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Photopolymerization of N,N-dimethylaminobenzyl alcohol as amine co-initiator for light-cured dental resins

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ABSTRACT

Objective. The present study was carried out in order to assess the suitability of N,N-dimethylaminobenzyl alcohol (DMOH) as co-initiator of camphorquinone (CQ) and 1-phenyl-1,2-propanedione (PPD) in light-cured dental resins.

Methods. DMOH was synthesized and used as co-initiator for the photopolymerization of a model resin based on {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane} (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA). Experimental formulations containing CQ or PPD in combination with DMOH at different concentrations were studied. The photopolymerization was carried out by means of a commercial light-emitting diode (LED) curing unit. The evolution of double bonds consumption versus irradiation time was followed by near-infrared spectroscopy (NIR). The photon absorption efficiency (PAE) of the photopolymerization process was calculated from the spectral distribution of the LED unit and the molar absorption coefficient distributions of PPD and CQ.

Results. DMOH is an efficient photoreducer of CQ and PPD resulting in higher polymerization rate and higher double bond conversion compared with dimethylaminoethylmethacrylate. The PAE for PPD was higher than that for CQ. However, the polymerization initiated by PPD progressed at a lower rate and exhibited lower values of final conversion compared with the resins containing CQ. This observation indicates that the lower polymerization rate of the PPD/amine system should be explained in terms of the mechanism of generating primary radicals by PPD, which is less efficient compared with CQ.

Significance. The DMOH/benzoyl peroxide redox system, has recently been proposed as a more biocompatible accelerator for the polymerization of bone cements based on poly(methyl methacrylate), because cytotoxity tests have demonstrated that DMOH possesses better biocompatibility properties compared with traditional tertiary amines. The results obtained in the present study reveal the suitability of the CQ/DMOH initiator system for the polymerization of light-cured dental composites.

1. Introduction

The camphorquinone (CQ)/amine initiator system is widely used for the free radical photopolymerization of methacrylate-based restorative dental materials. CQ produces free radicals on exposure to 450–500 nm radiation and this process is activated by the redox reaction with tertiary amines [1]. CQ is the most common photoinitiator but it possesses a noticeable

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yellowish color. For the majority of restorative work this is not an issue as natural tooth color also has a yellowish hue, but for cosmetic restoration this yellow color can be a significant factor. In addition CQ photobleaches [1] during photoinitiation so that its contribution to the color of the restoration can be variable depending on the extent of its reaction. For this reason, 1-phenyl-1,2-propanedione (PPD) has recently been proposed as photoinitiator due to the fact that it is more neutral in color when cured [2,3].

On the other hand, many amines have been suggested as accelerators, but owing to the inherent toxicity of many tertiary amines, research has been directed towards the use of alternative amines with improved biocompatibility [4–9]. The toxicity of restorative materials containing amine co-initiator is connected with the mobility of the amine molecule if other components are essentially non-toxic. A way to reduce its leaching into tissue is to increase the size of the molecule by bulky substituents, the polarity of the molecule so that it does not diffuse out of the resin, or by using polymerizable amines that are incorporated into the polymer chain. It should be noted that the photoredox products of CQ and an amine are a pinicol radical from the CQ molecule and a carbon-based amine radical. Since only the latter initiates polymerization [1] the amine fragment is incorporated into the network. Thus, only the unreacted amine can have a toxic effect. Vázquez et al. developed a new tertiary amine *N*,*N*-dimethylaminobenzyl alcohol (DMOH) as activator of benzoyl peroxide in bone cement formulations based on poly(methyl methacrylate) [5]. DMOH was proposed to replace the *N*,*N*-dimethyl-4-toluidine (DMPT), which is the activator present in conventional bone cement formulations. Although there is no unequivocal evidence about the carcinogenic effect of DMPT, it has been suggested that the toxicity of DMPT containing a methylated phenyl ring, after contact with the skin tissue or by inhalation, might have carcinogenic potential in humans. Liso et al. studied the biocompatibility of DMOH and compared it to that of DMPT [7]. The authors carried out toxicity studies by intravenous injection of DMPT and DMOH in mice. The lethal dose of DMOH was around 3.5 times higher than that of DMPT. In addition, the cytotoxicity can be assessed by the biochemical reaction of the transformation of pyruvate in lactate [7]. From this test, Liso et al. found that while the cytotoxicity of DMPT increases monotonically with its concentration, the cytotoxicity of DMOH reached a level lower than 30%. Moreover, an additional antimicrobial activity of DMOH was found after the incubation of different kinds of micro-organisms, including Gram-negative and Gram-positive bacteria. The marked improvement in biocompatibility of DMOH reported by the aforementioned authors encouraged further research with regard to the use of DMOH for the photopolymerization of dental resins.

