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# Effect of different photoinitiator systems on conversion profiles of a model unfilled light-cured resin

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## ABSTRACT

**Objective.** The aim of this study was to compare the efficiency of different camphorquinone (CQ)/amine photo-initiating systems for the photopolymerization of a model dental resin based in Bis-GMA/TEGDMA.

**Methods.** The monomer conversion versus exposure time was measured in resins containing different types and concentrations of photoinitiators and subjected to different irradiation procedures. The conversion profiles during photopolymerization were investigated using near-infrared spectroscopy (NIR). CQ was used in combination with dimethylaminoethylmethacrylate (DMAEMA), ethyl-4-dimethylaminobenzoate (EDMAB), 4-(N,N-dimethylamino)phenethyl alcohol (DMPOH), and N,N-3,5-tetramethylaniline (TMA) at different concentrations.

**Results.** From the conversion profiles, the approximate order of the accelerating ability of the respective amines were EDMAB  $\approx$  DMPOH > TMA > DMAEMA. The conversion profiles of all resins were sensitive to the illumination period. For a given exposure time, samples cured by sequential illumination resulted in lower conversion than samples cured by continuous irradiation. These results were attributed to a combination of both photo and thermal effects. NIR demonstrated to be a convenient method to follow the evolution of the monomer conversion during the photopolymerization of dental resins and, consequently, it is of great utility as a method for determining the relative efficacy of different photoinitiator.

**Significance.** The DMPOH/benzoyl peroxide redox system, has been recently proposed as a more biocompatible accelerator for the polymerization of acrylic resins. The results obtained in the present study reveal the potential usefulness of the DMPOH amine in light-cured dental composites.

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## 1. Introduction

Photocuring of multifunctional monomers is a well-known method applied in clinical restorative dentistry. Polymerization of dental resins is generally initiated by camphorquinone (CQ)/amine photo-initiating system, which produces free radicals on exposure to 450–500 nm radiation. The efficiency of this

system affects clinically important properties such as the rate of polymerization, the depth of cure and the final monomer conversion.

The room-temperature polymerization of dimethacrylates usually leads to glassy resins in which only part of the available double bonds are reacted. Before the completion of conversion, the vitrification phenomenon decelerates

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the reaction to hardly perceptible rate. Clinically, there are concerns raised if photocurable composite materials are under-cured. If inadequate levels of conversion are achieved in the polymerization, mechanical properties and wear performance can be compromised. In addition, with incomplete cure, leachable residual monomer and initiator become greater incompatibility issues and color stability may decline as well. However, if conversion is maximized to reduce these difficulties, then alternative problems of polymerization shrinkage of the composite become more critical. It is important, therefore, to be able to assess rapidly and conveniently, at least on a relative basis, the extent of polymerization of any dental monomer system, which can be polymerized under controlled conditions that are clinically relevant.

The most widely used techniques to assess the extent of polymerization in dental composites have been the physical determination of surface hardness, the measurement of the heat of reaction liberated during polymerization by differential scanning calorimetry (photo-DSC) and the direct chemical analysis of conversion by mid-infrared (mid-IR) spectroscopy. The photo-DSC technique has been extensively used to follow the reaction kinetics of many photoinitiated polymerization reactions of dimethacrylate monomers and comonomer mixtures [1-5]. However, photo-DSC suffers from rather long response time, which makes it impossible to monitor very fast reactions. In addition, because reaction rate rather than conversion is monitored, the technique is not adequate to monitor accurately the slow increase in monomer conversion when the vitrification process decelerates the reaction rate. Alternatively, a variety of infrared spectroscopic techniques, which enable the direct measurement of monomer conversion, have been an extremely valuable tool for the general characterization of dental resins. Among them, the near-IR spectroscopy (NIR) has been recently applied to the measurement of conversion in methacrylate networks that are characteristic of photocured dental resins and composites [6-9].

Although the final monomer conversions values of many dimethacrylate monomers and comonomers mixtures have been widely reported, little information can be found in the literature regarding the evolution of the monomer conversion during the photopolymerization. The aim of this study was to explore the hypothesis that the efficiency of different CQ/amine photo-initiating systems can be compared by the measurement of the conversion profiles as a function of the exposure time using the NIR technique. Consequently, NIR was used to assess the effect of various types and concentrations of photo-initiators on the extent of conversion. In addition, the influence of the photopolymerization procedure on the degree of conversion was assessed from the conversion profiles of samples irradiated at different exposure intervals.

## 2. Materials and methods

The resins were formulated from blends of {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxyl)phenyl]propane} (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) at mass fractions 70:30 Bis-GMA/TEGDMA. Bis-GMA (Esstech, Essington, PA) and TEGDMA (Aldrich) were used as received. The resins were activated for visible light polymerization

by the addition of camphorquinone (CQ) and amines reducing agent. The amines were dimethylaminoethylmethacrylate (DMAEMA, Aldrich), ethyl-4-dimethylaminobenzoate (EDMAB, Aldrich), 4-(*N,N*-dimethylamino)phenethyl alcohol (DMPOH, Aldrich) and *N,N*-3,5-tetramethylaniline (TMA, Aldrich).

