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Preparation and Properties of Dental Composite Resin Cured under Near Infrared Irradiation

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A composite resin (CR) with photo-polymerization is widely used for dental filling material. Current CR has a restriction on the photo-polymerization depth because of the scattering of irradiated blue visible (VIS) light. Rare earth doped Y_2O_3 particles (Y_2O_3:RE) are known to emit blue VIS light under near infrared (NIR) excitation by an upconversion process. The particles can act as both filler to reinforce and illuminator to cure the resin by emitting blue VIS light under the irradiation of the NIR light, which propagates more deeply due to its longer wavelength. In this study, CR with Y_2O_3:RE was prepared. The Young's modulus of CR with Y_2O_3 was comparable with that of commercial CR, however, the hardness was lower than that of commercial CR. CR with Y_2O_3:RE was successfully cured with NIR irradiation. Then, the feasibility of Y_2O_3:RE as the NIR polymerization initiator using its upconversion emission for CR was suggested.
Keywords:composite resin, upconversion, near infrared, photo-polymerization

1. Introduction

The dental filling materials consist of the methylmethacrylate polymer and the glass particles (filler), which called as "composite resin (CR)" are widely used for the restorative dentistry. Glass fillers assist the high abrasion resistance and estheticity of CR. CR is provided as the uncured paste containing photo-polymerization initiator. For the currently used CR, a blue visible (VIS) light (450-510 nm) is required for the curing of the CR. However, since the CR contains glass fillers with high content (more than 50 vol%), the transmittance of VIS, especially short wavelength light, is scattered strongly and results in a shallow curing depth. For this reason, multilayered curing is necessary for the restoration of deep defect more than 2mm[1].

On the other hand, rare-earth (RE) doped inorganic materials are used for various photonic applications. The author had developed the europium (Eu) containing glass filler for CR to visual identification of CR with near UV irradiation[2]. The upconversion (UC) emission from NIR to VIS is one of the characteristic phenomena of Rare-earth. UC occured through a multi step excitation among the discrete energy levels of RE. Y_2O_3 doped with erbium (Y_2O_3:Er) exhibit an UC to emit VIS light (550 and 660 nm) by a near infrared (NIR) excitation at 980 nm[3-6]. The Y_2O_3 is also known as a ceramic with a certain mechanical properties. By using the Y_2O_3:Er particles as the filler, the particles plays both roles as a wavelength upconverter for curing by the NIR irradiation and a reinforcing agent.

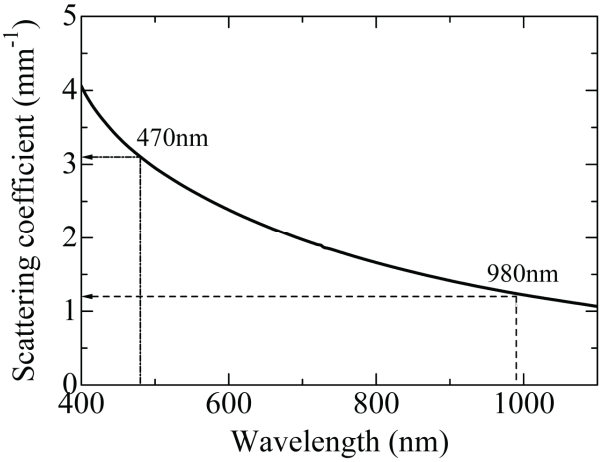

Fig.1 Wavelength dependence of the scattering coefficient of CR.

Fig.1 shows the scattering coefficient of the dental composite resin within the visible light. The scattering of NIR was approximately 1/3 of that of blue VIS. Thus, NIR would be transmitted deeply into CR without scattering. The use of the NIR for curing light source should increase the curing depth due to the longer wavelength of the NIR and achieve the above mentioned large volume restoration in a single step.

The purpose of this study is to evaluate the mechanical properties of the CR with Y_2O_3 filler by comparing the Young's modulus and hardness with those of a commercial CR. The NIR curing possibility of CR with Y_2O_3:RE was also estimated.

2. Experimental procedure

Three kinds of CR samples were prepared for the measurements of the mechanical properties; (a) cured CR with up to 40 vol% of Y_2O_3 particles with an average diameter of 55 nm (CR/Y_2O_3 as follows), (b) cured CR with up to 40 vol% of commercial SiO_2 glass particles (CR/SiO_2) and (c) cured commercial CR with more than 70wt% (>50vol%) glass filler.

