

Highly cross-linked networks for dental applications obtained by photocuring of tris[2-(acryloyloxy)ethyl]isocyanurate, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate, and pentaerythritol triacrylate

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Highly cross-linked networks have been obtained by photoinitiated camphorquinone–amine polymerization of tris[2-(acryloyloxy)ethyl]isocyanurate alone and/or with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate or pentaerythritol triacrylate, which can be considered a new class of dental restorative resins. The most effective coinitiators in this system are amines such as ethyl-4-dimethylaminobenzoate, N,N-dimethyl-benzylamine, and 2,4,6-tris(dimethylaminomethyl)phenol. The volume shrinkages of polymerized samples were 8%–13%. The hardness of photocured resins in the presence of an inorganic filler (aluminum/fluoro/silicate glass, Ketac-Fil) was slightly less than that of a restorative composite material (Z100 MP). □ *Camphorquinone–amine; curing kinetics; dental composites; photoinitiators; photopolymerization*

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The development of resin-based dental composites has long challenged dental material researchers (1–4). Different mono-, di-, and trifunctional base resins have been investigated in an effort to further enhance the quality of the polymeric matrix. Free radical polymerization of resin-based dental materials is initiated chemically by redox systems, or photochemically by visible light (400–500 nm) using camphorquinone–amine hybrid photoinitiator systems (5–11). The major component of dental composites is usually the reinforcing filler (50%–85% by weight) (2). The reinforcing filler performs many functions in a composite, such as stiffening the lower modulus resin binder and thereby increasing the mechanical properties; enhancing dimensional stability; reducing water sorption; and polymerization shrinkage. Clinical photocuring of restorative resins occurs under special conditions that differ from any other type of industrially applied curing conditions. In dentistry the whole photocuring procedure is made *in vivo*; thus, it is restricted by biophysiological demands such as a temperature not exceeding human body temperature and must occur under visible light irradiation, in the shortest time possible, with high rates of polymerization and monomer conversion, and uninfluenced by air, water, blood, or saliva. The components of a dental resin should not be toxic, neurotoxic, carcinogenic, mutagenic, or allergenic.

In our laboratory we took the approach to study the photopolymerization kinetics of multifunctional monomers leading to networks with highly cross-linked density and high hardness similar to that of commercially available dental composites. For these studies we chose the tris[2-(acryloyloxy)ethyl]isocyanurate (TAEI) monomer, which

has found a wide application in microlithography techniques, laser video- and compact discs, and coatings for optical fibers, and as spherical lenses (12–15). The object was for the isocyanurate to react with the -OH or -NH₂ groups in the dentin mineral or organic components. TAEI was copolymerized with two other trifunctional monomers, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA) and pentaerythritol-triacrylate (PETA). Photopolymerizations of pure monomers with or without filler were carried out in the presence of camphorquinone and different amines, and the kinetics of polymerization were studied in air and N₂ by means of photocalorimetry.

Materials and methods

Camphorquinone (CQ, Aldrich, Milwaukee, Wis., USA) in mixtures with different amines (Table 1) (all from Aldrich) was used as a hybrid photoinitiator system. The following monomers were used as received: the solid tris[2-(acryloyloxy)ethyl]isocyanurate (CAS name: 2,4,6-trioxo-1,3,5-triazine-1,3,5-(2H,4H,6H)triyyl-2,1-ethanediyl ester, CAS no: 40220-08-4) (TAEI, Aldrich); 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate (TMPTA, Aldrich); and pentaerythritol triacrylate (PETA, Alfa, Danvers, Mass., USA) (structures and states shown in Table 2). A commercially produced inorganic aluminum/fluoro/silicate glass filler (Ketac-Fil, ESPE, Seefeld, Germany) was bought on the open dental market and used as delivered. The Ketac-Fil glass was not silanized and therefore was

