Color Change of Newly Developed Esthetic Restorative Material Immersed in Food-simulating Solutions

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INTRODUCTION

Currently, various types of esthetic material with different physical characteristics and colors are available1–3). In particular, resin composites are widely used because they have excellent esthetic properties and can be bonded to dentin or enamel. Further, their increasing popularity is fueled by demands from patients for tooth-colored restorations.

Recently, however, a new esthetic material was developed. It is a polymer-based dental tooth coating material (WHITE COAT, Kuraray Medical Inc., Tokyo, Japan) to be applied on the enamel surface to improve the esthetic appearance of discolored teeth with a thin layer of resin-based material without cutting the tooth surface.4–13.

Color changes in resins occur from intrinsic and extrinsic factors. One major intrinsic factor causing long-term discoloration of resins in the past was oxidation of the monomers or catalysts. However, light-cured formulations have dramatically reduced intrinsically mediated discolorations because benzoyl peroxide is excluded from these systems.6–7. Extrinsic factors such as adsorption or absorption of extrinsic stains, on the other hand, are still a major problem for esthetic restorations.8–10. Be it intrinsically or extrinsically mediated, the degree of color change is affected by a number of factors, including incomplete polymerization, water sorption, chemical reactivity, diet, oral hygiene and surface smoothness of the restoration. Vogel reported that extrinsic stains result from discoloration of pellicle and bacterial plaque.6 Eriksen and Nordbø further suggested that there are at least three mechanisms that may contribute to the formation of extrinsic stains: (a) production of colored components in plaque by chromogenic bacteria; (b) retention of colored substances from dietary constituents passing through the oral cavity; and (c) formation of colored products from the chemical transformation of pellicle components. Studies measuring the accumulation of pellicle in humans suggested that factors such as diet (coffee, tea, and red wine), smoking, use of antimicrobial agents,14 and daily teeth cleaning contribute to extrinsic stain development.15,16 Drinks such as coffee, tea, and wine are commonly consumed between meals, and frequent brushing as a result exposes the surface of composite restorations.

The objective of this study was to compare the staining effects of three drinks — coffee, green tea, and red wine — on a contemporary composite, with an oral environment simulated by artificial saliva containing a clinically relevant concentration of mucin. The null hypothesis of this study was that the color stability of esthetic materials used in this study would not be affected by immersion medium nor period.

Recently, an esthetic tooth coating material has been developed. The material consisted of a primer solution, a base coat, and a top coat. The purpose of this study, therefore, was to evaluate the color change of this tooth coating material and two resin composites after immersion in food-simulating, staining solutions. To this end, the newly developed coating material with and without its top coat, a flowable resin composite, and a hybrid resin composite were employed for the evaluation.

The specimens were subjected to an experimental 24-hour staining cycle: 7-hour immersion in coffee, green tea or red wine, then 17-hour immersion in artificial saliva solution containing 0.3% mucin. After 24 hours, 3 days, 1, 2, and 4 weeks of immersion, the color changes of all specimen surfaces were measured.

Compared with the other materials, the ΔE* value of coating material without its top coat tended to increase as the immersion period increased until 4 weeks. On the other hand, the ΔE* value of coating material with its top coat measured the lowest among the materials tested. Based on the results obtained, it was concluded that when using this recently developed tooth coating material in dental clinics, its top coat should be properly applied.

Key words: Tooth coating material, Translucency, Chroma

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MATERIALS AND METHODS

Test materials and specimens preparation
A polymer-based dental tooth coating material (WHITE COAT, Kuraray Medical Inc., Tokyo, Japan), a flowable resin composite (Flow Line, Heraeus Kulzer GmbH & Co., KG, Hanau, Germany; code: FL), and a hybrid resin composite (Clearfil AP-X, Kuraray Medical Inc., Tokyo, Japan; code: AP-X) were used in this study (Table 1). The polymer-based dental tooth coating material consisted of a primer solution, BASE COAT and TOP COAT. The primer of WHITE COAT was a self-etching primer for enamel pretreatment. BASE COAT (WH) was a light-curing resin coating material while TOP COAT was a light-curing surface glaze material.

Translucent acrylic plate of 2.0 mm thickness with 10-mm-diameter hole was used to make disk specimens. Each mold was filled with test material, covered with a clear celluloid strip on both the top and bottom surfaces, and then pressed between two glass slides to achieve uniform thickness of the disk specimens. The top and bottom surfaces of each specimen were light-cured for 40 seconds using a light-curing device (Optilux 401, Demetron Kerr, CT, USA). After being removed from the molds, the specimens were stored at 37°C and 100% humidity for 24 hours. Then, the resin composite specimens were wet-polished with SiC papers of 800-, 1000-, 1500-, and 2000-grit successively such that the resultant surface with the 2000-grit was equivalent to a highly polished clinical surface. On the other hand, half of WH specimens were coated with TOP COAT (WHT) (Transparent coating material, WHITE COAT, Kuraray Medical Inc., Tokyo, Japan) using a brush according to the manufacturer’s instructions and light-cured for 40 seconds.

