# Photopolymerization of poly(melamine-*co*-formaldehyde) acrylate for dental restorative resins

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**Abstract: This paper describes the investigation of photoinitiated polymerization of poly(melamine-*co*-formaldehyde) acrylate (PMFA) by camphorquinone (CQ) and amines (AMH) by visible light ($\lambda > 400$ nm). It was shown that as the concentration of CQ and/or AMH increases, the rate of polymerization reaches a maximum and then decreases. The double bond conversion of PMFA was 20–35%, whereas monomer conversion was 90–96%, depending on the polymerization conditions. Addition of inorganic filler up to 70 wt% did not significantly influence the polymerization kinetics. The final hardness of the photocured samples (with 70 wt% filler) was about half that found in a commercial dental restorative composite. The shrinkage of a composite with 70 wt% filler was 2.12%. Dental formulations based on photocuring of PFMA can be considered for clinical applications, after biological and toxicological evaluation.**



**Keywords:** photopolymerization; poly(melamine-*co*-formaldehyde)acrylate; photoinitiator; camphorquinone–amine

## INTRODUCTION

Photocuring of multifunctional monomers is now a well known and well functioning method applied in clinical restorative dentistry.[1–7] During polymerization, initiated by visible light photoinitiation camphorquinone–amine (hydrogen atom donor) systems, crosslinking of these monomers occurs without any thermal energy contribution.[6,8–10] Restorative dental resins based on this photopolymerization process become insoluble in organic solvents as well as in human saliva. A limited number of crosslinks are usually sufficient to transform the resin into a firm crosslinked network. A special approach, however, must be used to cure resins in the oral cavity to make them suitable for application in clinical dentistry.[2,5]

Photopolymerization must occur in air, and there is a need to overcome the inhibiting effect of oxygen which has two major effects on the photocuring process: it may quench the excited state of the photoinitiator, and it may retard the free radical polymerization, especially at the surface. Very reactive unsaturated monomers must be used with a rapid polymerization process (not exceeding 40 s).

The photoinitiator must be adapted to the visible part of the spectrum ($\lambda > 400$ nm), which is almost harmless for human tissues. Because photoinitiators having absorptivity at wavelengths greater than 400 nm are, by definition coloured, their use (if they are not photobleached) may not be acceptable due to aesthetic requirements.

Because of the toxic, carcinogenic and mutagenic ingredients that may be present in most photoinitiating systems, they must be used at the smallest possible concentrations in restorative dentistry. Naturally, all formulations are system dependent, and the scientist must test a range of formulations in order to find the best concentration for any new system. Because light will be absorbed and scattered by the composite components (resin fillers and pigments), the depth of cure will be dependent on the different curing conditions.

Nowadays a dental practitioner is offered a wide range of dental restorative resins. In spite of many new commercial products available on the market, it is becoming increasingly important to develop better, less toxic and non-allergenic resins that can fulfil very specific requirements for their applications in clinical dentistry.

In this study, concern is mainly focused on the photocuring of poly(melamine-*co*-formaldehyde) acrylate by camphorquinone with different amine

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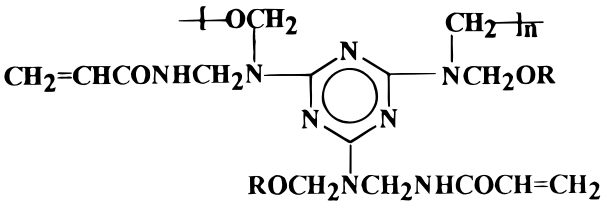
systems, using visible light ($\lambda > 400$ nm) in air. The object of this work was to study the kinetics of photopolymerization at different photoinitiator concentrations and at different temperatures. Therefore, a study of the influence of an inorganic filler and of saliva on the kinetics of photopolymerization and attained hardness of the resins had to be undertaken in order to determine their potential use as dental restorative materials.

## EXPERIMENTAL

Camphorquinone (bornanedione; 1,7,7-trimethylbicylo(2,2,1)heptane-2,3-dione) (CQ; Aldrich) was used as a photoinitiator, alone or with different amines (hydrogen donors) (AMH), at various concentrations (Table 1). The CQ–amine combinations working at 480 nm are the most common photoinitiating systems utilized in clinical dentistry. The photocurable resin used in this study was poly(melamine-*co*-formaldehyde) acrylate (PMFA) [(1-methyl-1,2-ethanediyl)bis(oxy(methyl-2,1-ethanediyl)) ester] (Aldrich). All substances were used as received. In one series of experiments, photocuring was carried out after mixing monomer with up to 70 wt% of an inorganic filler (alumina/barium/silica glass, KETAC DG, ESPE) and after covering the sample with an artificial saliva prepared according to a standard prescription.[11]




Poly(melamine-*co*-formaldehyde) acrylate (PMFA)

