

## PHOTOCURING STUDY OF NEW DENTAL RESINS BASED ON MULTIFUNCTIONAL ACRYLIC ISOCYANURATE BY PHOTOCALORIMETRY

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**Abstract** Photocuring of new dental resins composed of tri(2-hydroxyethyl) isocyanurate triacrylate (THITA) alone and its mixtures with trimethylolpropane triacrylate (TMPTA) or pentaerythritol triacrylate (PETA) initiated by camphorquinone/amine system was studied by photocalorimetry. Among several different amines as coinitiators, 2-ethyl-4-dimethylaminobenzoate (AM-3), *N,N*-dimethylbenzylamine (AM-5) and 2,4,6-[tri(dimethylaminomethyl)]phenol (AM-6) are most effective. Upon irradiation, photopolymerization can occur immediately and no induction period appears in  $N_2$  nor in air. Comparing the THITA/TMPTA and THITA/PETA mixtures, the parameters of photopolymerization and hardness of photocured samples show a small difference and only change slightly with varying molar ratios of mixture. In the presence of inorganic filler, the hardness of photocuring resins is almost the same as that for commercial products.

**Keywords** Multifunctional acrylates, Photocuring, Dental resin, Network

The development of new resins based on dental composites has long challenged dental material researchers. Although 2,2-bis[*p*-(2'-hydroxy-3'-methacryloxy propoxyphenyl)]propane (BIS-GMA) is widely used in commercial dental resin formulations as a major or base monomer, alternative mono-, di- and tri-functional base resins have been investigated in an effort to further enhance the quality of the polymeric matrix<sup>[1]</sup>. Since clinical photocuring of restorative resins occurs under special conditions, it differs from any type of industrially applied curing, i.e., the whole procedure of photocuring is made *in vivo*, and it is restricted by biophysiological requirements such as temperatures not exceeding 50°C and the presence of visible light irradiation with high rates of polymerization, high percentages of monomer conversion, and the absence of air, water, blood, saliva. Besides that, the components of dental material should not be toxic, neurotoxic cancerogenic, mutagenic or allergenic.

Monomer tri(2-hydroxyethyl)isocyanurate triacrylate (THITA) has been widely applied in microlithograph, laser video or compact discs, coatings for optical fibers and aspherical lenses<sup>[2-4]</sup>. Therefore we choose THITA as dental restorative resin and camphorquinone/amines as photoinitiation systems. Polymerization of pure THITA resin and its copolymerization with two trifunctional monomers such as trimethylol propane triacrylate (TMPTA) or pentaerythritol triacrylate (PETA) were studied by photocalorimetry. A method of obtaining a high degree of photo-polymerization of multifunctional monomers is used in this work, for which the networks

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formed with high crosslinking density and high hardness are similar to that of commercially available dental composites (e.g. 3M products)

## EXPERIMENTAL

Couples of camphorquinone and different amines, 3-dimethylamino-1-propanol (AM-1), tetra-methylethyldiamine (AM-2), 2-ethyl-4-dimethylaminobenzoate (AM-3), 4,4'-bis(dimethylamino) benzophenone (AM-4), N,N-dimethylbenzylamine (AM-5) and 2,4,6-tri(dimethylaminomethyl) phenol (AM-6) commercially available from Aldrich were used as combination photoinitiation systems. Tri(2-hydroxyethyl)isocyanurate triacrylate (THITA, Aldrich) and its mixtures with trimethylol propane triacrylate (TMPTA, Aldrich) or pentaerythritol triacrylate (PETA, Alfa) purified by aluminium oxide filled in chromatographical column were used as base resins. Commercially produced inorganic filler (Ketac-Fil) was delivered by ESPE.

The polymerization kinetic was monitored by a differential scanning calorimeter (Perkin-Elmer DSC-4) adapted to photochemical measurements. The polymerization was conducted at a temperature of  $40 \pm 0.01^\circ\text{C}$  (close to the temperature of the human body,  $37^\circ\text{C}$ ). Accurately weighed samples ( $\sim 20$  mg) of the photocurable formulation were polymerized in a 6.5 mm diameter open aluminum DSC pans. A Philips 500 W lamp (type PF 318 E/49) emitting visible light from 400 nm was used in the polymerization. The light intensity at the surface of cured samples was  $60 \text{ mW} \cdot \text{cm}^{-2}$ .