The purpose of this study was to examine the suitability of DMOH as co-initiator of CQ and PPD for the polymerization of a model dental resin based on Bis-GMA–TEGDMA. The efficiency of DMOH/CQ and DMOH/PPD initiator systems was assessed by monitoring the conversion versus irradiation time profiles by FTIR. The effectiveness of DMOH was compared to that of dimethylaminoethylmethacrylate (DMAEMA) which is used in commercial dental restorative formulations [10].

2. Materials and methods

2.1. Materials and techniques

The resins were formulated from blends of {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane} (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) at mass fractions 70:30 Bis-GMA/TEGDMA. Bis-GMA (Esstech, Essington, PA, USA), TEGDMA (Aldrich) and methyl methacrylate (MMA) (Súbiton Laboratories-Argentina) were used as received. The resins were activated for visible light polymerization by the addition of CQ (Aldrich) and PPD (Aldrich). DMAEMA (Aldrich) was used for comparison purposes.

Calorimetric measurements were made with a Shimadzu TA 50 calorimeter, provided with software, which enables data processing generated by each run. The calorimeter was calibrated with indium standard. Two liquid samples were prepared, one of them consisted of Bis-GMA monomer containing 1 wt% BPO (L_1) and the other consisted of MMA monomer containing 0.5 wt% amine (DMPOH or DMPT) (L_2). The liquid mixtures were prepared by hand mixing for 30 s at room temperature in a proportion L_1/L_2 equal to 1 by weight. Samples (8–10 mg) were sealed in hermetic aluminum pans and tested immediately. Runs were carried out in the isothermal mode at 40 °C in air atmosphere and an empty capsule served as a reference. The variation of rate of heat output as a function of time was recorded. The sample pans were reweighed after completion of the test to determine any loss of monomer during the measurements.

The light source employed to cure the resins was a light-emitting diode (LED) unit (Ultralume2, Ultradent, USA) with a wavelength range 410–530 nm and light intensity of 400 mW/cm^2. The emission spectrum was measured with a calibrated monochromator (CVI) and a Si-photodetector. The power of the photocuring source was measured with a calibrated laser probe thermopile sensor. Light irradiance was determined by dividing the output power by the area of the light exit window.

The UV absorption spectra of CQ and PPD were measured with a UV–vis spectrophotometer 1601PC Shimadzu in 10 mm cuvettes using ethanol as solvent. The concentrations of CQ and PPD (in mol/l) were 3.65×10^{-3} and 1.25×10^{-3}, respectively.

FTIR spectra were acquired with a Genesis II Mattson FT-IR (Madison, WI, USA). The near-infrared spectroscopy (NIR) spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution. Unfilled resins were sandwiched between two glass plates separated by a 3 mm rectangular rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned vertically, the light source was placed in contact with the glass surface. The specimens were irradiated at regular time intervals equal to 10 s, by manually controlling the curing light. Spectra were collected immediately after each exposure interval. The background spectra were collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at

6165 cm^{-1}. Three replicates of each of the resins were used in the measurement of conversion.

2.2. Synthesis of N,N-dimethylaminobenzyl alcohol

DMOH was synthesized by reduction of 4-*N*,*N*-dimethylbenzaldehyde with sodium borohydride in an alkaline medium. A 1 M solution of the benzaldehyde in methanol was placed in a three-necked flask equipped with a mechanical stirrer, a thermometer and a burette. While stirring, an alkaline solution of sodium borohydride (0.037 mol $NaBH_4$ in 2 ml of 2 M sodium hydroxide diluted with 18 ml of water) was added slowly with occasional cooling to keep the reaction temperature at 18–25 °C. After the reaction, the methanol was removed by evaporation for 48 h, and then the residue was diluted with 100 ml of water and extracted with ether. The organic phase was washed with water and it was dried rapidly with a little anhydrous magnesium sulfate. After ether removal by evaporation, the reaction product was distilled under reduced pressure. The synthesized amine compound was characterized by ^{1}H NMR spectroscopy with a Broker AM-500 spectrometer using deuterated chloroform as solvent and tetramethylsilane as an internal reference. The ^{1}H NMR spectra of 4-*N*,*N*-dimethylbenzaldehyde, and DMOH showed that the signal at 9.8 ppm assigned to the aldehyde proton of the 4-*N*,*N*-dimethylbenzaldehyde became a sharp peak at 4.5 ppm in the spectrum of the DMOH, corresponding to the methylol protons, as a consequence of the reduction reaction.

