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Phenylpropanedione; A New Visible Light Photosensitizer for Dental Composite Resin with Higher Efficiency than Camphorquinone

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Chemical or light induced polymerization resin system has been used as an esthetic and permanent restorative dental composite resin in dentistry.¹ Light induced polymerization system is more widely used than chemical resin system because it has many advantages² such as higher color versatility, better color stability, less bubble generation, and one paste system.

The light induced polymerization system has been used for the preparation of dental composite resin, denture, dental adhesives, and impression material. It can be divided into two types based on the light source; UV or visible light. Recently, visible light is mostly used to avoid harmful effects of UV light. Camphorquinone (CQ) is the most widely used photosensitizer for the visible light cured composite resin,³ but it has some drawbacks such as low polymerization efficiency and toxicity. Low polymerization efficiency of camphorquinone results in low mechanical properties of the composite resin and toxic effects to the human body because of the residual monomers. To overcome these drawbacks, a photosensitizer with high polymerization efficiency is necessary. However, only a few studies have been done to replace camphorquinone.^{4,5}

In the previous study,⁶ we reported on the visible light-cured restorative dental composite resin with low water absorption. The present paper deals with the properties of di-

acetyl (DA) and phenylpropanedione (PD) as a new photosensitizer for dental composite resin and those of dental composite resin containing them.

Physical state of DA and PD is yellow liquid and that of CQ is solid at room temperature. Figure 2 shows UV absorption spectra (Model V-550, Jasco, Japan) of three photosensitizers. The λ_{\max} of CQ, DA, and PD in ethyl alcohol is 468, 418.5, 393 nm and ϵ_{\max} is 80, 50, 20 respectively. The ϵ_{\max} values of 20-80 and blue shift of absorption maximum with increasing solvent polarity indicate ($n-\pi^*$) transitions.

Photopolymerization efficiency of the resin was studied by the IR absorption spectroscopy. A mixture of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)]phenyl propane (bis-GMA, 1.0 g),⁷ *N*-dimethylaminoethyl methacrylate (DAEM, 0.001 g), and 2.0 wt% of photosensitizer based on bis-

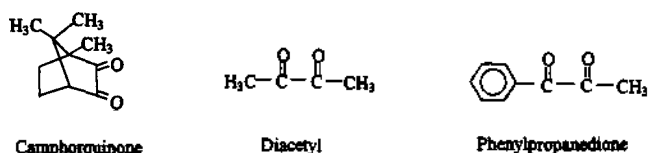


Figure 1. Photosensitizers used in this experiment.

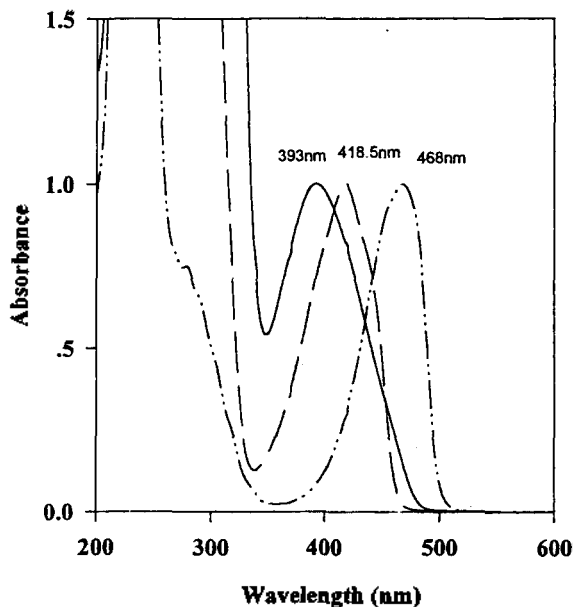


Figure 2. UV-VIS absorption spectra of CQ (····), PD (—) and DA (---) in ethyl alcohol.

GMA was coated on KBr plate. IR absorption spectra were measured for various irradiation times. Irradiations were carried out with a Curing Light XL 3000 (3M Co. Germany). Remaining double bond (RDB) of the resins^{8,9} after irradiation was determined based on the difference of absorbance at 1635 cm⁻¹ between before and after irradiation for a given period. The value was normalized with the difference between absorbance at 1581 cm⁻¹.

The photopolymerization efficiency of the resins increased with the photosensitizer concentration up to 1 wt%, but not any more with the photosensitizer concentration above 1 wt%. The reason is that the photosensitizer absorbs all the irradiated light at the photosensitizer concentration

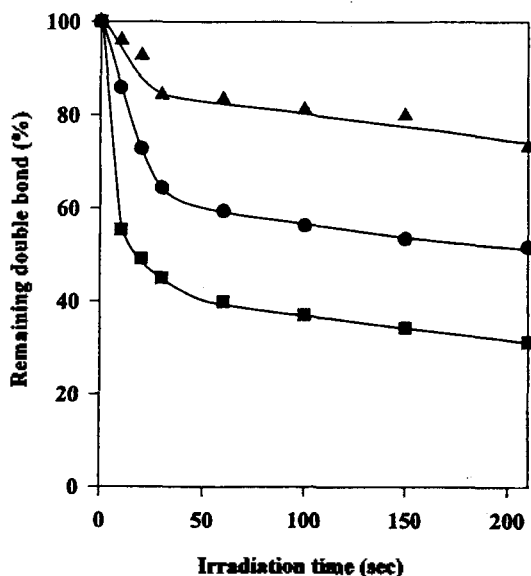


Figure 3. The relationship between irradiation time and % of remaining double bond of composite resin containing 2.0 wt% of photosensitizer: (●), CQ; (■), PD; (▲), DA.

around 1 wt%. Figure 3 shows RDB of the resins containing 2 wt% of three different photosensitizers as a function of irradiation time. The relative photopolymerization efficiency increased in the order of DA < CQ < PD. The RDB of CQ decreased up to 60%, but that of PD decreased up to 30% after 210 sec of irradiation. This result indicates that PD has better photopolymerization efficiency than CQ or DA.