The following photocuring kinetic parameters (shown in Fig 1) were monitored with a differential scanning calorimeter (Perkin-Elmer DSC-4) adapted for photochemical measurements. The curves of rate of polymerization ($R_p$, $s^{-1}$) versus time were calculated by dividing the value of the heat flow $dH/dt$ (expressed in kJ $mol^{-1} \cdot s^{-1}$) at each polymerization point by the theoretical heat of the reaction, $\Delta H_0$ (86 kJ $mol^{-1}$); the highest rate of polymerization ($R_p^{max}$, $s^{-1}$) corresponds to the reciprocal value of the time it would need to go from 0 to 100% conversion, at the maximum rate. Two formulations having the same $R_p^{max}$ value but different initial double bond contents actually have different polymerization rates, different double bond conversions ($p$, %), dissimilar highest degree of double bond conversions ($p_{max}$, %), different time at which $R_p^{max}$ is reached ($t_{max}$, s), and also different times of inhibition ($t_{inh}$, s) and $R_p$ versus $p$ relations. These experimental procedures are described in detail elsewhere.[12,13]

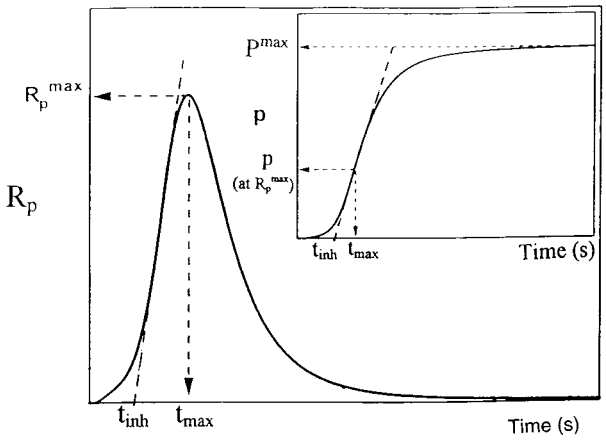



**Figure 1.** A thermogram recorded by photo-DSC and indications of the various parameters measured.

A Philips 500 W curing lamp (type PF 318 E/49) emitting visible light above 400 nm was used to initiate the polymerization, which was carried out in 0.6–1 mm increments in the presence of air. The light intensity measured with an EG & G Model 550-1 photometer, at the level of the surface of the cured samples was 60 mW $cm^{-2}$. All polymerizations were made in air under clinical-like conditions.

Polymerization shrinkage of the photopolymerized

| *Name* | *Abbreviation* | *Structure* | *State* |
|---|---|---|---|
| 2-(Dimethylamino) ethyl methacrylate | AMH1 | $CH_2{=}C(CH_3)COOC_2H_4N(CH_3)_2$ | Liquid |
| Poly(2-(dimethylamino)ethyl methacrylate) | AMH2 | $-[CH_2C(CH_3)-]_n$ <br> $COOC_2H_4N(CH_3)_2$ | Solid |
| Ethyl-4-dimethylamino benzoate | AMH3 | $(CH_3)_2NC_6H_4COOC_2H_5$ | Solid |
| 4,4′-Bis(dimethyl amino) benzophenone | AMH4 | $(CH_3)_2NC_6H_4COC_6H_4N(CH_3)_2$ | Solid |
| *N*,*N*-Dimethyl-*p*-toluidine | AMH5 | $CH_3{-}C_6H_4N(CH_3)_2$ | Liquid |
| *N*,*N*-Dimethylaniline | AMH6 | $C_6H_5N(CH_3)_2$ | Liquid |
| 2,4,6-Tris(dimenthyl amino methyl) phenol | AMH7 | $OH{-}C_6H_2[CH_2N(CH_3)_2]_3$ | Liquid |

**Table 1.** Name, abbreviation and structure of amines used

samples was calculated using the following relationship:[14]

$$\text{Shrinkage}(\%) = \left[1 - \frac{d(\text{uncured})}{d(\text{cured})}\right] \times 100$$

Specific densities ($d$) were measured by a pycnometric method.[15]

Hardness was measured with a Shimadzu Micro Hardness Tester, Type M. The Vickers hardness number (VHN) was calculated using the equation

$$\text{VHN} = 1854.4 \times p\tau^{-2}$$

where $p$ is the load factor (used: $p = 100\,\text{g}$) and $\tau$ is the mean of diagonal indentations (μm).

Extraction of unreacted monomer and initiator systems (sol/gel analysis) from the polymerized samples was carried out using ethanol, acetone or artificial saliva during 12 h at 37°C with slow agitation. The gel remaining after extraction was dried for 24 h at 40°C *in vacuo* and weighed ($w_t$). The soluble fraction ($Ex_m$) in wt% was determined according to the relation $Ex_m = (w_o - w_t)100/w_o$, where $w_o$ is the weight of sample before and $w_t$ the weight after extraction; monomer conversion $p_m = 100 - Ex_m$.

## RESULTS AND DISCUSSION

Poly(melamine-*co*-formaldehyde)acrylate (PMFA) is a high viscosity liquid, and has not yet been studied for its potential use in dental restorative resins.