The polymerization rate ( $R_p$ ) versus time was calculated by dividing the peak height of  $dH/dt$  (expressed in  $\text{kJ/mol} \cdot \text{s}^{-1}$ ) at each polymerization point by the theoretical heat of the reaction,  $\Delta H_0$  86 kJ/mol per double bond<sup>[5]</sup>. The dependencies of the fraction of double bond conversion ( $p\%$ ) on the rate polymerization time were obtained by integrating the polymerization rate. The DSC data were corrected from changes in the base line. After the extraction of non-reacted monomer and initiating components from polymerized samples with synthetic saliva, the percentage of gel conversion ( $G\%$ ) was determined for a period of 12 h at  $37^\circ\text{C}$ . Hardness was measured using an M-Shimadzu Micro Hardness Tester

## RESULTS AND DISCUSSION

Photocalorimetry (photo isothermal differential scanning calorimetry, photo-DSC) can directly yield information on the polymerization rate ( $R_p$ ,  $\text{s}^{-1}$ ), the highest polymerization rate ( $R_p^{\text{max}}$ ,  $\text{s}^{-1}$ ), the percentage of double bond conversion ( $p$ , %), the highest degree of double bond conversion ( $P^{\text{max}}$ , %) and the induction period ( $t_{\text{inh}}$ , s). The reproducibility of results was  $\pm 5\%$ .

From Fig. 1, it can be seen that polymerization of THITA and TMPTA mixtures photoinitiated by CQ- amine couple occurs in  $\text{N}_2$  as well as in air, but both  $R_p^{\text{max}}$  and  $P^{\text{max}}$  are slightly higher in  $\text{N}_2$  than in air. Polymerization commences very fast, immediately after irradiation, and thus the induction time ( $t_{\text{inh}} \sim 0$ ) is nearly zero in both  $\text{N}_2$  and air (Fig. 1a). The plots of  $R_p$  versus  $p$  (Fig. 1c) show that  $R_p$  reached a maximum at 3% of double bond conversion ( $p$ ), then dropped rapidly when  $p$  reached 8%, and finally approached zero at 23%~25% of  $p$  after irradiation for 400 s. This behavior has been interpreted as an evidence of rate acceleration due to the gel effects<sup>[6, 7]</sup>. For a polymerization, the termination reaction is generally considered to pass through the stages of segmental diffusion control ( $k_t$  independent of molecular weight), transitional diffusion control ( $k_t$  dependent on chain radical size), and ends by propagation of the radical end. For network-forming systems, e.g. THITA/TMPTA, due to their multifunctional groups and rapid increase in viscosity, the first segmental diffusion stage would end immediately at very low conversions ( $\sim 0\%$ ) and then translation diffusion would dominate. Once the gel is formed, the translation diffusion can only occur for radicals not attached to the gel, and thus results in an acceleration of  $R_p$  when the percentage of double bond ( $p$ ) is less than 3% (this is known as the Trommsdorff effect). However,

the Trommsdorff effect should only be operative up to conversions slightly past the gel point because the probability that a propagating chain radical crosslinks during its lifetime is quite high. For the remainder of the polymerization, termination should proceed by propagation of the chain ends<sup>[7]</sup>.

