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Properties of 2,3-butanedione and 1-phenyl-1,2-propanedione as new photosensitizers for visible light cured dental resin composites

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Abstract

Two 1,2-diketones, 1-phenyl-1,2-propanedione (PD) and 2,3-butanedione (BD) were investigated as new visible light photosensitizers for formulating a dental resin composite of bis-GMA in order to improve the physical properties of the resin composite. The results were then compared with those of camphorquinone (CQ), the most widely used photosensitizer. Photodecomposition of the photosensitizers with and without amine was studied through UV absorption spectroscopy. The photopolymerization efficiency of bis-GMA containing the photosensitizer increased with irradiation time and with the amount of photosensitizer. The increase was in the order: BD $<$ CQ $<$ PD. The experimental resin composite of bis-GMA containing BD or PD showed better mechanical properties than that which contained CQ. The reason for the higher mechanical properties of the resin composite containing BD or PD as compared with that containing CQ is discussed through the study of a model reaction. It was observed that BD or PD serves not only as a photosensitizer but also as a crosslinking agent.

Keywords: Visible light photosensitizer; Dental resin composite; 1,2-diketone

1. Introduction

When the hard tissue of teeth in the oral cavity is damaged by dental caries or trauma, the standard treatment has been to replace it with amalgam, metal, or dental ceramics. However, not only do patients regard the metallic hue of amalgam and metal restorations to be far from aesthetic, but the use of amalgam is especially harmful due to the presence of mercury in the amalgam [1]. On the other hand, dental ceramics, although aesthetically satisfactory, have certain drawbacks, such as fragility and the reduction of tooth tissue. Therefore, dental resin composites have become popular both for their excellent aesthetics and positive physical properties [2].

Light-induced polymerization systems have been used as permanent restorative dental resin composites in dentistry. They can be categorized into two types, based on the light source; UV or visible light. Recently, visible light-cured composite resins are used mostly because they are safer and easier to use than UV activated resin composite systems. They are composed of organic monomers, inorganic fillers, a photosensitizer, and a coinitiator. Among them, the photosensitizer is one of the most important additives since it initiates the photopolymerization of the resin composite.

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 [4]. The low polymerization efficiency of CQ results in low mechanical properties of the resin composite, as well as possible toxic effects to the human body from residual monomers. Thus, it is of great interest to find an effective photosensitizer for the visible light curing process. However, only a few studies have been carried out in the search for alternatives for CQ. The photopolymerization efficiencies of benzil and acenaphthenoquinone were found to be lower than that of CQ [5]. 2,3-butanedione (BD, diacetyl) was studied as a crosslinking agent rather than as a photosensitizer [6–10].

In a previous study, we reported that phenylpropanedione (PD) is a new visible light photosensitizer for dental resin composites with higher surface hardness and greater photopolymerization efficiency than that of CQ [11]. This current study presents a detailed study on the properties of BD and PD, compared with those of CQ (Scheme 1), as new visible light photosensitizers for dental resin composites.

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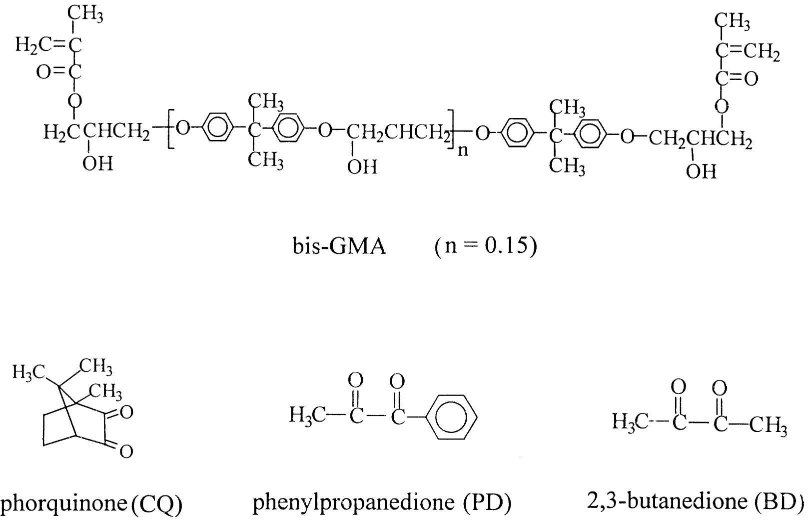

Scheme 1. Chemical structures of bis-GMA and photosensitizers.

