

A Comparison of Efficiency of Two Photoinitiators for Polymerization of Light-Cure Dental Composite Resins

P. P. Lizymol, V. Kalliyana Krishnan

Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Thiruvananthapuram 695012, Kerala, India

Received 25 October 2006; accepted 3 June 2007

DOI 10.1002/app.27493

Published online 28 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The purpose of the study was to compare the effect of two photoinitiators, (–)camphorquinone (CQ) and 1-phenyl-1,2-propanedione (PPD) on curing performance of light-cure dental composite resins. Bisphenol A-glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA) monomer mixture was used as the resin matrix. The resin matrix was mixed with CQ and/or PPD along with 0.25% of 4-(dimethyl amino) phenethyl alcohol (DMAPEA) catalyst. The effect of photoinitiator on curing performance was evaluated and compared in terms of properties such as depth of cure, diametral tensile

strength (DTS), flexural strength (FS), flexural modulus (FM), vickers hardness number (VHN), water sorption (WS), and solubility of cured composite. Statistical evaluation using Analysis of Variance (single factor) showed that the photosensitization efficiency of CQ and PPD are comparable. However, their combination showed synergistic effect for properties such as DTS and solubility. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3337–3342, 2008

Key words: biomaterials; composites; dental polymers; mechanical properties; photopolymerization

INTRODUCTION

The use of light-cure composites for restoring cavities in teeth has increased rapidly in recent years. Synthetic resins have evolved as restorative materials principally because of their aesthetic characteristics. Composites have good aesthetics and they are less expensive when compared with cast gold inlays and ceramic inlays.¹ Dentistry has an ever-expanding variety of restorative materials that require curing by photoinitiation.

Light-cure composites generally contain three main components. The major component is the inorganic filler mainly quartz or radiopaque glass along with or without fumed silica. In a composite restorative material, the filler forms 30–80% by weight of the product and it is the dispersed phase. The high filler content dilutes the resin and causes the thermal expansion characteristics of this mixture to be significantly lower than that of the resin itself, more closely matching that of the tooth structure. The second important component is the binding resin usually comprising high-molecular weight dimethacrylates [Bisphenol A-Glycidyl methacrylate (BIS GMA) or urethane dimethacrylate (UDMA)] mixed with low-

viscosity dimethacrylates like triethylene glycol dimethacrylate (TEGDMA). The resin is the binder for the filler and it is the continuous phase. The properties and chemistry of the binder contributes significantly to the acceptability and biocompatibility of the restoration. The third component is an organosilane coupling agent (3-methacryloxy-propyl trimethoxy silane) to achieve a good bonding between the resin and the inorganic filler. Along with these materials, traces of photoinitiator, activator, UV stabilizer, and inhibitor are added to light-cure composite. The most commonly used photoinitiator is (–) camphor quinone which is a diketone with a λ_{\max} at 473 nm. In the present study a comparison was made between CQ and the new photoinitiator 1-phenyl-1,2-propanedione (PPD), which has a λ_{\max} at 409 nm in terms of properties of cured dental composite. Photopolymerization implies both the light-induced increase of molecular weight by monomer to polymer conversion as well as crosslinking of developing or preexisting macromolecules.² There is a consensus that improved conversion of double bonds during photopolymerization is critical for the optimization of mechanical properties,^{2–6} biocompatibility,⁷ and color stability⁸ of light-activated dental restorative resins. The efficiency of several α -diketones as visible light photoinitiators for the crosslinking of waterborne latex dispersions in the presence of acrylic monomers was evaluated by Bibaut-Renaud et al.⁹ Among the eight α -diketones studied, camphorquinone allows the fastest curing speed, and the curing

Correspondence to: P. P. Lizymol (lizymol@rediffmail.com).

Contract grant sponsor: Science, Technology and Environment Department of Government of Kerala, India.

of the acrylic waterborne coating is not affected by the presence of oxygen.

