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Color matching ability of resin composites incorporating supra-nano spherical filler producing structural color

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ABSTRACT

Objective. The aim of this study was to evaluate the optical properties of supra-nano spherical fillers with different diameters and the color matching ability of resin composites (RC) incorporating these fillers.

Methods. Two types of SiO_2–ZrO_2 nano fillers with different diameters (150 nm and 260 nm) were used. The size distribution of each filler was measured and filler morphology was observed. The colors and spectral reflection spectra were measured by a spectral reflectometer. Experimental RCs incorporating ϕ150-nm/ϕ260-nm filler (D150RC/D260RC) were prepared. For the base dentin part, disc specimens (Estelite Astelia: A1B, A2B, A3B, A3.5B, or A4B) were prepared with a cylindrical cavity. Estelite Astelia with NE shade was layered on top as the enamel layer. Disk specimens with different cavity depths were prepared using A3B shade. Experimental RC was used to fill the cavity, and spectral reflection spectrums were obtained and analyzed. Filtek Supreme Ultra (FSU) with A3B shade was used (n = 10) as a control.

Results. Both ϕ150-nm and ϕ260-nm nano fillers showed uniform spherical shape and exhibited no aggregation. The maximum peaks of the spectral reflection spectra of the ϕ150-nm and ϕ260-nm nano fillers were 380 nm and 580 nm, producing structural colors close to blue and yellow, respectively. The spectral reflection spectrum of FSU had a broad peak at 540 nm, and D150RC had a significant peak at 420 nm. The D260RC specimen had a broad peak at 680 nm. The peaks of D150RC and D260RC significantly decreased in accordance with the shift in base RC shade from A1B to A4B. There was no significant difference in the peak of the reflection spectral spectra among different cavity depths of D260RC. These results suggest that the experimental RC could reflect base RC colors *via* the matrix resin, and the amount of transmitted light from the base RC was not much different with cavity depth.

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Significance. D260RC producing structural color demonstrated a broad spectrum and reduction in brightness and chromatic value by adapting to surrounding restorative materials, suggesting its ability to enhance the chameleon (blending) effects to improve color matching. D260RC showed better color matching ability than resin composite containing uniformly sized ϕ150-nm SiO_2–ZrO_2 supra-nano spherical filler.

1. Introduction

Dental resin composites (RCs) are the material of choice for most anterior restorations [1–3], and the use of RCs as a posterior restorative is increasing worldwide [4]. RCs are widely used because of their exceptional esthetics, conservative tooth preparation, and acceptable longevity in the treatment of anterior [5] and posterior teeth [6]. The Vitapan Classical shade guide (Vita Zahnfabrik, BadSackingen, Germany) is a gold standard in dentistry for selecting shades of RC [5,7]. However, the Vitapan Classical shade guide only covers approximately 6%–11% of natural teeth shades [8]. Therefore, a less-than-perfect color match between a restoration and natural tooth can occur without the corresponding shade in the shade guide of the restorative material, inaccurate shade selection, or reproduction [9,10]. Thus, a new approach to achieve perfect color matching of natural teeth and RC is required.

A structural color is a brilliant iridescent color caused by interaction between visible light and periodical refractive index structured materials [11]. Structural color can be observed in biological tissues such as peacock feathers [12], *Chrysochroa fulgidissima* [13], and Cabot's tragopan [12]. When the index variation has only a short-range order, the structural color is independent of angle, such as Morpho butterfly wings [14–16].

Spherical symmetric nano fillers with a diameter smaller than the wavelength of visible light (< approximately 380 nm) could produce angle-independent structural color without the addition of pigments [17,18]. Various structural colors could produce from SiO_2 particles with diameters between 200 and 300 nm [19]. Because production of structural color depends on the size and distribution of fillers, the use of optimized nano fillers (sharp unimodal distribution) can possibly improve the color matching capability of RC. However, detailed information about the size of nano fillers and their structural color production is not available.