The kinetics of photopolymerization of PFMA in the presence of camphorquinone (CQ) ($6 \times 10^{-2}$ M) and different amines (AMH) (Table 1) show that the most effective CQ–AMH photoinitiators are based on AMH1, AMH3 and AMH4 (Table 2). The most effective hydrogen atom donor in this system is 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) with an $R_p^{max}$ value of $10.65 \times 10^{-3}\,\text{s}^{-1}$ (Table 2), which has also been reported by us elsewhere.[8] The shortest times to reach $R_p^{max}$ were for AMH4 ($t_{max} = 22.5$ s) and AMH1 ($t_{max} = 23.5$ s) (Table 2). The highest double bond conversions ($P_{max}$) were, however, almost the same for all amines tested between 25% and 35% (Table 2). A limited number of crosslinks were enough to transform the monomer into a network. Michler's ketone (AMH4) is unique in that it contains both the benzophenone chromophore and a tertiary amine group in its structure. The effects of this molecular coinitiator combination are twofold: firstly, the amine groups are immediately available for the abstraction of hydrogen atoms, and secondly, the amine substituents on the benzophenone chromophore result in a greatly enhanced charge transfer absorption (especially at longer wavelengths in the vicinity of 366 nm), and an enhanced ability to form exciplexes with aromatic ketones.[16] The CQ–AMH4 system is a very effective system for the photocuring of monomers.[8] For the CQ–AMH1, CQ–AMH3 and CQ–AMH4 systems, there was no measurable inhibition time ($t_{inh} = 0$); however, for the other CQ–AMH systems, $t_{inh}$ was between 10 and 20 s (Table 2). The effect of oxygen on the inhibition and polymerization processes originated from two interactions: quenching of the excited state of CQ*, and reaction with AM$^{\cdot}$ and monomeric (M$^{\cdot}$) radicals to form non-reactive peroxy radicals (AMOO$^{\cdot}$ and/or MOO$^{\cdot}$). These peroxy radicals are not energetic enough to initiate any further polymerization, but may abstract hydrogen, producing an amine or monomer (or polymer-) hydroperoxide (AMOOH, MOOH) plus some alkyl radicals (R$^{\cdot}$).[13,17] These latter reactions form a chain sequence resulting in the efficient consumption of oxygen. In this manner, the formation of one alkyl amino radical may remove as many as 12 molecules of oxygen from the formulation[18] with the expected result that crosslinking of the polymer is reduced because of the competition of oxygen for the growing free radical chains.

The results above indicate that the photoinitiating activity of CQ–AMH systems may depend on the following:[8,10]

(1) The structure of AMH which forms an exciplex with an excited triplet state of the $^3$CQ* at diffusion controlled rates according to the scheme

$$^3\text{CQ}^* + \text{AMH} \rightarrow [\text{CQ–AMH}]^* \qquad (1)$$

and formation of a complex with AMH which efficiently completes the energy transfer to oxygen.

(2) The importance of hydrogen atom abstraction from AMH, and the formation of an amine active

**Table 2.** Kinetics of photopolymerization of PMFA at [CQ] = $6 \times 10^{-2}$ M, with different amines ($1.5 \times 10^{-2}$ M) in air

| *Amine* | $R_p^{max} \times 10^3$ ($s^{-1}$) | $t_{max}$ (s) | $P_{max}$ (%) | $p_m$ (%)* | $t_{inh}$ (s) |
|---|---|---|---|---|---|
| AMH1 | 9.22 | 23.5 | 28.7 | 93.5 | 0 |
| AMH2 | 6.71 | 31.0 | 25.5 | 91.7 | 15 |
| AMH3 | 10.25 | 25.5 | 34.8 | 95.4 | 0 |
| AMH4 | 10.65 | 22.5 | 34.5 | 94.9 | 0 |
| AMH5 | 6.31 | 35.5 | 25.7 | 96.0 | 20 |
| AMH6 | 8.94 | 27.5 | 29.1 | 92.8 | 10 |
| AMH7 | 4.29 | 35.6 | 26.5 | 90.5 | 20 |

Extraction of unreacted monomer was made with saliva.

radical (AM$^{\cdot}$) according to the reaction

$$[\text{CQ–AMH}]^{*} \rightarrow \text{CQH}^{\cdot} + \text{AM}^{\cdot} \qquad (2)$$

In order to function, the AMH used must have a hydrogen atom alpha in relation to a nitrogen atom on one or more of the substituent groups.