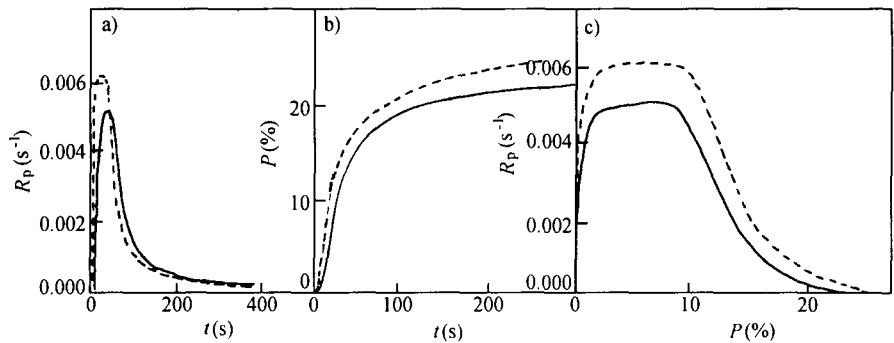


**Fig. 1** Photopolymerization of THITA/TMPT mixture initiated by CQ/AM-3 [CQ] =  $6 \times 10^{-2}$  mol/L, [AM-3] =  $6 \times 10^{-2}$  mol/L, THITA/TMPT (molar ratio) = 1:1  
a)  $R_p$ ~time, b)  $p$ ~time, c)  $R_p$ ~ $p$

Table 1 outlines the data of photopolymerization kinetics of THITA and TMPTA mixtures using CQ alone or CQ and different amines as photoinitiation systems. It shows that 2-ethyl-4-dimethylaminomethyl phenol (AM-3), *N,N*-dimethylbenzylamine (AM-5) and 2,4,6-tri(dimethylaminomethyl) phenol (AM-6), are most effective coinitiators (H-donors). For these three CQ/amine systems, the  $R_p^{max}$  values are significantly higher than that of CQ alone, whether in  $N_2$  or in air, although the  $p^{max}$  values are rather low (20%~35%). They are also slightly superior to CQ alone, but for all systems, the percentages of gel conversions are very high (90%~100%). Furthermore, for three such CQ-amine systems, although the hardness of the photocured samples shows significant differences, their hardness values were also much higher than that of CQ alone. As Refs. [8] and [9] describe, the reactivity of different amines in H-abstraction by triplet CQ mainly depends on the ability of amine to form an exciplex with CQ.

**Table 1.** Data of photopolymerization kinetics of THITA/TMPTA mixtures initiated by the couples of CQ and different amines

|         | $R_p^{max} \times 10^3 \text{ (S}^{-1}\text{)}$ |       | $P^{max} \text{ (%)}$ |       | $G \text{ (%)}$ |       | Hardness (VH) |       |
|---------|-------------------------------------------------|-------|-----------------------|-------|-----------------|-------|---------------|-------|
|         | air                                             | $N_2$ | air                   | $N_2$ | air             | $N_2$ | air           | $N_2$ |
| CQ      | 4.19                                            | 4.14  | 21.3                  | 23.2  | 91              | 99.5  | 16.14         | 16.29 |
| CQ/AM-1 | 4.31                                            | 4.59  | 16.0                  | 19.1  | 90              | 99.5  | 12.88         | 14.02 |
| CQ/AM-2 | 4.09                                            | 4.35  | 18.9                  | 20.9  | 91              | 99.5  | 16.14         | 18.54 |
| CQ/AM-3 | 5.14                                            | 6.19  | 23.0                  | 26.4  | 96              | 99.5  | 21.11         | 22.84 |
| CQ/AM-4 | 4.52                                            | 4.72  | 19.0                  | 23.7  | 92              | 99.5  | 23.05         | 25.97 |
| CQ/AM-5 | 5.27                                            | 5.55  | 21.7                  | 35.1  | 92              | 100   | 20.81         | 24.78 |
| CQ/AM-6 | 5.34                                            | 5.98  | 25.5                  | 30.5  | 97              | 99.5  | 23.41         | 28.97 |

[CQ] = [AM] =  $6 \times 10^{-2}$  mol/L, THITA/TMPTA (molar ratio) = 1:1

The effect of amine concentration on photopolymerization of THITA/TMPTA mixtures initiated by CQ/amine system was further studied. Table 2 shows that the values of  $p^{max}$  and hardness of photocured samples increase with increasing AM-3 concentration, whereas  $R_p^{max}$  increases with the increase of AM-3 at low concentration ( $6 \times 10^{-2}$  mol/L), but decreases at high concentration either in  $N_2$  or in air. This is because high amine concentration may result in the quenching of triplet state of CQ by excess amine that does not participate in the formation of exciplex<sup>[8, 10]</sup>. This means that for each CQ/amine photoinitiation system, there is an optimum

amine concentration at which the rate of polymerization and efficiency of initiation are the highest. In addition, it is important that AM-3 concentration has no significant effect on gel conversion for photocuring of dental resins based on THITA/TMPTA. Due to the toxicity and cancer-ogenicity of amine, it is generally recommended as little amine as possible is used to approach an optimal effect<sup>[11]</sup>.