Table 1. Name, abbreviation, and structure of amines

Name	Abbreviation	Structure	State
3-Dimethylamino-1-propanol	AMH1	$\text{HOCH}_2\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Liquid
N,N,N',N'-Tetramethylethylenediamine	AMH2	$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$	Liquid
Ethyl-4-dimethylaminobenzoate	AMH3	$\text{CH}_3\text{CH}_2\text{OCOC}_6\text{H}_4\text{N}(\text{CH}_3)_2$	Solid
4,4'-Bis(dimethylamino)-benzophenone	AMH4	$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{COC}_6\text{H}_4\text{N}(\text{CH}_3)_2$	Solid
N,N-Dimethylbenzylamine	AMH5	$\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2$	Liquid
2,4,6-Tris(dimethylaminomethyl)phenol	AMH6	$[(\text{CH}_3)_2\text{NCH}_2]_3\text{C}_6\text{H}_2(\text{OH})$	Liquid

expected not to increase hardness of the formed materials to a level of that of a commercial dental composite.

The polymerization kinetics were monitored by a differential scanning calorimeter (Perkin-Elmer DSC-4) adapted for photochemical measurements. A Perkin-Elmer 3600 Data Station was employed to read and store data on floppy disks.

The polymerization was carried out at a temperature of $40 \pm 0.1^\circ\text{C}$. Accurately weighed samples ($\cong 20$ mg) of the photocurable composition were polymerized in open aluminum DSC pans, 6.5 mm in diameter. When polymerization was carried out in an inert (nitrogen) atmosphere, the sample was first allowed to reach equilibrium in the apparatus under a stream of oxygen-free nitrogen for 5 min (time sufficient to complete replacement of oxygen), and then a very slow nitrogen flow was allowed during irradiation.

A Philips 500 W lamp (type PF 318 E/49), emitting visible light from 400 to 800 nm, was used for initiation of the polymerization. This type of lamp is equipped with a

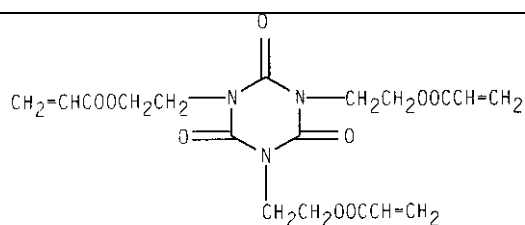
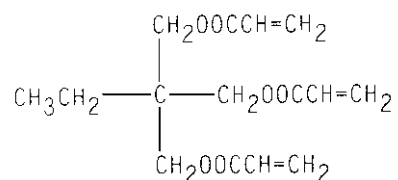
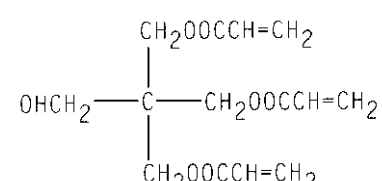
spherical reflector that gives an emitted light at the same intensity over a large surface area.

The light intensity at the level of the surface of cured samples was 60 mW cm^{-2} and was measured using a photometer (EG&G model 550-1). The light intensity (mW cm^{-2}) could easily be changed by increasing or decreasing the distance from the lamp to the polymerization sample.

Some photocurings were made using a commercially available dental curing lamp (type VCL 500, Demetron, Kerr, Danbury, Conn., USA) equipped with a photocell for measuring light intensity. The light intensity at the level of the surface of cured samples was 220 mW cm^{-2} .

The reaction rates versus time were calculated by dividing the dH/dt (expressed in $\text{kJ/mol}\cdot\text{s}$), at each polymerization point, by the theoretic heat of the reaction, $\Delta H_0 = 86 \text{ kJ/mol}$ per one double bond (16). Double bond conversions on the polymerization were determined by integration of the polymerization rate. Conversion at the time at which the polymerization rate decreased to 0 was

Table 2. Name, abbreviation, and structure of monomers

Name	Abbreviation	Structure	State
Tris[2-(acryloyloxy)-ethyl]isocyanurate	TAEI		Solid
2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate	TMPTA		Liquid
Pentaerythritol triacrylate	PETA		Liquid