(3) The reactivity of AM$^{\cdot}$ radical with the monomer (PMFA):

$$\text{AM}^{\cdot} + \text{PMFA} \rightarrow \text{AM–PMFA}^{\cdot} \qquad (3)$$

It is also believed that the semi-benzopinacol radical (CQH$^{\cdot}$) acts as a terminator of the propagation reaction.[19] The different AM$^{\cdot}$ radicals have different reactivities. Small energetic free radicals, having a high diffusion coefficient, will diffuse more rapidly to react with vinyl groups than large, bulky radicals. This diffusability becomes more important in the later stages of the curing process because large, bulky free radicals will not reach the residual reactive sites. This results in incomplete conversion of monomers to polymers.[20–22]

The presence of oxygen on amino radicals gives

$$\text{AM}^{\cdot} + \text{O}_2 \rightarrow \text{AMOO}^{\cdot} \qquad (4)$$

because all free alpha amino radicals have the ability to react preferentially with oxygen, resulting in the formation of peroxy radicals (AMOO$^{\cdot}$).[13]

Because all amines are toxic, mutagenic and carcinogenic to some extent,[23,24] we decided to use AMH1 for further experiments in this study. AMH1 could be copolymerized with PMFA during the photocuring process, and was not extracted in saliva.

Kinetic measurements of the photopolymerization of PMFA in the presence of CQ–AMH1 at a constant concentration of AMH1 of $1.5 \times 10^{-2}$ M, but different concentrations of CQ (Figs 2 and 3, Table 3), showed that when [CQ] increased, the $R_p^{max}$ reached a maximum and then decreased (Fig 3a). It was reported that the efficiency of photoinitiators in free radical polymerization decreases beyond a certain optimum concentration of the initiator, because of screening and/or quenching by the initiator itself.[25–29] Deviations observed at low [CQ] due to pseudo first-order consumption of CQ probably resulted from the consumption of radicals by adventitious inhibiting impurities.[10] The yellowness of the cured resin increased with increasing [CQ].

The $t_{max}$ value decreased with increasing [CQ] (Fig 3b), and the maximum double bond conversion ($p_{max}$) increased slightly (Fig 3c), whereas $t_{inh}$ decreased even to zero (Table 3). The photoinitiator concentration would also be expected to be an important factor in the degree of oxygen inhibition.[30]

The plot of $R_p$ versus $p$ (Fig 2c) showed that $R_p^{max}$ was obtained at about 10% double bond conversion, for almost all the concentrations of CQ tested.

In fact, it could be concluded from these results that up to a certain concentration, the main function of CQ is to absorb incident light. It could perhaps also be speculated that the higher the concentration of CQ, the more AMH$^{\cdot}$ radicals, produced by a given quantity of photons, are concentrated near the surface.

As AMH$^{\cdot}$ radical entrapped in a 'monomer cage' is surrounded by monomer molecules, it is unlikely to react with another AMH$^{\cdot}$ radical produced in a separate photochemical event. It is also unlikely to react with CQH$^{\cdot}$ and will most probably react with monomer to initiate polymerization.

The AMH$^{\cdot}$ radicals generated are initially trapped where they may recombine with CQH$^{\cdot}$, terminate with another nearby radical, transfer by hydrogen abstraction, or initiate polymerization. Recombination of two AMH$^{\cdot}$ radicals or/and reaction of AMH$^{\cdot}$ with oxygen, and termination of AMH$^{\cdot}$ by a propagating polymer radical are responsible for lowering the overall efficiency.

Measurements of the kinetics of photopolymerization of PMFA in the presence of CQ–AMH1 at constant $[\text{CQ}] = 6 \times 10^{-2}$ M, but different [AMH1] (Fig 4, Table 4) showed the following:

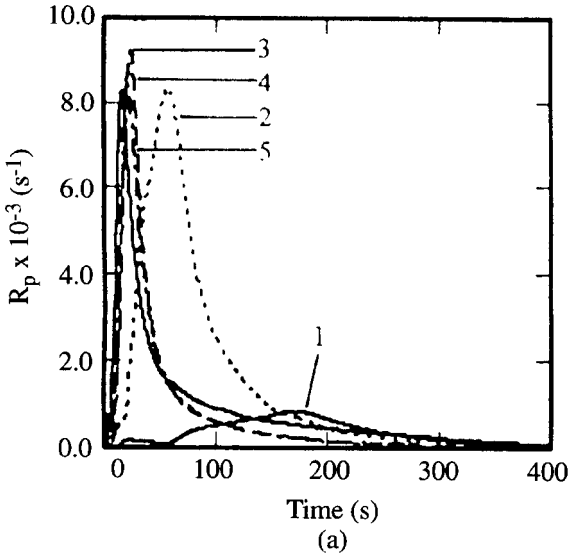
(1) As [AMH1] increased, $R_p^{max}$ reached a maximum ($R_p^{max} = 9.22 \times 10^{-3}\,s^{-1}$ at $[\text{AMH}] = 1.5 \times 10^{-2}$ M) and then decreased (Fig 4a). This effect is the result of quenching of the triplet state of $^3$CQ* by excess AMH.[13] As a consequence of this quenching, it could be expected that there would be a critical relationship between CQ and AMH concentrations.