3. Results and discussion

3.1. Measurement of the conversion

NIR spectroscopy was used for the characterization of conversion versus exposure time of the experimental formulations. The non-destructive nature of the NIR technique provides a simple means to follow conversion on individual specimens as a function of time and gives bulk monomer conversion data on sample dimensions that are relevant to clinical practice. A further advantage of the NIR method is that glass has a very weak absorption at approximately 4500 cm^{-1}, so spectra can be obtained through glass substrates [11–14]. The effect of the radiation dose on the extent of polymerization was examined by illuminating four samples for different intervals. One sample was irradiated in 2 s intervals up to 10 s and then it was irradiated in 10 s increments. The other three samples were irradiated using 10 or 20 or 40 s irradiation periods. In each of these experiments there was a 2 min data acquisition and software data processing interval between two successive irradiations periods. Fig. 1 illustrates the conversion profiles for the different illumination periods. For the 2 and 10 s exposure times, the samples achieved lower conversion than samples cured by more continuous irradiation. However, for the 20 and 40 s exposure intervals, the final conversion was almost the same. This influence of the exposure period on the monomer conversion can be attributed to the temperature rise in the sample due to the exothermic reaction. The maximum temperature reached during polymerization

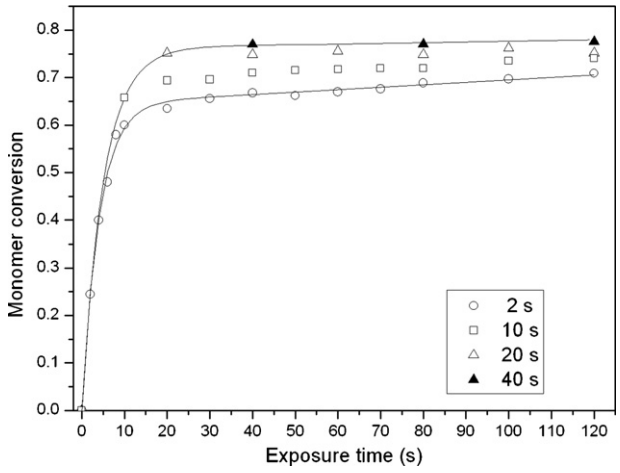

Fig. 1 – Conversion profiles measured at different exposure intervals.

depends on the relative rate of heat generation to heat transfer between the sample and the surroundings [15]. As described above, the cure schedule of the samples consisted of the illumination period followed by the 2 min data acquisition period. During the latter period, the sample is not illuminated and no exotherm is generated, but heat transfer to the environment still occurs, which contributes to a decrease in the sample temperature. Thus the temperature of samples irradiated for shorter periods does not rise as high as samples with longer irradiation periods. A higher sample temperature increases the mobility of the reaction environment (i.e. monomer, radical and polymer) and consequently increases the reaction rate parameters [16,17]. Thus, the greater double bond conversion in samples subjected to relatively continuous illumination is attributed to a combination of both photo and thermal effects. In addition, polymerization of these monomers causes the glass transition temperature (T_g) to rise [16]. Once the T_g approaches the photocuring temperature, the material will vitrify and the reaction will stop [16], thus limiting maximum conversion. Therefore, the samples which were continuously photoirradiated for longer periods attained a higher temperature and therefore reached a higher limiting conversion. In practice, the photopolymerization of dental resins is carried out by continuous exposure of the restoration at intervals of around 40 s. For the remainder of the present work, an illumination interval equal to 10 s was selected in order to focus on the initial stages of the polymerization, i.e. the time before which the double bond consumption reaches a plateau.