EXPERIMENTAL

Materials

Bis GMA (Aldrich Chem, Milwaukee, WI) was used as the binder resin, and purified silanated quartz was used as the filler for the preparation of restorative paste. Both 1-phenyl-1,2-propanedione (PPD) and/or (–)camphorquinone (CQ) (Aldrich Chem) were used as the photoinitiators. Other chemicals (all from Aldrich Chem) used were triethylene glycol dimethacrylate (TEGDMA), 4(dimethylamino) phenethyl alcohol (DMAPEA), 4-methoxy phenol, phenyl salicylate, 2-hydroxy-4-methoxy-benzophenone, and 2,6-di-tert-butyl-4-methyl-phenol.

Characterization of photoinitiators

PPD and CQ were dissolved separately in HPLC grade *n*-hexane and scanned between 190 and 700 nm range in a UV-VIS spectrophotometer (CARY 100 BIO UV-Visible Spectrophotometer). Absorbance was plotted against wave length, and absorbance maxima at specific wavelength were noted. Fourier-transform infra red spectra of PPD and CQ were recorded using a JASCO FTIR spectrophotometer (Model 6300, Japan; resolution 0.07 cm⁻¹) using a NaCl cell for PPD and diffuse reflectance accessory for CQ.

Silanation of filler

A coupling agent 3-trimethoxy silyl propyl methacrylate (Aldrich Chem) was used directly without further purification. A 1% solution of 3-trimethoxy silyl propyl methacrylate (silane) in acetone with respect to filler was prepared and added to the filler. The mixture was stirred at 40°C in a water bath till the solvent evaporated completely. Then the filler was heated at 120°C for 1 h in an air oven, cooled, and used for preparing dental composite paste.

Dental composite paste preparation

Triethylene glycol dimethacrylate (TEGDMA) was used as the diluent monomer for the BisGMA resin which also acted as a crosslinking agent. Seventy parts of BisGMA was mixed with 30 parts of TEGDMA. To this mixture, 0.25% by weight of photoinitiator (CQ, PPD, or CQ-PPD combination), catalyst, inhibitor, and UV stabilizer were mixed to prepare three different batches of pastes. The prepared resin mixture was mixed with 280–300% of silanated quartz and 12% pyrogenic silica in a wear resistant

agate mortar to obtain a uniform paste. The paste prepared using PPD, CQ, and PPD/CQ combinations were coded as **VLCPPD**, **VLCCQ**, and **VLC**, respectively.

Evaluation of dental composites

FTIR analysis

FTIR spectra of uncured BIS GMA and cured composites were recorded using a JASCO FTIR spectrophotometer (Model 6300, Japan; resolution 0.07 cm⁻¹). Peak height ratios at 1635–2966 cm⁻¹ because of unsaturated —C=C— and —C—H stretching, respectively, were calculated for uncured BIS-GMA and cured composite to confirm monomer conversion during the composite preparation.

Depth of cure

Brass moulds with 3-mm diameter and 6-mm depth were used to prepare the samples for depth of cure measurements. The mould was placed on a strip of transparent sheet on a glass slide, and composite paste was packed in to the mould. A second strip of transparent sheet was placed on the top followed by a second glass slide. The mould and strip of film between the glass slides were pressed to displace excess material. The glass slide covering the upper strip was removed and the paste was exposed to visible light (LED light source, 3M, ESPE) for 40 s. The sample was then taken from the mould and the uncured part of the paste was removed using a metallic spatula. The depth of the cured part was measured accurately to the nearest millimeter using a digimatic vernier caliper of accuracy 0.01 mm. Divide the value by 2 to get the depth of cure. Mean and standard deviation were calculated.