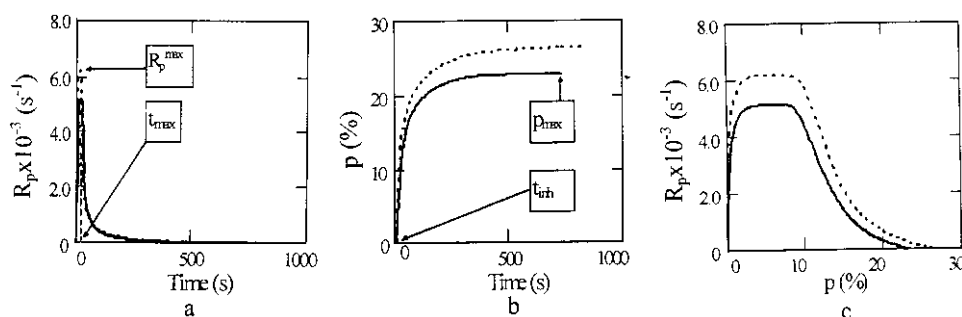


Fig. 1. a) Rate of polymerization (R_p), b) double bond conversion (p), and c) R_p versus p of TAEI:TMPTA = 1:1 (molar ratio) photopolymerized in the presence of $[CQ] = [AMH3] = 6 \times 10^{-2}$ M in N_2 (---) and in air (—), using a 500 W Philips lamp (60 mW cm^{-2}). TAEI = tris[2-(acryloyloxy)ethyl]isocyanurate; TMPTA = 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate.

taken as the final conversion. The DSC data obtained were corrected for changes in the baseline.

Extraction and/or removal of non-reacted monomers and initiators from polymerized samples (sol/gel analysis) was carried out using acetone or saliva for 12 h at 37°C . The time of extraction was controlled by UV/Vis spectrometric measurement with a Beckman DU7500 spectrophotometer for up to 3 days. After 12 h there was no measurable extraction. The remaining gel was dried for 24 h at 40°C in a vacuum and weighed (w_t). The soluble fraction was determined as the average of five samples, according to this formula: $Ex_m (\text{wt}\%) = (w_o - w_t) 100/w_o$, where w_o is weight of sample before extraction.

Polymerization shrinkage of photopolymerized samples was calculated using the following equation (17): shrinkage (%) = $[1 - d (\text{uncured})/d (\text{cured})] \times 100$. Specific densities (d) were measured by a pycnometric method (18).

Hardness was measured using a Shimadzu Micro Hardness Tester, Type M. The Vickers hardness number (VHN) was calculated with the following equation: $VHN = 1854.4 \text{ pd}^{-2}$, where the p is the load factor ($p = 100 \text{ g}$) and d is the mean diagonal indentation (μm). The Vickers Hardness Tester gives relative data at different times, and does not allow for measuring time dependent recovery (entropy elasticity). Photocured samples of a dental restorative composite (Z100 MP, 3M, Malakoff, France) were used as controls. The samples were photopolymerized in the same way as the samples of the investigated materials.

Results and discussion

Photocalorimetry (isothermal photo-differential scanning calorimetry, or photo-DSC) directly yields information on the rate of polymerization (R_p , s^{-1}), the highest rate of polymerization (R_p^{max} , s^{-1}), the double bond conversion (p , %), the highest degree of the double bond conversion (p_{max} , %), time in which R_p^{max} appears (t_{max} , s), time of inhibition (t_{inh} , s), and R_p versus p (19). The reproducibility

of measurements was $\pm 5\%$. Typical experimental curves of photo-DSC from which R_p , R_p^{max} , p_{max} , t_{max} , and t_{inh} can be extracted are presented here for photocuring of TAEI and TMPTA (1:1 molar ratio) (Fig. 1a,b).