3.2. Efficiency of CQ/DMOH and BPO/DMOH systems

The efficiency of the DMOH in activating the CQ photosensitizer was assessed from the conversion versus irradiation time profiles of formulations prepared with 0.25, 0.5, 0.75, 1 and 1.5 wt% CQ in combination with equal molar ratios of DMOH. The double bond consumption of a sample containing 1.5 wt% CQ without added amine was also measured for comparison purposes. Fig. 2 shows that DMOH is an efficient co-initiator for CQ because a fast reaction and high conversions are obtained with concentrations as low as 0.25 wt% CQ. Conversely, in the

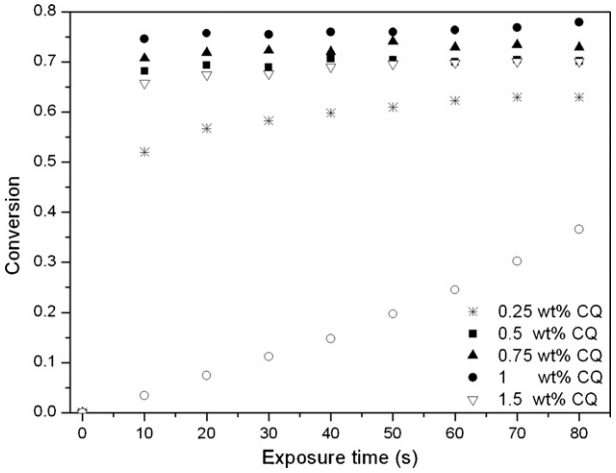

Fig. 2 – Conversion vs. exposure duration for resins containing different concentrations of CQ and molar CQ/DMOH equal to 1. The hollow circles correspond to a sample containing 1.5 wt% CQ in the absence of amine. The exposure interval was 10 s.

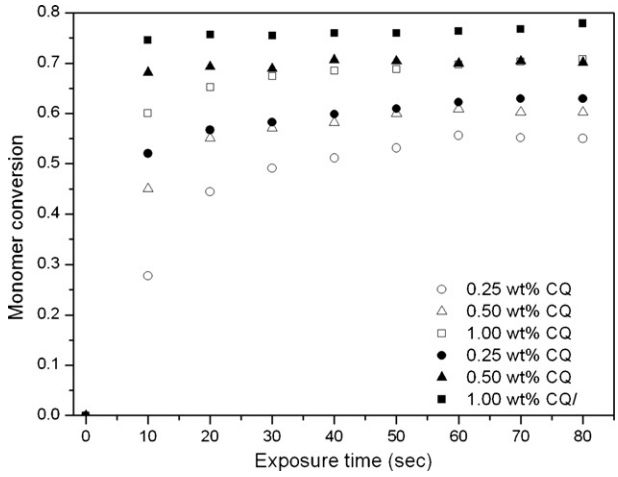

Fig. 3 – Conversion vs. exposure duration for resins containing 0.25, 0.5 and 1 wt% CQ and molar ratio CQ/DAEMA or CQ/DMOH equal to 1. The solid points represent the CQ/DMOH system. The hollow points represent the CQ/DMAEMA system. The exposure interval was 10 s.

absence of amine polymerization progresses at a slower rate. The photodecomposition of CQ may be attributed to the presence of an impurity or hydroxy groups present in the Bis-GMA monomer which can act as a reducer. The double bond conversion in resins containing CQ/DMOH experienced a rapid rise during the first 10 s irradiation, after which it exhibited a plateau, probably caused by vitrification of the network as discussed above. The final conversion increased appreciably on increasing the CQ photoinitiator concentration up to 1 wt%. However, the data shown in Fig. 2 indicate that the increase in the amount of photosensitizer from 1 to 1.5 wt% resulted in a marked decrease in the monomer conversion. In fact the final double bond conversion of samples containing 1.5 wt% CQ was similar to that of samples having 0.5 wt% CQ. This result is attributed to a 'self-screening' effect due to attenuation of the radiation through the sample thickness by CQ [1].

The effectiveness of the CQ/DMOH system was compared with that of the CQ/DMAEMA. Fig. 3 shows the conversion versus exposure time of samples containing 0.25, 0.5 and 1 wt% CQ in combination with equal molar ratios of DMAEMA. The curves for the formulations prepared with equal amounts of DMOH are also shown for comparison purposes. In the resins formulated with DMAEMA, the polymerization progressed at a slower rate and exhibited significant lower values of conversion compared with the resins containing DMOH. For the resin containing 0.25 wt% CQ/DMAEMA, the conversion did not reach a plateau during the whole illumination time, so the time for maximal cure with this formulation would be longer than that recommended for commercial resins (20–40 s). Moreover, the final monomer conversion in resins containing 0.5 wt% CQ with DMOH was equivalent to that in samples containing 1 wt% CQ with DMAEMA.