2. Experimental

2.1. Materials

1-Phenyl-1,2-propanedione, camphorquinone, and γ-(trimethoxysilyl)propyl methacrylate were purchased from Aldrich Chemical Company and used without further purification. *N,N*-dimethylaminoethyl methacrylate (DAEM) and BD were obtained from Tokyo Kasei Chemical Company. Diglycidyl ether of bisphenol A (DGEBA) was obtained from Dow Chemical company (epoxy resin 331). 2,2-bis[4-(2-hydroxy-3-methacryloxy-propoxy)-phenyl]propane (bis-GMA) was prepared by the reported procedure [12]. Silica (silicon dioxide) was purchased from Shinyo Chemical Company and used after passing through a USA standard testing sieve (325 mesh, <44 μm). Silanization was carried out with γ-(trimethoxysilyl)propyl methacrylate by the reported procedure [13]. Poly(vinyl alcohol) (PVA, M_w; 20 000, saponification number; 86.5–98 mol%) was obtained from Kanto Chemical Company.

2.2. Instruments

UV spectra were obtained with a Jasco model V-550 spectrophotometer. FT-IR spectra were recorded on a Shimadzu Model 8201PC infrared spectrophotometer. ^{1}H-NMR spectra were obtained from a Bruker ASX-32 300 MHz FT-NMR spectrometer. Thermal gravimetric analysis (TGA) was run on a DuPont model 951 at a heating rate of 10°C/min. The Vickers hardness reading was done under a 500 g load for 20 s on a microhardness tester (Model No. 3212.001, Zwick, Germany) using a Vickers diamond indentor. The measurements of diametral tensile strength (DTS) and flexural strength (FS) were performed using a Shimadzu Model AGS-100A universal testing machine. Irradiations are carried out with a Curing Light XL 3000 (3M Co., Germany).

2.3. Photodecomposition of photosensitizers

The photodecomposition of photosensitizers was studied by UV absorption spectroscopy. The photosensitizer was dissolved in ethanol, and the absorbance at its maximum wavelength (λ_{max}) was adjusted to 1.0. The relative rate of photodecomposition of photosensitizers was measured by the percent decrease in absorbance at λ_{max} with irradiation time. In order to study the effect of amine on photodecomposition of the photosensitizer, the absorbance of a photosensitizer solution containing 10^{-3} M of DAEM was adjusted to 0.8 at its absorption maximum (ϵ_{max}), and the relative rate was measured by the same procedure mentioned above.

2.4. Remaining double bond determinations

Remaining double bond (RDB) was determined by IR absorption spectroscopy. A mixture of bis-GMA (1.0 g), DAEM (2 mg, 0.6 mol% of bis-GMA), and 0–3.0 mol% of the photosensitizer based on the amount of bis-GMA was coated manually on the KBr plate. The absorbance of this mixture on the KBr pellet was adjusted to be in the range of 0.85–1.2. IR absorption spectra were measured as a function of irradiation time. RDB of the resins after irradiation was determined from the difference in absorbance at 1635 cm^{-1} before and after irradiation for a given period. Values obtained were normalized with the difference between absorbance at 1581 cm^{-1} [14–16].

2.5. Specimen preparation

The photosensitizer (0–6.0 mol% of bis-GMA) was added to a mixture of bis-GMA (1.0 g), silanized silica (1.0 g), and DAEM (2 mg). The compounds were mixed

Table 1
Physical properties of photosensitizers used in this experiment

Photo-sensitizers	Physical state (m.p. or b.p.)	λ_{max}[a] (nm)		ϵ_{max}[a]
		Ethanol	Cyclohexane	
CQ	Solid (199°C)	468	482.5	80
BD	Liquid (88°C)	419	423.5	50
PD	Liquid (217°C)	393	408	20

[a] In ethanol.

together until the photosensitizer was completely dissolved. Specimens were prepared by inserting the unpolymerized material into a brass mold designed according to the specifications for testing mechanical properties. The specimens were further prepared by the reported procedure [17]. The top surface of the specimen was exposed to light through the polypropylene film and glass cover, then irradiated for 40 s with a photo-curing light source. Once the top surface was cured, the mold was inverted and the lower surface was cured in the same manner. After removal from the mold, the specimens were visually inspected for defects, and those deemed acceptable were stored in darkness at room temperature for 1 day prior to testing.