Polymerization of TAEI, TMPTA, and their mixtures (mixed with the ultrasonic method) photoinitiated by CQ-amine occurs just as well in N_2 as in air (Fig. 1). Both R_p^{max} and p_{max} are higher in N_2 than in air, but the difference is not big. Polymerization starts very fast, immediately after switching on irradiation, and there is a very short, almost immeasurable, inhibition period ($t_{\text{inh}} \cong 0$) in air as well as in N_2 (Fig. 1a). The R_p versus p (Fig. 1c) shows that R_p is reached after 3% of double bond conversion and then decreases rapidly after about 8% conversion. $R_p^{\text{max}} \cong 0$ at 23%–25% conversion is reached after about 400 s (Fig. 1b). In the solid state of TAEI monomer and its mixture with TMPTA or PETA (8:2 and 9:1 ratios, Tables 5 and 6, respectively), the polymerization occurs by propagation through functional groups, which have a very limited mobility. The formation of a supermolecular structure network (polymer structure features observable at a level above that of individual polymer molecules) hinders the movement of propagating free radicals, which are entrapped in the dense network (8, 20). The propagation mechanism in the solid state is physically different from polymerization mechanisms in the liquid state, since the latter involve diffusion of polymer macro-radicals and chain segments to bring radicals within a reaction zone before terminating (21). In the case of TAEI-TMPTA the first segmental diffusion stage (rate constant of termination (k_t) is independent of molecular weight) would end at very low conversions, after which the translation diffusion (k_t is dependent on chain radical size) would dominate. However, once a gel has been formed (22), translational diffusion can occur for radicals not attached to the gel. Thus, termination by translational diffusion, which results in acceleration of the R_p (the Trommsdorff effect), should only be operative up to conversions slightly passing the gel point, since the probability that a propagating chain will acquire a cross

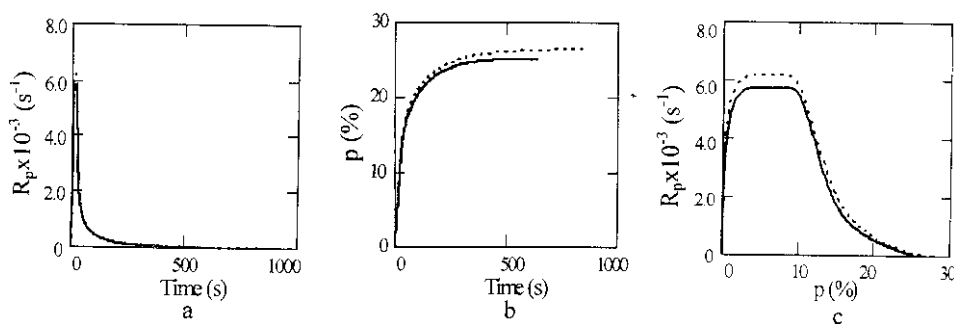


Fig. 2. a) Rate of polymerization (R_p), b) double bond conversion (p), and c) R_p versus p of TAEI:TMPTA = 1:1 (molar ratio) photopolymerized in the presence of $[\text{CQ}] = [\text{AMH3}] = 6 \times 10^{-2} \text{ M}$ in N_2 using a 500 W Philips lamp: 17 mW cm^{-2} (—) and 60 mW cm^{-2} (- -). For abbreviations see Fig. 1.

link during its life is rather high. For the remaining polymerization, termination probably proceeds by propagation of the chain ends. Some of propagating radicals are trapped in polymer networks, and they can be identified by the electron spin resonance even after 10 h. In the polymerization of TAEI and TMPTA a diffusion-controlled propagation may occur before vitrification. This is likely if the vinyl groups are separated by a rigid space unit (high-density network) that reduces the mobility and thus the reactivity of the pendant vinyl groups. In the case of TAEI the vinyl groups are not attached to flexible chains as in TMPTA. This may result in the propagation reaction never being under control through the whole conversion range (23, 24). The mobility of radicals through segmental diffusion falls well before their mobility through reaction diffusion at very low functional group conversion. Decreasing the light intensity from 60 mW cm^{-2} to 17 mW cm^{-2} has a very limited effect on the photopolymerization kinetics (Fig. 2).

Photopolymerization kinetics measurements of TAEI:TMPTA (1:1) using the photoinitiating system combining CQ and different amines (0.06 M each) show that the most effective coinitiators (H-atom donors) are AMH3 (ethyl-4-dimethylaminobenzoate) ($R_p^{\text{max}} = 6.2 \times$

