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Rare earth oxide containing fluorescent glass filler for composite resin.

(Running Title : FLUORESCENT GLASS FILLER FOR COMPOSITE RESIN)

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Abstract

In recent dental care, esthetic restorative materials such as composite resin and porcelains 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 add visual inspection ability with small change in color. The Eu_2O_3 containing filler provided clear and visible fluorescence with irradiation by near ultraviolet light. The fluorescence intensity of the prepared composite resin was increased with the increase of the Eu_2O_3 content in the glass filler and the filler/resin ratio in the composite resin. The effect of the addition of Eu_2O_3 up to 10wt% to the glass filler on the color of the composite resin was quite small. Tb_4O_7- and Dy_2O_3-added fillers also showed clear fluorescence as Eu_2O_3-added filler. Therefore, fluorescent glass fillers for composite resins were successfully prepared with small change in color.

Keywords: rare earth oxide, europium, fluorescence, filler, composite resin

Introduction

In recent dental care, the esthetic property is important for patients; therefore, restorative materials such as composite resin and porcelains 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 is difficult for dentists. Usually, exploring the tactile difference in the tooth surface has been used as a detection method. If the composite resin shows some distinct optical feature, easy visual inspection of the restored part could be achieved. Fluorescence is a good property for use as a non-contact detection method in various materials and has already been applied in many fields[9-11]. The authors have also applied the fluorescence detection method for the discrimination of esthetic restoratives[12,13].

Rare earth oxides are well known and widely used fluorescent materials[14]. Silicate glass, which comprises the glass filler of composite resin, provides wide solubility for other oxides containing rare earth oxides. A rare earth oxide contained in the glass filler would show fluorescence, which would make visual inspection possible.

The purpose of this study was to prepare a fluorescent glass filler for use in a composite resin to add visual inspection ability without changing in color.

Experimental procedure

(1) Preparation of fluorescent glass filler

The glass was prepared by mixing reagent grade chemicals $Na_2B_4O_7$, B_2O_3, Al_2O_3 and SiO_2 to form 10 $Na_2O \cdot 49B_2O_3 \cdot 1Al_2O_3 \cdot 40SiO_2$ (wt%). Rare earth oxides (Eu_2O_3, Dy_2O_3, Tb_4O_7, Nd_2O_3, Ho_2O_3, Er_2O_3 and Sm_2O_3) were added to the above mixture at 2, 5, 7 and 10wt%. The mixture was melted at 1100°C for 2 hours in air using an alumina crucible. The melt was cast into a brass mold as a thin sheet and quenched. The prepared glass was crushed and sieved to be under 53μm and provided for the composite resin preparation.

(2) 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 0.3wt% as a photo-cure catalyst. The prepared glass filler and UDMA were mixed at filler/resin weight ratio (f/r) of 1/1, 2/1 and 3/1. The mixture was put in a plastic mold (8mm in diameter, 2mm in thickness) and cured with a light curing unit (JetLight 3000, Morita, Tokyo, Japan) for 30 seconds from both sides. The cured specimen was applied following optical measurement without polish.

(3) Measurement of optical properties

The fluorescence spectra of prepared composite resin were measured using a

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

Results

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

Fig.1

The dependence on Eu_2O_3 content in the glass filler and filler/resin ratio (f/r) of fluorescence intensity at 613nm excited at 396nm is shown in Fig. 2. The intensity was increased with the increases in both the Eu_2O_3 content and filler/resin ratio. Each intensity curve was saturated with the increase in the Eu_2O_3 content of the glass filler. This was caused by self absorption or concentration quenching of fluorescence. More than 50% maximum emission (at f/r=3/1 with 10% Eu_2O_3 filler) was achieved with 5% Eu_2O_3 filler with the f/r=2/1 composite resin.

