Rare Earth Oxide-containing Fluorescent Glass Filler for Composite Resin

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In recent dental care, esthetic restorative materials such as composite resin and porcelain have been widely used and studied. However, their good esthetics makes the visual inspection of restored teeth difficult. In this study, a fluorescent glass filler containing rare earth oxides – which are well-known fluorescent materials – was prepared and used in composite resin to enhance visual inspection capability with small change in color. For example, when irradiated with near ultraviolet light, an Eu₂O₃-containing filler fluoresced clearly and visibly. The fluorescence intensity of the prepared composite resin increased with increase of Eu₂O₃ content in the glass filler and with filler/resin ratio in the resin. Despite the clear fluorescence, the effect of Eu₂O₃ on the color change of composite resin was quite small – even when up to 10 wt% Eu₂O₃ was added to the glass filler. Tb₄O₇- and Dy₂O₃-added fillers also showed clear fluorescence, just like Eu₂O₃-added filler. Therefore, fluorescent glass fillers for composite resins, resulting in small color change in the latter, were successfully prepared in this study.

Key words: Rare earth oxide, Europium, Fluorescence, Filler, Composite resin

INTRODUCTION

In recent dental care, esthetics is of paramount importance to patients. Therefore, restorative materials such as composite resin and porcelain have been widely used and studied^{1–8)}. However, because of their good esthetics, the visual inspection of restored teeth becomes difficult. In particular, quick and accurate inspection in mass dental health examinations becomes increasingly difficult for dentists. This is because detection is usually done by exploring the tactile difference on the tooth surface. If the composite resin shows some distinct optical feature, then visual inspection of the restored part could be easily achieved. Fluorescence is a good property for use as a non-contact detection method for various materials. As such, it has already been applied in many fields^{9–11)}. In the current study, the authors applied the fluorescence detection method to discriminate between esthetic restoratives and teeth^{12,13)}.

Rare earth oxides are well-known and widely-used fluorescent materials¹⁴⁾. Silicate glass, which constitutes the glass filler of composite resin, provides good solubility for other oxides containing rare earth oxides. Leveraging on this solubility property, a rare earth oxide-containing glass filler could then fluoresce – making visual inspection possible.

The purpose of this study was to prepare a fluorescent glass filler for use in a composite resin to

enhance visual inspection capability without change in color.

MATERIALS AND METHODS

Preparation of fluorescent glass filler

Glass was prepared by mixing reagent grade chemicals Na₂B₄O₇, B₂O₃, Al₂O₃, and SiO₂ to form 10Na₂O·49B₂O₃·1Al₂O₃·40SiO₂ (wt%). Rare earth oxides (Eu₂O₃, Dy₂O₃, Tb₄O₇, Nd₂O₃, Ho₂O₃, Er₂O₃, and Sm₂O₃) were added to the above mixture at 2, 5, 7, and 10 wt%. The mixture was melted at 1100°C for two hours in air using an alumina crucible. The melt was cast in a brass mold into a thin sheet, and quenched. The prepared glass was crushed and sieved to be under 53 μm, and supplied for composite resin preparation.

Preparation of composite resin

Urethanedimethacrylate (UDMA; Shin Nakamura Kagaku, Wakayama, Japan) was used as the resin matrix. Camphoroquinone (Tokyo Kasei, Tokyo, Japan) was added to UDMA at 0.3 wt% as a photocure catalyst. The prepared glass filler and UDMA were mixed at filler/resin weight ratios (f/r) of 1/1, 2/1, and 3/1. The mixture was put in a plastic mold (8-mm diameter × 2-mm thickness) and cured with a light curing unit (JetLight 3000, Morita, Tokyo, Japan) for 30 seconds from both sides. The cured

specimen was applied for optical measurement without polish.