The aim of this study was to evaluate the optical properties of supra-nano spherical fillers with different diameters and the color matching ability of RC incorporating these supra-nano spherical fillers with structural color.

2. Materials and methods

2.1. Supra-nano spherical fillers and their size distribution

Two SiO_2–ZrO_2 fillers with different diameters (150 nm and 260 nm) were obtained from Tokuyama Dental (Tsukuba, Japan) (Fig. 1). The fillers were observed by SEM (JSM-7800F Prime, JEOL, Tokyo, Japan) and the mean diameters were obtained by image analysis. Each filler was dispersed in ion-exchanged water (0.125 g/mL) and homogenized by an ultrasonic homogenizer (Sonifier 450, Branson, Danbury, CT, USA) for 20 min under 40% output. The size distribution of each filler was determined with a laser diffraction particle size analyzer (LS-230, Beckman Coulter, Atlanta, GA, USA).

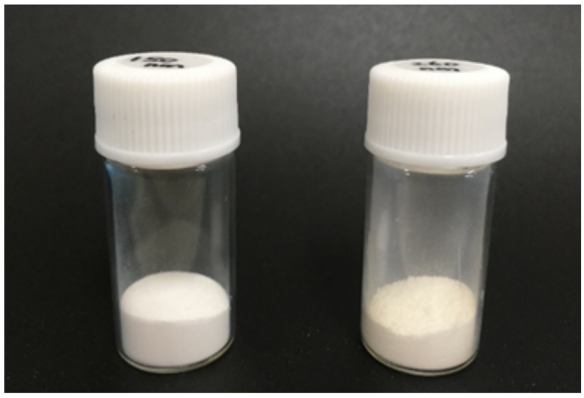

Fig. 1 – SiO_2–ZrO_2 fillers with a diameter of ϕ150 nm (left) and ϕ260 nm (right).

Each nano filler was dispersed in 70% ethanol by 43 kHz ultrasonication for 10 s and then placed on 150-mesh copper grids (NP-C15, Okenshoji, Tokyo, Japan). A transmission electron microscope (TEM) (H-800, Hitachi, Tokyo, Japan) operated at 200 keV was used for observation of each nano filler particle under ×100,000 or ×300,000 magnification.

2.2. Measurement of the spectral reflection spectra of the fillers

Each nano filler immersed in 70% ethanol was spread as a thin layer on test black paper (TP Giken, Osaka, Japan). The color difference ΔE^*_{ab} (CIELAB) between the two nano fillers was calculated from color L*, a*, and b* (n = 10) under the black background. The spectral reflection spectrum from 380 to 780 nm of each filler was obtained. The colors and spectral reflection spectra were measured by a spectral reflectometer using a ϕ3-mm fiber scope (ZE6000, Nippon Denshoku, Osaka, Japan).

Table 1 – Materials composition of each resin composite used in this study. UDMA: urethane dimethacrylate, UDA: urethane diacrylate, TEGDMA: triethyleneglycol dimethacrylate, Bis-GMA: bisphenol A-diglycidyl methacrylate, Bis-EMA: bisphenol A-lolyethylene diethe dimethacrylate, PEGDMA: polyethylene glycol dimethacrylate.

Product	Code	Manufacturer	Composition		
			Monomer	Filler	Filler content (wt%)
Experimental resin composite	D150RC		UDMA TEGDMA	SiO_2–ZrO_2 filler (150 nm)	79
Experimental resin composite	D260RC		UDMA TEGDMA Bis-GMA	SiO_2–ZrO_2 filler (260 nm)	82
Filtek Supreme Ultra, A3B	FSU	3M ESPE	UDMA TEGDMA Bis-EMA PEGDMA	SiO_2 filler (20 nm) ZrO_2 filler (4–11 nm) SiO_2/ZrO_2 cluster (0.6–20 μm)	78.5