**Table 2.** Effect of amine concentration on photopolymerization of THITA/TMPTA initiated by CQ/AM-3 couple

| [AM] × 10 <sup>2</sup> (mol/L) | R <sub>p</sub> <sup>max</sup> × 10 <sup>3</sup> (S <sup>-1</sup> ) |                | P <sup>max</sup> (%) |                | G (%) |                | Hardness (VH) |                |
|--------------------------------|--------------------------------------------------------------------|----------------|----------------------|----------------|-------|----------------|---------------|----------------|
|                                | air                                                                | N <sub>2</sub> | air                  | N <sub>2</sub> | air   | N <sub>2</sub> | air           | N <sub>2</sub> |
| 0                              | 4.19                                                               | 4.14           | 21.3                 | 23.2           | 96.0  | 99.5           | 16.14         | 16.29          |
| 1.5                            | 4.46                                                               | 4.33           | 21.3                 | 24.5           | 96.5  | 99.0           | 17.65         | 19.78          |
| 3.0                            | 4.89                                                               | 5.13           | 24.2                 | 27.7           | 97.0  | 99.5           | 19.31         | 20.99          |
| 6.0                            | 5.14                                                               | 6.19           | 23.0                 | 26.4           | 96.0  | 99.5           | 21.22         | 22.84          |
| 12                             | 4.79                                                               | 4.94           | 24.8                 | 28.1           | 99.0  | 99.5           | 23.60         | 25.67          |
| 24                             | 5.39                                                               | 4.45           | 25.7                 | 26.3           | 96.0  | 99.5           | 28.97         | 30.32          |

[CQ] = 6 × 10<sup>-2</sup> mol/L, THITA/TMPTA (molar ratio) = 1:1

Samples of THITA and TMPTA can be mixed well in one another and will show different states, solid or liquid, depending on the molar ratio of THITA and TMPTA. Comparisons of photopolymerization of samples with different THITA/TMPTA molar ratios were carried out in N<sub>2</sub> and in air. From Table 3, we can see that the R<sub>p</sub><sup>max</sup> values for THITA alone in both air and N<sub>2</sub> are respectively higher than that for TMPTA alone. It indicates that the reactivity of THITA is higher than that of TMPTA. The higher the molar ratio of THITA/TMPTA, the higher are the values of R<sub>p</sub><sup>max</sup> and hardness of photocured samples. Due to the formation of networks of THITA and TMPTA in photopolymerization, the percentages of gel conversion have almost no change with varying molar ratios of THITA and TMPTA in both air and N<sub>2</sub>. Therefore it is possible that the solid samples of THITA and its mixtures with TMPTA at molar ratio 9/1 and 8/2 may have some practical advantages in the clinical filling of teeth.

**Table 3.** Data of photopolymerization of THITA and TMPTA with different molar ratio initiated by CQ/AM-3

| THITA/TMPTA (molar ratio)                                          |                | 0:10   | 1:9    | 3:7    | 5:5    | 7:3   | 8:2   | 9:1   | 10:0  |
|--------------------------------------------------------------------|----------------|--------|--------|--------|--------|-------|-------|-------|-------|
| State                                                              |                | liquid | liquid | liquid | liquid | iquid | solid | solid | solid |
| R <sub>p</sub> <sup>max</sup> × 10 <sup>3</sup> (S <sup>-1</sup> ) | air            | 4.12   | 4.57   | 5.00   | 5.14   | 5.56  | 5.93  | 6.47  | 6.73  |
|                                                                    | N <sub>2</sub> | 4.38   | 4.68   | 5.38   | 6.19   | 6.82  | 6.90  | 7.01  | 7.16  |
| P <sup>max</sup> (%)                                               | air            | 22.0   | 20.7   | 22.6   | 23.0   | 25.4  | 22.8  | 20.3  | 23.6  |
|                                                                    | N <sub>2</sub> | 22.2   | 24.1   | 25.2   | 26.4   | 30.0  | 28.0  | 26.4  | 31.9  |
| G (%)                                                              | air            | 97.5   | 97.0   | 94.5   | 95.0   | 96.0  | 95.1  | 94.1  | 95.0  |
|                                                                    | N <sub>2</sub> | 99.5   | 99.5   | 99.5   | 99.5   | 99.5  | 99.5  | 99.5  | 99.0  |
| Hardness (VH)                                                      | air            | 16.29  | 16.89  | 20.81  | 21.22  | 23.41 | 25.07 | 25.07 | 25.97 |
|                                                                    | N <sub>2</sub> | 17.65  | 18.54  | 21.22  | 22.84  | 25.61 | 27.58 | 27.58 | 28.83 |

