Microstructural Properties and Surface Properties of a New Resin Composite Employing Structural Color Technology

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Abstract: In this study, we performed alkaline degradation testing to investigate the microstructural properties of a new resin composite composed of a single paste containing no pigments that still has the same basic structure as conventional pigment-containing composites. Our aim was to identify factors that affect the matching of various shades of teeth using structural color technology. The effect of these structural properties on the surface properties of the resin composite was also investigated. We found that the structural properties of the new composite included a wide distribution of many spherical organic fillers of various sizes. In addition, spherical inorganic filler of 260 nm in diameter was uniformly distributed at almost the same density both within the organic filler and within the base resin surrounding it. The organic filler and base resin, which are regarded as difficult to couple, were strongly bound without any gaps forming even after alkaline degradation testing. Although the surface layer of the organic filler was vulnerable to alkaline degradation, the center part exhibited very low degradation similar to the matrix surrounding the organic filler. In the new resin composite, the bonding state between the base resin and the various fillers was significantly improved. Furthermore, the microstructural properties were inferred to be effective factors for producing structural color, including the shape, particle diameter, distribution mode and density of the fillers as well as the properties of the base resin. However, these structural properties were not found to affect surface properties such as the line roughness, surface roughness, gloss, discoloration, and wettability.

Key words: Structural color, Resin composite, Microstructural properties, Surface properties, Alkaline degradation test

Introduction

The colors of conventional resin composites are produced by absorption or reflection of visible light by pigments added to fillers and base resin of the material. However, structural color technology has recently been introduced to a composite that has the same base constituents as a conventional one (e.g., fillers and base resin) but that has no pigment added. A new type of resin composite has been developed that is a single paste suitable for matching various shades of teeth.

Unlike coloration by pigments in which particular wavelengths of light are reflected or absorbed, structural coloration is a phenomenon in which a pigment-free material produces color through interactions between light and fine structures smaller than the wavelength of visible light. This newly developed resin composite investigated in this study does not contain any pigments, but has a uniform distribution of spherical filler of 260 nm in diameter that produces red to yellow colors. With this resin, color is produced not only by structural coloration, but also by blending of light reflected off the resin surface and diffuse light reflected with the color of the filler and base resin constituting the resin composite and the color of the surrounding tooth material, which makes this material suitable for matching various shades of teeth.

However, some conventional resin composites also contain particles of similar sizes to this resin and the color is mainly produced by pigments. Thus, to produce high color compatibility without any pigments, we envisioned that the filler and base resin constituting the material and the silane treatment technology for coupling them would need to be improved or modified. However, such an approach has not been reported in detail previously.

Kishimoto measured surface roughness, gloss, and discoloration as indicators of the surface properties of various conventional resin composites, and investigated the relationships between these properties to clarify the differences between the composites. To search for relevant factors, they focused on the structure of the composite and performed accelerated degradation tests under an alkaline environment (alkaline degradation testing), which promotes hydrolysis of siloxane bonds formed by silane treatment. As a result, it was found that differences in surface properties are closely related to factors such as the particle size and distribution mode of the filler, which affect the structure of the resin, as well as the density, base resin, and bonding state between the filler and base resin. Furthermore, alkaline degradation testing has been shown to be useful for accurately obtaining information about these structures. Accordingly, alkaline degradation testing is expected to be significant for understanding the factors that produce high color compatibility in the new pigment-free resin composite with structural color, through investigation of the particle sizes and distribution mode of the filler, density, and the bonding state between the filler and base resin.

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The aim of this research was to understand the factors behind how structural color technology makes a new pigment-free resin composite that is a single paste compatible with various shades of teeth, with a particular focus on the structure of the resin as one of these factors. For comparison, we used a conventional resin composite from the same manufacturer that contains spherical inorganic filler of 200 nm in diameter, spherical organic filler, and pigment, and we performed alkaline degradation testing to investigate particle sizes, distribution mode, and density of the filler contributing to the structure of each resin, the base resin, and the binding state between the filler and base resin. We hypothesized that these structural properties would affect the color of the new resin composite. Furthermore, we investigated the effects of differences between these structures in terms of surface properties such as surface roughness, gloss, discoloration, and wettability of both resins.