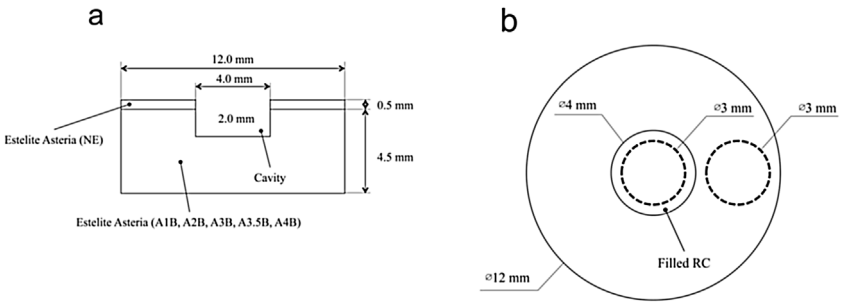

Fig. 2 – (a) Schematic illustration and dimensions of the model cavity. Base dentin part and enamel layer. (b) Measurement area of the reflection spectral spectrum by a ϕ3-mm fiber scope of the spectral reflectometer on a disk specimen filled with RC (black dotted line).

2.3. *Color matching ability of resin composite incorporating supra-nano spherical filler for various shades*

Experimental RCs incorporating ϕ150-nm/ϕ260-nm SiO_2–ZrO_2 supra-nano spherical filler (D150RC/D260RC) were prepared (Table 1). Using commercial RC (Estelite Asteria, Tokuyama Dental), disc specimens (ϕ12 × 5.0 mm) with a cylindrical cavity (ϕ4 × 2 mm) were prepared. For the base dentin part with a thickness of 4.5 mm, RC with a shade of A1B, A2B, A3B, A3.5B, or A4B was used, and RC with a shade of NE was layered on top at a thickness of 0.5 mm as the enamel layer (Fig. 2a). D150RC and D260RC were filled into each cavity. The surface of each specimen was polished by #1500 water proof paper and finished by mirror polishing using diamond paste. These specimens were stored in water at 37 °C for 24 h. Spectral reflection spectra from 380 to 780 nm of each specimen were obtained by a spectral reflectometer using a ϕ3-mm fiber scope (ZE6000, Nippon Denshoku) (Fig. 2b). The surface of each specimen was observed by optical microscope (SMZ-745T, Nikon, Tokyo, Japan). Filtek Supreme Ultra (3M ESPE; FSU) restorative composite with the shade of A3B was used (n = 10) as a control.

To evaluate the influence of the depth of cavities on the color matching ability, disk specimens with different cavity depths (1 mm, 3 mm) and the same geometry as the above specimens were prepared using A3B shade as the base dentin. D260RC was used to fill the cavity. Spectral reflection spectra from 380 to 780 nm of each specimen were obtained by a spectral reflectometer using a ϕ3-mm fiber scope.

2.4. *Statistical analysis*

The means of the peak reflectance among different shades of RCs were statistically analyzed by one-way analysis of variance (ANOVA) with partial eta-squared statistics followed by Bonferroni tests using p values <0.05 (IBM SPSS Statistics Subscription, IBM, Armonk, NY, USA).

3. Results

3.1. *Size distribution of the supra-nano spherical fillers*

The diameter of each nano filler was 128 ± 49 nm (d10 = 71 nm, d50 = 120 nm, d90 = 196 nm) and 288 ± 52 nm (d10 = 223 nm, d50 = 283 nm, d90 = 360 nm). Both nano fillers showed uniform spherical shape and no aggregation (Fig. 3).

3.2. *Spectral reflection spectra of the fillers*

The color difference (ΔE^*_{ab}) of the two nano fillers was 15.314 ± 1.178, exceeding the threshold for a visually noticeable difference (approximately equal to 2.3 [20]). Although the ϕ150-nm and ϕ260-nm nano fillers appeared white (Fig. 1), the spectral reflection spectrum of the ϕ150-nm nano filler on the test black paper had a maximum peak at 380 nm and the ϕ260-nm nano filler had a peak at 560 nm (Fig. 4), for structural colors close to blue and yellow, respectively (Fig. 5).