The light source employed to cure the resins was a LED unit Ultralume2, Ultradent USA, wavelength range 410-490 nm, light intensity 400 mW/cm<sup>2</sup>.

FT-IR spectra were acquired with a Genesis II Mattson FT-IR (Madison, WI). A standard FT-IR sample holder with a 15 mm × 10 mm opening was used. The NIR spectra were acquired in absorbance mode over the range of 4500-7000 cm<sup>-1</sup> from 16 coadded scans at two wavenumber resolution. Unfilled resins were sandwiched between two glass plates separated by a 2 mm rectangular rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned in vertical position, the light source was placed in contact with the glass surface. The specimens were irradiated at different time intervals equal to 2, 10, 20 and 40 s, by manually controlling the curing light. After collection of the uncured resin NIR spectrum, spectra were collected immediately after each exposure interval. The background spectra were collected through an empty mould 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<sup>-1</sup> as described by Stansbury and Dickens [6]. Three replicates of each of the resins were used in the measurement of conversion.

## 3. Results and discussion

### 3.1. Measurement of conversion

The copolymerization of multifunctional vinyl monomers leads to a cross-linked network polymer having residual insaturation in the form of pendant vinyl groups and non-reacted monomer. Therefore, the properties of this complex network copolymer will be determined not only by the chemical structure and composition of the monomer system, but also by the degree of conversion of the vinyl groups. The presence of non-reacted monomer can have a plasticizing effect on the polymer, thereby altering the physical and mechanical properties of the hardened material [10-14]. In addition, the presence of residual insaturations can make the polymeric matrix more susceptible to oxidative degradative reactions. In dental composites materials, such chemical degradative reactions can lead to poor aesthetics (i.e. color instability) and poor durability (i.e. loss of anatomic form). It is important, therefore, to be able to assess, at least on a relative basis, the degree of residual insaturation remaining after the polymerization.

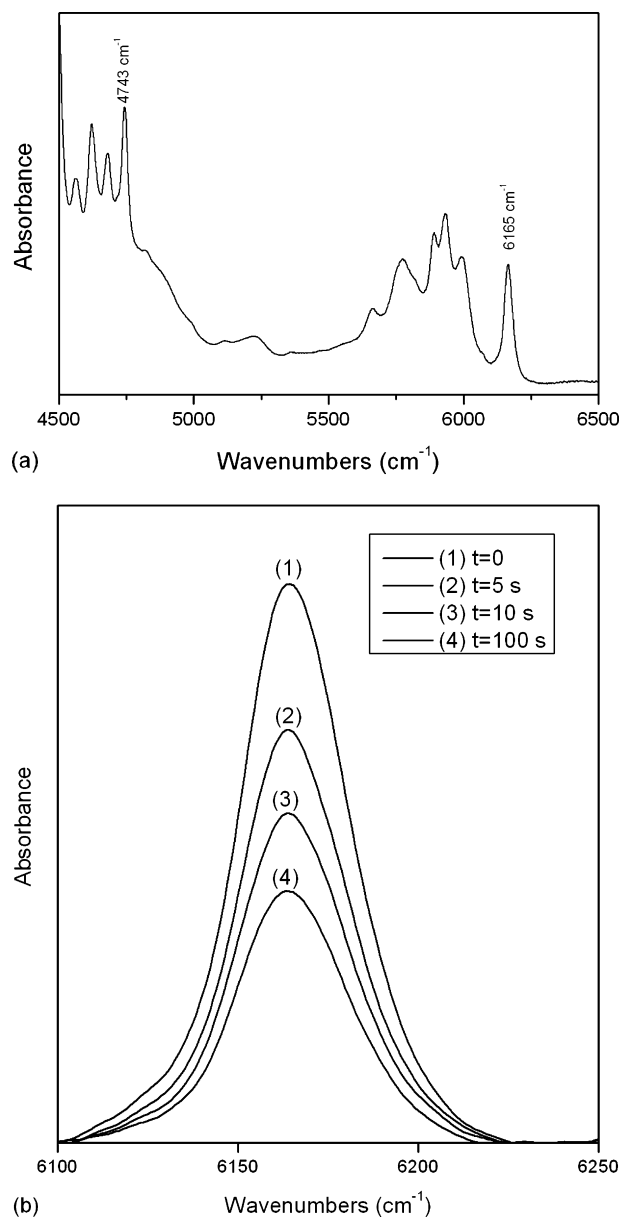
NIR spectroscopy has been recently applied to the characterization of conversion in visible light-cured dental composite resins [6-9]. There are several advantages associated with the use of NIR for measurements of conversion in dental resins. The non-destructive nature of the NIR technique provides a simple means to follow conversion on individual specimens as a function of time. As it was reported by

Stansbury and Dickens [6], NIR spectroscopy provides equivalent methacrylate conversion values to those obtained by traditional mid-IR techniques whereas the use of an internal standard reference peak is not required. In addition, NIR gives bulk monomer conversion data on sample dimensions that are relevant to clinical practice. A further advantage favoring the NIR method is that glass has a very weak absorption at approximately  $4500\text{ cm}^{-1}$ , so, spectra can be obtained through glass substrates.

