via a sol-gel process by varying the reaction conditions. There is a pronounced difference in the shell thickness and morphology when adjusting the concentration of the zirconium butoxide (TBOZ). The core-shell particles are shown in Figs. 1(a-c), in which ZrO₂ shell appears as a dark ring around the SiO₂ core, showing a uniform shell with a smooth surface. In contrast, irregularly coated particles with rough surface were obtained (Fig. 1(d)), and self-aggregation of the ZrO₂ particles occurred, resulting in homo-aggregates in the product.

As shown in Fig. 2, the ZrO₂ shell thickness increased significantly with the increment of the TBOZ concentration. The formation of zirconia shell is related to the nucleation and growth of the particle. The zirconia molecules and nuclei are generated by the hydrolysis and condensation process of zirconium alkoxide [11,12]. These nuclei are precipitated in a labile super-saturated solution due to its low solubility and coalesced fast onto the SiO₂ core surface. The growth of nuclei take place through polycondensation or aggregate with each other. In general, the relationship between nucleation and the growth rate as a function of the degree of super-saturation. This is expressed as follows [13]:

$$Growth\ rate = k_1 \frac{Q-S}{S} \quad (1)$$

$$Nucleation\ rate = k_2 \left(\frac{Q-S}{S}\right)^n \quad (2)$$

Here, Q is the amount of the dissolved material, S is the solubility, $\frac{Q-S}{S}$ is the degree of relative super-saturation and k_1 and k_2 are constants. When increasing the concentration of TBOZ, the degree of super-saturation is increased.

In the dilute region of solute material, particle growth is dominant to nucleation because of low nucleation rate. The shell thickness of core-shell particle was increased linearly up to 0.045M as the degree of super-saturation following the linear dependence of growth rate in precipitation. Once formed, the nuclei grow by aggregation and form the shell where deposit on the SiO₂ core surface. In this region all the materials supplied by hydrolysis and condensation was used for growing and thickening of zirconia shell.

Generally in the high concentration region, nucleation is dominant and the rate follows power law dependence as a function of concentration. However, in the region beyond 0.045M of TBOZ, the shell was thickened in the low rate of linear increase. It is caused by evolution of homo aggregate from homogeneous nucleation and growth. In this region almost materials supplied by hydrolysis and condensation was used for homo aggregate, only small part of materials was used for thickening of zirconia shell. Therefore, the uniform core-shell particles for filler of restorative composites could be synthesized in the condition of up to 0.045M of TBOZ concentration.

The amount of the H₂O is relatively less susceptible to increase zirconia shell as opposed to the TBOZ concentration. Fig. 3 shows that the shell thickness of the core-shell particles decreased as the H₂O concentration increased. The higher the water concentration, the lower concentration of TBOZ in the reaction solution, and the smaller shell thickness obtained. Therefore, the shape of core-shell particles is directly dictated by the ZrO₂ nano-particle generation and its deposition and growth on the SiO₂ core particles.

Fig. 4 and Table 1 show the radiopacity values of the experimental composite resins containing prepared SiO₂/ZrO₂ core-shell fillers, Ba glass and SiO₂ core particles. The samples fabricated with the TBOZ concentrations of 0.015, 0.030, 0.045 and 0.1M are simply denoted here as Zr-b015, Zr-b030, Zr-b045 and Zr-b100, respectively. There was a

significant difference between the radiopacity values of the different composites, with SiO₂ composites showing the lowest radiopacity and Zr-b100 composites the highest. According to ISO-4049, composite resins filled with core-shell particles should have radiopacity that at a minimum matches the thickness of an aluminum. All of the composites met this criterion except for the SiO₂ composite. The SiO₂ composite was virtually radiolucent. The Zr-b015 and Zr-b030 composites were judged as having suitable radiopacity for diagnoses. Of the composites assessed here, the Zr-b045 and Zr-b100 composites exhibited equal or higher radiopacity values, respectively, than the Ba-Glass composite.

The radiopacity-value based clinical requirements for the composites incorporating core-shell fillers were compared with those of human dentine and enamel. The radiopacity values of human enamel and dentine at an equivalent sample thickness of 2 mm were taken from the work of Tsuge [14]. He found that the mean radiopacity values for enamel and dentine were 4.3 and 2.3 mm, respectively, for Al/2mm specimen. For a rough comparison, only Zr-b015 was less radiopaque than enamel and dentine. Zr-b030 showed radiopacity characteristics similar to those of enamel. Zr-b045 and Zr-b100 exhibited high radiopacity values as compared to dentin. Therefore, these composites were deemed to be suitable for diagnostic purposes.