**Materials and Methods**

**Materials used**

The new resin composite with structural color technology was OMNICHROMA (OC) (Tokuyama Dental Corp., Tokyo, Japan). The conventional resin composite, Estelite Σ Quick (EQ) (A3, Tokuyama Dental) was used for comparison (Table 1).

**Preparation of mirror-polished specimens**

Each of the resin composites was packed into a silicone mold (length 20 mm × width 10 mm × height 4 mm) and compressed using slide glass via a polyethylene film. Then, to fabricate resin block specimens, the resins were exposed to light for 60 s using a curing light (VALO Curing Light, Ultradent Products, Inc., South Jordan, UT, USA). These resin block specimens, an oxygen absorber/carbon dioxide generator (AnaeroPack, Mitsubishi Gas Chemical Company, Inc., Tokyo, Japan), and an oxygen indicator (Anaerobic Indicator, Mitsubishi Gas Chemical Company) were placed into an anaerobic cultivation jar (2.5 l standard rectangular jar, Mitsubishi Gas Chemical Company). The jar was held in a constant temperature bath at 37˚C in a carbon dioxide environment for 24 h. One face of the resin block specimen (20 mm × 10 mm) was progressively polished under running water using #800, #1200, #1500, and #2000 waterproof silicon carbide abrasive paper using an automatic rotary polisher (Ecomet3000, Buehler Ltd., Lake Bluff, IL, USA), and a mirror-polished surface was prepared using 1.0 μm and 0.3 μm aluminum oxide powders and polishing buff. Ultrasonic cleaning in distilled water (5 min × 3 times) was performed between each polishing step.
The procedure, including the experiments discussed below, is shown in Fig. 1.

**Detection of unpolymerized resin in the resin block specimens**

To examine whether any unpolymerized monomer remained in the resin block specimens, staining was performed using Astra Blue alcohol solution (30% ethanol, 2% isopropyl alcohol, 0.5% Astra Blue) (ScyTek Laboratories Inc., West Logan, UT, USA). Specimens were cut in half along the centerline in the lengthwise direction of the mirror-polished surface, and the obtained cross section (20 mm × 4 mm) was mirror-polished. Each mirror-polished surface was coated with the staining solution for 2 min, fully rinsed with flowing water, and air dried. Then, the presence or absence of stain was examined under a digital stereomicroscope (SZ61, Olympus Corp., Tokyo, Japan).

**Accelerated degeneration testing in an alkaline environment**

The completely polymerized mirror-polished specimens were immersed in 0.1N NaOH solution (60°C, pH 12.7) for 1 day and then ultrasonically cleaned (5 min × 3 times). Gold was deposited on the surface by evaporation to a thickness of 10 nm (MSP-1S, Vacuum Device, Ibaraki, Japan), and the micromorphology of the erosion surface was observed by scanning electron microscopy (SEM; VE-9800, Keyence Corp., Osaka, Japan). The specimen was embedded in epoxy resin and cut in half near the centerline of the specimen in the lengthwise direction. The cut surface was mirror polished, and gold was evaporation deposited onto the surface. Then, the micromorphology of the cross section was observed by SEM.

**Surface roughness measurements (line roughness and surface roughness)**

The surface roughness of the mirror-polished surface was measured in terms of line roughness and surface roughness. For the line roughness, the arithmetic mean roughness (Ra) was determined using a surface roughness meter (Surfcom130A, Tokyo Seimitsu Co., Ltd., Tokyo, Japan) at a feed rate of 0.15 mm/s. Measurements were performed three times near the center of each specimen, and the mean value was taken as the line roughness of the specimen.

Furthermore, for the surface roughness, a standard surface of the specimen was automatically analyzed over an area of 5812 × 4357 μm using a 3D laser scanning microscope (VK-X150/160, Keyence Corp., Osaka, Japan) with a beam spot diameter of 0.2 μm and 100× objective lens, and then the arithmetic mean height (Sa) was found. Measurements were performed five times near the center of each specimen, and the mean value was taken as the surface roughness of the specimen.