Through the present work, NIR spectroscopy was used to measure double bond conversion as a function of exposure time in resins subjected to different irradiation procedures. Samples were irradiated at consecutive illumination intervals and after each exposure interval NIR spectra were collected. Representative NIR spectra are displayed in Fig. 1. Fig. 1(a) shows a typical NIR spectrum obtained after irradiation. The absorption of  $=\text{C}-\text{H}$  is located at about  $4743\text{ cm}^{-1}$  while the first overtone is at  $6165\text{ cm}^{-1}$ . Because the base line drops sharply in the vicinity of the  $4743\text{ cm}^{-1}$  band, reliable peak area measurements are difficult in this region. Conversely, the region at  $6165\text{ cm}^{-1}$ , is very stable and there is no ambiguity in baseline construction. Therefore, the methacrylate double bond conversion was followed by measuring the overtone band at  $6165\text{ cm}^{-1}$ . Fig. 1(b) is a magnified plot of the  $6165\text{ cm}^{-1}$  band used to obtain peak heights and areas at different collection times.

A possible dark reaction during the NIR measurement was checked by irradiating a sample for 5 s after which NIR spectra were recorded. The first spectrum was collected immediately after exposure and five successive spectra were acquired after irradiation was interrupted at intervals of 90 s while the sample was kept in the sample holder. The procedure was repeated eight times. Fig. 2 shows the conversion calculated from each spectrum. It can be seen that, the conversion of the resin measured during storage in the sample holder was practically the same as that measured immediately after irradiation.

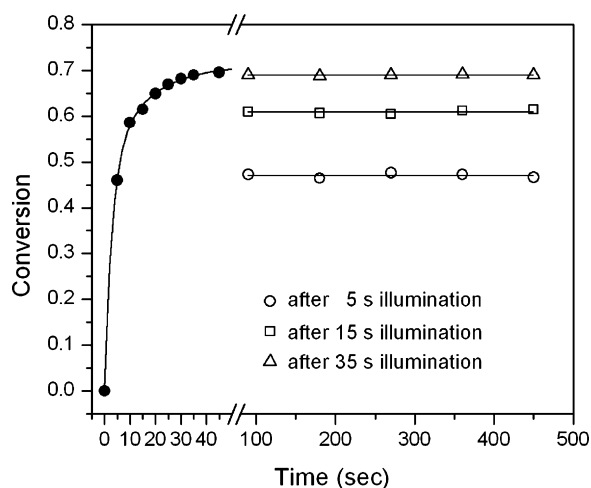
The kinetic of the 75/25 Bis-GMA/TEGDMA system has been studied by previous workers [15–17]. Lovell et al. [15] found that after 4 days dark storage, the specimens conversion increased by 5–10%. Similarly, Halvorson et al. [16] reported post-irradiation polymerization in commercial formulations over the first 24 h. This additional “dark cure” was attributed to the presence of free radical in the network after irradiation had ceased. The extent of post-polymerization was greater in samples with lower initial conversion due to a greater mobility of the network compared to samples that were more highly converted. On the other hand, Decker and Moussa [17] studied the photopolymerization of multifunctional monomers under ultraviolet light. The authors reported that when samples were stored in the dark, the polymerization of the remaining acrylic unsaturations proceeded slowly. For example, the degree of conversion of a sample irradiated for 1 s increased from 22% just after UV exposure to 26% after 7 h of storage at  $25\text{ }^{\circ}\text{C}$ . It is worth noting that in all the aforementioned studies, post-irradiation polymerization was detected after storage periods much longer than the duration of the NIR measurements carried out in the present work. Therefore, from the results presented in Fig. 2 it emerges that the storage of the sample in the sample holder during the 90 s spectral acquisition time had no influence on the double bond conversion.