Diametral tensile strength

Stainless steel moulds with 6-mm diameter and 3-mm thickness were used for the preparation of specimens for diametral tensile strength (DTS) measurements. Samples were prepared as per ADA specification.¹⁰ The mould was kept on a transparent sheet on a metallic plate. The paste was packed into the mould and a second transparent sheet was kept on top followed by a second metallic plate. The mould and strip of film between the metallic plates were pressed to displace excess material. The plates were removed and the paste was exposed to visible light for duration of 40 s on both sides through the transparent sheet. The cured samples were removed from the mould and kept at 37 ± 1°C for 23 h and 22 ± 2°C for 1 h before testing. The diametral tensile strength was determined as described before¹¹ using

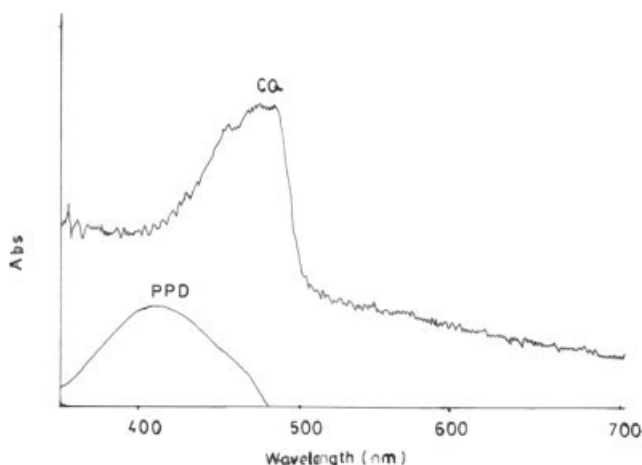


Figure 1 UV-visible spectra of CQ and PPD.

a Universal Testing Machine (Instron, Model 1011, UK) with a crosshead speed of 10 mm/min. The load at which break occurs was noted and diametral tensile strength was calculated using the following equation.

$$DTS = 2P/\pi DL$$

where P is the load in Newtons, D is the diameter, and L is the thickness of the specimen in mm. Mean and standard deviation of six values were calculated.

Flexural strength

Flexural strength test specimens were prepared as per ISO specification No. 4049-2000(E) (25-mm length, 2-mm depth, and 2-mm thickness). The paste was packed into the mould as described for depth of cure and exposed to visible light for duration of 3 min on both sides.

The flexural strength was determined using the Universal Testing Machine with a crosshead speed

of 1 mm/min. The samples were placed horizontally on two metal rods of 2-mm diameter fixed 20 mm apart on an aluminum platen. Load was exerted at the mid point of the specimen. Load at break was noted and flexural strength was determined using the formula

$$FS \text{ (MPa)} = 3FL/2bd^2$$

where F = load at break in Newtons,

L = length of the specimen between two metal rods at the base plate in mm,

b = width of the specimen in mm,

d = depth of the specimen in mm, and

Five samples were tested and the mean value and standard deviation were calculated.

Flexural modulus was measured using the same equipment and samples used for the flexural strength measurement. The following formula was used to calculate flexural modulus E ,

$$E \text{ (MPa)} = FL^3/4bd^3D$$

F = load at break in Newtons,

L = length of the specimen between two metal rods at the base plate in mm,

b = width of the specimen in mm,

d = depth of the specimen in mm, and

D = deflection in mm at load F from computer data.

Vickers hardness number

Vickers hardness number (VHN) was measured for each side of the sample using a Vickers microhardness Tester (Model HMV2, Shimadzu, Japan). The samples used for Vickers hardness (VHN) measurements are similar to those used for DTS measurements. Hardness was measured without polishing the surface of the specimen. Vickers hardness tester