Color change ($\Delta{E^*}$) measurement
Five different solutions (distilled water, artificial salvia, coffee, green tea, and red wine) were used to test the discoloration of resin composites (Table 2). The artificial salvia composition was selected based on the major organic constituents of human saliva and the inorganic components of commercially available artificial saliva. To evaluate the staining effect of each test solution, four types of specimens were distributed into five groups.

Before exposure, the color of all specimen groups was measured with a colorimeter (OFC-300A, Nippon Denshoku, Tokyo, Japan) using CIEL*a*b* against a white background. For the two control groups, five specimens of each control group were placed in either distilled water or artificial saliva. For the other groups, specimens were first immersed in artificial saliva for 17 hours, and then placed into one of the beverages for seven hours. All specimens were stored at 37°C, and these 24-hour protocols were repeated daily. CIEL*a*b* of each specimen was then measured after 24 hours, at 3 days, 1, 2, and 4 weeks. All measurements were repeated five times for each of the five specimens. Color change of each material was determined by calculating the color difference between $E_{\text{period}}$ and $E_{\text{before}}$, according to the fol-

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**Table 1** Products used for test materials

<table>
<thead>
<tr>
<th>Material (Code)</th>
<th>Composition</th>
<th>Batch No.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>WHITE COAT</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BASE COAT</td>
<td>UDMA, HEMA, photoinitiator, specially treated sodium fluoride, microfiller</td>
<td>0007AA</td>
<td>Kuraray Medical Inc., Tokyo, Japan</td>
</tr>
<tr>
<td>TOP COAT (Light-curing surface glaze material)</td>
<td>Multifunctional methacrylate, photoinitiator</td>
<td>0005AA</td>
<td></td>
</tr>
<tr>
<td>Flow Line (FL)</td>
<td>TEGDMA, methacrylate, microfiller</td>
<td>010102</td>
<td>Heraeus Kulzer GmbH &amp; Co., KG, Hanau, Germany</td>
</tr>
<tr>
<td>Clearfil AP-X (AP-X)</td>
<td>Bis-GMA, TEGDMA, photoinitiator, glass fiber, microfiller</td>
<td>0851AA</td>
<td>Kuraray Medical Inc., Tokyo, Japan</td>
</tr>
</tbody>
</table>

**Table 2** Products used for staining effects

<table>
<thead>
<tr>
<th>Product</th>
<th>Brand</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green tea</td>
<td>Green Tea (Itoen, Tokyo, Japan)</td>
<td>2.1g /120 cc hot water</td>
</tr>
<tr>
<td>Coffee</td>
<td>Nescafé Excella (Nestlé Japan, Kobe, Japan)</td>
<td>2 g / 140 cc hot water</td>
</tr>
<tr>
<td>Red wine</td>
<td>Cuvée Prestige 2003 (Bordeaux, France)</td>
<td>12.5%, v/v alcohol</td>
</tr>
</tbody>
</table>
lowing equation:

\[ \Delta E^* = \left[ (L^*_{E_{\text{period}}}-L^*_{E_{\text{before}}})^2 + (a^*_{E_{\text{period}}}-a^*_{E_{\text{before}}})^2 + (b^*_{E_{\text{period}}}-b^*_{E_{\text{before}}})^2 \right]^{1/2} \]

where the subscripts "E_{\text{period}}" and "E_{\text{before}}" refer to the CIEL*a*b* values for each material on the white backing. In this study, \( \Delta E^* \) values greater than or equal to 3.3 were considered as a clinically unacceptable color change and can be detected by the naked eye\(^{2,3,16-20} \).

**SEM observation**

Material surface before and after four weeks of staining was sputter coated with platinum to have the surface morphology examined under a scanning electron microscope (S-4000, Hitachi, Tokyo, Japan).

To observe the relationship between material and staining substances, specimens were cut vertically and embedded in epoxy resin (Specifix-20, Struers, Denmark). After curing of the epoxy resin, the specimens were ground and polished with SiC paper and diamond pastes (800-, 1000-, 1500-, and 2000-grit, 3 \( \mu \)m, and 1 \( \mu \)m successively). The specimens were subsequently sputter coated with carbon to be examined by a scanning electron microscope (S-2380N, Hitachi, Tokyo, Japan) in SEI mode. For the SEI mode, specimens were also observed by a scanning electron microscope (S-4000, Hitachi, Tokyo, Japan).