Measurement of optical properties

One human third molar was sliced perpendicular to the tooth axis to expose the enamel, and then polished with $\phi 2 \mu\text{m}$ alumina slurry to expose the dentin. Their fluorescence spectra were measured using a fluorescence spectrophotometer (F-2500, Hitachi, Tokyo, Japan) under the following conditions: slit width=2.5 nm, wavelength scanning speed=300 nm/min. When irradiated by a purple light-emitting diode (purple-LED[®]; Toyoda Gosei Co. Ltd., Nakajima-gun, Aichi, Japan), the fluorescence image was observed and recorded with a digital camera (D60, Canon Co. Ltd., Tokyo, Japan). The camera was attached with a sharp cut filter (O56, Hoya Co. Ltd., Tokyo, Japan) to cut off irradiating light. The effect of Eu_2O_3 content — in the filler — on the color of composite resin was estimated with a color-difference meter (OFC-300A, Nihon Denshoku Kogyo Co. Ltd., Tokyo, Japan). For each condition, the fluorescent measurement and color estimation were carried out once for each specimen.

RESULTS

The excitation and emission spectra of 10 wt% Eu_2O_3 -containing filler mixed at $f/r=3/1$ are shown in Fig. 1. Sharp peaks were observed in both the excitation and emission spectra. Strong excitation bands were distributed in the wavelengths below 400 nm and strong peaks were observed at 395 nm and 382 nm. As for the emission spectrum, strong peak was observed at around 613 nm.

Fig. 1 The excitation and emission spectra of 10 wt% Eu_2O_3 -containing filler mixed at $f/r=3/1$.

As shown in Fig. 2, the fluorescence intensity at 613 nm when excited at 396 nm was dependent on two factors: Eu_2O_3 content in the glass filler and filler/resin ratio (f/r). Fluorescence intensity increased with increase in both the Eu_2O_3 content and filler/resin ratio. Each intensity curve was saturated with increase in Eu_2O_3 content in the glass filler. This was caused by self-absorption or concentration quenching of fluorescence. At 5 wt% Eu_2O_3 filler and $f/r=2/1$, more than 50% of maximum emission (i.e., 10 wt% Eu_2O_3 filler and $f/r=3/1$) was already achieved.

The fluorescence image of Eu_2O_3 -containing composite under purple-LED (383 nm) irradiation is shown in Fig. 3. For comparison purpose, a conventional commercial composite (Vita Shade, 3M) was also shown in the figure. A clear fluorescence visibly emitted from the Eu_2O_3 -containing composite, where the composite could be easily identified by the fluorescence through macroscopic observation. By contrast, the commercial composite did not show clear fluorescence under the same irradiation conditions.

Fig. 2 The dependency of fluorescence intensity (at 613 nm under excitation at 396 nm) on filler/resin ratio (f/r) and Eu_2O_3 content in glass filler.

Fig. 3 The fluorescence image of Eu_2O_3 -containing composite under purple LED (383 nm) irradiation.

The effect of Eu_2O_3 addition – to the filler – on the color change of composites is shown in Table 1. At $f/r=2/1$, Table 1 shows the L^* , a^* , and b^* parameters of the CIE color system for composites with Eu_2O_3 -containing fillers and filler without Eu_2O_3 . The effect of Eu_2O_3 content on color change was very small, such that any difference in color among the composites was not distinctly visible to the eye. Therefore, the effect of Eu_2O_3 on the color change of composite resin was negligible.

Fig. 4 shows the emission spectra of Eu_2O_3 -containing composite, enamel, and dentin under exci-

Table 1 The effect of Eu_2O_3 content on color of composites (at $f/r=2/1$)

Eu content (%)	L^*	a^*	b^*
0	50.6	-1.0	1.0
5	49.6	-0.7	1.4
10	52.3	-1.0	2.2

Fig. 4 The emission spectra of Eu_2O_3 -containing composite, enamel, and dentin under excitation at 396 nm.

Fig. 5 The emission spectra of the composites with Tb_4O_7 - and Dy_2O_3 -containing fillers (10 wt%).