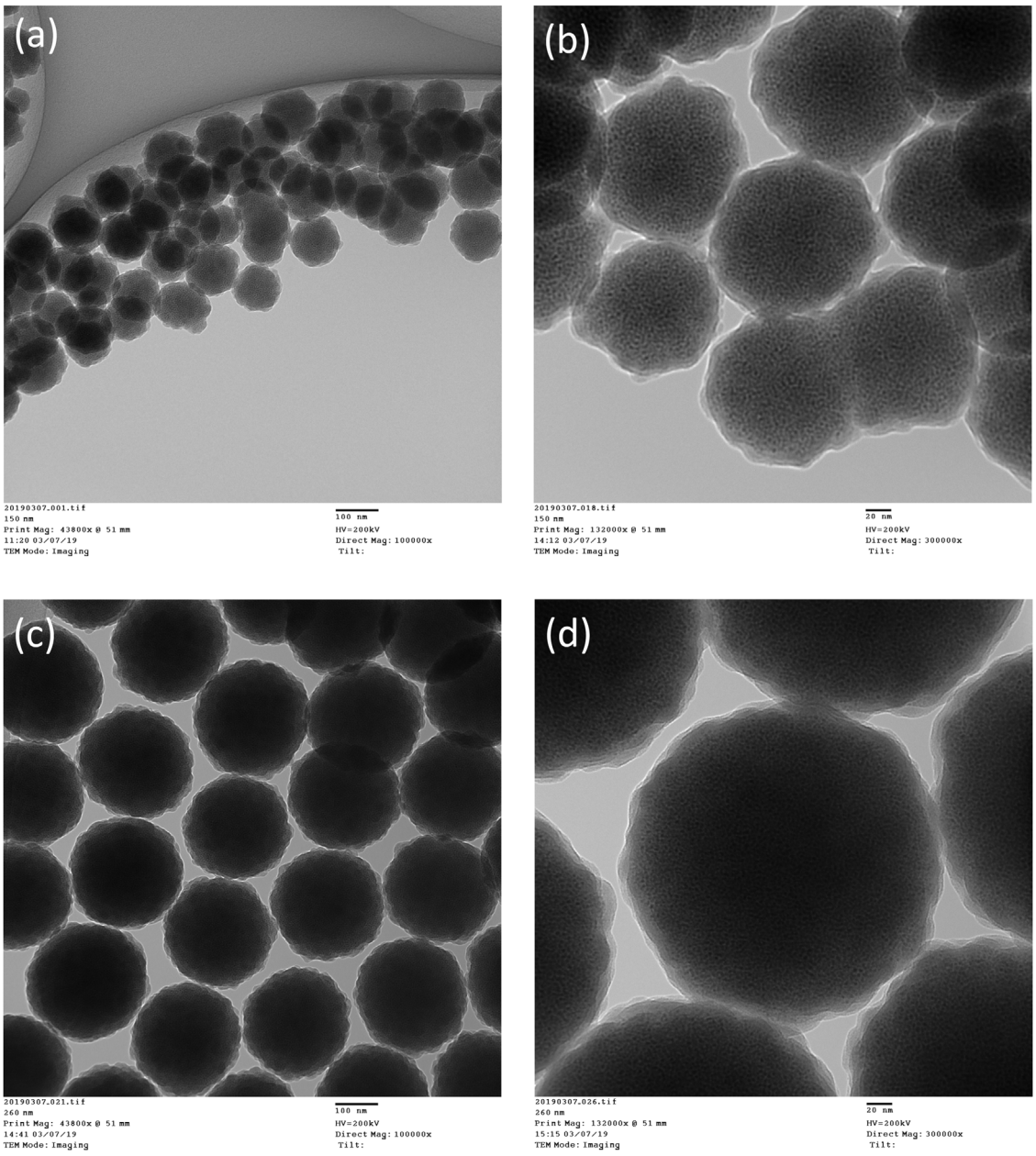

Fig. 3 – Transmission electron microscope (TEM) images of ϕ150-nm nano filler at (a) 100,000 and (b) 300,000 magnification. TEM images of ϕ260-nm nano filler at (c) 100,000 and (d) 300,000 magnification.