2.6. Measurements

2.6.1. Vickers hardness number

Specimens for the measurement of Vickers hardness testing were prepared in a cylindrical stainless-steel mold (height: 1.5 mm; diameter: 6 mm). The hardness was then measured at six different sites on each specimen, and the mean value was calculated. For each type of composite resin, the hardness was determined from the mean value obtained from two specimens. Vickers hardness number (VHN) was determined from the following equation [18]:

$$\mathrm{VHN} = 1.854\frac{P}{d^2} \tag{1}$$

where P is the load (kg) and d the length of the diagonal indentation (mm).

2.6.2. Diametral tensile strength

As a general tensile strength test method (ASTM method) is not suitable for measuring the tensile strength of brittle materials. An alternative method, the diametral tensile strength (DTS) test was utilized [19]. DTS test specimens (height: 3 mm; diameter: 6 mm) were produced in a cylindrical brass mold, then loaded to failure with a crosshead speed of 10 mm per min, using 500 kgf load cell. DTS was determined by the following standard:

$$\mathrm{DTS} = 2f/(\pi \times d \times l) \tag{2}$$

where f is the load at failure, d the specimen diameter, and l the specimen thickness. Five specimens for each experimental group were tested and their mean value was calculated.

2.6.3. Flexural strength

The samples for measuring flexural strength (FS) were prepared in a rectangular brass mold (length: 10 mm; height: 2.0 mm; width: 2.0 mm). The specimens were placed on a three-point bending fixture with a span of 6 mm between supports, and loaded to failure at a crosshead speed of 1 mm per min using a 100 kgf load cell [7]. FS was calculated from the following equation:

$$\mathrm{FS} = (3 \times c \times f)/(4 \times b \times a^2) \tag{3}$$

where f is the force at fracture, a the specimen height, b the specimen width and c the distance between the supports. Five specimens for each experimental group were tested and their mean value was determined.

2.7. Photocrosslinking of PVA

Four drops of PVA solution (5 wt% in water), containing BD (2 wt% of PVA), were placed on the aluminum plate (3×7 cm^2, thickness: 0.2 mm) and spread evenly. The plate was dried under vacuum at 70°C for 1 h. The film on the aluminum plate was irradiated with 500 W tungsten–halogen lamp (Taewoo Co., Korea) under atmospheric conditions and then immersed in distilled water for 2 min at 50°C. The weight of the plate (W_3) was measured after drying at reduced pressure. The insoluble fraction of the PVA film was determined from the following equation:

$$\text{insoluble fraction(\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \tag{4}$$

where W_1 is the weight of the uncoated plate, W_2 the weight of the coated plate, and W_3 the weight of the coated plate after irradiation and dipping.

3. Results and discussion

3.1. Physical properties

Table 1 shows the physical properties of the photosensitizers. BD and PD are yellow viscous liquids, while CQ is a solid at room temperature. Their physical state allows BD and PD to have good compatibility with the resin components and to serve as a diluent.

Fig. 1 shows the UV absorption spectra of the three photosensitizers. The maximum wavelength (λ_{max}) of CQ, BD and PD in ethanol is 468, 419, and 393 nm, respectively, while the molar absorption coefficient at maximum wavelength (ϵ_{max}) is 80, 50 and 20. CQ intrinsically has a yellow color, which does not make it possible to be applied in large amounts, resulting in the low mechanical properties of the resin composite. One advantage of PD or BD over CQ is a shorter λ_{max}. This allows it to be applied in a relatively larger amount into the resin composite.