Fig.2

The fluorescence image of the Eu_2O_3-containing composite under purple-LED (383nm) irradiation is shown in Fig. 3. For comparison, a conventional commercial composite (Vita Shade, 3M) was also shown in the figure. The clear fluorescence emission from the Eu_2O_3-containing composite was observed and the composite was easily identified by the fluorescence with macroscopic observation. In comparison, the commercial composite did not show clear fluorescence under the same irradiation conditions.

Fig.3

The effect of Eu_2O_3 addition in filler on the color of the composites is shown in Table 1. The L*, a* and b* parameters in the CIE color system of the composites with Eu_2O_3-containing fillers and filler without Eu_2O_3 mixed at f/r=2/1 are shown. The effect of Eu_2O_3 addition on color was very small. The difference in color of these composites could not

Table 1

identified by eye. Therefore, the effect of Eu_2O_3 on the color of the composite resin could be ignored.

Figure 4 shows the emission spectra of the Eu_2O_3-containing composite, enamel and dentin under excitation at 396nm. 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 560nm and the Eu_2O_3-containing composite showed higher emission intensity at wavelengths longer than 560nm. Using the appropriate filter to pass wavelengths longer than 560nm, the emission of Eu_2O_3-containing composite could be clearly differentiated from dentin.

Fig.4

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

Fig.5

Fig.6

Discussion

Because of the recent improvement of esthetic restorative materials such as composite resin and porcelain, greater skill has been required for the dentists to detect resin filled teeth. As shown in Fig. 3, the Eu_2O_3-containing glass filler gives a strong fluorescent property to composite resin with irradiation by purple and near ultraviolet light. The fluorescence from such composite resin was easily identified by eye. The addition of Eu_2O_3 did not affect the color of the filler and composite resin as shown in Table 1. This means the affect by the addition of Eu_2O_3 on color of the composite resin is quite small. As a light source, a purple or near ultraviolet LED can be used. These LED light sources were small in size, with a sharp emission spectrum and low electricity consumption compared to the conventional light source. It's emission The small size and low electricity consumption of LED is appropriate for inspection in oral cavity and the sharp emission wavelength distribution makes for efficient excitation of fluorescence. The authors have studied the discrimination of esthetic restorative materials from their fluorescent properties[12,13]. Most commercial porcelains and composite resins show typical fluorescence at the longer wavelengths under irradiation by blue light. Thus, the possibility of non-contact discrimination of these materials was suggested. The present study would provide an easy and clear method for discrimination of composite resins. The present method using rare earth oxides can also be applied to porcelains.

Fig.3

Table 1

As shown in Figs. 5 and 6, Tb_4O_7- and Dy_2O_3-containing composite resins also showed clear fluorescence like that with Eu_2O_3 and their emissions could be easily assigned. This indicates the possibility of recording data by changing the combination and

Figs. 5,6

composition of these rare earth oxide-containing glass fillers. The presence (or absence) of three rare earth oxide could expresses three bits of datas. For example, containing with Er and Tb but without Dy could be assigned to the expression of (1,1,0). Using the composition of rare earth oxide in filler as the parameter, more informations could be expressed. With this method, the recording of information would be possible. For example, product information such as the lot number could be recorded.

Conclusions

In this study, we developed fluorescent glass filler and used it in composite resin to add visual inspection ability with small change in color of the resin. The Eu_2O_3-containing filler provided clear and visible fluorescence with irradiation by a purple or near ultraviolet light. The fluorescence intensity of the prepared composite resin was increased with the increase of the Eu_2O_3 content in glass fillers and the filler/resin ratios in the composite resins. The addition of Eu_2O_3 up to 10wt% 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 for those elements and easily assigned. Therefore, fluorescent glass fillers for composite resins were successfully prepared with small change in color and data recording ability was also suggested.

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

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

Figure captions

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

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

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

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

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

Fig. 6 The emission spectra of the composites with both Eu_2O_3 and Tb_4O_7 or Dy_2O_3

(5wt%, respectively).