3.3. *Color matching ability of resin composite incorporating supra-nano spherical fillers*

The spectral reflection spectra and optical microscopic images of the surface of each specimen with A3B shade are shown in Fig. 6. The spectral reflection spectrum of FSU had a broad peak at 540 nm (Fig. 6a), and D150RC had a significant peak at 420 nm (Fig. 6b). The D260RC specimen had a broad peak at 680 nm (Fig. 6c).

The peaks of the reflection spectral spectra, *i.e.*, the brightness and chromatic value, of D150RC and D260RC significantly decreased in accordance with the shift in shade of the base resin composite from A1B to A4B ($p < 0.05$, partial $\eta^2 = 0.544$), while the peaks for FSU showed no significant difference ($p > 0.05$, partial $\eta^2 = 0.02$). The optical microscopic images of each specimen are summarized in Fig. 7. There was no significant difference among 1-mm, 2-mm, and 3-mm cavity depths of D260RC ($p > 0.05$, partial $\eta^2 = 0.126$).

4. Discussion

The ϕ150-nm and ϕ260-nm nano fillers showed a spherical shape and uniform-sized distribution with no aggregation while the 20-nm SiO_2 and 4-nm ZrO_2 fillers in Filtek Supreme Ultra (FSU) can produce a 0.6–20.0-μm cluster [21]. Such spherical fillers are fabricated on the basis of the sol–gel method, and RC containing these spherical fillers can provide natural

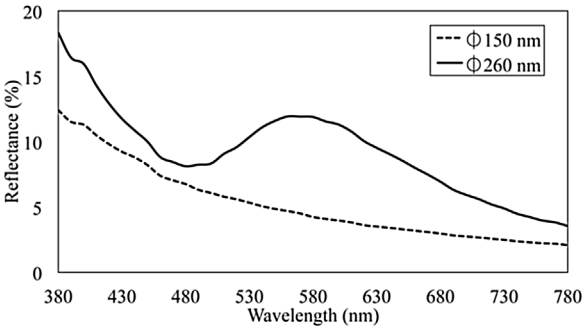

Fig. 4 – Spectral reflection spectra from 380 nm to 780 nm of thin layers of ϕ150-nm and ϕ260-nm nano filler on test black paper.

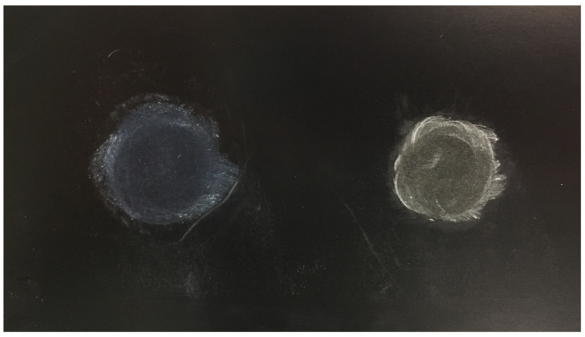

Fig. 5 – Structural color produced by thin layers of ϕ150-nm nano filler and ϕ260-nm on test black paper.

color matching with teeth by diffusing and refracting light [22]. Nano filler with a diameter smaller than the wavelength of visible light can produce structural color without the addition of any pigments. Because the production of structural color depends on the size and distribution of fillers [11], use of the optimized nano fillers can possibly improve color matching of resin composites. The spectral reflection spectra of ϕ260-mm nano fillers indicated a significant peak near 560 nm, close to yellow, while that of ϕ150-mm nano fillers indicated a peak near 380 nm, close to blue. The whiteness and yellowness of natural teeth are two particularly important visual attributes [23,24], suggesting that ϕ260-mm nano fillers are better to synthesize RCs than ϕ150-mm nano fillers. According to the TEM images, both of the nano fillers showed uniform size and spherical symmetrical shape, with angle-independent structural color.