The absorption of x-rays by an object is determined by the composition of the material and by the nature of the atoms. μ as the x-ray attenuation coefficient and the characteristic of the substance is related to its atomic number (Z). It is expressed as follows [15]:

$$\mu = k\lambda^3 Z^4 + b \quad (3)$$

Here, λ is the wavelength of the x-ray beam and k and b are constants. Zirconium exhibits a high atomic number (40) compared to silicon (14); consequently, it presents high radiopacity. It was assumed that the adsorption or attenuation of an x-ray is mostly attributable to the ZrO₂ shell.

As shown in Fig. 5, radiopacity value of composite resins increased in a non-linear manner in response to an increase in the shell thickness. This behavior can be explained by the Beer-Lambert formula [12]:

$$I = I_0 e^{-\mu x} \quad (4)$$

Here, I_0 is the intensity of the incident radiation, and I is the value at a depth of x . Equation (4) shows

that I_0 decreases as a function of the thickness (x) of the material. As the ZrO₂ shell thickness (x) in uniform core-shell particles increases, the intensity of the transmitted light (I) decline. Thus, a decrease in the x-ray optical density (I/I_0) appears brighter on an x-ray film according to the increase in the ZrO₂ shell thickness of the core-shell particles (Fig. 6).

4. Conclusion

The core-shell particles with uniform shell thicknesses were prepared by adjusting the reaction condition, including the TBOZ and H₂O concentrations. In this experiment, it was confirmed that there was the upper limit of the reactant concentrations to control the shell thickness and contents. Moreover, a non-uniform coating and severe agglomerates were arisen beyond this upper limit. These facts demonstrate that the dominance of the nucleation rate and the growth rate as a function of TBOZ concentration influences the shell thickness and uniformity of the ZrO₂. Excellent composite radiopacity was observed for high radiopacity of the ZrO₂ shell itself. The radiopacity composite could be easily and precisely controlled by adjusting the shell thickness of the SiO₂/ZrO₂ core-shell filler. An analysis of the present results led to the conclusion that a composite filled with SiO₂/ZrO₂ core-shell filler presents acceptable radiopacity to allow diagnostic discrimination.

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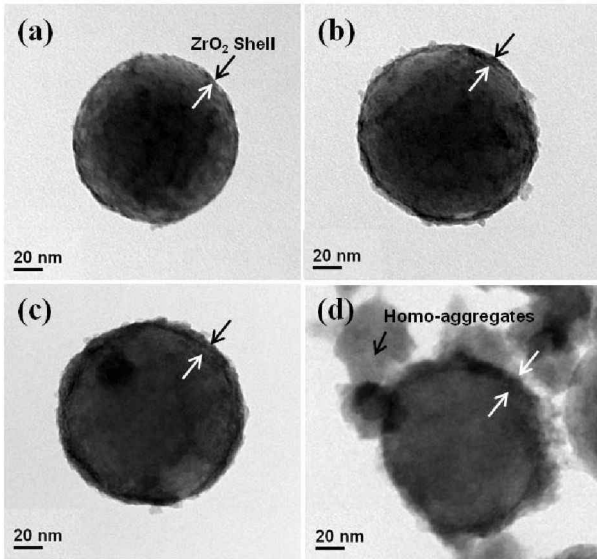


Fig. 1. TEM image of SiO₂/ZrO₂ core-shell fillers prepared at concentrations of (a) 0.015M, (b) 0.03M, (c) 0.045M, (d) 0.1M of TBOZ

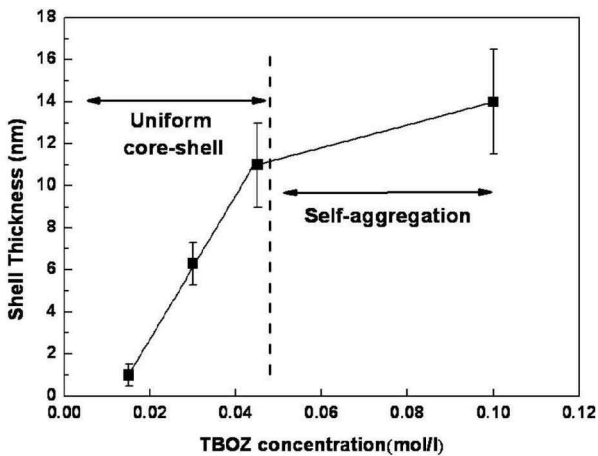


Fig. 2. Influence of the TBOZ concentration on the shell thickness. The H₂O level was fixed at 0.28 mol/l.