10^{-3} s^{-1} in N_2), AMH5 (N,N-dimethylbenzylamine) ($R_p^{\text{max}} = 5.6 \times 10^{-3} \text{ s}^{-1}$ in N_2), and AMH6 (2,4,6-tris(dimethylaminomethyl)phenol) ($R_p^{\text{max}} = 6.0 \times 10^{-3} \text{ s}^{-1}$ in N_2) (Table 3). The effectiveness of the coinitiators can also be evaluated from comparison of p_{max} data. The effectiveness of different amines in the H-atom abstraction by the triplet state of CQ depends mainly on the structural ability of amines to form an exciplex with CQ (5, 23). The kinetic measurements made in air (oxygen inhibition effect) and N_2 showed that R_p^{max} is only slightly higher in the latter (Table 3). The highest double bond conversions (p_{max}) are rather low, about 16%–35%. However, the monomer conversions are very high (90%–100%), and they are almost the same in air as in N_2 (Table 3). Surprisingly, the hardness of photocured TAEI:TMPTA samples in the presence of CQ mixed with different amines is almost the same (Table 3). On the basis of results presented in Table 3, we used the CQ–AMH3 photoinitiating system for further studies. In addition, since AMH3 is a solid, this decreases its ability to evaporate easily from the network.

Increasing the AMH3 concentration in the CQ–amine photoinitiating systems first causes an increase and then a decrease in R_p^{max} , whereas the maximum double bond

Table 3. Data on kinetics of photopolymerization of TAEI:TMPTA = 1:1 (molar ratio), $[\text{CQ}] = [\text{AMH}] = 6 \times 10^{-2} \text{ M}$, and different amines, using a 500 W Philips lamp (60 mW cm^{-2}). Highest rate of polymerization (R_p^{max} , s^{-1}), time in which R_p^{max} appears (t_{max} , s), highest degree of double bond conversion (p_{max} , %), monomer conversion (p_m , %), and Vickers hardness number (VHN)

Photoinitiator	$R_p^{\text{max}} \times 10^3 \text{ (s}^{-1}\text{)}$		$t_{\text{max}} \text{ (s)}$		$p_{\text{max}} \text{ (\%)}$		$p_m \text{ (\%)}$		Hardness (VHN)	
	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2
CQ	4.2	4.1	26.0	18.0	21.3	23.2	91.0	99.5	16.1	16.3
CQ + AMH1	4.3	4.6	17.0	12.5	16.0	19.1	90.0	99.5	12.9	14.0
CQ + AMH2	4.1	4.4	17.0	13.5	18.9	20.9	91.0	99.5	16.1	18.5
CQ + AMH3	5.1	6.2	20.0	12.5	23.0	26.4	96.0	99.5	21.1	22.8
CQ + AMH4	4.5	4.7	16.0	11.0	19.0	23.7	92.0	99.5	23.1	26.0
CQ + AMH5	5.3	5.6	19.5	12.0	21.7	35.1	92.0	100	20.8	24.8
CQ + AMH6	5.3	6.0	24.5	17.0	25.5	30.5	97.0	99.5	23.4	29.0

TAEI = tris[2-(acryloyloxy)-ethyl]isocyanurate; TMPTA = 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; CQ = camphorquinone; AMH = amine.

Table 4. Data on kinetics of photopolymerization of TAEI:TMPTA = 1:1 (molar ratio), [CQ] = 6×10^{-2} M, and different concentrations of AMH3 using a 500 W Philips lamp (60 mW cm^{-2}). Highest rate of polymerization (R_p^{max} , s^{-1}), highest degree of double bond conversion (p_{max} , %), monomer conversion (p_m , %), and Vickers hardness number (VHN) of photocured samples

Measured values	(AMH3) $\times 10^{-2}$ M					
	0	1.5	3.0	6.0	12	24
$R_p^{\text{max}} \times 10^3$ in air (s^{-1})	4.2	4.5	4.9	5.1	4.8	4.4
$R_p^{\text{max}} \times 10^3$ in N_2 (s^{-1})	4.1	4.3	5.1	6.2	4.9	4.5
p_{max} in air (%)	21.3	21.3	24.2	23.0	24.8	25.7
p_{max} in N_2 (%)	23.2	24.5	27.7	26.4	28.1	26.3
p_m (%) in air	96.0	96.5	97.0	96.0	99.0	96.0
p_m (%) in N_2	99.5	99.0	99.5	99.5	99.5	99.5
Hardness (VHN) curing in air	16.1	17.7	19.3	21.2	23.6	29.0
Hardness (VHN) curing in N_2	16.3	19.8	21.0	22.8	25.7	30.3