**Fig. 1 – (a) Typical NIR spectra of a Bis-GMA/TEGDMA blend at 70/30 mass fraction. (b) Magnified methacrylate double bond region in the NIR spectra showing the decrease of the absorption at  $6165\text{ cm}^{-1}$  at different collection times.**

### 3.2. Influence of the photoinitiator system on the conversion profile

In general, the type and concentration of photosensitizer and reducing agent in light-cured dental polymers are fixed by manufacturers and vary from product to product. The concentration of photo-initiator in the resin must be such that it will react at the proper time. In the present work, 0.5 and 1.5 wt.% CQ and a CQ/amine equimolar ratio were added to a 70/30 (w/w) blend of Bis-GMA and TEGDMA. Resins containing 0.25 wt.% CQ with DMAEMA and EDMAB were also prepared in order to assess the polymerization behavior of resins with reduced initiator concentrations. Taking into account that



**Fig. 2 – Conversion vs. time measured during storage of a photo-activated resin in the sample holder. The sample was illuminated for 5 s after which six spectra were acquired at intervals of 90 s. The procedure was repeated eight times. Only representative points, connected by a straight line, are shown to make the plot clearer.**

dental resins contain about 70 wt.% of filler, the initiator concentrations based in the unfilled resin are equivalent to about 0.075, 0.15 and 0.45 wt.% based in the composite resin. The efficiency of different photoinitiator systems was assessed by the measurement of the degree of double bonds conversion as a function of the irradiation time. Fig. 3(a)–(d) illustrates the influence of the concentration and chemical nature of the amine co-initiator on the photopolymerization and Table 1 shows the conversion measured at 10 and 120 s irradiation for the different resins. For EDMAB, DMPOH and TMA aromatic amines, the double bond conversion experienced a rapid rise during the first 10 s of irradiation and increased slowly with further illumination. In resins prepared with 0.5 wt.% CQ, the conversion reached about 61–65% from 10 s exposure, and then increased slowly up to 66–68% after 120 s illumination. No significant differences in the final conversion among the formulations were found. As expected, the increase in the CQ concentration resulted in a significant increase in the final monomer conversion. When 1.5 wt.% CQ was used in combination with EDMAB, TMA or DMPOH, the extent of conversion was over 20% higher than that in resins containing 0.5 wt.% CQ. The double bond conversion was 68–76% when irradiated

for 10 s and increased up to 74–79% upon prolonged exposure. Differently, for the resins formulated with DMAEMA, the polymerization progressed at lower rate and exhibited significant lower values of conversion compared with the aromatic amines. The slow-acting accelerative nature of this amine is demonstrated by its sluggish polymerization compared to the much more rapid polymerization by a fast-acting accelerator such as EDMAB. For the resin containing 0.25 wt.% CQ/DMAEMA, the conversion increased steadily during about 90 s, therefore, this formulation exhibited a cure time longer than that recommended in commercial resins (20–40 s).

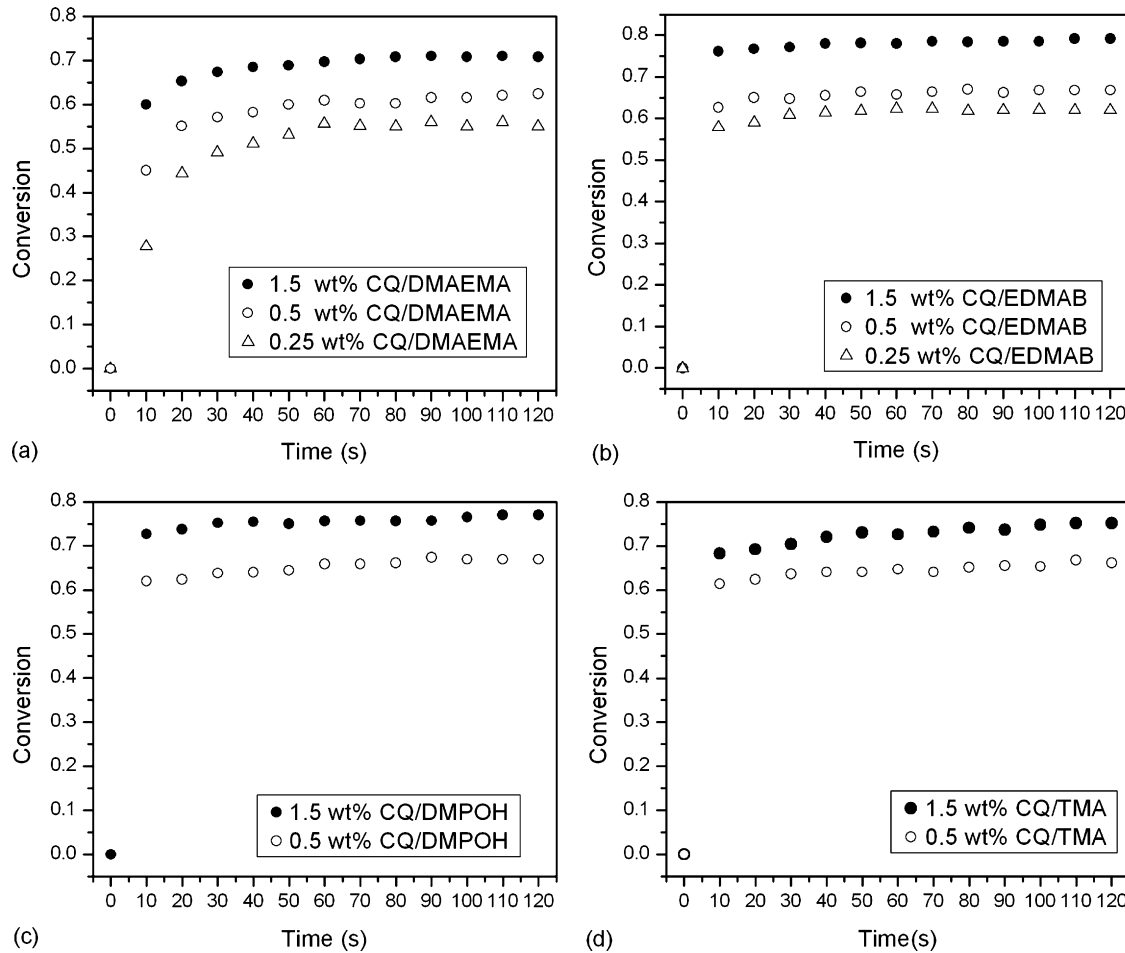
Fig. 4 shows that when 1.5 wt.% of CQ was used as the only photoactivator in the resin, a conversion of the vinyl group of only 49.2% was obtained after 120 s exposure. In light-cured systems, the absorption of one quantum of radiation promotes the carbonyl group to an excited singlet state. This excited state may return to the ground state by fluorescence or a radiationless transition or it may decompose to another species. The excited singlet may also undergo intersystem crossing to the triplet state. The excited triplet then forms an exciplet with the amine reducing agent by charge transfer from the nitrogen lone pair to carbonyl, thus producing two radical ions. This reaction is significantly more efficient than the photolysis of the photo-oxidant in the absence of a reducing agent. On the other hand, previous workers attributed the polymerization in the absence of added amine to the presence of reducing agents in the Bis-GMA monomer [1].