The spectral reflectance spectrum of FSU showed a similar tendency to a base RC constructed by Estelite Asteria. On the basis of the optical microscopic images, the brightness of FSU appears greater than that of the base RC given the greater reflectance across the whole range of the wavelength in spectral reflectance spectrum. The spectrum of FSU was broader than D260RC, contributing to greater brightness of the restorative than the base RC for FSU. The peak value at 420 nm was confirmed in the spectral reflectance spectrum of D150RC and shifted 40 nm compared with the spectrum of ϕ150-nm nano filler (380 nm). By changing the test black paper to matrix resin with transparency, the structural color

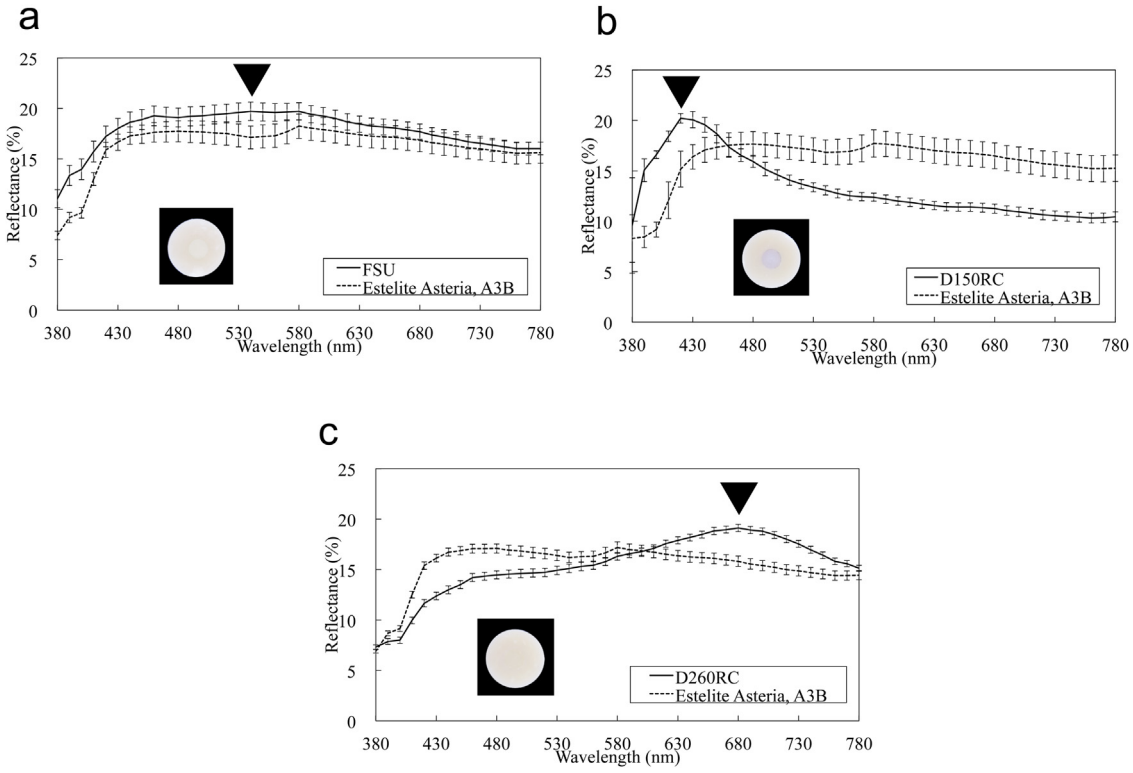

Fig. 6 – Spectral reflection spectra and optical microscopic images of the specimen. (a) Filtek Supreme Ultra, A3B shade, (b) D150RC, and (c) D260RC in the cavity at the center of specimen. The A3B shade in the base dentin part around the cavity is Estelite Astelia.