TAEI = tris[2-(acryloyloxy)-ethyl]isocyanurate; TMPTA = 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate.

conversion (p_{max}) increases slightly with increased amine concentration (Table 4). The decrease in R_p^{max} with increasing amine concentration is a result of quenching of the triplet state of CQ by the excess of amines that do not participate in the exciplex formation (5, 25). For each CQ-amine photoinitiating system, there is an optimum of the amine concentration in which the amine itself is the most efficient part for the initiation of polymerization. Decreasing amine concentration has, however, no effect on the monomer conversion (Table 4). This is an important result for photocuring of dental resins based on TAEI:TMPTA because it is recommended that use of amines be minimized, since they generally are toxic and carcinogenic (26–28). The hardness of photocured samples increases little with increasing amine concentration (Table 4).

The TAEI and TMPTA monomers mix well in one another, giving solid or liquid samples depending on the molar ratios (Table 5). When cured in N_2 , the R_p^{max} of TAEI is $7.2 \times 10^{-3} \text{ s}^{-1}$, higher than that of TMPTA, $4.4 \times 10^{-3} \text{ s}^{-1}$ (Table 5). This indicates that TAEI is more reactive than TMPTA. When photopolymerization is

carried out in air, the R_p^{max} for both TAEI and TMPTA is slightly lower than when cured in N_2 (Table 5). The maximum double bond conversions (p_{max}) for TAEI and TMPTA photopolymerized in air are almost the same, 23.6% and 22.0%, respectively (Table 5). When photopolymerization is carried out in N_2 , the p_{max} for TAEI and TMPTA are 31.9% and 22.2%, respectively (Table 5). Monomer conversions (p_m) in N_2 for TAEI, TMPTA, and their mixtures at different molar ratios are the same (p_m 99.5%). Monomer conversion close to 100% at 20%–30% of double bond conversions can be explained by the fact that some of the monomers are quickly trapped in the polymer network and cannot easily be extracted by the solvents.

The hardness of photocured TAEI (VHN = 28.8 in N_2 and 26.0 in air) is slightly higher than the hardness of TMPTA (VHN = 17.7 in N_2 and 16.3 in air). The changing of the TAEI:TMPTA molar ratio has very little effect on the polymerization parameters and relative measurements of hardness of photocured samples (Table 5). Solid, but soft, samples of TAEI and its mixtures, with

Table 5. Data on kinetics of photopolymerization of TAEI:TMPTA at different molar ratios, [CQ] = [AMH3] = 6×10^{-2} M, using 500 W Philips lamp (60 mW cm^{-2}); and hardness of photocured samples. Highest rate of polymerization (R_p^{max} , s^{-1}), highest degree of double bond conversion (p_{max} , %), monomer conversion (p_m , %), and Vickers hardness number (VHN) of photocured samples

Measured values	TAEI:TMPTA (molar ratio)											
	0:10	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1	10:0	
State	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Solid	Solid	Solid
$R_p^{\text{max}} \times 10^3$ in air (s^{-1})	4.1	4.6	4.7	5.0	5.1	5.1	5.2	5.6	5.9	6.5	6.7	
$R_p^{\text{max}} \times 10^3$ in N_2 (s^{-1})	4.4	4.7	5.2	5.4	5.7	6.2	6.4	6.8	6.9	7.0	7.2	
p_{max} in air (%)	22.0	20.7	20.4	22.6	20.9	23.0	28.6	25.4	22.8	20.3	23.6	
p_{max} in N_2 (%)	22.2	24.1	23.3	25.2	30.2	26.4	33.3	30.0	28.0	26.4	31.9	
p_m in air (%)	97.5	97.0	97.0	94.5	94.9	95.0	95.1	96.0	95.1	94.1	95.0	
p_m in N_2 (%)	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	99.5	
Hardness (VHN), curing in air	16.3	16.9	18.5	19.8	20.8	21.2	22.8	23.4	24.5	25.1	26.0	
Hardness (VHN), curing in N_2	17.7	18.5	19.3	21.0	21.2	22.8	24.5	25.6	26.3	27.6	28.8	

TAEI = tris[2-(acryloyloxy)-ethyl]isocyanurate; TMPTA = 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate.

