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The effect of 4,4'-bis(N,N-diethylamino) benzophenone on the degree of conversion in liquid photopolymer for dental 3D printing

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PURPOSE. The purpose of this preliminary study was to investigate the effects of adding 4,4'-bis(N,N-diethylamino)benzophenone (DEABP) as a co-initiator to a binary photoinitiating system (camphorquinone-amine) to analyze on the degree of conversion (DC) of a light-cured resin for dental 3D printing. **MATERIALS AND METHODS.** Cylindrical specimens (N=60, n=30 per group, ø5 mm × 1 mm) were fabricated using bisphenol A glycerolate dimethacrylate (BisGMA) both with and without DEABP. The freshly mixed resins were exposed to light in a custom-made closed chamber with nine light-emitting diode lamps (wavelength: 405 nm; power: 840 mW/cm^2) for polymerization at each incidence of light-irradiation at 10, 30, 60, 180, and 300 seconds, while five specimens at a time were evaluated at each given irradiation point. Fourier-transform infrared (FTIR) spectroscopy was used to measure the DC values of the resins. Two-way analysis of variance and the Duncan post hoc test were used to analyze statistically significant differences between the groups and given times (α=.05). **RESULTS.** In the DEABP-containing resin, the DC values were significantly higher at all points in time (P<.001), and also the initial polymerization velocity was faster than in the DEABP-free resin. **CONCLUSION.** The addition of DEABP significantly enhanced the DC values and, thus, could potentially become an efficient photoinitiator when combined with a camphorquinone–amine system and may be utilized as a more advanced photopolymerization system for dental 3D printing. *[J Adv Prosthodont 2015;7:386-91]*

KEY WORDS: Photopolymer; Photointiator; Degree of conversion, 4,4'-bis(N,N-diethylamino)benzophenone; 3D Printing

INTRODUCTION

3D printing is one of the advanced technologies for the

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fabrication of objects from computer aided design (CAD) data via layer-by-layer processing of the material.[1,2] There are various additive processes both in the way layers are deposited to create parts and in the materials that are used.[3] Stereolithography (SLA) is the first 3D printing technique, introduced to production systems by Charles W. Hull in 1986.[4] SLA utilizes liquid ultraviolet (UV)-curable photopolymer and a UV light source to build parts of an object based on cross-sectional patterns made by computer design. To elaborate, after a first resin layer has been established, the second one is then exposed to a light source to be solidified and adhered on the top of the first.[5] Traditionally, the photopolymer used in SLA processing is a compound of oligomers, monomers, and photoinitiator, requiring excellent control of the photopolymerization process to acquire high-quality solid 3D objects.[6] Although high resolution and accuracy are advantages of this method, a post

curing process is required in most cases after printing because the liquid photopolymer is not completely cured inside the vat.[5] The post curing process can cause warping or curling in the relatively thin area of the product.

The degree of conversion (DC) of resin materials is the number of carbon double bonds (C=C) that are converted into carbon single bonds (C–C) of the methacrylate groups involved in the curing process.[7,8] There is much scientific evidence that the DC relates to the mechanical properties, amount of residual uncured monomer, color stability, water sorption, solubility, and volumetric shrinkage of the polymerized product.[8-12] For light-cured dental resins, the DCs are highly influenced by the characteristics and concentrations of the photoinitiators.[8] Currently, a binary photoinitiating system, such as a camphorquinone (CQ)-amine complex, is the most widely used among commercial light-cured packable dental resins.[13,14] However, CQ is inherently yellow, so the shade may cause esthetic problems in the anterior teeth.[9,14,15] On top of that, its inner shielding effect and poor solubility in water have been noted as other drawbacks of CQ.[11] Hence, these limitations have encouraged further research into new initiators to improve photo activating systems.[11,16-19]

4,4'-Bis(N,N-diethylamino)benzophenone (DEABP) was first introduced as a photo-reactant in 1970.[20] DEABP is a benzophenone derivative and a hydrogen abstraction-type free radical-generating photoinitiator.[12] The molecule of DEABP contains both ketone and amine functional groups, causing it to exhibit a strong absorption of UV A irradiation, but does not absorb significantly in the visible light region, so color can be maintained better than with CQ systems.[15] The photochemistry of benzophenone derivatives has been investigated in terms of various solvents, the molar absorptivity, the rate of bleaching, concentrations, and the thickness of materials.[15,21]

In the SLA system, to remove or reduce the post curing process, increasing the DC is indispensable during the printing process. Therefore, several studies have attempted to increase the DC values of photopolymers by improving the photoinitiating system.[19,22] However, there has been no research investigating the effect of DEABP on the DC of liquid photopolymer under SLA-simulative conditions. Accordingly, this preliminary study was designed to analyze the curing of a liquid photopolymer in a custom chamber and to examine the efficiency of adding DEABP into the CQ-amine initiating system by measuring the DC of a light-cured resin using a Fourier transform infrared (FTIR) spectrophotometer. The null hypothesis was that the DEABP-containing resin possesses similar DC values to that of the DEABP-free resin.