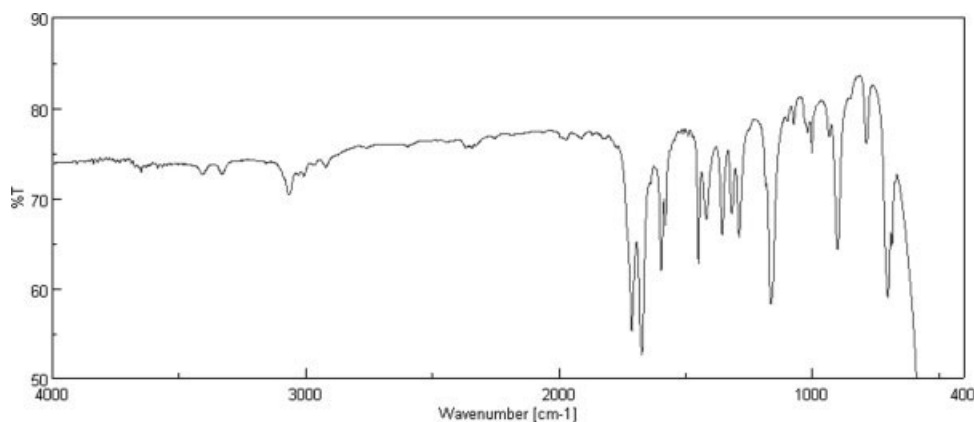


Figure 2 Fourier-transform infra red spectrum of PPD.

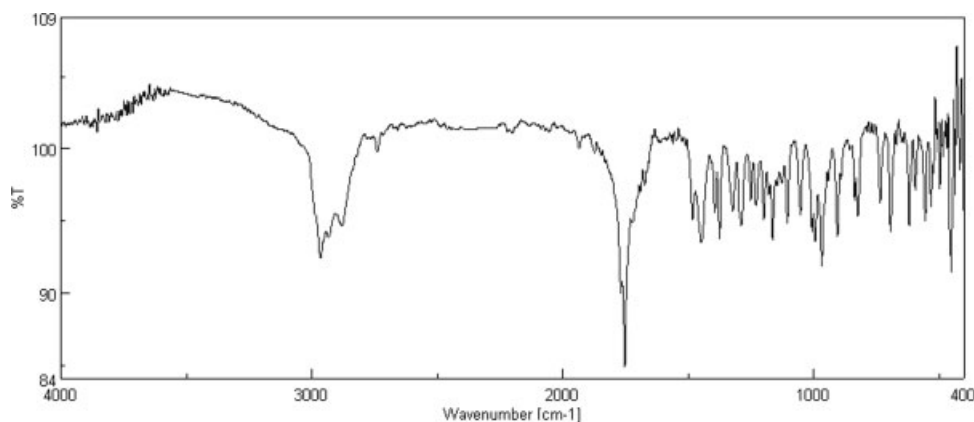


Figure 3 Fourier-transform infra red spectrum of CQ.

employs a diamond in the shape of square based pyramid. The specimen was placed flat on the microscope stage. The specimen surface was examined microscopically, and the indenter was then moved into position, and the microscope stage was raised automatically until the indenter upon the specimen applied the required load. In all cases, a load of 100 g was applied. The load was held for 15 s. before the microscope stage was steadily lowered. The indenter was then replaced with the objective lens and the image of the indentation was focused. The contrast of the image was optimized using differential filtering, and the size of the diagonal of the indentation was measured. Vickers hardness was calculated from the following equation. The mean value of six measurements was taken as the VHN.

$$H_v = \frac{0.1891F}{d^2}$$

where H_v = hardness number,

F = Test load (N),

d = mean length of the indentation diagonal length (mm).

Determination of water sorption and solubility

Cured samples of 10-mm diameter and 2-mm thickness were prepared. The surface of the specimens was polished using 240 grit silicon carbide paper and washed with distilled water and dried in a desiccator till constant dry weight (W_1) was achieved. The desiccator contains silica dried at 120°C for 5 h. Then the samples were stored in distilled water at 37°C for 7 days. After storage for 7 days, the surface adherent water was removed from the samples and weighed (W_2). The samples were then again dried at 37°C in vacuum desiccator till constant dried weight (W_3) was obtained. The water sorption and solubility were determined using the following equations,

$$\text{Water sorption (WS), } \mu\text{g/mm}^3 = (W_2 - W_3)/V$$

$$\text{Solubility (S), } \mu\text{g/mm}^3 = (W_1 - W_3)/V$$

where, W_1 is the initial dry weight in micrograms,

W_2 is the weight in micrograms after storage of the specimen in distilled water,

W_3 is the final dry weight in micrograms,

V is the volume of the sample in cubic millimeter, and

Mean and standard deviation of five samples were reported.