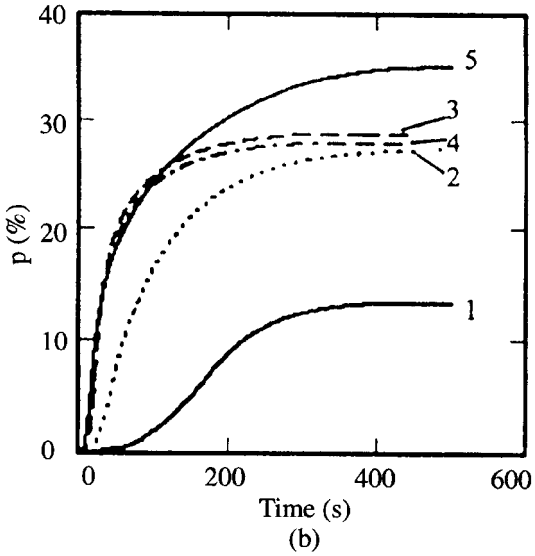
(2) The shortest $t_{max} = 23.5$ s was also obtained at $[\text{AMH1}] = 1.5 \times 10^{-2}$ M, but it increased with increasing [AMH] (Fig 4b);

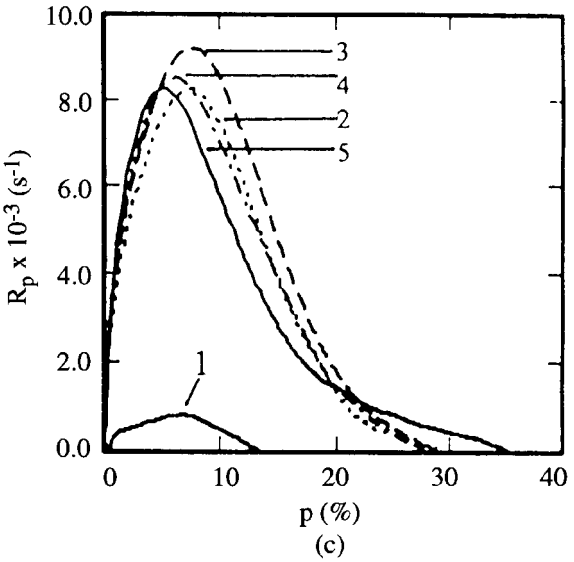
(3) Increasing [AMH] had only a slight effect on $p_{max}$ (Fig 4c);

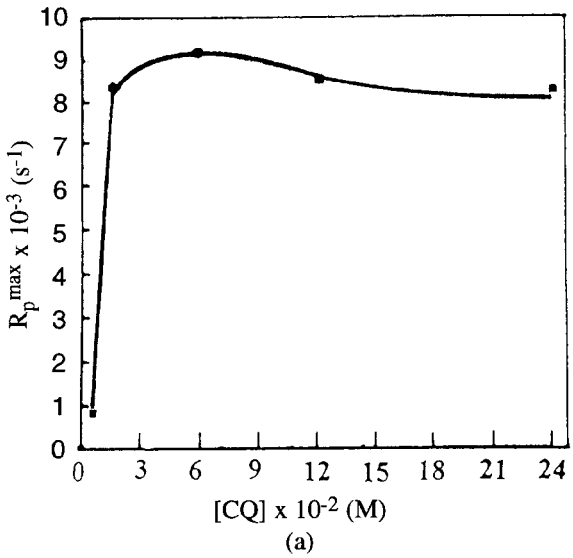
**Table 3.** Kinetics of photopolymerization of PMFA at $[\text{AMH1}] = 1.5 \times 10^{-2}$ M, and different concentrations of CQ in air

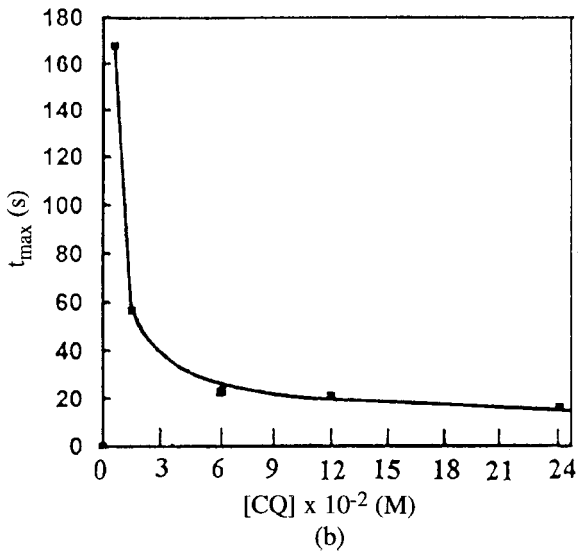
| $[CQ] \times 10^2$ (M) | $R_p^{max} \times 10^3$ ($s^{-1}$) | $t_{max}$ (s) | $p_{max}$ (%) | $t_{inh}$ (s) |
|---|---|---|---|---|
| 0.6 | 0.83 | 168 | 13.4 | 70 |
| 1.5 | 8.34 | 56.5 | 27.6 | 25 |
| 6 | 9.22 | 23.5 | 28.7 | 0 |
| 12 | 8.52 | 21.0 | 27.9 | 0 |
| 24 | 8.26 | 16.0 | 35.2 | 0 |