Fig. 6 The emission spectra of the composites with $\text{Eu}_2\text{O}_3/\text{Tb}_4\text{O}_7$ or $\text{Eu}_2\text{O}_3/\text{Dy}_2\text{O}_3$.

tation at 396 nm. The Eu_2O_3 -containing composite showed higher emission intensity than enamel within the observed wavelength range. Dentin had higher emission intensity at wavelengths shorter than 560 nm, while Eu_2O_3 -containing composite showed higher emission intensity at wavelengths longer than 560 nm. By using an appropriate filter to pass wavelengths longer than 560 nm, the emission of Eu_2O_3 -containing composite could be clearly differentiated from dentin.

Fig. 5 shows the emission spectra of the composites containing fillers with Tb_4O_7 and Dy_2O_3 (10 wt%). Both Tb_4O_7 and Dy_2O_3 showed clear emissions, but not so for composites that contained other rare earth oxides. Fig. 6 shows the emission spectra of composites with both Eu_2O_3 and Tb_4O_7 or Dy_2O_3 (5 wt% respectively). The emissions from Eu, Tb, and Dy were easily identified and assigned.

DISCUSSION

Due to the recent improvement of esthetic restorative materials such as composite resin and porcelain, greater skills are now required of dentists to detect resin-filled teeth. As shown in Fig. 3, an Eu_2O_3 -containing glass filler lent a strong fluorescent property to the composite resin when the latter was irradiated by purple or near ultraviolet light. The fluorescence could be observed visually. Further, as shown in Table 1, the addition of Eu_2O_3 did not affect the color of composite resin. This meant that the effect of Eu_2O_3 content on the color change of composite resin was negligibly small.

As for the light source, a purple or near ultraviolet LED was used. Compared to conventional light sources, these LED light sources wielded several advantages: small in size, sharp emission spectrum, and low electricity consumption. And these advantages were the reasons that made LED an appropri-

ate inspection device in the oral cavity.

The authors have studied the discrimination of esthetic restorative materials based on their fluorescent properties^{12,13)}. Most commercial porcelains and composite resins show typical fluorescence at the longer wavelengths when irradiated by blue light. Therefore, the possibility of non-contact discrimination of these materials was suggested. To confirm this possibility, the present study designed an easy and clear method to discriminate between composite resin and tooth using rare earth oxides — which could likewise be applied to porcelains.

As shown in Figs. 5 and 6, Tb_4O_7 - and Dy_2O_3 -containing composite resins also showed clear fluorescence, just like Eu_2O_3 , and their emissions also easily assigned. This indicated the possibility of systematic recording of data when the combination and/or composition of these rare earth oxide-containing glass fillers were changed. For example, in the current study, the presence (or absence) of the three rare earth oxides could be expressed as three bits of data. If a glass filler contained Er and Tb but without Dy, the expression could be assigned as (1,1,0). By including the composition of rare earth oxide in the filler as a parameter, more information could be expressed. Thus, with this method, it would be possible to systematically record information on rare earth oxide-containing glass fillers — apart from product information such as lot number.

CONCLUSIONS

In this study, we developed a fluorescent glass filler which induced a small color change in composite resins. We then used it in a composite resin to enhance the latter's visual inspection capability. The Eu_2O_3 -containing filler fluoresced clearly and visibly when irradiated with purple or near ultraviolet light. Fluorescence intensity of the prepared composite resin increased with increase of Eu_2O_3 content in the glass filler and with filler/resin ratio in the resin. Nevertheless, addition of up to 10 wt% Eu_2O_3 to the glass filler did not change the color of the composite resin. Tb_4O_7 - and Dy_2O_3 -added fillers also showed clear fluorescence. The emissions of Eu_2O_3 , Tb_4O_7 , and Dy_2O_3 were characteristic of these elements, and hence easily identified and assigned in the spectra. Therefore, in the present study, fluorescent glass fillers for composite resins were successfully prepared — where color change in composite resin was negligibly small and that the possibility of systematic data recording was also suggested.

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