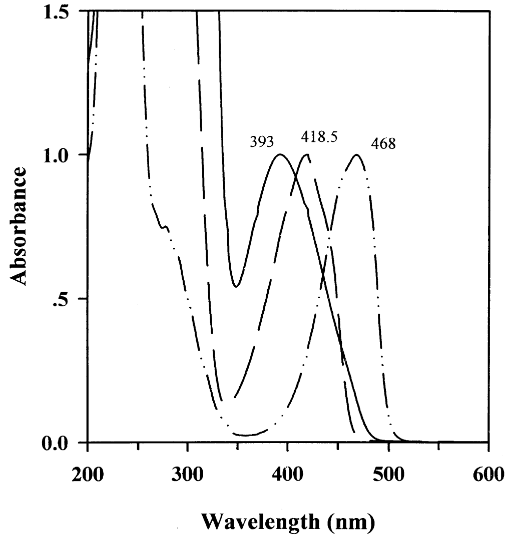

Fig. 1. UV–VIS absorption spectra of CQ (– · · –), PD (——) and BD (– – –) in ethyl alcohol. The concentration of the sensitizers is 2, 1, and 8×10^{-3} M, respectively.

The effect of solvent on the UV–VIS absorption spectra of the sensitizers was studied in order to find out whether the absorption band around 350–500 nm is a (n–π^*) or (π–π^*) transition. Generally, the $\epsilon_{\max}$ of (n–π^*) transition is below 100 and the $\lambda_{\max}$ is shifted to a shorter wavelength with increasing solvent polarity [20]. With the change of solvent from ethanol to cyclohexane, the $\lambda_{\max}$ shifted about 4–15 nm towards a longer wavelength. Both the $\epsilon_{\max}$ values of 20–80 and the shift of $\lambda_{\max,}$ about 4–15 nm, to a shorter wavelength upon change of solvent from cyclohexane to ethanol, indicate (n–π^*) transitions.

3.2. Photodecomposition

The UV absorption spectra of the photosensitizers show that the absorption band around 350–500 nm decreased with irradiation due to the photodecomposition of the sensitizers. The relative photodecomposition rate of the photosensitizers was measured by the percent decrease in absorbance at the maximum absorption wavelength.

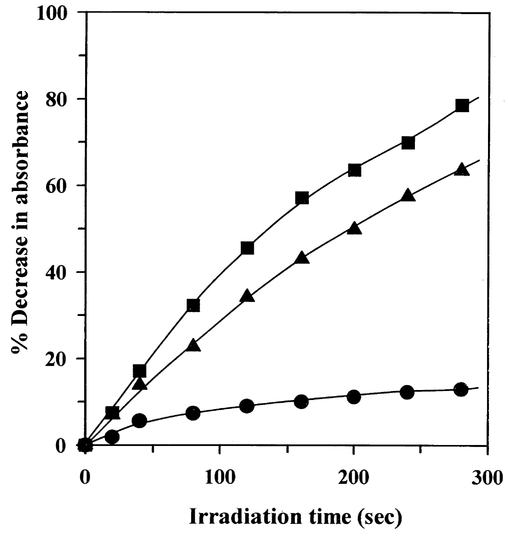

Fig. 2. Relative photodecomposition of photosensitizers as a function of irradiation time in ethyl alcohol: (●), CQ; (■), PD; (▲), BD.

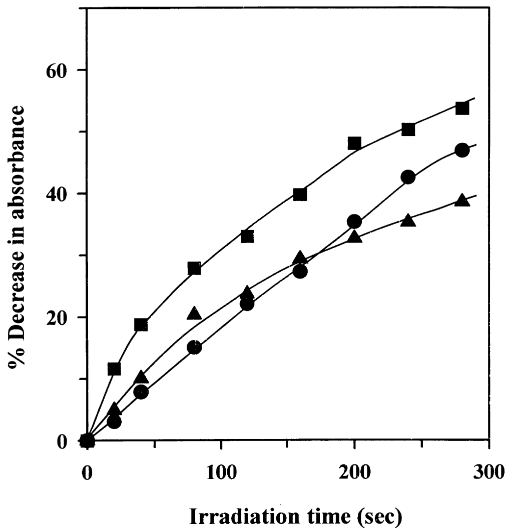

Fig. 3. Relative photodecomposition of photosensitizers as a function of irradiation time in the presence of DAEM (1×10^{-3} M) in ethyl alcohol: (●), CQ; (■), PD; (▲), BD.