Y_2O_3 and Y_2O_3:RE(Er, Tm and Tb) particles were prepared by a homogeneous coprecipitation method reported in literature[7]. Y_2O_3 particles without RE were used for the mechanical priperties evaluation. SiO_2 glass particles (Tatsumori, Tokyo, Japan), which are used as the silica filler of the commercial CR, were used to compare the effect of filler material.

The mixture of bis-phenol A di-glycidyl methacrylate (Bis-GMA; Shin Nakamura Kagaku, Wakayama, Japan) and triethyleneglycol dimethylmethacrylate (TEGDMA; Kanto Kagaku, Tokyo, Japan) was used as the base resin matrix. Bis-GMA and MMA were mixed to be 2:1 in weight ratio. 1 wt% of a photo-polymerization initiator (Irgacure784, Ciba Specialty Chemicals Inc.) was added to the base resin.

To prepare CR, Y_2O_3 and SiO_2 fillers and the base resin matrix were mixed in a mortar to be a certain filler content. The mixture was filled into the cylindrical mold (4mmϕ×6mm$t$) and cured by blue VIS. The density of cured CR was evaluated by the Archimedian method. Also, the cured CR was sliced into disk shape and polished for the mechanical test. Hardness and Young's modulus were measured on the polished specimens by using a dynamic ultra micro hardness tester (DUH-W201, Shimadzu, Tokyo, Japan). The test load was varied from 50 to 300 mN with the Berkovich probe. The commercial CR (Beautifil, Shofu, Kyoto, Japan) was also cured and evaluated with same method as the reference material.

UC emission spectrum Y_2O_3:Er was estimated using a fluorescence spectrometer (RF-5000, Shimadzu, Tokyo, Japan). CR with Y_2O_3:Er was cured using laser diode (980nm, 1W, L9418-04, Hamamatsu-Photonics, Hamamatsu, Japan) and curing possibility with NIR was estimated.

3. Results and Discussion

Fig.2 shows the SEM images of the prepared Y_2O_3 particles. The secondary particles (Fig.2a) with several ten micrometers in diameter consist of the primary particles (Fig.2b). The secondary particles showed porous microstructure.

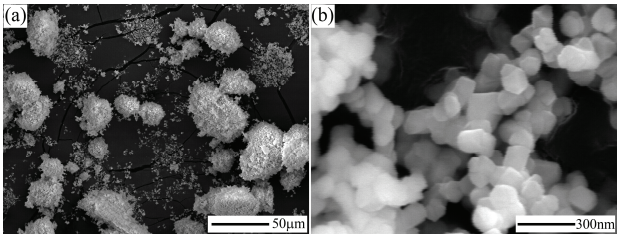

Fig.2 SEM images of Y_2O_3 particles with (a) low and (b) high magnifications.

Fig.3 shows the relative density of prepared CR using Y_2O_3 and SiO_2 particle. The relative density was estimated by the density of each component (resin:ρ=1.2; Y_2O_3:ρ=5.0; SiO_2:ρ=2.2 g/cm^3) and their composition. Contrast to CR/SiO_2, the relative density of CR/Y_2O_3 was decreased with the Y_2O_3 content. As shown in Fig.2, the Y_2O_3 secondary particles are porous and the resin matrix (Bis-GMA) is highly viscous. Therefore, the pores among the Y_2O_3 primary particles were not densely packed with the resin matrix, thus, the relative density would decreased with Y_2O_3 content.

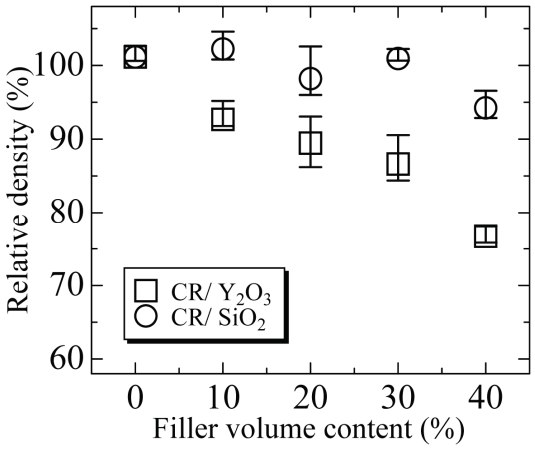

Fig.3 Relative density of prepared CR using Y_2O_3 and SiO_2 with various filler content.