MATERIALS AND METHODS

DEABP-free liquid resin was prepared by mixing 70.0 wt% bisphenol a glycerolatedimethacrylate (BisGMA) and 30.0 wt% triethylene glycol dimethacrylate (TEGDMA) (Sigma-Aldrich, St. Louis, MO, USA); 0.5 wt% of CQ and 1.0 wt%

of ethyl-4-dimethylaminobenzoate (DMAEMA) (Sigma-Aldrich) were then added to the mixture. The DEABP-containing liquid resin was obtained by adding 1.0 wt% of DEABP (Alfa Aesar, Ward Hill, MA, USA) to the DEABP-free liquid resin. The liquid resin mixtures were agitated for 2 hours at 25°C (room temperature). The chemical structures of CQ, DMAEMA, and DEABP are shown in Fig. 1.

Sixty cylindrical specimens (5.0 mm in diameter, 1.0 mm in height) were fabricated for two groups, with and without DEABP, and were light-irradiated for durations of 0, 10, 30, 60, 180, and 300 seconds with 5 specimens for each condition. The freshly mixed resins both with and without DEABP were poured into silicone molds, and then were covered by polyester film and 1.0 mm thick glass slides in sequence (Fig. 2). To apply standardized pressure, two circular weights (50.0 g each) were placed on both the left and right sides of the glass slides.

The liquid resin mixtures were cured in a custom-made closed chamber in an air environment and 25.0°C. The chamber consisted of a specimen table and a light source unit (Fig. 3). The height of the table was controllable, and the light unit, composed of nine light-emitting diode (LED) lamps (wavelength: 405 ± 5 nm, power: 780 mW/cm^2) (LG Innotek, Seoul, Korea), was mounted. The distance between the light unit and the specimen table was set at 10 mm. Every specimen was analyzed immediately after each individual curing process.

The DC values of the materials were measured using an FTIR spectrophotometer (IRPrestige-21; Shimadzu, Kyoto, Japan) with an attenuated total reflectance (ATR) unit (MIRacle; Pike Technologies Inc., Madison, WI, USA).[23-25] The absorbance spectra were obtained by scanning the
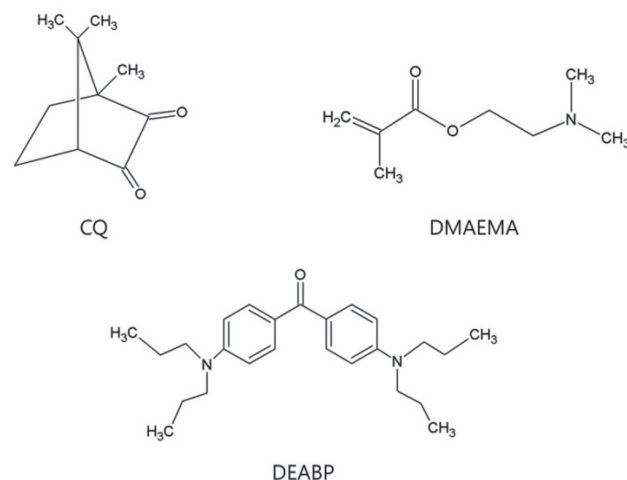