**Gloss measurement**

The gloss of the mirror-polished surface was measured as the 60° specular gloss in accordance with the JIS standards by using a handheld gloss meter (PG-1M, Nippon Denshoku Industries Co., Ltd., Tokyo, Japan). Measurements were performed five times near the center of each specimen, and the mean value was taken as the gloss of the specimen.

**Measurement of discoloration**

Three teabags (Nittoh Tea 2 g, Mitsui Norin Co., Ltd., Tokyo, Japan) were steeped in 250 ml of distilled water for 5 min, and the mirror-polished specimens were immersed for 7 days in the liquid tea, which was held at 37°C. The color of the resin surface before and after immersion was measured under a standard black plate or standard white plate using a dental spectrophotometer (SpectroShade, Dentsply Sirona Inc., New York, USA), and the difference between the measured values (ΔE*ab) was calculated and used as the degree of discoloration. Measurements were performed three times near the center of each specimen, and the mean value was taken as the discoloration of the specimen.

**Wettability measurement**

A 0.5 μl droplet of distilled water was placed on the mirror-polished surface, and the contact angle was measured using the 0/2 method with an automatic contact angle meter (DMs-400, Kyowa Interface Science Co., Saitama, Japan). Measurements were performed three times near the center of each specimen, and the mean value was taken as the contact angle of the specimen.

**Statistical analysis**

The correlations between the line roughness, surface roughness, gloss, degree of discoloration, and wettability obtained from the OC or EQ were analyzed by using the Pearson product-moment correlation coefficient (α=0.05).

**Results**

**Detection of unpolymerized resin in provided specimens**

None of the resin block specimens treated with the 0.5% Astra Blue alcohol solution were found to be stained (Fig. 2), meaning that no unpolymerized monomer was detected for the polymerization method used in this experiment.

**Morphology after alkaline degradation testing**

At the surface of OC, various sizes of circular organic filler, circular inorganic filler, and base resin were clearly observed. Uniformly sized fine inorganic fillers were evenly distributed at almost the same density both within the organic filler and within the base resin, and the state of degradation was almost the same between the inorganic filler and the base resin and between the inorganic filler at the center of the organic filler and the base resin (Fig. 3A). Near the surface layer of the organic filler, a degradation layer of approximately 4 μm thick was clearly observed at the interface with the base resin, and many voids were found due loss of the inorganic filler (Fig. 3B, C). Furthermore, a phenomenon was observed where the fine voids present at the interface between the inorganic filler and base resin became connected, forming a single continuous void (Fig. 3D).

Circular fine inorganic fillers, various sizes of semicircular and circular organic fillers, and base resin were clearly observed in the OC cross section as on its surface (Fig. 3E). At the surface of the EQ, the interfaces between square organic fillers, circular inorganic fillers, and base resin were clearly observed, and...
voids were found in the contact area between the organic filler and base resin (Fig. 4A, B, C). Unlike OC, the organic filler was appeared uniformly degraded down to the interior, and loss of inorganic filler from within the organic filler was more significant than the loss of inorganic filler from within the surrounding base resin (Fig. 4B, C).

Square organic fillers were also clearly observed in the base resin in the cross section of EQ, and voids were found at the point of contact between this filler and the base resin (Fig. 4D).

Table 2. Surface characteristics

| Code | Line roughness (μm) | Surface roughness (μm) | Gloss (%) | Color change (black) (ΔE*ab) | Color change (white) (ΔE*ab) | Contact angle (degrees) |
|------|---------------------|------------------------|-----------|------------------------------|-----------------------------|-------------------------|
| OC   | 0.066 (0.005)       | 1.59 (0.16)            | 71.62 (7.10) | 5.32 (1.02)                  | 7.26 (1.28)                 | 72.90 (2.51)            |
| EQ   | 0.065 (0.005)       | 1.14 (0.10)            | 70.44 (4.05) | 2.75 (1.28)                  | 2.22 (1.23)                 | 69.27 (3.01)            |