Fig.4 and 5 show the Young's modulus and hardness of the CR with Y_2O_3 and SiO_2. Both Young's modulus and hardness were increased with the filler content. Significant difference of those parameters was not observed between Y_2O_3 and SiO_2 fillers. The Young's modulus of the prepared CR attained to that of commercial CR (10GPa) with 40vol% of filler content. The hardness of CR with 40vol% of filler content was half of that of commercial CR. The hardness of CR is necessary for its wearing durability. One reason of this low hardness would be low relative density of CR/Y_2O_3, then the hardness would be increased by the improvement of packing density of Y_2O_3 in CR.

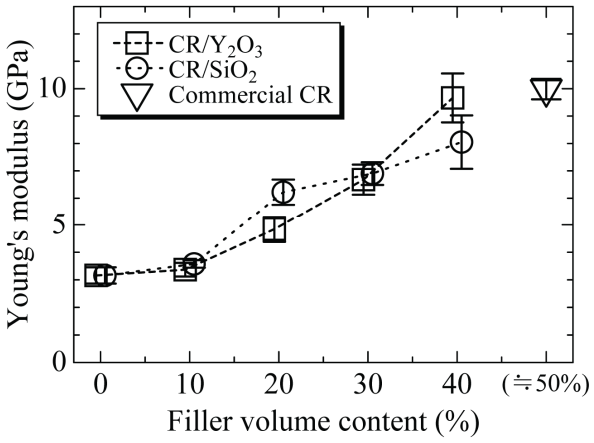

Fig.4 Dependence of Young's modulus on the filler content of CR.

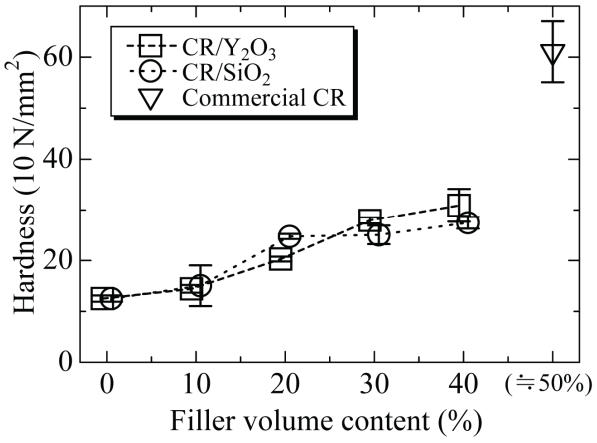

Fig.5 Dependence of the hardness on the filler content of CR.

The scheme of UC emission from Er^{3+}/Y_2O_3 was shown in Fig.6. Er^{3+} is excited with two photons of NIR (980nm), then emit VIS (530-660nm). Fig.7 was observed UC emission spectrum from 5mol% Er containing Y_2O_3 (Y_2O_3:5Er) and absorption spectrum of Irgacure784 used as the photo-polimerization initiator of CR. UC emission from Er^{3+} overlaped with the absorption spectrum of Irgacure, then the CR/Y_2O_3:5Er could be successfully cured with NIR laser irradiation for 5 minutes as shown in Fig.8. As shown in Fig.7, the overlap of the emission and absorption spectrum was quite small. Then, the upconversion emission from Er^{3+} was not effectively used for the photo polymerization.

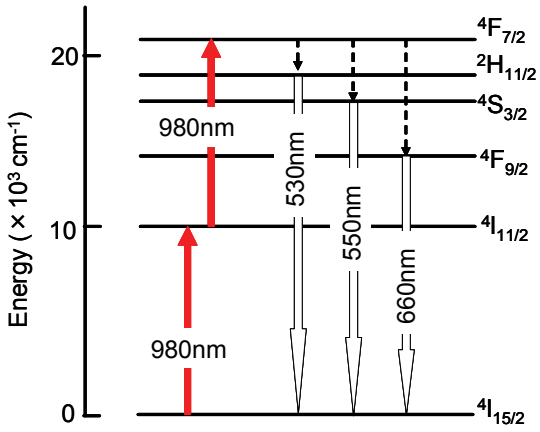

Fig.6 Energy diagram of Er^{3+} and UC emission process.