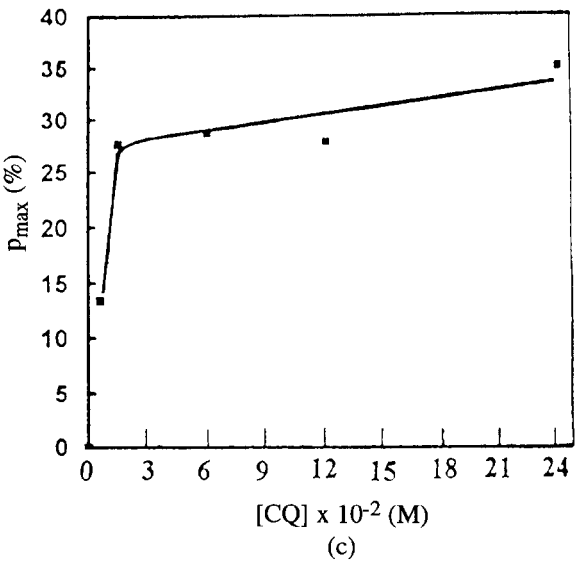




**Figure 2.** (a) Rate of polymerization ($R_p$); (b) double bond conversion (%); and (c) $R_p$ versus $p$ (load factor) of PMFA polymerization at [AMH1] = $1.5 \times 10^{-2}$ M, and different concentrations of CQ. Curve 1, $0.6 \times 10^{-2}$ M CQ; curve 2, $1.5 \times 10^{-2}$ M; curve 3, $6 \times 10^{-2}$ M; curve 4, $12 \times 10^{-2}$ M; curve 5, $24 \times 10^{-2}$ M.

**Figure 3.** (a) Kinetics of photopolymerization; (b) maximum rate of polymerization ($R_p^{max}$); (c) time when $R_p^{max}$ appears ($t_{max}$). maximum double bond conversion ($p_{max}$, %) of PMFA Polymerization at [AMH1] = $1.5 \times 10^{-2}$ M, and different CQ concentrations.

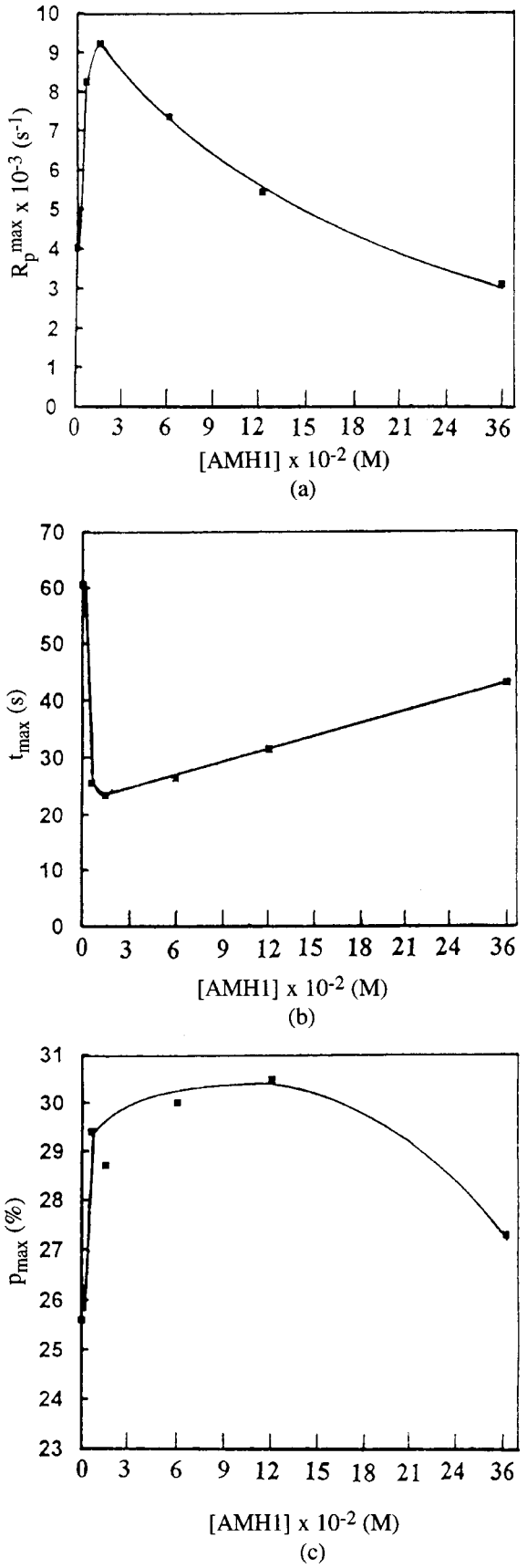



**Figure 4.** (a) Kinetics of photopolymerization; (b) maximum rate of polymerization ($R_p^{max}$); (c) time when $R_p^{max}$ appears ($t_{max}$). maximum double bond conversion ($p_{max}$, %) of PMFA at [CQ] = 6 × $10^{-2}$ M, and different AMH1 concentrations.