RESULTS AND DISCUSSION

Figure 1 shows the combined UV-visible spectrum of (-) camphorquinone having a λ_{max} at 473 nm and 1-phenyl-1,2-propanedione (PPD) at 409 nm. Figures 2 and 3 show that the FTIR spectra of PPD and CQ, respectively. While the carbonyl absorption occurs at 1713 cm^{-1} in the PPD spectrum, whereas it is shifted

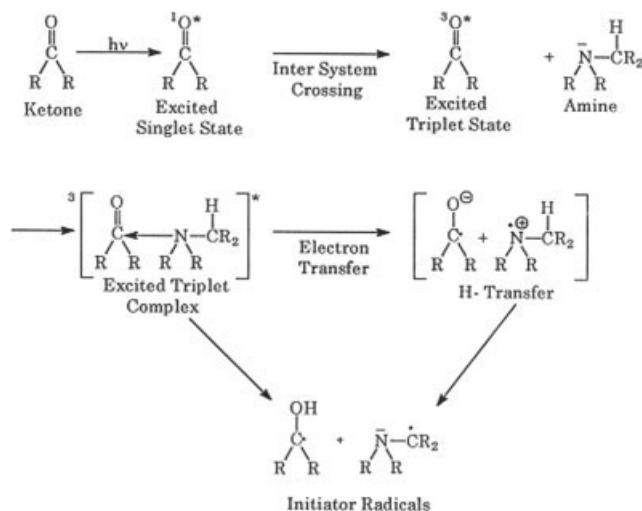


Figure 4 Mechanism of photoinitiation.

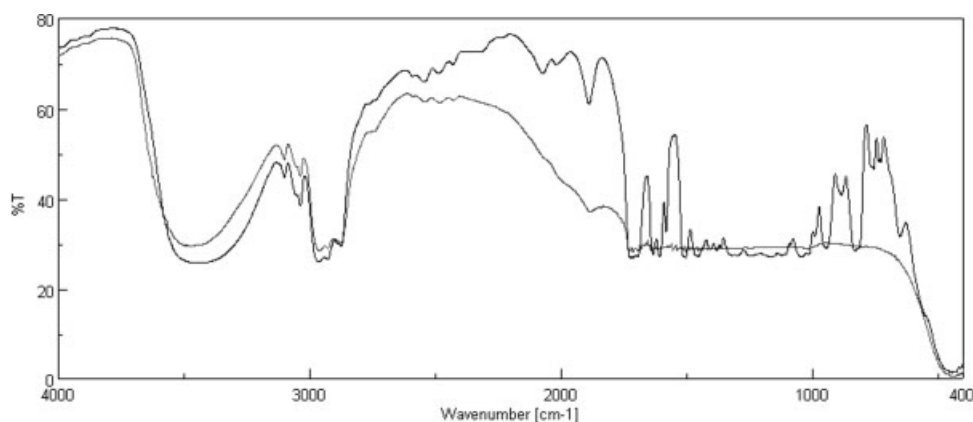


Figure 5 Overlay FTIR spectra of uncured Bis GMA and cured composite showing monomer conversion.

to 1752 cm^{-1} in CQ due to its ring structure, the —C—H stretching absorption occurring at 2965 cm^{-1} in CQ occurs at 3067 cm^{-1} in PPD due to the aromatic ring.