Many amines have been suggested as accelerators, but biocompatibility and esthetic requirements have greatly limited the number of compounds, which can be used for dental applications. EDMAB, which is a very effective hydrogen donor, has been widely used in combination with CQ in dental resins formulations. With this amine, rapid cures are obtained even at low accelerator concentrations [15]. The DMAEMA reducing agent polymerizes to harmless polymer, which brings about improved biocompatibility. For this reason, the CQ/DMAEMA photoinitiator system is the most common one used in the current photoactivated dental materials. However, in agreement with previous workers [1,18], the results presented in Fig. 3(a), show that DMAEMA is the less efficient photoreducer resulting in low polymerization rate and lower conversion compared with the aromatic amines. The lower reactivity of DMAEMA has been attributed to the fact that DMAEMA is more prone to combine with oxygen than aromatic amines. In addition, since DMAEMA carries a methacrylate group with a carbon–carbon double bond, DMAEMA molecules produce DMAEMA-dimers or oligomers when radicals exist [18].

**Table 1 – Degree of conversion (DC) at 10 and 120 s of samples containing 0.5 and 1.5 wt.% CQ in combination with equimolar proportions of amine**

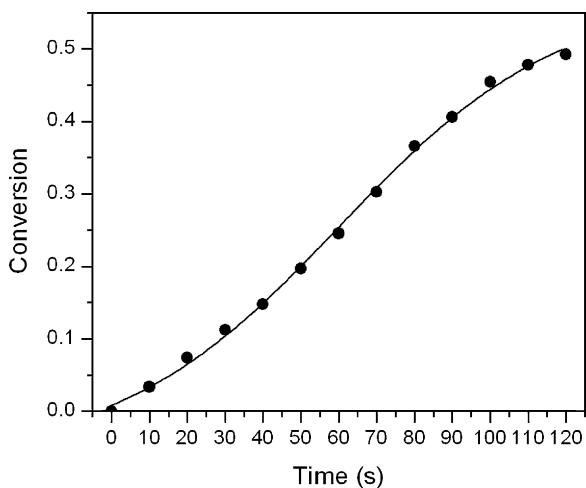
Amine reducing agent	0.5 wt.% CQ		1.5 wt.% CQ	
	DC at 10 s	DC at 120 s	DC at 10 s	DC at 120 s
DMAEMA	0.45	0.62	0.60	0.71
EDMAB	0.65	0.68	0.76	0.79
DMPOH	0.63	0.67	0.73	0.78
TMA	0.61	0.66	0.68	0.75

The standard deviation of the DC: 0.005.