(4) Increasing [AMH] decreased $t_{inh}$, even to zero (Table 4).

However, at very high [AMH], where AM$^{\cdot}$ radical concentration was also very high, almost no oxygen inhibition occured.

As polymerization proceeded and viscosity increased, the CQ–AMH efficiency decreased, because initiator fragments were trapped in the 'monomer cage' for longer times and hence had more opportunity to terminate.[31] A loss of molecular mobility of AM$^{\cdot}$ radicals at high crosslink densities may also result in an additional decrease in CQ–AMH efficiency. Decreasing efficiency may, in fact, be simultaneous with the onset of radical trapping, because both are diffusion-limited phenomena on roughly the same molecular scale.[32]

The main factor to be considered was how to avoid using unnecessarily large quantities of AMH, because of the toxicity, carcinogenity and mutagenity of these compounds.[23,24] This can be evaluated from the photo-DSC measurements shown in (Fig 4).

It was concluded that because of the reaction of propagating radicals with oxygen, forming unreactive peroxy radicals (AM–PMFA–OO$^{\cdot}$) at the sample/air interface where the oxygen concentration was highest, there is competition between the propagating reaction of polymerization and the reaction of free radicals (AM–PMFA$_n^{\cdot}$) with oxygen. The ratio of these reaction rates depended on the reactivity of monomers, the oxygen diffusion rate, the photoinitiator concentration and the light intensity. Still another effect might simply be the dilution effect of non-polymerizable material. Surface and mixing effects are also important and have been studied elsewhere.[33]

$R_p^{max}$ increased with temperature up to 40°C and then decreased slightly (Table 5). For some unknown reasons, an elevation of temperature did not result in the expected increase of the maximum conversion, possibly suggesting that above this temperature, termination through chain transfer suppressed the autoacceleration.[34] Generally, in the polymerization of (meth)acrylates, an elevation of temperature causes higher conversions.[35]

Inorganic fillers effectively absorb a portion of the incident light; therefore one might expect their presence to play a role in photopolymerization kinetics. Increasing the filler content in the polymerized samples had little effect on the polymerization kinetics, although the hardness (VHN) increased (Table 6). Maximum hardness depended on the percentage of filler. The VHN of PMFA at 70 wt% filler load was 20.99, ie much less than that of 3 M restorative Z100 MP (VHN = 49.84), the commercially available dental resin used as control. Several factors have been found to influence the hardness of restorative resins, such as the content and type of initiator,[36,37] content and type of monomer,[38] and degree of double bond conversion,[36,39] the degree of

| $[AMH1] \times 10^2$ (M) | $R_p^{max} \times 10^3$ ($s^{-1}$) | $t_{max}$ (s) | $p_{max}$ (%) | $t_{inh}$ (s) |
|---|---|---|---|---|
| 0 | 4.02 | 60.5 | 25.6 | 33 |
| 0.06 | 7.43 | 30.5 | 29.9 | 20 |
| 0.60 | 8.25 | 25.5 | 29.4 | 0 |
| 1.50 | 9.22 | 23.5 | 28.7 | 0 |
| 6.00 | 7.34 | 26.5 | 30.0 | 0 |
| 12.0 | 5.42 | 31.5 | 30.5 | 0 |
| 36.0 | 3.10 | 43.0 | 27.3 | 0 |

**Table 4.** Kinetics of photopolymerization of PMFA at $[CQ] = 6 \times 10^{-2}$ M, and different concentrations of AMH1 in air

below-surface curing will affect surface hardness and scratch resistance.[40,41] Glossy and scratch-resistant polymerized samples can be obtained only by sanding and polishing the surface. Thus it can be concluded that the most difficult thing to achieve is a good surface curing of polymeric dental resins. This problem can be solved to a certain extent by using high-intensity dental curing lamps[42–44] high photoinitiator concentrations, or some surface coating. It is expected that a high-photon dose rate combined with an increased sample optical density will produce such a high concentration of radicals that the oxygen inhibiting effect will be swamped. However, in clinical practice, a given restorative resin will not always be photocured with the light sources recommended by the manufacturer or with the most efficient light unit, and the effects of photocuring will differ.

Increasing the saliva content of the photopolymerized samples, decreased $R_p^{max}$, $p$ and VHN values (Table 7). The amount of saliva which can come into contact with a curing sample depends on the way the curing procedure is carried out by the dentist. The surface of the tooth and each increment of added resin should be absolutely dry in order to obtain good adhesion between the layers of a polymer filling.