Vickers hardness (Zwick, Model 3212.001, Germany) was measured to study the physical properties of the dental composite resin containing three kinds of photosensitizers. The composite resin for measurement of Vickers hardness was prepared as follows: Bis-GMA (1.0 g), silanized silica (1.0 g), and DAEM (0.002 g) were mixed with the photosensitizer (1.0 wt% of bis-GMA). The mixture was poured into a cylindrical stainless-steel mold (height, 1.5 mm; diameter, 6 mm) and irradiated between two pieces of transparent polypropylene film with visible light curing unit for a given time on each side. The hardness was then measured at six different sites on each specimen, and the mean value was calculated. For each type of polymer, the hardness was taken as the mean value obtained from three specimens. Vickers hardness number (VHN) was determined from the following equation:¹⁰

$$\text{Vickers hardness number (VHN)} = 1.854 \frac{P}{d^2}$$

where *P* is the load (Kg) and *d* is the length of the indentation's diagonal.

Figure 4 shows the relationship between irradiation time and VHN of dental composite resin containing 1 wt% of photosensitizer. The hardness of the composite resin increased with irradiation time and increased in the order of CQ < PD < DA. The resin containing DA has higher VHN than that of CQ or PD. This can be explained by the effect of DA which acts as not only a photosensitizer but also a cross-linker.⁸ It is not consistent with the result of pho-

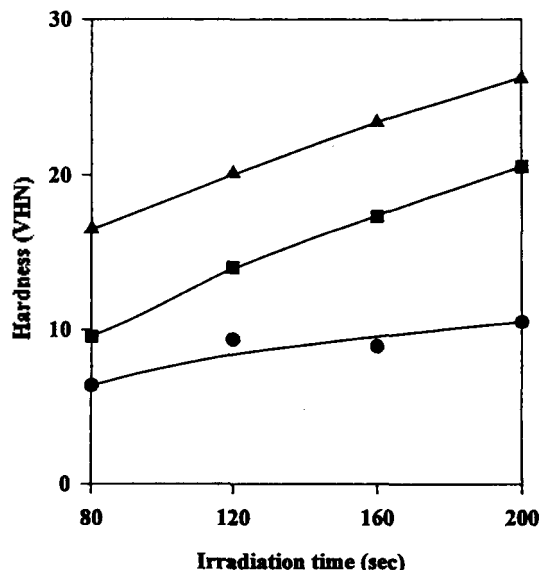


Figure 4. The relationship between irradiation time and Vickers hardness number for dental composite resins containing 1.0 wt% of photosensitizer: (●), CQ; (■), PD; (▲), DA.

topolymerization efficiency of the three photosensitizers. One possibility is that enol form of DA increases RDB of the composite resin containing DA. Another possibility is that Vickers hardness is surface property of the resin, while RDB is bulk property of the resin.

The photodecomposition of photosensitizers was studied by UV absorption spectroscopy. The photosensitizer was dissolved in ethanol and the absorbance at its λ_{max} was adjusted to 1.0. The relative rate of photodecomposition of photosensitizers was measured by the decrease in absorbance at the absorption maximum with irradiation time. The relative absorbance decrease of CQ, PD, and DA was 87, 30, and 43% respectively after 240 sec of irradiation time. The relative rate of photodecomposition for three photosensitizers increased in the order of $\text{CQ} < \text{DA} < \text{PD}$. The photodecomposition efficiency of CQ was lower than that of DA or PD. This can be explained as follows: Photolysis of diketone leads to homolytic cleavage of C-C bond between the two carbonyl groups resulting in the production of two carbonyl radicals. The radical pair can undergo cage escape to form photodecomposed product. However, the two carbonyl radicals in CQ are structurally connected each other and the probability of recombination of the two carbonyl radicals in CQ is greater than that of DA or PD.

The effect of amine to the photodecomposition of photosensitizer was also studied. The absorbance of photosensitizer solution containing 10^{-3} M of DAEM was adjusted to 0.8 at its absorption maximum, and relative rate of photodecomposition of photosensitizers was measured by the same procedure as described above. The photodecomposition rate of CQ increased about 35%, but that of PD or DA decreased about 25% by the addition of amine. The relative photodecomposition rate increased in the order of $\text{CQ} \leq \text{DA} < \text{PD}$, but the difference was not so large. The reason is that different mechanism is operating for the photodecomposition of photosensitizers in the presence of amine. Irradiation of diketone and amine mixture results in the formation an exciplex via electron transfer

from amine to excited diketone. Hydrogen transfer from α hydrogen of amine to the diketone in the exciplex results in the production of aminyl radical and hydryl radical. These two radicals initiate the polymerization of bis-GMA.

The results indicate that PD is a new visible light photosensitizer for dental composite resin with higher surface hardness and photopolymerization efficiency than those of CQ. The more study on the properties of dental composite resin containing PD or DA will be pursued further at this laboratory.

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