Fig. 1. Chemical structures of the photoinitiators and amine synergist. CQ: camphorquinone; DMAEMA: ethyl-4-dimethylaminobenzoate; DEABP: 4,4'-bis(diethylamino)benzophenone.
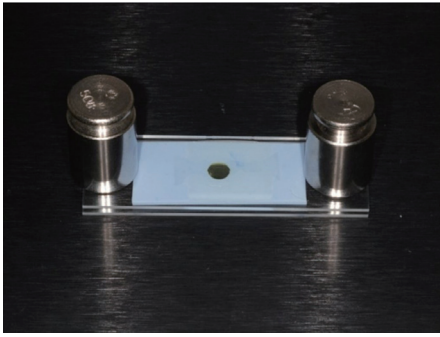
Fig. 2. Specimen fabrication; A small amount of freshly mixed material was placed into a silicone mold, and then covered with polyester film and a glass slide to be pressed.
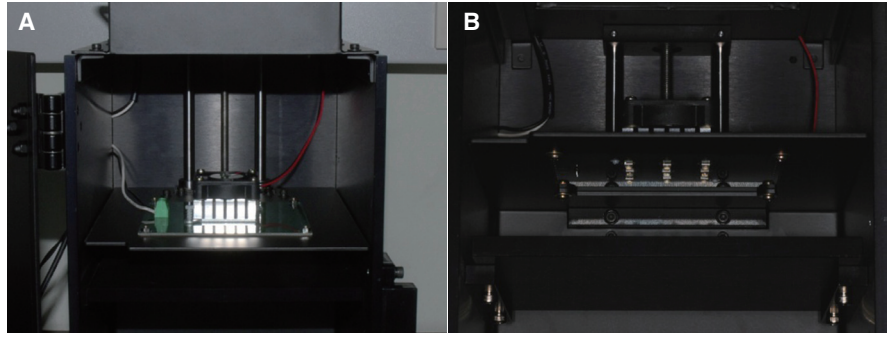

Fig. 3. (A) Custom-made closed chamber with an adjustable light-irradiation distance and (B) nine LED lamps with adjustable light-irradiation duration.

specimens 20 times in the 1670-1550 cm^{-1} range with a resolution of 4 cm^{-1}. The aliphatic C=C bond (with a peak at 1638 cm^{-1}) was used for the DC calculations, while the aromatic C=C bond (with a peak at 1608 cm^{-1}) was used for the internal calibration. The DC values were calculated by comparing the height of the peak for the methacrylate vinyl group in the cured resin against that in the uncured resin, using the following equation:

$$DC\ (\%) = (1 - cured/uncured) \times 100, \qquad (1)$$

where *cured* and *uncured* are the absorption peak heights for the cured and uncured resins, respectively.

The mean DC values were then fitted with a non-linear least square method. The calculated regression curve followed the equation of the ratio of two polynomials as below.

$$DC\ (\%) = \frac{a_0 + a_1 x + a_2 x^2}{b_0 + b_1 x + b_2 x^2} \qquad (2)$$

The initial velocity of polymerization was calculated using the equation during the first 5 seconds. The final DC was calculated using L'Hôpital's, when time was set to infinity, as below:

$$\text{Final DC\ (\%)} = \lim_{n \to \infty} \frac{a_0 + a_1 x + a_2 x^2}{b_0 + b_1 x + b_2 x^2} \qquad (3)$$

$$= \lim_{n \to \infty} \frac{a_1 + 2a_2 x}{b_1 + 2b_2 x} = \lim_{n \to \infty} \frac{2a_2}{2b_2} = \frac{a_2}{b_2}$$

The data were evaluated with two-way analysis of variance (ANOVA) to assess the effects of the addition of DEABP and the duration of light-irradiation, using SPSS software Version 22.0 for Windows (SPSS Inc., Chicago, IL, USA). Post hoc comparisons were performed using the Duncan test at a significance level of 0.05.

RESULTS

Fig. 4 shows the regression curve of the DC results of the two experimental resins as functions of the irradiation times. The DC values increased rapidly during the initial period and then plateaued. The coefficients, the corresponding value of standard error of estimate (S$_{y,x}$), and the coefficient of determination (R^2) of the regression equations are listed in Table 1. The initial velocity of polymerization and final DC were greater in the DEABP-containing resin than in the DEABP-free resin (Table 2). Two-way ANOVA
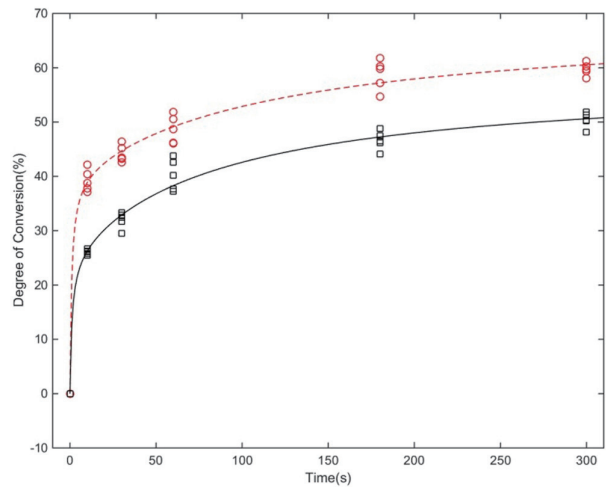

Fig. 4. Degree of conversion of the C=C bonds (%) as functions of the irradiation time. The lines are calculated fits of the experimental data of the equations. The solid line represents DEABP-free resin, whereas the dotted line indicates DEABP-containing resin.