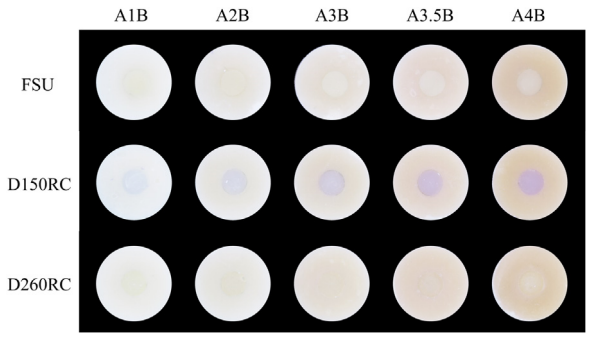

Fig. 7 – Optical microscopic images of the surface of each specimen.

produced by experimental RC can possibly change [11,25] compared with SiO_2–ZrO_2 supra-nano fillers alone. A spectrum with the peak value at 420 nm produces purple color, which is not appropriate for use as RC. The peak value at 680 nm was confirmed for a spectral reflectance spectrum of D260RC and shifted 120 nm compared with the spectrum of ϕ260-nm nano fillers (560 nm). Compared with the spectral reflection spectrum at the base RC, D260RC showed a mirror-reversed shape. Even with such a spectrum, the difference in color between the dentin part and restorative part was not recognized, suggesting that the structural color from the ϕ260-nm nano filler was diluted by the color of the base RC, while the transmitted light from base RC, *i.e.*, the chameleon (blending) effect [9], was enhanced. Thus, D260RC is more appropriate for use as RC than FSU or D150RC.

The peak value of the spectral reflectance spectrum for D150RC and D260RC was significantly varied according to the different base RCs, while there was no significant difference among the other peaks of the spectrum for FSU. These results suggest that D150RC and D260RC can reflect the base RC colors *via* matrix resin. D260RC especially showed better adaptability than D150RC (producing a purple color) in terms of its color matching ability.

In 1-mm to 3-mm cavity depths, there was no significantly different peaks in the spectral reflection spectrum, suggesting that the amount of transmitted light from the base RC *via* matrix resin containing ϕ260 nm nano fillers was not much different, even with different cavity depth. Thus, D260RC has better color matching than the base RC (Estelite Asteria: A1B, A2B, A3B, A3.5B, and A4B).

Various reflective indexes of SiO_2–ZrO_2, urethane dimethacrylate (UDMA), and triethylenglycol dimethacrylate (TEGDMA) have an effect on the structural color of SiO_2–ZrO_2 supra-nano fillers and are difficult to use for *in vitro* investigations. *In silico* finite-difference time-domain modeling would be useful to clarify the detailed mechanism of producing color [26,27] of the RC used in this study using the real morphology determined by nano scale cryo-electron microscopic images [28].

As the limitation of this study, color matching ability of D260RC appropriately works on background color. In case of specific cavity such as class IV (partially no background), the background RC will be recommended. The influence of different preparations reflecting clinical conditions on the optical properties of restoratives with natural teeth will be investigated in another study.

5. Conclusion

Resin composite containing uniformly sized ϕ260-nm SiO_2–ZrO_2 supra-nano spherical filler (D260RC) demonstrated a broad spectrum and a reduction in brightness and chromatic value by adapting to surrounding restorative materials, suggesting its ability to enhance the chameleon (blending) effects to improve color matching. D260RC showed better color matching ability than resin composite containing uniformly sized ϕ150-nm SiO_2–ZrO_2 supra-nano spherical filler.

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