The DMAEMA reducing agent can copolymerize with the other monomers to form a harmless polymer, which brings about improved biocompatibility. For this reason, the CQ/DMAEMA photoinitiator system is the one most commonly used in current photoactivated dental materials. Unfortunately, the good biocompatibility properties of DMAEMA are accompanied by a sluggish polymerization. Teshima et al. studied the production of primary radicals formed during irradiation of CQ/amine systems by electron spin resonance (ESR) [18]. The amine primary radical is difficult to observe because its lifetime is extremely short. By applying the spin-trapping method with phenyl-*tert*-butyl nitrone (PBN) as trapping agent, short-lived radicals could be observed by ESR. The combination of an amine radical and PBN generates a PBN amine radical which can be quantified. The authors found that, for the same irradiation time, the quantity of radicals generated using CQ/DMAEMA was around 30% of that using CQ/dimethyl-*p*-toluidine (DMTP). The lower production of primary radicals in the CQ/DMAEMA system was attributed to the following facts. First, tertiary aliphatic amines with an electron-withdrawing substituent are less effective electron donors than tertiary aromatic amines with a para electron donating substituent and, consequently, DMAEMA is less inducible by the excited CQ than DMPT [18]. Second, Teshima et al. [18] argued that DMAEMA is more prone to combine with oxygen than aromatic amines because fewer PBN–DMAEMA radicals were detected by the ESR technique, suggesting that they combine with dissolved oxygen instead.

Exploratory differential scanning calorimetry (DSC) measurements were carried out in order to compare the reactivity of DMOH/BPO and DMPT/BPO redox initiator systems. The exothermic peak due to the polymerization reaction is accurately detected; therefore, DSC is a suitable technique to measure the rate of heat generation during the chemical reaction and, in turn, the rate of polymerization. Fig. 4 shows typical traces of reaction rate versus time for the DMOH/BPO and DMPT/BPO systems. The reaction started after the consumption of hydroquinone inhibitor present

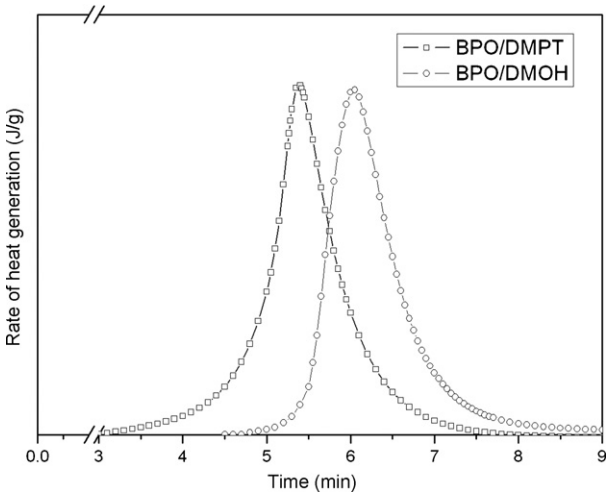

Fig. 4 – Typical DSC traces of reaction rate vs. time. The traces are displaced to make the plot clearer.

in the MMA monomer. The traces are displaced to make the plot clearer; however, the induction time was similar in the two redox initiators tested. The heat of polymerization of the resins (kJ/g) was obtained from the area under the curve of the thermogram. No statistically significant differences in the heat of polymerization between the formulations tested were found. Thus, from DSC measurements it emerges that the reactivity of DMOH was comparable to that of DMPT. Mateo et al. [19] studied the reactivity of radicals derived from CQ/amine systems in acrylic photopolymerization. The authors found that the reactivity of the amine radicals increased as the electron-withdrawing character of the groups attached in the para position increased, which is in agreement with the observation that the amine ethyl-4-dimethylaminobenzoate, is an efficient co-initiator with CQ [20]. The electron withdrawing character of the $COOCH_2CH_3$ substituent in ethyl-4-dimethylaminobenzoate is considered responsible for its high reactivity. Similarly, the high reactivity displayed by DMOH is explained in terms of the electron withdrawing character of its CH_2OH substituent in para position.