Table 6. Data on kinetics of photopolymerization of TAEI:PETA at different molar ratios, $[CQ] = [AMH3] = 6 \times 10^{-2}$ M, using a 500 W Philips lamp (60 mW cm^{-2}). Highest rate of polymerization (R_p^{\max} , s^{-1}), highest degree of double bond conversion (p_{\max} , %), monomer conversion (p_m , %), and Vickers hardness number (VHN) of photocured samples

Measured values	TAEI:PETA (molar ratio)						
	0:10	1:9	3:7	5:5	7:3	9:1	10:0
State	Liquid	Liquid	Liquid	Liquid	Solid	Solid	Solid
$R_p^{\max} \times 10^3$ in air (s^{-1})	4.5	4.9	5.1	5.2	5.7	6.7	6.7
$R_p^{\max} \times 10^3$ in N_2 (s^{-1})	4.8	5.2	5.6	6.6	7.0	7.1	7.2
p_{\max} in air (%)	25.8	25.6	24.9	23.2	21.5	21.3	23.6
p_{\max} in N_2 (%)	29.4	27.9	27.3	29.0	27.7	23.1	31.9
p_m in air (%)	99.0	98.5	97.5	97.0	98.5	97.5	95.0
p_m in N_2 (%)	99.5	99.5	99.5	99.5	99.5	99.5	99.5
Hardness (VHN), curing in air	18.5	19.3	21.2	22.9	23.6	25.3	26.0
Hardness (VHN), curing in N_2	21.0	21.2	23.6	24.7	26.3	27.6	28.8

TAEI = tris[2-(acryloyloxy)-ethyl]isocyanurate; PETA = pentaerythritol triacrylate; CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate.

Table 7. Polymerization shrinkages of photocured monomers alone and in the presence of filler, $[CQ] = [AMH3] = 6 \times 10^{-2}$ M

Sample	Density		Volume shrinkage (%)
	Uncured (g/mL)	Cured (g/mL)	
No filler			
TAEI	1.337	1.461	8.5
TAEI:TMPTA = 1:1 (mol)	1.231	1.360	9.5
TAEI:PETA = 1:1 (mol)	1.264	1.407	10.1
TMPTA	1.094	1.229	11.0
PETA	1.187	1.368	13.2
50 wt% filler			
TAEI	2.131	2.153	1.0
TAEI:TMPTA = 1:1	2.034	2.057	1.1
TAEI:PETA = 1:1	2.069	2.113	1.1
TMPTA	1.927	1.968	2.1
PETA	1.985	2.029	2.2

CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate; TAEI = tris[2-(acryloyloxy)-ethyl]-isocyanurate; TMPTA = 2-ethyl-2-(hydroxymethyl)-1,3-propanediol triacrylate; PETA = pentaerythritol triacrylate.

TMPTA at molar ratios of 9:1 and 8:2, respectively, can have some practical advantages in the clinical placing of fillings, because it is easier to work with soft, semi-solid materials in paste form than with liquid suspensions.

We have also studied photocuring of a mixture of TAEI with pentaerythritol triacrylate (PETA). The polymerization parameters (Table 6), as well as shrinkage (Table 7) and hardness numbers for TAEI:PETA (Table 8), are very similar to those obtained for mixtures of TAEI:TMPTA (Table 5).

The polymerization shrinkage is dependent on the type of monomer employed and the amount of unpolymerized monomer present. The volume shrinkages measured for TAEI, TMPTA, PETA, TAEI:TMPTA 1:1, and TAEI:PETA 1:1 are presented in Table 7. The lowest volume shrinkage was measured for TAEI (8.5%), in comparison with TMPTA (11.0%) and PETA (13.2%).