Results are presented as the Mean(SD). n=10

Table 3. Correlation between each surface characteristics (Pearson's correlation test)

|                  | Line roughness | Surface roughness | Gloss | Color change (black) | Color change (white) | Contact angle |
|------------------|----------------|-------------------|-------|----------------------|----------------------|---------------|
|                  | Line roughness | Surface roughness |       |                      |                      |               |
|                  | r  | p  | r  | p  | r  | p  | r  | p  | r  | p  | r  | p  | r  | p  |
| Line roughness   |   | -  | -  |   | 0.165 |       | -0.498 | 0.929 | -0.395 | 0.871 | 0.567 |       | 0.956 |
| Surface roughness|   | -  | -  |   | 0.851 | 0.999 | -0.665 | 0.982 | -0.569 | 0.957 | 0.060 | 0.565 | -0.209 | 0.719 |
| Gloss            |   | -  | -  |   | -0.606 | 0.968 | -0.573 | 0.958 | -0.091 | 0.648 | -0.019 | 0.774 |
| Color change (black) |   | -  | -  |   | -0.042 | 0.546 | 0.469 | 0.914 | -0.066 | 0.572 | 0.005 | 0.506 | -0.258 | 0.864 |
| Color change (white) |   | -  | -  |   | -0.282 | 0.785 | 0.210 | 0.720 | 0.233 | 0.741 | 0.024 | 0.526 | -0.091 | 0.648 |
| Contact angle    |   | -  | -  |   | 0.178 | 0.719 | 0.369 | 0.853 | -0.417 | 0.885 | -0.258 | 0.864 | -0.258 | 0.864 |

No statistical difference was found between the surface characteristics (p>0.05).
Various surface properties and their correlations

Table 2 shows the measurement results for line roughness, surface roughness, gloss, discoloration, and wettability. The line roughness of the OC was 0.062 μm, the surface roughness was 1.59 μm, the gloss was 71.83%, the color change was 5.32 (standard black plate) and 7.26 (standard white plate), and the contact angle was 72.90°. The line roughness of the EQ was 0.063 μm, the surface roughness was 1.14 μm, the gloss was 70.93%, the color change was 2.75 (standard black plate) and 2.22 (standard white plate), and the contact angle was 69.27°. No correlations were found between any of these measured values in each resin composite (p>0.05) (Table 3).

Discussion

Effects of structural properties of the new resin composite on structural color

The new OC resin composite employing structural color technology has exactly the same base composition as a conventional resin composite but does not have any pigments added. Spherical filler of 260 nm in diameter, which has red to yellow structural color is uniformly distributed in the base resin. This gives high color compatibility with teeth that is similar to conventional composite resin colored using pigments. To investigate the factors behind this, we performed alkaline degradation test to determination that the inorganic filler, organic filler, or base resin constituting OC, and the silane treatment technology that couples these into a solid were modified and improved, and that their structural properties affect structural color. In addition, we also investigated the relationship between the structural properties and OC surface properties.

The notable structural properties of OC that were clarified by the alkaline degradation testing include that there was wide dispersion of spherical organic fillers with a distribution of various particle sizes, spherical inorganic fillers of 260 nm in diameter were evenly distributed at almost the same density both within the organic filler and within the base resin surrounding it, but the organic filler and base resin, which are thought to be difficult to couple, were strongly bound without any gaps forming in an alkaline environment; although the surface layer of the organic filler experienced alkaline degradation, the center part had little alkaline degradation, similar to the matrix surrounding the organic fillers. Kishimoto observed the state of alkaline degradation of various conventional resin composites containing pigments, and noted that, in all of the resins, the interface between the organic filler and the base resin in particular became less tight and gaps form more readily in an alkaline condition. In OC, the inorganic and organic fillers maintained extremely tight contact with the base resin, even under an alkaline environment. Furthermore, the degradation in the organic filler was localized to the surface layer and there was little degradation, the extent of which was almost the same as that of the surrounding matrix. This showed that the coupling technology for each of the interface areas was significantly improved in OC.