**Fig. 3 – Conversion vs. exposure duration for resins containing different concentrations of CQ and molar CQ/amine equal to 1. (a) CQ/DMAEMA, (b) CQ/EDMAB, (c) CQ/DMPOH and (d) CQ/TMA.**

On the other hand, tertiary aromatic amines have also been used together with benzoyl peroxide (BPO) as an effective initiation system in the free-radical polymerization of acrylic bone cements. The most commonly used amine is *N,N*-dimethyl-

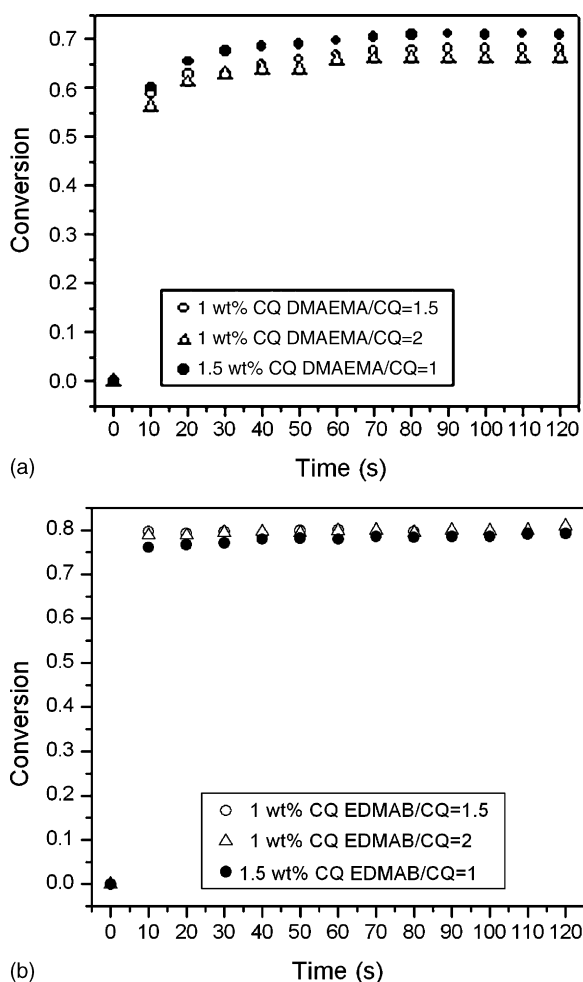


**Fig. 4 – Conversion vs. exposure duration for a resin containing 1.5 wt.% CQ in absence of added amine.**

*p*-toluidine (DMT), which is a suspected carcinogen. For this reason, several other amines have been proposed with better biocompatibility than DMT. Among them, DMPOH has been proposed as a more biocompatible and highly reactive accelerator for the polymerization of bone cement [19,20]. In fact, in 1996 DMT was replaced by DMPOH in a commercial bone cements based on methylmethacrylate (MMA). The kinetics of the BPO/DMPOH redox system for the polymerization of dental dimethacrylate monomers has been studied by Achillias and Sideridou [20]. The authors reported that the performance of formulations with BPO/DMPOH proved to be very satisfactory. Similarly, the results presented in Fig. 3(c) for the CQ/DMPOH photoinitiator system indicate the potential usefulness of this amine in light-cured dental composites.

Previous research [21] has suggested the use of DMAEMA/CQ molar ratios higher than 1:1 to increase the monomer conversion and in turn improve the mechanical properties of light cured resins. 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. Fig. 5(a) and (b) shows the conversion versus time profiles for CQ/DMAEMA and CQ/EDMAB respectively. The curves for the resins having 1.5 wt.% CQ and equimolar proportion of amine are also





**Fig. 5 – Conversion vs. exposure duration for resins containing 1 wt.% CQ and amine/CQ molar ratios equal to 1.5 and 2. The plot for the formulation containing 1.5 wt.% CQ and amine/CQ molar ratio equal to 1 is also shown for comparison. (a) CQ/DMAEMA and (b) CQ/EDMAB.**