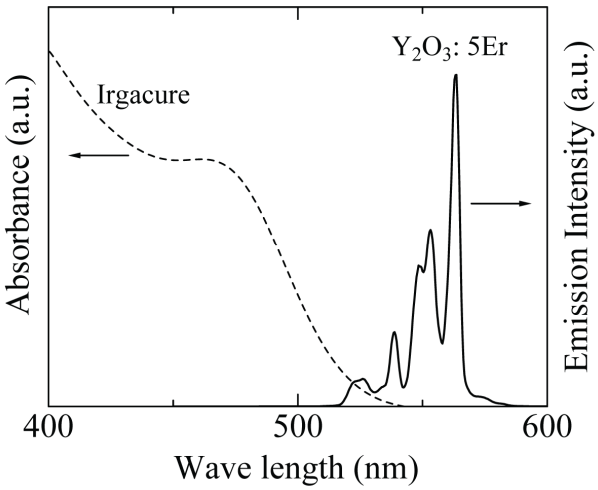

Fig.7 UC emission spectrum from Er^{3+}containing Y_2O_3 and the spectrum of the Irgacure.

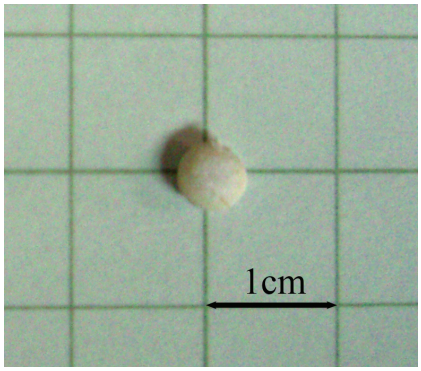

Fig.8 Cured CR/Y_2O_3:5Er with NIR laser (980nm) irradiation for 5 minutes.

UC from co-doped Tm^{3+} and Yb^{3+} in Y_2O_3 had been reported that blue VIS emission around 480nm induced by NIR excitation caused by the energy transfer between Tm^{3+} and Yb^{3+}[8, 9]. Fig.9 shows the scheme of UC emission from Tm^{3+} and Yb^{3+} and UC emission spectrum from Y_2O_3:0.1Tm, 5Yb. UC emission from Tm^{3+} and Yb^{3+} was around 480nm in which Irgacure showed high absorption. Thus, CR/Y_2O_3:Tm, Yb particles could also be successfully cured with NIR laser irradiation.

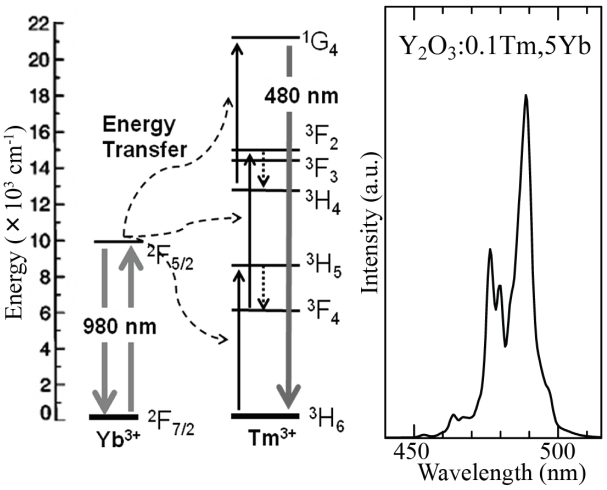

Fig.9 UC mechanism and observed UC emission spectrum from Y_2O_3:0.1Tm, 5Yb with NIR excitation (980nm).

4. Conclusions

Dental composite resin (CR) was prepared with Y_2O_3:RE. The Young's modulus of CR/Y_2O_3 was comparable with the commercial CR. The hardness was about half of the commercial CR because of the low relative density of CR. CR/Y_2O_3:RE(Er, Tm and Yb) was successfully cured with NIR irradiation. Then, the feasibility of Y_2O_3:RE as the NIR polymerization initiator using its upconversion emission for CR was suggested.

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