Fig. 2 shows the percent decrease of absorbance for the three photosensitizers at their $\lambda_{\max}$ as a function of irradiation time. The relative rate of decrease in absorbance increased in the order: CQ < BD < PD. Approximately 10% of the CQ decomposed after 280 s of irradiation time, while about 60–80% of PD and BD decomposed. This obviously indicates that CQ photodecomposes slower than BD or PD. This can be explained by the probable reactions of the carbonyl radicals. The photolysis of diketone leads to the homolytic cleavage of the C–C bond between the two carbonyl groups, resulting in two carbonyl radicals. This radical pair can undergo cage escape to form photodecomposed products. However, the two carbonyl radicals in CQ are structurally connected to each other and the probability of their recombination in CQ is greater than that in BD or PD.

The effect of amine on the photodecomposition of the photosensitizers was also studied. Fig. 3 shows the percent decrease in the absorbance of three photosensitizers containing DAEM as a function of irradiation time. The photodecomposition rate of PD and BD decreased somewhat with the addition of amine, while that of CQ increased. The photodecomposition rate of CQ increased about 35% with the addition of DAEM at irradiation time of 280 s, while that of PD and BD decreased about 20–30%. The relative photodecomposition rate increased in the order: BD ≤ CQ < PD with the addition of amine, but the difference was not significant.

The above result may be due to a different mechanism operating for the decomposition of photosensitizers in the

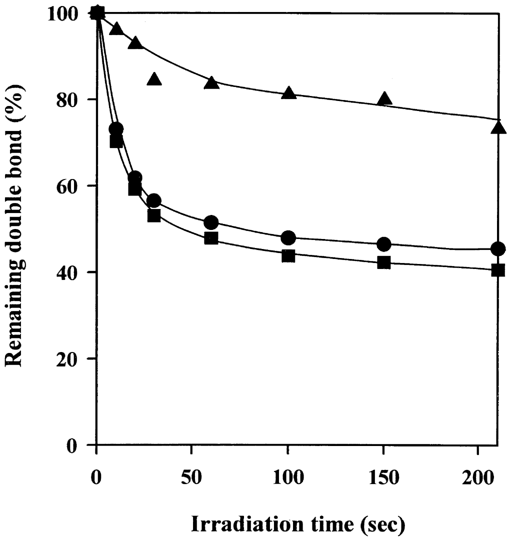

Fig. 4. The relationship between irradiation time and remaining double bond of bis-GMA in the presence of 3.0 mol% photosensitizers: (●), CQ; (■), PD; (▲), BD.

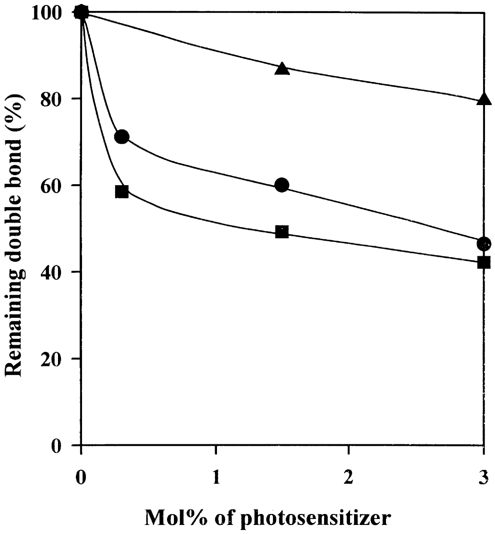

Fig. 5. The relationship between mol% of photosensitizers and remaining double bond of bis-GMA with an irradiation time of 80 s: (●), CQ; (■), PD; (▲), BD.

presence of amine. The irradiation of the diketone and amine mixture resulted in the formation of an exciplex via an electron transfer from amine to excited ketone [21]. A hydrogen transfer from α hydrogen of amine to the diketone in the exciplex resulted in the production of an aminyl radical and a hydryl radical. The aminyl radical is responsible for the initiation of the polymerization reaction, whereas the CQ hydryl radical is inactive [22]. The photodecomposition rate of CQ increased with the addition of amine, while that of PD or CQ decreased slightly. This result indicates that, in the presence of amine, an electron transfer mechanism is predominant for CQ, while a direct photodecomposition mechanism is predominant for BD or PD.