The incorporation of inorganic fillers causes several effects on a polymer composite, such as reduction of

polymerization shrinkage and improvements in mechanical properties. In general, a higher proportion of filler results in a lower final shrinkage (Table 7). The volume shrinkages for filled composites with 50 wt% of a filler are 1% for TAEI and 2% for the other samples, comparable with shrinkages of commercially developed dental resin composites (2.0%–4.0%). It is probable that 50 wt% filler would give almost the same reduction in volume shrinkage of the three different monomer mixtures. The polymerization shrinkage of the composite should be as low as possible, since this enhances marginal adaptation and so reduces the possibility of recurrent caries. Polymerization shrinkage has also been implicated as a primary source of interfacial breakdown. During the setting process, shrinkage stresses develop because the material is constrained by adhesion to the cavity walls. These stresses can be sufficient to cause breakdown of the interfacial bonds. The hardnesses of samples photocured with 10, 30, and 50 wt% of filler are significantly higher than those of the pure

Table 8. Comparison of hardness (Vickers hardness number, VHN) of differently photocured monomers alone and in the presence of filler (wt%), [CQ] = [AMH3] = 6×10^{-2} M

Photocured sample	Hardness (VHN) of samples cured in air	
	With Philips lamp (60 mW cm ⁻²)	With VCL lamp (220 mW cm ⁻²)
Z100 MP (3M product)	49.8	51.5
TAEI	26.3	31.3
TAEI + 10% filler	31.7	36.5
TAEI + 30% filler	35.7	43.6
TAEI + 50% filler	41.9	47.5
PETA	21.9	27.3
PETA + 10% filler	27.4	31.6
PETA + 30% filler	32.2	39.1
PETA + 50% filler	36.2	44.7
TAEI:PETA = 1:1	22.9	28.3
TAEI:PETA = 1:1 + 10% filler	29.1	33.1
TAEI:PETA = 1:1 + 30% filler	34.3	40.7
TAEI:PETA = 1:1 + 50% filler	39.0	46.0

CQ = camphorquinone; AMH3 = ethyl-4-dimethylaminobenzoate; TAEI = tris[2-(acryloyloxy)-ethyl]-isocyanurate; PETA = pentaerythritol triacrylate.

monomers or their mixtures (Table 8). For TAEI, and for its mixtures with PETA containing 50 wt% of a filler, the VHN values are almost the same as for the commercial restorative Z100 MP, which was used as a reference in hardness tests. However, several factors can influence the hardness of photocured samples, such as composition, content and type of initiator (27), initiator concentration (CQ-AMH) (7), content and type of monomer (28), and degree of conversion of double bonds (29–31). Measurements of hardness may give some indication of wear resistance, but this relation unfortunately breaks down at high filler loading (32).

Highly cross-linked networks obtained by photopolymerization of TAEI-TMPTA and TAEI-PETA mixtures are extremely difficult to characterize both experimentally and theoretically. These difficulties arise from the structural heterogeneity that develops in the polymer nets during the copolymerization of different trifunctional monomers. These monomers possess different reactivities. In the copolymerization system, not only is the reactivity of the functional group different, but the relative reactivity changes with the degree of polymerization. Any polymerization involving multifunctional monomers has this complexity of varying reactivity of the functional groups on the same molecule. The research reported here provided insight into the copolymerization kinetics of TAEI-TMPTA and TAEI-PETA mixtures. Unfortunately, the photo-DSC technique can provide information only about the average rate of copolymerization and the total conversion of the functional groups. The shrinkages of composites filled with 50 wt% of an inorganic filler are 1%–2%, similar to those reported for commercially available products. The hardnesses of the composite materials obtained by photocuring of these monomers mixed with 50 wt% of an inorganic filler (Ketac-Fil) are slightly less than that of a commercial dental composite

(Z100 MP). The highly cross-linked networks obtained by photopolymerization of TAEI-TMPTA and TAEI-PETA mixtures in the presence of CQ-amine photoinitiators can be used as the resin part in dental restorative materials. However, bonding composite to dentin would provide the advantage of eliminating, or at least significantly reducing, marginal leakage, thus reducing recurrent decay. Also, if adequate bonding could be achieved, more conservative cavity preparations could be used, and the strength of the clinical fillings could be approximate to that of tooth substance.

Studies on the toxicity of TAEI-TMPTA and TAEI-PETA are being considered in our Division of Toxicology and will be reported in a separate publication.

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