The color of conventional composite resin is mainly adjusted by blending with pigments. When the resin is exposed to light, the molecules in the pigment absorb light in a particular range of wavelengths, and the remaining wavelengths of light are reflected or transmitted to create color. Furthermore, a blending effect with the diffuse reflected light at various interfaces and the shade of teeth surrounding the resin composite are added to match the color of the filled tooth. The OC new resin composite has the same base composition as conventional resin but can match various shades of teeth even though it contains no pigment. As described above, the structural properties of OC are achieved by careful design of the following: spherical inorganic fillers with a uniform diameter of 260 nm, which produce a red to yellow color; a spherical organic fillers of various particle sizes in which the above spherical inorganic fillers are evenly distributed; the base resin that surrounds the fillers; and the coupling process that tightly joins these.

In other words, the light incident on OC is thought to be transmitted with almost no reflections or scattering at the interface between the base resin and various types of spherical fillers; this is particularly true at the interface with organic filler because the two are tightly joined. This suggests that adjustments can be made in OC so that “absorption”, “transmission”, “reflection”, and “scattering” occur uniformly between the spherical inorganic filler/spherical organic filler and the base resin, and between the inorganic filler in the organic filler and the base resin. When light is incident on OC, a particular range of wavelengths is absorbed, and the remaining light is transmitted, reflected, or scattered, and color close to the shade of teeth is reproduced by the diffuse reflected light. Furthermore, various shades of teeth can be matched by adding a blending effect for the resin composite that has these special structures and the shade of the surrounding teeth. This suggests that factors that effectively produce structural color are structural properties such as the properties of the base resin; the shape, particle size, distribution mode, and density of the filler; and the binding state between the filler and base resin.

Although the polymerization of the specimens fabricated in this experiment was conducted under anaerobic condition, the environment was set in air at 37°C by considering the oral cavity. However, the details of the fabrication conditions for the organic filler distributed inside the OC resin are not clear. At least industrially, the organic filler is fabricated with the spherical inorganic filler prepared by the sol-gel method under favorable conditions for the polymerization compared to that in air at 37°C. Therefore, we expected the degree of degradation between the inorganic or organic filler and the base resin in OC and EQ cured in air at 37°C to be larger than that between the inorganic filler and the base resin inside the industrially made organic filler under an alkaline environment, but the reverse was observed in this research (Fig. 3A, B and Fig. 4A, B), which is consistent with a report by Kishimoto. Furthermore, the mode of degradation of the organic filler in the two resins differed under the conditions used in this research. The surface layer was more strongly affected than the interior in OC, whereas a uniform effect was occurred in EQ. In both cases, the binding state between the organic filler and the base resin, that between the inorganic filler and the base resin inside the organic filler, and the degree of polymerization and cross-linking structure of the base resin are thought to contribute, and there is a need for further investigation into the detailed mechanisms.

Surface properties of the new resin composite with structural color

Although the base composition of OC and EQ was exactly the same except for the pigment, the structural properties differed as described above. The contact between the various fillers and the base resin in particular was tighter in OC. As a result, we expected that there would also be differences in surface properties such as line roughness, surface roughness, gloss, discoloration, and wettability, but no correlations were found among them. Although the measurement results were not as similar as the other surface properties, and we are planning to investigate this in the future with consideration of surface free energy.

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**Conflict of Interest**
The authors have declared that no COI exists.