3.3. Photopolymerization efficiency

FT-IR [14], HPLC [23], and NMR [24] have mainly been used for the determination of the photopolymerization efficiency of dental resins. However, the use of FT-IR absorption spectroscopy is the easiest and simplest method. In this experiment, the photopolymerization efficiency of bis-GMA in the presence of a photosensitizer was studied through the use of FT-IR absorption spectroscopy.

Bis-GMA was prepared by the reaction of DGEBA and methacrylic acid. The chemical structure of bis-GMA was confirmed by ^{1}H-NMR and FT-IR absorption spectroscopy. NMR spectra of prepared bis-GMA indicated a mixture of two isomers as reported by Brown et al. [13].

The IR spectra of bis-GMA containing the photosensitizer showed that the absorption band of aliphatic double bond at 1635 cm^{-1} decreased with irradiation, while that of the aromatic double bond at 1581 cm^{-1} was unchanged, indicating that photopolymerization of bis-GMA took place. Fig. 4 shows the relationship between irradiation time and RDB of bis-GMA containing 3.0 mol% of the photosensitizer in the presence of 0.5 mol% DAEM. RDB increased with irradiation time and the photopolymerization reaction was nearly completed within 50 s of irradiation time. The relative efficiency of photopolymerization increased in the order: BD $<$ CQ $<$ PD at the same irradiation time. This order is consistent with the photodecomposition rate of the photosensitizers in the presence of amine, as shown in Fig. 3.

Fig. 5 shows the relationship between the mole percent of the photosensitizer and RDB of bis-GMA in the presence of DAEM with an irradiation time of 80 s. The photopolymerization efficiency of the resins increased appreciably with the photosensitizer concentration up to 0.3 mol%, but not significantly over 3 mol%. The relative photopolymerization efficiency of the photosensitizers also increased in the order: BD $<$ CQ $<$ PD.

Fig. 6 shows the effect of DAEM concentration on the RDB of bis-GMA in the presence of 3.0 mol% of the photosensitizer. The photopolymerization efficiency of bis-GMA containing PD or BD was not significantly affected by the increase of DAEM concentration, while that containing CQ increased appreciably on increasing the DAEM concentration. The degree of RDB of bis-GMA containing CQ was not greater than that containing PD, up to the DAEM concentration of 6.0 mol%.

The above result may be attributed to the different mechanisms at work between CQ and PD or BD. As shown in Figs. 2 and 3, PD or BD photodecomposed at a faster rate than CQ without the addition of amine. However, the photodecomposition rate was similar in the presence of amine. Thus, CQ does not photodecompose readily, compared with PD or BD, due to its cage structure which

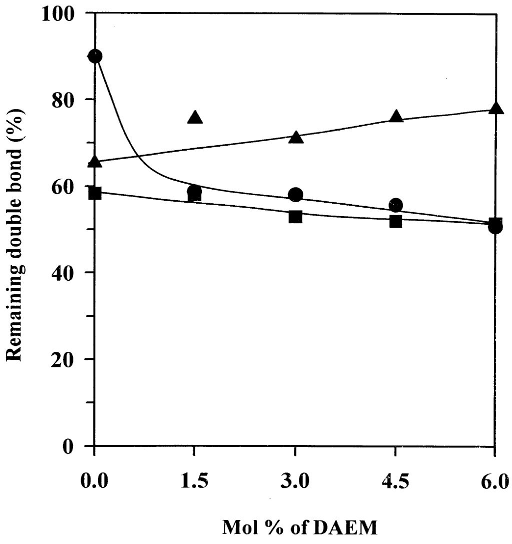

Fig. 6. The relationship between mol% of DAEM and degree of remaining double bond of bis-GMA containing 3.0 mol% of the photosensitizer with an irradiation time of 80 s: (●), CQ; (■), PD; (▲), BD.

inhibits photodecomposition. This result indicates that an electron transfer mechanism is operating for CQ in the presence of amine, while in the case of BD or PD, the radicals directly produced by the photodecomposition of the photosensitizer induce polymerization of bis-GMA independently of amine concentration.