Mechanism of photoinitiation

Both the diketones CQ and PPD absorb energy in the visible region and reach the excited singlet state. Because of intersystem crossing, the excited molecule reach the excited triplet state (Fig. 4) and extracts proton from the amine. The mechanism of photoinitiation is because of proton transfer. FTIR spectroscopic studies (Fig. 5) revealed the conversion of double bond at 1635.34 cm^{-1} of uncured BIS-GMA in photocured composite. The peak height ratio of peak I (1635.34 cm^{-1}) to peak II (2966.95 cm^{-1}) because of unsaturated —C=C— and —C—H stretching, respectively, in uncured BIS-GMA is found to be 0.701, whereas that of cured dental composite is 0.0889 which is an indication of monomer conversion because of photopolymerization.

Depth of cure

Depth of cure values of the composites, VLCPPD, VLCCQ, and VLC are given in Table I and their statistics are given in Table II. It can be observed that VLCCQ has shown statistically significant improvement in depth of cure when compared with VLCPPD composite. Similarly VLC showed improved depth of cure compared to VLCPPD and VLCCQ. This shows that CQ-PPD combination has better photopolymerization efficiency as compared with CQ or PPD. However, VLCPPD met the requirements as per international standard. As per international standard ISO 4049-2000(E),¹² depth of cure should not be less than 1 mm for a material to be used for restorative applications.

Diametral tensile strength

Tables I and II show that DTS values of VLCPPD (37.4 MPa) and VLCCQ (36.7 MPa) composites are comparable and DTS values are more than 34 MPa, which is the minimum value stipulated by international standards. On the other hand VLC (44.2 MPa) composite has higher DTS value when compared with VLCCQ and VLCPPD showing a synergistic effect when CQ and PPD are used together which may be due to the better curing performance of their combination.

Flexural strength and flexural modulus

From Tables I and II it can be seen that VLCPPD (123.4 MPa, 13.4 GPa) and VLCCQ (97.7 MPa, 11.4

TABLE I
Properties of Cured Dental Composites Contain CQ and PPD Photoinitiators

Sample code	Property evaluated	PI used	Values obtained
VLCPPD	Depth of cure (mm)	PPD	1.9 ± 0.061
VLCCQ		CQ	2.75 ± 0.039
VLC		PPD+CQ	2.85 ± 0.09
VLCPPD	DTS (MPa)	PPD	37.4 ± 0.69
VLCCQ		CQ	36.7 ± 2.14
VLC		PPD+CQ	44.2 ± 2.85
VLCPPD	FS (MPa)	PPD	123.4 ± 26.52
VLCCQ		CQ	97.7 ± 8.53
VLC		PPD+CQ	110.9 ± 6.0
VLCPPD	FM (MPa)	PPD	13470 ± 2669
VLCCQ		CQ	11400 ± 3254
VLC		PPD+CQ	9938 ± 1029
VLCPPD	VHN (kg/mm^2)	PPD	49.1 ± 1.98
VLCCQ		CQ	40.4 ± 1.40
VLC		PPD+CQ	39.7 ± 2.53
VLCPPD	WS ($\mu\text{g}/\text{mm}^3$)	PPD	20.9 ± 1.92
VLCCQ		CQ	21.7 ± 2.97
VLC		PPD+CQ	20.4 ± 4.01
VLCPPD	S ($\mu\text{g}/\text{mm}^3$)	PPD	5.9 ± 1.07
VLCCQ		CQ	6.0 ± 0.86
VLC		PPD+CQ	3.5 ± 0.77