**References**
1. Ishizaki T. Coloring based on structural colors. J Surf Finish Soc Jpn 61: 747-750, 2010
2. Mitomo H, Shimamoto N and Ijiro K. Biomimetic materials in imitation of eye-opening colors from nano-structure in nature. J Surf Finish Soc Jpn 64: 9-14, 2013
3. Kinoshita S. Colors due to different coloration mechanisms -Structural colors-. Journal of the ISJ 50: 543-555, 2011
4. Ono S, Ohara N, Matsuzaki K, Shibuya K, Yokoyama A, Takahashi K, Shinno Y, Yamaji K, Shimada Y and Yoshiyama M. Color matching evaluation using the visual analog scale. Jpn J Conserv Dent 63: 30-37, 2020
5. Kishimoto T. Evaluation of the mirror-polished surface characteristics and the alkaline deterioration behavior of the various latest composites. Jpn J Conserv Dent 58: 482-495, 2015
6. Mishima K. Cell reaction of cultured rat pulpal cells to various adhesive resins. J Hiroshima Univ Dent Soc 36: 117-134, 2004
7. de Gee AJ, Harkel-Hagenaar ET and Davidson CL. Color dye for identification of incompletely cured composite resins. J Prosthet Dent 52: 626-631, 1984
8. Hosoda H, Yamada T and Horie K. Study on degradation of posterior composite resins. Part I. Structural changes of resin surface under alkaline condition. Jpn J Conserv Dent 30: 863-882, 1987
9. Hosoda H, Yamada T and Inokoshi S. Study on degradation of posterior composite resins. Part 2. Structural changes in subsurface damage layer of resins under alkaline condition. Jpn J Conserv Dent 30: 1251-1265, 1987
10. Goto M, Harada C, Ikejima I and Momoi Y. A study on reproduction of discolored model tooth. Jpn J Conserv Dent 48: 94, 2005
11. Tokuyama Dental America Inc. OMNICROMA - Technical Report. https://www.tokuyama-us.com/omnicroma-dental-composite/ (cited 2020.8.10)
12. Kawase H, Kawamoto Y, Shima H, Kanakuri K, Kawahara K, Shimada K, Kakehashi Y, Igarashi T, Saitoh M and Nishiyama M. A study on repair restoration with high filler containing indirect composites -Surface treatment for light cured type resins-. J Jpn Prosthodont Soc 47: 769-778, 2003
13. Arksornnukit M, Takahashi H and Nishiyama N. Effects of silane coupling agent amount on mechanical properties and hydrolytic durability of composite resin after hot water storage. Dent Mater J 23: 31-36, 2004
14. Nihei T, Kurata S, Kondo Y, Unemoto K, Yoshino N and Teranaka T. Characterization of water-storage resin composites containing a filler treated with polyfluoroalkyltrimethoxysilane/3-methacryloyloxypropyltrimethoxysilane. Jpn J Conserv Dent 45: 797-807, 2002
15. Ohashi K, Nihei T, Mori R, Kurata S, Unemoto K and Teranaka T. Modified effect of adding catalyst with silane coupling treatment. Jpn J Conserv Dent 52: 161-167, 2009
16. Ishida S and Nishiyama N. Study on surface treatment of silica filler -Hydrolytic deterioration of the silane layer-. Jpn J Conserv Dent 8: 601-607, 1989
17. Miyamoto M. Light transmittance and color of light-cured composite resins. Jpn J Conserv Dent 29: 239-243, 2005
18. Nakaura K, Katayama T, Hatanaka T, Kijima S, Yamazaki N, Enya T, Katayama I and Motonomi T. Color change of visible light-cured composite resin by thickness (Part 2). Jpn J Conserv Dent 30: 839-846, 1987
19. Nakaura K, Yamashita M, Nagamine T, Kijima S, Yamazaki N, Enya T, Katayama I and Motonomi T. Color change of visible light-cured composite resin by the underlying background color. Jpn J Conserv Dent 37: 2004
20. Teranuma K and Murai H. Influence of chromatic color in background on the color of composite resin. Jpn J Conserv Dent 52: 81-93, 2009
21. Hosoya Y and Goto G. Evaluation of colorimetric values measured with the spectrophotometer sensor developed for semitranslucent objects (Report 1). Jpn J Ped Dent 37: 39-48 1999
22. Ando S, Oshiro M, Irokawa A, Fujimoto Y, Uyama S, Miyazaki M, Hosoya Y and Yamagata T. Color match of resin composite with two-layer technique. Jpn J Conserv Dent 49: 590-600, 2006
23. Oguri M, Kimura M and Kazama H. Tokuyama Dental’s adhesion technology. Adhes Dent 22: 50-55, 2004
24. Tokuyama Dental America Inc. Estelite Sigma Quick Instructions. https://www.tokuyama-us.com/estelite-sigma-quick-dental-composite/ (cited 2020.8.10)
25. Otsuka E, Tsujimoto A, Tsuchiya K, Ueda H, Kanazawa T, Hirai K, Takimoto M, Kawamoto R, Takamizawa T and Miyazaki M. Influence of surface treatment of glass-ionomer cements on bond strength with resin composite. Jpn J Conserv Dent 57: 325-332, 2014

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