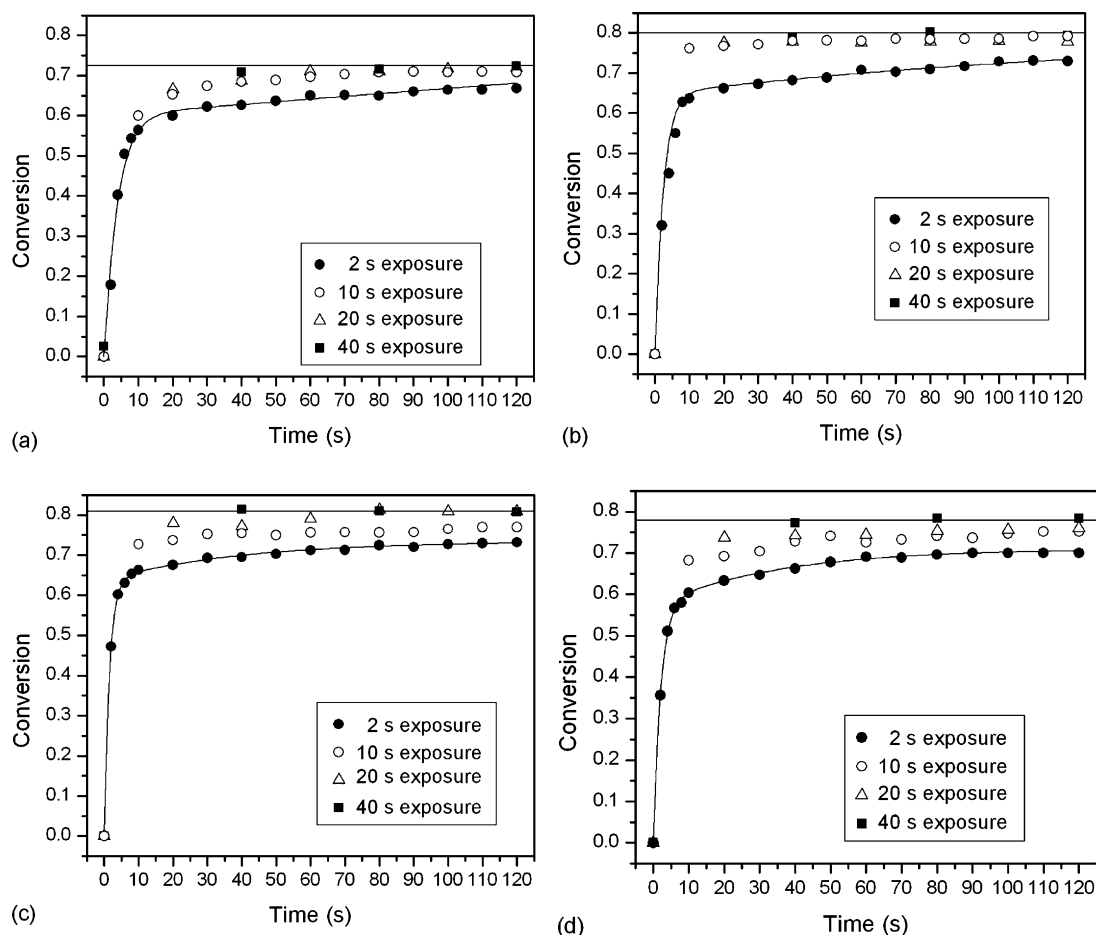
shown for comparison purposes. It is seen that for the CQ/EDMAB formulation, the conversion profiles were essentially independent of the concentration of amine and equal to that measured in formulations with 1.5 wt.% CQ. Similarly, the maximum conversion for the CQ/DMAEMA formulation is roughly the same at both CQ/amine molar proportions, showing slightly decreased values compared with the resin containing 1.5 wt.% CQ. Yoshida and Greener [22] studied the influence of varying concentrations of CQ and DMAEMA on the degree of conversion of unfilled resins. The concentration of both CQ and DMAEMA were in the range of 0.1–2 wt.%. The authors found that at CQ concentrations of above 1 wt.%, the monomer conversion was independent of the concentration of CQ. Furthermore, at CQ concentrations of above 0.5 wt.% and DMAEMA/CQ molar ratios above 1:1, the conversion values were essentially independent of the concentration of DMAEMA. On the other hand, Cook studied the photopolymerization kinetics of dimethacrylates using the CQ/amine initiator system at different concentrations [1]. The author reported that for low amine concentrations the rate of radi-

cal formation was dependent of the amine concentration and reactivity, while at high concentrations of amine the rate of radical formation was independent of amine concentration and only depended on the amine reactivity. In agreement with the above studies, the data shown in Fig. 5 indicates that in the range of concentration of photoinitiator studied, the increase of the DMAEMA/CQ or EDMAB/CQ molar ratio had no significant effect on the final monomer conversion. From these results it emerges that above a certain optimum value the use of increasing photoinitiator concentrations has no significant effect in increasing the degree of monomer conversion. The assessment of the optimum concentration of photoinitiator to be used in a given formulation results relevant to clinical practice. From an aesthetic consideration, the concentration of CQ should be as little as possible because the yellowness of the resin, which may affect the color adaptation to natural teeth. In addition, limits in the amount of amine may also be set by the tendency to internal discoloration of the resin.

### 3.3. Effect of the irradiation method on the monomer conversion

It is widely reported that polymerization shrinkage presents one of the major drawbacks of light cured dental composites [9,23–31]. Earlier works have shown that soft-start cure of the resins may give rise to reduced shrinkage [27–29]. Soft-start cure may be brought about by the so called pulse-delay cure, where the polymerization is initiated by short pulses of energy (controlled by the light intensity or the exposure duration) followed by a waiting time of several minutes before the final cure is performed. On the other hand, it has been reported that for a given monomer formulation, the curing shrinkage is closely related to the monomer conversion [27–31]. While studies have shown that pulse-delay polymerization mode results in lower shrinkage, it was also demonstrated that the resulting polymer exhibited increased susceptibility to softening in ethanol compared to the standard continuous technique [30]. The latter effect may be attributed to the presence of higher non-reacted monomer content, i.e. lower degree of conversion.