[CQ] = [AM] = 6 × 10<sup>-2</sup> mol/L

We have also studied the photocuring of mixtures of THITA and PETA (Table 4). The results demonstrate that parameters of polymerization for THITA/PETA mixtures are slightly higher than that of THITA/TMPTA mixtures.

The reinforcing filler is usually one of the major components in dental materials (50%~85%). It performs many functions in a composite, for instance stiffening the lower modulus resin binder and thus increasing the mechanical properties, enhancing dimensional stability, and reducing water sorption and polymerization shrinkage. From Table 5, it can be seen that the hardness of all photocured samples containing inorganic fillers is comparatively higher

**Table 4.** Data of photopolymerization of PETA and TMPTA with different molar ratios initiated by CQ/AM-3

| THITA/TMPTA<br>(molar ratio)                    |                | 0:10   | 1:9    | 3:7    | 5:5    | 7:3   | 9:1   | 10:0  |
|-------------------------------------------------|----------------|--------|--------|--------|--------|-------|-------|-------|
| State                                           |                | liquid | liquid | liquid | liquid | solid | solid | solid |
| $R_p^{max} \times 10^3 \text{ (S}^{-1}\text{)}$ | air            | 4.48   | 4.92   | 4.09   | 5.22   | 5.70  | 6.69  | 6.73  |
|                                                 | N <sub>2</sub> | 4.76   | 5.19   | 5.61   | 6.59   | 6.97  | 7.05  | 7.16  |
| $P^{max} \text{ (%)}$                           | air            | 25.8   | 25.6   | 24.9   | 23.2   | 21.5  | 21.3  | 23.6  |
|                                                 | N <sub>2</sub> | 29.4   | 27.9   | 27.3   | 29.0   | 27.7  | 23.1  | 31.9  |
| $G \text{ (%)}$                                 | air            | 99.0   | 98.5   | 97.5   | 97.0   | 98.5  | 97.5  | 95.0  |
|                                                 | N <sub>2</sub> | 99.5   | 99.5   | 99.5   | 99.5   | 99.5  | 99.5  | 99.0  |
| Hardness (VH)                                   | air            | 18.54  | 19.31  | 22.94  | 22.94  | 23.60 | 25.31 | 25.97 |
|                                                 | N <sub>2</sub> | 20.99  | 21.22  | 24.67  | 24.67  | 26.28 | 27.58 | 28.83 |

[CQ] = [AM] =  $6 \times 10^{-2}$  mol/L

**Table 5.** Comparison of hardness of photocured samples containing filler at different fractions

| Filler (wt%) | Hardness (HV) |       |                  |
|--------------|---------------|-------|------------------|
|              | THITA         | PETA  | THITA/PETA (1:1) |
| 0            | 26.28         | 21.93 | 22.89            |
| 10           | 31.69         | 27.38 | 29.05            |
| 30           | 35.67         | 32.19 | 34.33            |
| 50           | 41.93         | 36.17 | 38.95            |

[CQ] = [AM] =  $6 \times 10^{-2}$  mol/L, in air

than that of the photocured polymers of THITA or PETA, or their mixtures. For THITA or its mixture with PETA containing 50 wt% filler, the values of hardness are close to 49.84 for commercial 3M Restorative Z100 MP Resin under the same experimental conditions.

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