3.4. Mechanical properties of resin composites

In order to study the effect of three photosensitizers on the mechanical properties of resin composites, VHN, DTS, and FS of the resin composites containing photosensitizers were studied. The resin composites were prepared by mixing bis-GMA, silanized silica, sensitizer, and DAEM. Silanized silica was prepared through the treatment of silica with γ-(trimethoxysilyl)propyl methacrylate [13], and silanization was confirmed by FT-IR and TGA. ATR FT-IR spectrum of silanized silica showed that the absorption band of the –OH group at 3441 cm^{-1} decreased, and a new carbonyl absorption band of methacryl group appeared at 1687 cm^{-1}. TGA analysis of the silanized silica indicated about 1% of weight loss. These results indicate that silanization of the silica was successfully performed.

Table 2
Mechanical properties of resin composites (visible light was irradiated for 40 s to front and back sides) containing 3.0 mol% of photosensitizer with various irradiation times

Mechanical properties		Irradiation time (s)			
		40	60	80	100
VHN (kg/mm^2)	CQ	6	9	9	11
	PD	10	14	17	21
	BD	15	20	23	24
DTS (MPa)	CQ	27	29	31	31
	PD	33	34	34	35
	BD	30	31	32	34
FS (MPa)	CQ	23	93	93	97
	PD	85	101	104	106
	BD	89	100	101	103

Table 3
Mechanical properties of resin composites (visible light was irradiated for 40 s to front and back sides) in relation to photosensitizer content

Mechanical properties		Mol%			
		1.5	3.0	4.5	6.0
VHN (kg/mm^2)	CQ	5	6	12	15
	PD	9	10	14	15
	BD	13	15	16	17
DTS (MPa)	CQ	24	27	28	28
	PD	30	33	34	35
	BD	29	30	32	31
FS (MPa)	CQ	23	23	26	25
	PD	83	85	86	95
	BD	82	89	99	98

Table 2 shows the mechanical properties of experimental resin composites containing 3.0 mol% of the photosensitizer with various irradiation times. The mechanical properties of the resin composites improved with irradiation time. This may be due to an increase in the photopolymerization efficiency of the resin composites. The resin composites containing PD or BD showed 1.6–1.9 or 2.2–2.5 times higher VHN than that containing CQ, respectively. The relative VHN of the resin containing sensitizers increased in the order: CQ $<$ PD $<$ BD. The resin composite containing PD or BD also showed 1.1–1.2, and about 1.1 times higher DTS and FS than that containing CQ at the same irradiation time, respectively.

Table 3 shows the mechanical properties of resin composites with varying photosensitizer contents at an irradiation time of 40 s. All the mechanical properties of resin composites improved with increasing the amount of photosensitizer. Resin composites containing PD and BD had higher VHN than those containing CQ at the same sensitizer content. The relative VHN increased in the order: CQ $<$ PD $<$ BD. DTS of resin composite containing PD and BD was about 20–30%, and 10–20% higher than that containing CQ, respectively. The FS of resin composites containing PD or BD were in the range of about 82–98 MPa, while those containing CQ ranged about 23–25 MPa.

The effect of DAEM concentration on the VHN of the resin composites is shown in Fig. 7. The resin composites containing PD or BD show similar or slightly higher VHN with an increase in DAEM concentration, while that containing CQ rapidly increased. This may be attributed to an electron transfer mechanism, which is operating between CQ with amine, while, in the case of PD or BD,

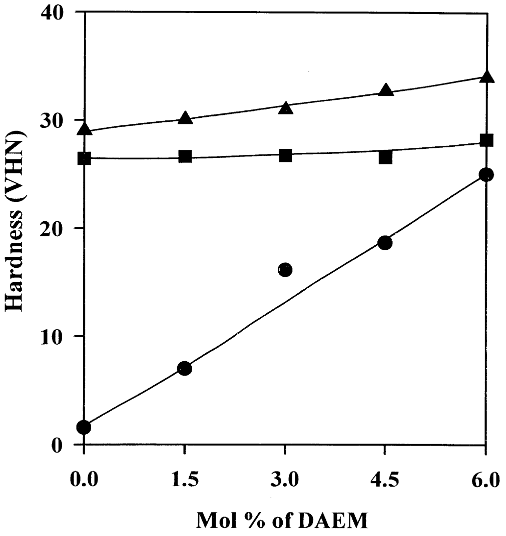

Fig. 7. The relationship between mol% of DAEM and VHN of resin composites with an irradiation time of 40 s: (●), CQ; (■), PD; (▲), BD.