3.3. *Influence of the CQ/DMOH molar ratio on the double bond consumption*

Previous research [21] suggested the use of amine/CQ molar ratios higher than 1:1 to increase the monomer conversion and in turn improve the mechanical properties of light-cured resins, although Cook [1] has shown that excessive levels of amine (>0.5 wt%) caused retardation in the rate through the reaction of the chain radicals with the amine to form less active species. In order to assess the effect of increased amine/CQ molar proportions on the final monomer conversion, samples containing 1 wt% CQ and amine/CQ molar ratios equal to 1.5 and 2 were evaluated. Table 1 shows the final conversion values of formulations containing CQ/DMOH and CQ/DMAEMA. It is seen that for the CQ/DMAEMA formulations, the final double bond conversions were essentially independent of the concentration of DMAEMA. Similarly, the final conversions for the CQ/DMOH formulations were roughly

Table 1 – Final double bond consumption of samples prepared with different CQ/amine molar ratios (the standard deviation is ±0.01)

Molar ratio, amine/CQ	Conversion	
	DMOH	DMAEMA
1.0	0.779	0.682
1.5	0.753	0.667
2.0	0.746	0.671

the same at both CQ/DMOH molar proportions, showing slightly decreased values compared with the resin containing 1:1 molar ratio CQ/DMOH. The data shown in Table 1 indicate that, in the range of concentration of photoinitiator studied, the increase of the DMAEMA/CQ or DMOH/CQ molar ratio had no significant effect on the final monomer conversion. These results are in agreement with previous research concerning the photopolymerization kinetics of dimethacrylates using the CQ/amine initiator system at different concentrations [1]. The author reported that for low amine concentrations (<0.1 wt%) the rate of radical formation was dependent of the amine concentration and reactivity, while at intermediate concentrations (between 0.1 and 0.5 wt%) of amine the rate of radical formation was independent of amine concentration and only depended on the amine reactivity. Since aromatic amines have been implicated in resin discoloration over time [22], a limit to the amount of amine used will enhance composite esthetics.

3.4. *Efficiency of PPD/DMOH initiator system*

CQ is the most common activator used in dental restorative composites, but as noted earlier, it possesses a noticeably yellowish color which is photobleached during irradiation [1]. PPD has been proposed as an alternative photosensitizer because it is less yellow in color, however it also photobleaches [2,3]. Therefore, the efficiency of DMOH to activate PPD was assessed in samples containing the same molar proportion of PPD as the samples prepared with CQ. Because the molecular weight of PPD (148 g/mol) is slightly lower than that of CQ (166 g/mol), the weight percent of PPD in these formulations was 0.225, 0.45, 0.675, 0.9 and 1.35 wt%. The double bond consumption of a sample containing 1.5 wt% PPD without added amine was also measured for comparison purposes. Fig. 5 shows that the polymerization initiated by PPD progressed at a slower rate and exhibited lower values of final conversion compared with the resins containing CQ. Moreover, the final monomer conversion in resins containing 0.9 wt% PPD was lower than that in samples containing 0.5 wt% CQ (Fig. 6).

In practice, the light absorption of dental photoinitiators should correlate with the spectral emission profiles of dental light curing units compared on an equivalent basis. Only those wavelengths where the photosensitizer strongly absorbs are useful for photopolymerization [23–25]. The molar absorption of CQ and PPD in conjunction with the emission spectrum of the curing lamp is shown in Fig. 7. It is seen that CQ is activated in the wavelength range 400–500 nm with an absorption peak at 470 nm and PPD is activated from below 350 to 480 nm with a maximum at around 400 nm. By comparison, the LED

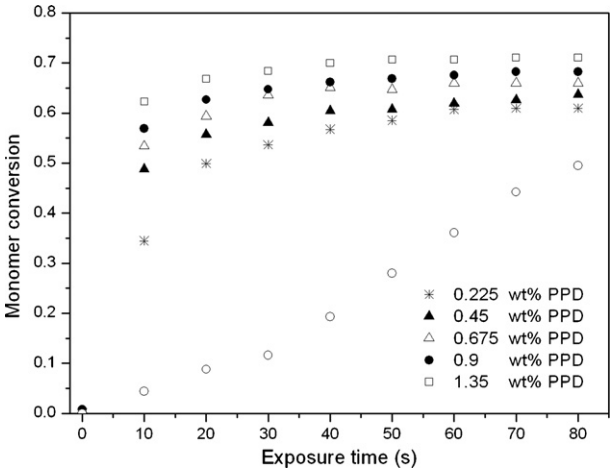

Fig. 5 – Conversion vs. exposure duration for resins containing different concentrations of PPD and molar PPD/DMOH equal to 1. The exposure interval was 10 s.