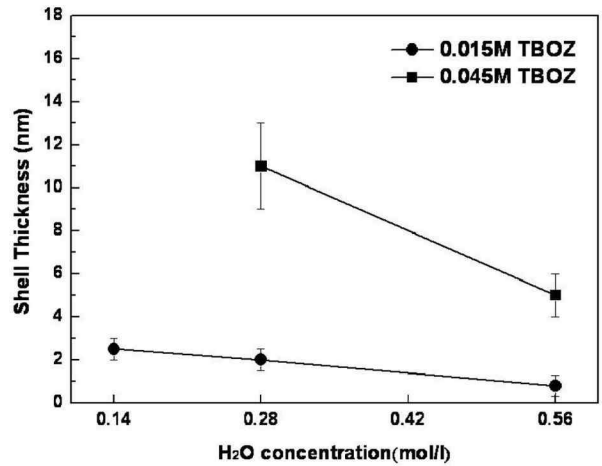


Fig. 3. Influence of the H₂O concentration on the shell thickness. The TBOZ level was fixed at 0.015mol/l and 0.045mol/l, respectively.

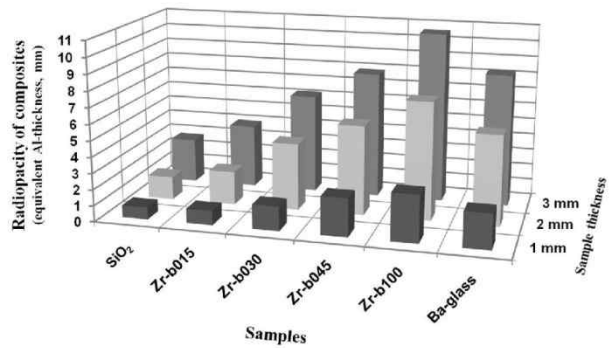


Fig. 4. Three-dimensional comparison of the radiopacity of six composite resins

Table 1. Radiographic density values of six composites filled with different fillers

Material	Sample thickness : mean (standard deviation)		
	1 mm	2 mm	3 mm
SiO ₂ Composite	0.75 (0.23)	1.44(0.08)	2.78(0.20)
Zr-b015 Composite	0.89(0.08)	2.08(0.25)	3.97(0.25)
Zr-b030 Composite	1.51(0.28)	4.18(0.20)	6.02(0.18)
Zr-b045 Composite	2.36(0.21)	5.58(0.34)	7.88(0.19)
Zr-b100 Composite	2.92(0.50)	7.32(0.29)	10.61(0.07)
Ba-Glass Composite	2.18(0.28)	5.60(0.25)	8.26(0.63)

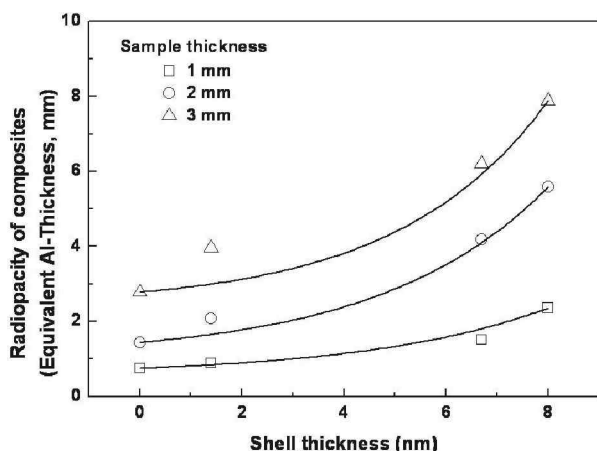


Fig. 5. Radiopacity of composites filled with core-shell particles versus the shell thickness.

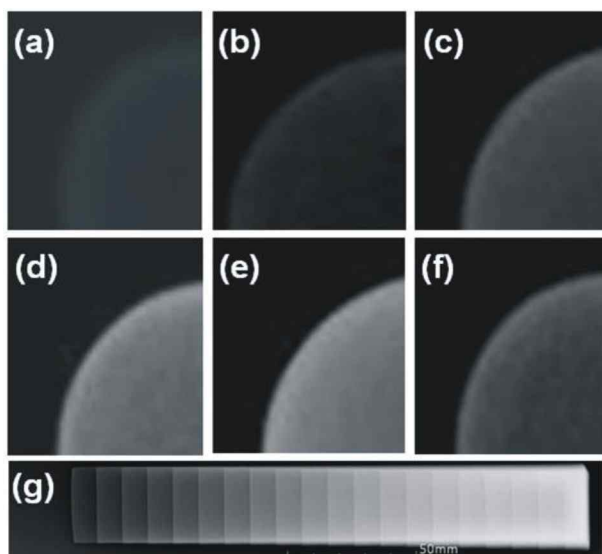


Fig. 6. X-ray image of composites (2mm in height) filled with various fillers: (a) SiO₂ (b) Zr-b015, (c) Zr-b030, (d) Zr-b045, (e) Zr-b100, (f) Ba-Glass and (g) aluminum step wedge as reference

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