Table 1. Coefficients of the regression equation of the DEABP-containing and DEABP-free resins

Resin	a_0	a_1	a_2	b_0	b_1	b_2	$S_{y,x}$*	$R^{2\dagger}$
DEABP-free resin	0.0001	22.5	0.58	1.0	0.88	0.01	2.3136	0.997
DEABP-containing resin	-0.010	38.0	0.55	0.9	0.95	0.008	1.9199	0.999

* $S_{y,x}$: Standard error of estimate.
† R^2: Coefficient of determination.

Table 2. Initial velocity of polymerization and degree of conversion (%) at given times

Light-irradiation durations	V_{ip} (%/s)*	Degree of conversion (mean ± SD)					
		10	30	60	180	300	Final
DEABP-free resin	22.5	26.1 ± 0.5[a1]	32.0 ± 1.5[b1]	40.4 ± 2.9[c1]	46.6 ± 1.7[c1]	50.4 ± 1.4[d1]	58.0
DEABP-containing resin	34.8	39.3 ± 2.1[a2]	44.2 ± 1.6[b2]	48.7 ± 2.5[c2]	58.7 ± 2.8[d2]	59.7 ± 1.1[d2]	68.7

* Vip: initial velocity of polymerization.
Significant differences are represented by different superscript lowercase letters or numbers (lowercase letters are within a row; numbers are within a column).
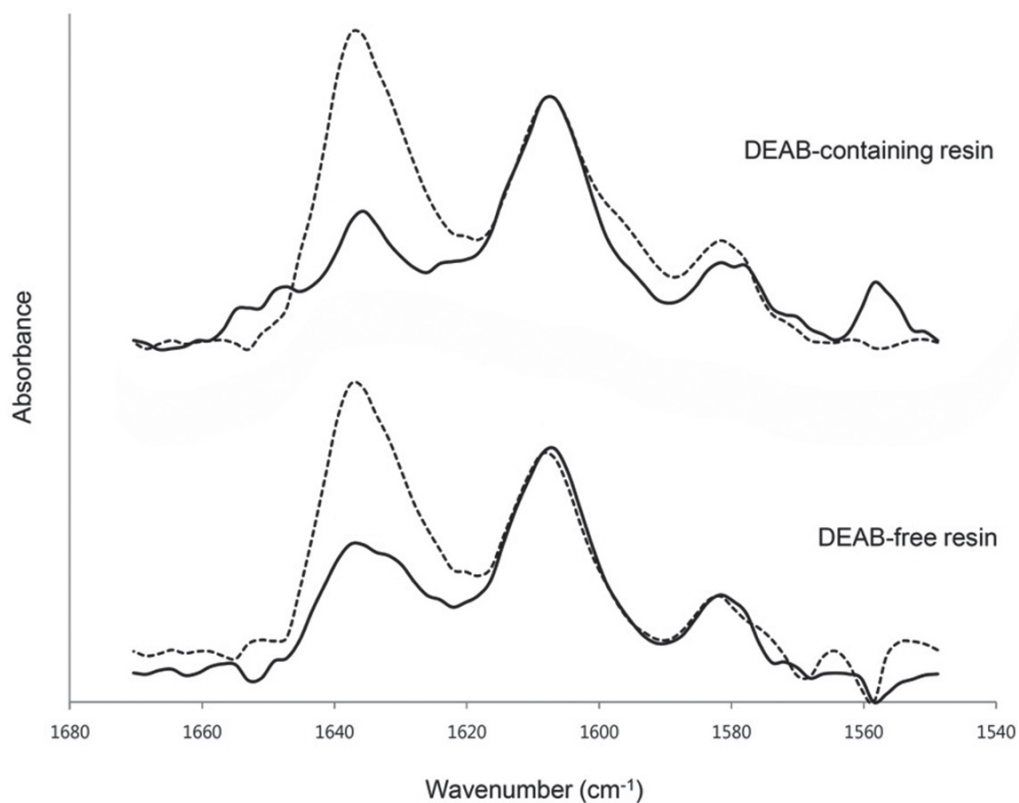

Fig. 5. FTIR spectra of DEABP-containing and DEABP-free resins. Dotted lines (uncured); solid lines (300 s of light irradiation).

revealed significant differences for the addition of DEABP ($P <$ .001), the light-irradiation time ($P <$ .001), and the interaction between these two factors ($P =$ .041). At each point in time, the DC value of the DEABP-containing resin was significantly greater than that of the DEABP-free resin (Fig. 5).