For clinical evaluation, the information on the amount of monomer extracted by human saliva ($Ex_m$) is of special importance. This unreacted monomer can be transported from the oral cavity to the intestine, where it can be absorbed and distributed into the circulatory system of the human body, thereby causing toxic effects. The amounts of unreacted PMFA monomer ($Ex_m$) extracted by different solvents were 14.8% for ethanol, 21.1% for acetone and 4.3% for saliva, for the photocured samples in the presence of $[CQ] = 6 \times 10^{-2}$ M and $[AMH1] = 1.5 \times 10^{-2}$ M, after 600 s irradiation, indicating that the extraction of unreacted monomer depends on the solvent used. PMFA is not soluble in saliva, and extraction occured only by removing the thin unpolymerized monomer layer from the surface exposed to air (oxygen inhibition). Considering that the whole amount (20–21%) of unreacted monomer

| Temperaures (°C) | $R_p^{max} \times 10^3$ ($s^{-1}$) | $t_{max}$ (s) | $p_{max}$ (%) | $t_{inh}$ (s) |
|---|---|---|---|---|
| 20 | 8.59 | 16.5 | 32.9 | 0 |
| 40 | 9.22 | 23.5 | 28.7 | 0 |
| 60 | 8.22 | 16.0 | 32.8 | 0 |
| 80 | 7.44 | 18.5 | 35.8 | 0 |

**Table 5.** Kinetics of photopolymerization of PMFA at $CQ = 6 \times 10^{-2}$ M, $[AMH1] = 1.5 \times 10^{-2}$ M and at different temperatures in air

| Filler (wt%) | $R_p^{max} \times 10^3$ | $t_{max}$ (s) | $p_{max}$ | $t_{inh}$ (s) | Volume shrinkage (%) | Hardness (VHN) |
|---|---|---|---|---|---|---|
| 0 | 9.22 | 23.5 | 28.7 | 0 | 13.7 | 5.57 |
| 30 | 9.32 | 23.0 | 27.7 | 0 | – | 13.59 |
| 50 | 9.51 | 27.0 | 35.7 | 0 | – | 18.54 |
| 70 | 11.39 | 20.0 | 38.6 | 0 | 2.12 | 20.99 |

**Table 6.** Kinetics of photopolymerization of PMFA at $[CQ] = 6 \times 10^{-2}$ M, $[AMH1] = 1.5 \times 10^{-2}$ M in the presence of different concentrations (wt%) of filler in air

| Saliva (wt%) | $R_p^{max} \times 10^3$ ($s^{-1}$) | $t_{max}$ (s) | $p_{max}$ (%) | $t_{inh}$ (s) | Hardness (VHN) |
|---|---|---|---|---|---|
| 0 | 11.39 | 20.0 | 38.6 | 0 | 20.99 |
| 1 | 8.53 | 33.0 | 37.7 | 0 | 12.88 |
| 3 | 8.13 | 27.0 | 25.9 | 0 | 10.97 |
| 5 | 7.97 | 27.0 | 27.1 | 0 | 9.02 |
| 10 | 6.29 | 28.0 | 24.9 | 0 | 8.30 |

**Table 7.** Kinetics of photopolymerization of PMFA at $CQ = 6 \times 10^{-2}$ M, $[AMH1] = 1.5 \times 10^{-2}$ M and 70 wt% of filler, in the presence of different amounts (wt%) of saliva in air

was extracted by acetone, we assume that the monomer conversion into crosslinked polymer networks was approximately 79–80% for a double bond conversion of around 35%.

The volume shrinkage of PFMA was 13.7%; however, when filled with 70 wt% of inorganic filler, this decreased to 2.12% (Table 6). Polymerization shrinkage causes formation of a contraction gap between the restoration and the cavity walls. Recurrent caries may develop if cariogenic bacteria subsequently invade the gap. However, polymerization shrinkage is not the only cause of dimensional change of a restoration. The adaptation of the restoration to the cavity walls may gradually deteriorate in the oral environment because of temperature variations and mechanical stress. In contrast, a contraction gap may be greatly reduced due to water sorption of the composite and subsequent expansion.

## CONCLUSIONS

Polymerization of poly(melamine-*co*-formaldehyde) acrylate could be easily photoinitiated by a combination of camphorquinone with different amines (hydrogen atom donors) in visible light ($\lambda > 400$ nm). Polymerization occurred quickly (within 25–35 s) in air. Oxygen inhibition manifested itself only as a thin layer of unpolymerized monomer on the surface of a sample exposed to light in the presence of air. The polymerization process levelled off at a double bond conversion of 35% at best. This was a surprisingly low value for a UV-curable acrylate system, especially considering that the crosslinked polymer was not very hard and was plasticized by the 20% extractable monomer. A limited number of crosslinks was enough to transform the resin into a crosslinked network. Rapid vitrification of the system caused immobilization of the double bonds and polymeric radicals, thus rendering them unavailable for further polymerization. An inorganic filler (up to 70 wt%) had only a slight influence on the polymerization kinetics; however, it increased the hardness of the resin and decreased polymerization shrinkage.

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