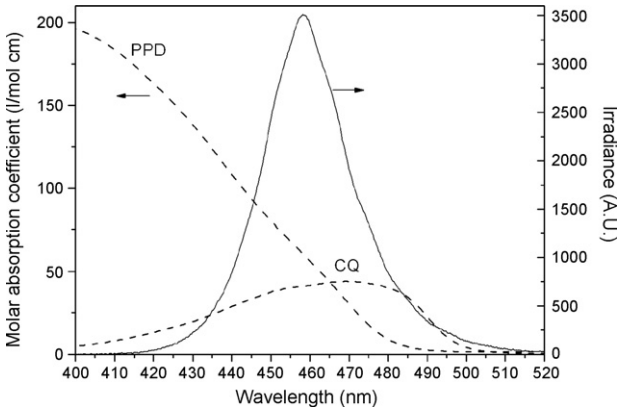

Fig. 7 – Light irradiance of the LED unit in arbitrary units (a.u.) and molar extinction coefficients of the photoinitiators CQ and PPD.

light source employed in the present work emits in the wavelength range 410–530 nm with a peak around 470 nm. Although the absorption peak for PPD is in the UV region, its absorption curve extends into the visible range and, in fact PPD exhibits a molar absorbance at 470 nm equivalent to that of CQ. This observation suggests that the LED unit should polymerize formulations containing PPD/DMOH with similar efficiency to CQ/DMOH. Cook proposed a way to quantify of the efficiency of a given curing unit to excite a given photoinitiator [23], from the spectral irradiance of the curing unit ($I(\lambda)$) and the molar absorption coefficient distribution of the photoinitiator ($\varepsilon(\lambda)$). This quantity was originally defined [23] as the photocuring efficiency but it might be better termed the 'photon absorption efficiency' (PAE), a term coined by Newman et al. [24], because this parameter does not take into account the probability that the excited initiator creates active radicals. The PAE can be assessed as follows. If $I(\lambda)$ (in W/m^2) is the energy incident to an area per unit time, then the number of photons of a given

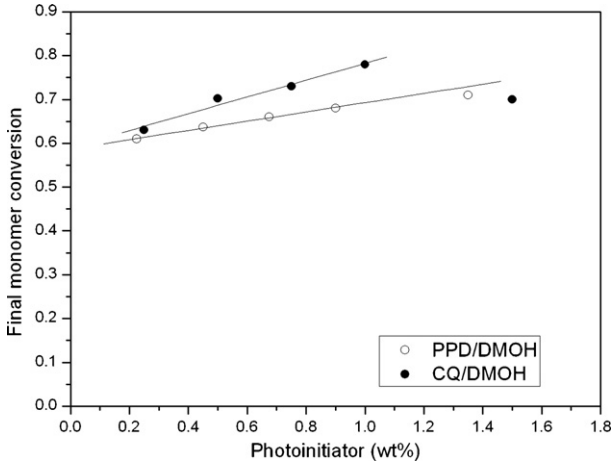

Fig. 6 – Final double bond conversion for formulations containing different concentration of CQ or PPD and molar ratio CQ/DMOH or PPD/DMOH equal to 1. The exposure interval was 10 s.

wavelength ($N(\lambda)$) is equal to the irradiance of the source at the wavelength λ divided by the energy of one photon:

$$N(\lambda) = \frac{I(\lambda)\lambda}{hc}\frac{\text{photons}}{\text{m}^2\text{s}} \tag{1}$$

where h is the Plank constant, c the speed of light and hc/λ is the energy of one photon. The total number of photons of the incident light (N_t) is given by the summation of the photons produced at each wavelength.

$$N_t = \sum_{\lambda_1}^{\lambda_2} N(\lambda)\,\Delta\lambda = \int_{\lambda_1}^{\lambda_2} \frac{I(\lambda)\lambda}{hc}\,d\lambda \tag{2}$$

where λ_1 and λ_2 are the limits of the wavelength emission of the source. For radiation passing through a layer of sample of thickness dL containing a concentration of photoinitiator c (molecules/cm^3), the fraction of absorbed photons (f_{abs}) is:

$$f_{abs} = \frac{\text{Number of photons absorbed}}{\text{Number of photons incident}} = 1 - 10^{-\varepsilon(\lambda)c\,dL} \tag{3}$$

assuming that the material obeys the Lambert–Beer model. For an infinitely thin layer, this equation may be simplified to

$$f_{abs} = 2.303\varepsilon(\lambda)c\,dL \tag{4}$$

Hence, the theoretical number of photons available to be absorbed by the sample per unit time in the volume $A\,dL$ is obtained by combining Eqs. (2) and (4) to give Eq. (5) where K is a constant. This equation provides a means of measuring the efficiency that a particular photoinitiator can utilize the radiation of a given light source to produce an excited state. If these excited states all produce radicals then this is the photocuring efficiency (PE) of the source-initiator pair.