**RESULTS**

Fig. 1 shows the relationship between \( \Delta E^* \) and the immersion period in each solution. Water and saliva caused no visible color changes (\( \Delta E^* < 3.3 \)) regardless of immersion time. With green tea, the \( \Delta E^* \) values tended to remain stable for 2 weeks and thereafter increased until 4 weeks (\( \Delta E^* > 3.3 \)). With coffee, the graphs could be divided into two main \( \Delta E^* \) groups. WHITE COAT without TOP COAT (WH) specimen immersed in coffee solution tended to show gradual increase in \( \Delta E^* \) value until 4 weeks, and \( \Delta E^* \) value of this higher \( \Delta E^* \) value group exceeded 5 after three days (\( \Delta E^* > 3.3 \)). WHITE COAT with TOP COAT (WHT) and resin composite specimens (FL and AP-X) belonged to the lower group, where \( \Delta E^* \) values seemed to be stable for 2 weeks (\( \Delta E^* < 3.3 \)) and thereafter increased until 4 weeks (\( \Delta E^* > 3.3 \)). With wine, the graphs could be divided into three \( \Delta E^* \) groups. WH specimen belonged to higher \( \Delta E^* \) value group where \( \Delta E^* \) value exceeded 4.8 after 24 hours (\( \Delta E^* > 3.3 \)). The resin composite specimens (FL and AP-X) belonged to the in-between \( \Delta E^* \) value group where \( \Delta E^* \) values were higher than 3.3 after three days. WHT specimen belonged to the lowest \( \Delta E^* \) group where color change was visible only one week later. For all groups, \( \Delta E^* \) values tended to increase with time.

The surface of each material before and after
four weeks' immersion in each solution was shown in Figs. 2-4. Before immersion, all the surfaces appeared intact (Fig. 2). After four weeks of immersion in red wine, enormous flaky substances were seen on the surface of the resin composite materials (AP-X and FL) such that the original intact surface could barely be seen (Figs. 3(a) and (b)). On the other hand, WH and WHT samples revealed partial adsorption of amorphous substances on the surface, with the original intact surface shown in other parts (Figs. 3(c) and (d)).

As for the AP-X specimens, their typical images after immersion in distilled water, artificial saliva, coffee, and green tea are shown in Fig. 4. Upon comparison among the different immersion media, the surface of the specimens did not show any major change nor differences. However, numerous amorphous substances appeared to be absorbed onto the surface of specimens.

Fig. 5 shows the back-scattered electron images of the specimens, which were immersed in wine and which were cut vertically across the surface. The average thickness of TOP COAT was approximately 20 μm. For resin composite specimens (AP-X and FL), a layer of adsorbed substances was observed on the top of the surface (Figs. 5(a) and (b)), and which was approximately 2-3 μm thick and showing the darkest image. On the other hand, no adsorbed substances were found on the top of the surfaces of WH and WHT (Figs. 5(c) and (d)).

Fig. 6 shows the scanning electron images of the specimens, which were immersed in wine and which were cut vertically across the surface. The surfaces of WH and WHT specimens appeared intact (Figs. 6(c) and (d)). However, for resin composite specimens (AP-X and FL), surface cracks with 2-3 μm-wide gaps propagated along the filler-matrix interface at the top of the specimen surface. Loss of filler particles at the top of the surface was also observed (Figs. 6(a) and (b)).

**DISCUSSION**

In the oral environment, dental restorative materials are inevitably exposed to saliva as well as food components and beverages of all sorts. Against this background, the present study sought to investigate the staining effect of some of these chemicals on the surface of esthetic restorative materials. Ruyter *et al.* 17 concluded that ΔE* values greater than or equal to 3.3 are visually perceptible. Therefore, in this study, any value greater than 3.3 was considered as a clinically unacceptable color difference.

Specimens immersed in distilled water and saliva showed no visible color changes regardless of immersion time (ΔE* < 3.3), except for WH at 3 days (ΔE* = 3.3, Fig. 1(b)). For specimens immersed in distilled water, their surfaces appeared intact under SEM — that is, similar to the way they were before immersion. On the other hand, for specimens im-

![Fig. 2](image-url) Surface of each material before immersion in test solutions at 2000× magnification: (a) AP-X; (b) FL; (c) WH; and (d) WHT. All the surfaces appeared intact.
Fig. 3 Surface of each material at 4 weeks after immersion in red wine (2000× magnification): (a) AP-X, (b) FL: Surfaces of AP-X and FL showed presence of enormous flaky substances such that the original surface was barely shown; (c) WH, (d) WHT: Surfaces of WH and WHT revealed partial adsorption of amorphous substances on the surface, while intact surface was shown in other parts.