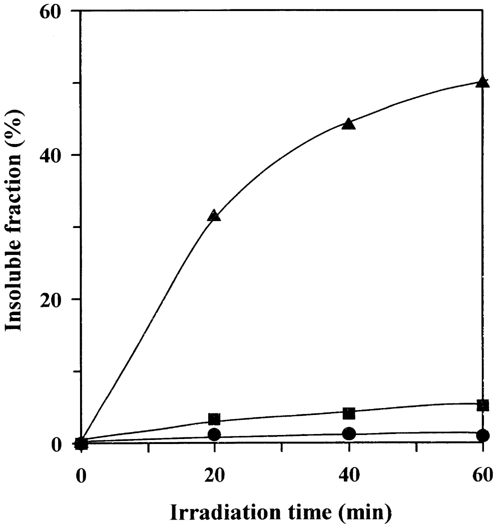

Fig. 8. The effect of irradiation time on the insoluble fraction of PVA film containing 2 wt% of photosensitizer in H_2O with a dipping time of 2 min: (●), CQ; (■), PD; (▲), BD.

a direct photodecomposition mechanism is operating, as mentioned above.

3.5. Photocrosslinking of PVA

The relative photopolymerization efficiency of bis-GMA containing the photosensitizer increased in the order: BD < CQ < PD. However, the relative mechanical properties of the resin composite containing the photosensitizer improved in the order: CQ < PD < BD. Thus, the results of the mechanical properties of the resin containing BD were not consistent with those of photopolymerization efficiency. A possible reason for the higher mechanical properties of BD or PD, compared with CQ, is that BD or PD may serve as a photocrosslinking agent. It was reported that either BD or propanal are able to improve the mechanical properties of dental polymers. This may be indicative of these compounds serving as crosslinking agents [6–8].

The photocrosslinking reaction of PVA, a model polymer for cured resin composites, in the presence of the photosensitizer, was studied to clarify the role of BD or PD as a crosslinking agent. PVA was selected as a model polymer of bis-GMA since it contains –OH groups in the main polymer chain similar to bis-GMA. Fig. 8 shows the insoluble fraction of PVA containing photosensitizers as a function of irradiation time. The insoluble fraction of PVA film containing photosensitizers increased in the order: CQ < PD < BD, indicating that an efficient photocrosslinking reaction took place in the presence of BD. The rate of photocrosslinking reactions of PVA containing PD was slower than that containing BD, but somewhat faster than those containing CQ. Thus, the enhanced mechanical properties of the resin composites containing BD or PD, compared with that containing CQ, may be caused by this photocrosslinking reaction of BD or PD with the resins.

4. Conclusion

The physical state of BD and PD allows them good compatability with the resin and well suited to serve as a diluent, as opposed to CQ. The radicals directly produced by the photodecomposition of BD or PD induce polymerization of bis-GMA independently of amine concentration. However, CQ does not photodecompose readily, due to its cage structure. This property of CQ may indicate a predominant electron transfer mechanism operating in the presence of amine.

The photopolymerization efficiency of bis-GMA and the mechanical properties of the experimental resin composites increased with the amount of photosensitizer and irradiation time. The better mechanical properties of the resin composite containing BD or PD, compared with that containing CQ, were due to the photocrosslinking reaction of BD or PD with the resins. The present study shows that BD and PD serve not only as photocrosslinking agents, but also as effective photosensitizers for dental resin composites with a higher efficiency than CQ. Thus, PD or BD can be utilized as new visible light photosensitizers, suitable for dental resin composites.

Acknowledgements

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