$$PE = K\int_{\lambda_1}^{\lambda_2} I(\lambda)\varepsilon(\lambda)\lambda\,d\lambda \tag{5}$$

Fig. 8 shows the product of the spectral distribution of the light source times the molar absorption coefficient distribu-

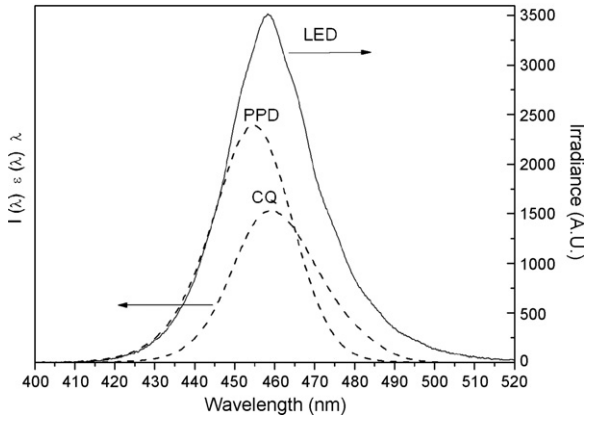

Fig. 8 – Product of the spectral distribution of the light source times the molar absorption coefficient distribution of CQ and PPD. The photon absorption efficiency (PAE) was calculated from the integrated areas.

tion of CQ and PPD. The PAE for PPD, from the integrated curves, is about 40% higher than the PAE for CQ. Therefore the lower polymerization rate of PPD compared with CQ can not be attributed to an inefficient overlap of the PPD absorption spectrum with the spectral emission of the light source, but to a lower efficiency of PPD to generate active initiating species.

Previous research proposed that PPD produces initiating radicals by α-cleavage of the C–C bond between the carbonyls [3]. However, the Norrish Type I unimolecular mechanism is independent of the presence of amine. From results presented in Fig. 5 it is clear that the polymerization of resins with PPD in the absence of amine progressed at a slow rate. Moreover, the increase in the polymerization rate in the presence of amine co-initiator lends support to the fact that PPD decomposes through a bimolecular redox mechanism. It is worth noting that the relationship between the chemical nature of the initiator system and the rate of polymerization is difficult to predict because it depends on a variety of factors such as quantum yield of the photoinitiator as well as various side reactions. From the results obtained in the present work, it may be concluded that although PPD has a high absorption coefficient which contributes to a high photon absorption efficiency, the slower polymerization rate produced by PPD compared with CQ, is attributed to a lower quantum yield of PPD for converting the photon into a radical.

4. Conclusions

The co-initiator DMOH was synthesized by reduction of 4-*N*,*N*-dimethylbenzaldehyde, which resulted in a high purity compound.

The differential scanning calorimetry technique, which is a convenient method to assess polymerization rates, revealed that the reactivity of DMOH/BPO redox initiator system was comparable to that of the DMPT/BPO.

NIR was demonstrated to be a convenient method to follow the evolution of the double bond consumption during photopolymerization of the resins; consequently, it is of great use as a method for determining the relative efficacy of different photoinitiators.

DMOH is an efficient co-initiator for CQ because fast reactions and high conversions are obtained with concentrations as low as 0.25 wt% CQ. Moreover, the effectiveness of the CQ/DMOH was higher than that of the CQ/DMAEMA photoinitiator system. The high efficiency of the DMOH was attributed to the electron-withdrawing character of the $-CH_2OH$ group attached in the para position, which generates highly reactive amine radicals.

The final conversion increased appreciably on increasing the CQ photoinitiator concentration up to 1 wt% and a molar ratio DMOH/CQ equal to 1. However, a further increase in the amount of photosensitizer from 1 to 1.5 wt% resulted in a marked decrease in the monomer conversion due to attenuation of the radiation through the sample thickness by CQ.

The photopolymerization initiated by PPD/DMOH progressed at a slower rate and exhibited lower values of final conversion compared with the resins containing CQ/DMOH. These results were attributed to a lower efficiency of PPD to generate active initiating species compared with CQ.

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