The purpose of this experimental part was to study the influence of the photopolymerization procedure on the degree of conversion and in turn in the degree of conversion. Resins with 1.5 wt.% CQ and equimolar proportion of amine were illuminated at different intervals equal to 2, 10, 20 and 40 s, with 2 min data acquisition between two successive illuminations. The 2 s radiation interval was used during the first 10 s exposure and then followed by a 10 s irradiation interval. Fig. 6(a)–(d) illustrates that the conversion profiles of all resins were sensitive to the illumination period. For a given exposure time, samples cured by sequential illumination resulted in lower conversion than samples cured by continuous irradiation. The difference in conversion between samples cured by steps and samples cured continuously was more marked for the shorter illumination periods and for the more reactive initiators. The conversion of the resin containing CQ/DMAEMA cured by 10 s continuous illumination was only 6% higher than that of the resin subjected to five successive 2 s illumination while for the CQ/EDMAB system the 10 s continuous exposure resulted in a conversion about 20% higher



**Fig. 6 – Conversion profiles measured at different exposure intervals in resins containing 1.5 wt.% CQ and amine/CQ molar ratio equal to 1. (a) DMAEMA, (b) EDMAB, (c) DMPHOH and (d) TMA.**

than that of the 2 s incremental exposure. Considering the larger exposure intervals, that is 20 and 40 s, the conversion attained during continuous illumination is roughly the same as that reached by incremental exposures. The results shown in Fig. 6 are attributed to the non-isothermal nature of the photopolymerization, which gives as a result different temperature profiles in samples cured under different exposure periods. The release of reaction heat and the heating of the sample by the curing lamp result in a temperature rise during exposure. On the other hand, the maximum temperature reached during polymerization depends on the relative rate of heat generation to heat transfer between the sample and the surroundings [14]. As it was described above, the sequential cure of the sample consists of the illumination period followed by 2 min data acquisition. During the latter period, the sample is not illuminated and heat transference is present, which contribute to decrease the temperature of the sample. Conversely, during continuous light exposure the rate of heat production is much higher than the rate of heat transfer to the surroundings, therefore, a considerable part of the energy liberated is accumulated into the system, which results in a higher increase in temperature compared with the sequential illumination procedure. On the other hand, as the heat released is related to the monomer conversion, resins

containing more reactive initiators are expected to develop a higher temperature compared with the less reactive systems. Thus, the difference in temperature rise between 10s continuous illumination and 2s incremental illumination for the CQ/DMAEMA is expected to be lower than that for the more reactive CQ/aromatic amine initiators. Previous researches have shown that increasing the temperature increases the mobility of the reaction environment (i.e. monomer, radical and polymer) and increases the reaction rate parameters [8,13,14]. All of these effects increase the polymerization rate and account for the higher conversion values in samples cured by higher exposure intervals. Thus, the greater double bond conversion in samples subjected to continuous illumination is attributed to a combination of both photo and thermal effects. From the results presented in Fig. 6, it emerges that the reduced polymerization contraction reported in resins cured by soft-start techniques may be attributed to lower conversion values compared with that reached by traditional continuous photopolymerization.

Free-radical polymerization reactions involving multi-functional monomers are markedly influenced by diffusional effects arising due to the formation of an infinite network. As the extent of polymerization advances, it passes through several physical and kinetics landmarks, including the gel point,

auto-acceleration leading to a rate maximum, vitrification and residual instaurations in the final polymer. The reaction kinetics of many dimethacrylate monomers and comonomers mixtures has been extensively studied by DSC. However, the analysis of conversion kinetics in methacrylate monomers by DSC have some limitations. As the polymerization proceeds, vitrification effects begin to limit the mobility of even small molecules such as the monomer or primary initiator radicals. Before completion of the conversion the vitrification process decelerates the reaction to a hardly perceptible rate. Under these conditions, the sensitivity of DSC is not adequate to accurately monitor the subtle continuous increase in conversion that occurs as the limiting conversion is approached in glassy polymers [32]. Conversely, FT-IR spectroscopy, in which the absorbance of the C=C double bond rather than reaction rate is monitored, is more suited for conversion measurements of very slow processes. It should be emphasized that one of the distinct advantages of NIR spectroscopy is to allow a fast and precise evaluation of the degree of conversion at any stage of the reaction and in sample thicknesses representative of clinical practice. This is a valuable information, with respect to practical applications, because the NIR specimen dimensions are compatible with a variety of laboratory test specimens used to evaluate dental resins. Therefore, physical and mechanical properties can be assessed on the same NIR specimen used to measure the degree of conversion.

It is worth noting that the experimental procedure used in the present work allows double bonds conversion data after a selected exposure time. Because with the development of high-powered dental curing lamps most of the monomer reacts during the first 20 s illumination [33–35], the selected procedure provides limited information during the initial stage of the reaction. However, this limitation may be overcome by the use of real-time infrared spectroscopy (RTIR), which possesses a high temporal resolution and consequently permits to follow extremely rapid kinetic processes such as the photopolymerization of dental resin composites [7,8].

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