Fig. 4 Typical images of AP-X specimens after immersion in each solution at 2000× magnification: (a) distilled water; (b) artificial saliva; (c) green tea; and (d) coffee.
Fig. 5  Back-scattered electron images of specimens cut vertically across the surface at 2000× magnification: (a) AP-X, (b) FL: A layer of adsorbed substances (2-3 μm) was observed on the top of the surface; (c) WH, (d) WHT: No adsorbed substances were found on the top of the surfaces.

Fig. 6  Scanning electron images of the specimens cut vertically across the surface at 2000× magnification: (a) AP-X, (b) FL: Surface cracks with 2-3 μm-wide gaps propagated along the filler-matrix interface at the top of the specimen surface; (c) WH, (d) WHT: Surface of specimens appeared intact.
When immersed in coffee and green tea, $\Delta E^*$ values of the resin composites (AP-X and FL) and WHT seemed to be stable for up to two weeks, as compared with WH. However, at 4 weeks, the $\Delta E^*$ values of all these materials exceeded 5. Once again, it could that the mucin mediated the stainability of the materials. Nonetheless, it is still not clear why there was an abrupt change in $\Delta E^*$ at 4 weeks. Future study is indeed required to evaluate the periodical accumulation of mucin in vitro.

Previous findings revealed that tea and coffee contained yellow colorants with different polarities. Higher polarity components (like those in tea) were eluted first, and lower polarity components (like those in coffee) were eluted at a later time. Therefore, discoloration by tea might be due to adsorption of polar colorants onto the material surface, which could be removed by toothbrushing. On the other hand, discoloration by coffee might be due to both adsorption and absorption of colorants. This absorption and penetration of colorants into the organic phase of the materials were probably due to compatibility of the polymer phase with the yellow colorants of coffee.

With wine, $\Delta E^*$ values of all the materials increased over time as compared with the other beverages. The $\Delta E^*$ values of AP-X and FL specimens exceeded 3.3 after three days. This meant that the color change of the resin composite materials was visually perceptible. As revealed in the scanning electron micrographs at 4 weeks, the surface of resin composite materials (AP-X and FL) displayed propagation of surface cracks along the filler-matrix interface (Figs. 6(a) and (b)). It is not clear why the cracks were present at 3 days, but probably these cracks were induced by a slight change in surface texture. It has been previously reported that alcohol showed some degradation effect on the surface properties of resin composites. Indeed, a rougher, degraded surface provides an extensive surface area for the adsorption of pigments, thereby leading to more staining. Therefore, alcohol in red wine could have roughened the composite surface, leading to increased staining. As revealed in BEI and SEI modes, absorbed substances were clearly present. These substances could also be one of the causes for color change.

Compared with the other test materials, WH specimens yielded the highest $\Delta E^*$ values (Fig. 1(e)). After 24 hours, the $\Delta E^*$ value of WH specimen exceeded 4. It meant that the color change of this material was not clinically acceptable as it exceeded the threshold value. It should be noted that the surface of WH specimen did not show any surface crack (Fig. 6(c)) nor the presence of adsorbed substances (Fig. 5(c)). Nonetheless, WH showed the greatest discoloration when immersed in staining solutions. A possible reason for the severe staining of this material over time lies in its composition. WH material was composed of 2-hydroxyethyl methacrylate (HEMA). The molecular structure of HEMA is composed of both hydrophilic and hydrophobic portions. A hydroxyl functional group of HEMA makes it hydrophilic even after polymerization. It is known that hydrophilic materials have a high water sorption degree. Moreover, it might also absorb the hydrophobic substances. Therefore, surface staining of WH might be influenced by such physicochemical properties as water sorption and hydrophilic properties of the resin matrix.

Among the test materials, WHT specimens yielded the lowest $\Delta E^*$ values. As seen in the SEM images, neither cracks (Fig. 6(d)) nor absorbed substances (Fig. 5(d)) were seen on the surface of WHT specimens. The components of TOP COAT were hydrophobic. Hydrophobic materials tend to show a low capacity for water sorption. This could be one of the key reasons why hydrophobic materials like TOP COAT seemed to be more stain-resistant than hydrophilic ones. However, a little staining on the surface of TOP COAT might be derived from mucin of artificial saliva as well as adsorption of polar colorants. The mucin itself and combination of mucin and stain could have acted as some kind of mediator for the stainability of the material.

In conclusion, when using WHITE COAT in dental clinics, BASE COAT should be absolutely covered with a thin layer of TOP COAT using a flat brush. On this note, clinicians should pay special attention when applying TOP COAT because this material is highly transparent. Leveraging on the results of this study, further study is needed to evaluate the effect of brushing on stain removal from TOP COAT-coated surfaces.

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