DISCUSSION

In this preliminary laboratory study, the addition of DEABP to a resin with a CQ-amine binary photoinitiating system was highly effective in enhancing its DC value. Thus, the null hypothesis that the DEABP-containing resin possesses similar DC values to that of the DEABP-free resin was rejected. In a previous study,[26] the addition of the p-octyloxy-phenyl-phenyl iodonium hexafluoroantimonate (OPPI) photoinitiator increased the DC of a CQ-DMAEMA containing resin by 3.29% after 300 seconds of light irradiation. Another study concerning the behaviors of acylphosphine oxide (APO) and bisacylphosphine (BAPO) derivatives in light-cured dental resins found that although the BAPO photoinitiator exhibited greater reactivity than did the CQ-amine system, there were no significant differences in the DC values of these systems.[19] Also, the result of a study using 4-(N,N-dimethylamino)phenethyl alcohol (DMPOH) as an alternative co-initiator showed that there were similar DC values using DMPOH and CQ-ethylamine benzoate.[14] On the other hand, in the present study, the DC increased by up to 9.31% when DEABP was added, probably indicating the high photon-absorption efficiency of the photoinitiator.[16] Moreover, the DEABP-containing resin demonstrated a higher initial velocity of polymerization than did the DEABP-free resin. These findings imply that DEABP improved the rate of polymerization, contributing to increased productivity.

The effect of each layer's thickness on the irradiance is important according to the Beer-Lambert law, since the transmittance of the material sample is related to its optical depth (T) and its absorbance (A):

$$T = \Phi_e^t / \Phi_e^i = e^{-\tau} = 10^{-A}, \qquad (4)$$

where Φ_e^t is the radiant flux transmitted by the material sample and Φ_e^i is the radiant flux received by the material sample. Current CQ-based packable dental resins should be incremented in thickness of no greater than 2 mm per layer thickness with more than 20 seconds of activation time each; however, 1mm is the most ideal.[27,28] As for DEABP, Schroeder et al.[15] showed that DEABP was completely consumed at less than 0.5 mm of depth, but the resin in thicknesses of 2 mm was just partially polymerized, possibly due to the effect of the photoinitiator absorptivity that caused radiation attenuation throughout the depth of cure. Therefore, the authors concluded that DEABP was not efficient as a photoinitiator for packable dental resin. However, the curing conditions are totally different in 3D printing. Since the output of 3D printing is formed through a layer-by-layer technique, a single layer, 0.05 to 0.15 mm,[5] is thin enough to be polymerized. Thus, DEABP can be used for 3D printing processes. Furthermore, based on our findings of its positive effect on the DC, DEABP may even be more suitable than CQ in 3D printing applications.

The gun-type LED lamp is widely used as a light source for experimental studies,[29-31] as it features a narrow spectra-range output and good efficiency on the DC of monomer.[7] The gun-type LED lamp has also commonly been used for curing packable dental resins. The possibility of using UV LEDs instead of conventional light sources used in SLA technology has been demonstrated in a previous study.[32] In the present study, as the closed chamber with multiple LED lamps mimics the conditions of a SLA-type 3D printer, the experimental conditions might be more practical than the gun-type light source for researching photoinitiators that can be applied for 3D printing.

The DC value is affected by not only the natures of the photoinitiators,[11] but also by the chemical structure of the resin matrix, the viscosity, and the radiation sources.[7,10,15] Although this controlled study confirmed that DEABP had a positive effect on polymerization, no optimized conditions were identified. Accordingly, to develop more efficient DEABP-containing photopolymers for 3D printing, further experiments incorporating various matrices, radiation sources, photoinitiator concentrations, and other mechanical properties will be needed.

CONCLUSION

Within the limitations of the present study, the addition of DEABP significantly improved the DC values and initial velocity of polymerization of the system. Therefore, DEABP is highly recommended as a co-initiator of the CQ-amine system of a light-cured resin, especially for 3D printing processes.

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