TABLE II
Statistical Analysis of Various Properties

Property evaluated	Group A	Group B	P value
Depth of cure	VLCPPD	<u>VLCCQ</u>	1.04 E ⁻¹³
	VLCPPD	<u>VLC</u>	1.4 E ⁻¹²
	VLCCQ	<u>VLC</u>	0.0005
DTS	VLCPPD	<u>VLCCQ</u>	0.5
	VLCPPD	<u>VLC</u>	0.0002
	VLCCQ	<u>VLC</u>	0.0004
FS	VLCPPD	<u>VLCCQ</u>	0.35
	VLCPPD	<u>VLC</u>	0.9
	VLCCQ	<u>VLC</u>	0.02
FM	VLCPPD	<u>VLCCQ</u>	0.43
	<u>VLCPPD</u>	<u>VLC</u>	0.04
	<u>VLCCQ</u>	<u>VLC</u>	0.36
VHN	<u>VLCPPD</u>	<u>VLCCQ</u>	5.11 E ⁻⁶
	<u>VLCPPD</u>	<u>VLC</u>	3.18 E ⁻⁵
	<u>VLCCQ</u>	<u>VLC</u>	0.66
Water sorption	VLCPPD	<u>VLCCQ</u>	0.99
	VLCPPD	<u>VLC</u>	0.39
	VLCCQ	<u>VLC</u>	0.435
Solubility	VLCPPD	<u>VLCCQ</u>	0.77
	VLCPPD	<u>VLC</u>	0.004
	VLCCQ	<u>VLC</u>	0.001

Note: Underlined group has significant improvement ($P < 0.05$).

GPa) have comparable FS and FM values. FS value of VLC (110.9 MPa) composite is comparable with that of VLCPPD. Compared to VLCCQ, VLC has statistically significant improvement in FS. On the other hand, in the case of FM, VLCPPD has significantly improved FM when compared with VLC. FM values of VLCCQ and VLC are comparable.

Vickers hardness number

Table I shows the VHN of the three composites. From statistical calculations shown in Table II, it can be seen that VLCPPD has significant improvement over VLCCQ and VLC composites which shows that by changing the photoinitiator from CQ to PPD, composite becomes harder resulting to a higher VHN value. It can be seen that there is no significant difference in hardness number when CQ alone and CQ/PPD combinations are used.

Water sorption and solubility

Table I shows that water sorption values of all the three composites are comparable and within standard deviation limits. The solubility values of VLCCQ and VLCPPD are comparable. Statistically significant reduction in solubility is observed for VLC compos-

ite. As per international standard ISO 4049, water sorption value should be less than 40 $\mu\text{g}/\text{mm}^3$ and solubility should be less than 7 $\mu\text{g}/\text{mm}^3$ for a material to be used for restorative applications. It can be seen that all the three composites met the requirements as per ISO standards.

CONCLUSIONS

The results of this study shows that photosensitization efficiency for the initiation of dental resin polymerization of both CQ and PPD are almost comparable. Depth of cure is higher for composite containing the photo initiator CQ than composite containing PPD. When both the initiators are used together, synergistic effect is observed for depth of cure, DTS, and solubility. On the other hand, statistically significant improvement observed for FM and VHN when PPD alone was used as the photoinitiator. All other properties including aesthetic appearance are comparable. Statistically no significant difference in properties such as DTS, FS, WS, and solubility was observed for composites containing either CQ or PPD photo initiators.

The authors are extremely grateful to The Director, Sree Chitra Tirunal Institute for Medical Sciences and Technology and Head, BMT Wing for providing facilities to carry out the project.

References

- Manhart, J.; Kunzelmann, K.-H.; Chen, H. Y.; Hickel, R. *J Biomed Mater Res (Appl Biomater)* 2000, 53, 353.
- Park, Y. J.; Chae, K.-H.; Rawls, H. R. *Dent Mater* 1999, 15, 120.
- Ferracane, J. L.; Greener, E. H. *J Biomed Mater Res* 1986, 20, 121.
- Ferracane, J. L.; Mitchem, J. C.; Condon, J. R.; Todd, R. *J Dent Res* 1997, 76, 1508.
- Peutzfeldt, A.; Asmussen, E. *J Dent Res* 1992, 71, 1847.
- Peutzfeldt, A.; Asmussen, E. *Dent Mater* 1996, 12, 103.
- Rietschel, R. L. *Occup Med* 1986, 1, 301.
- Imazato, S.; Tarumi, H.; Kobayashi, K.; Hiraguri, H.; Oda, K.; Tsuchitani, Y. *Dent Mater J* 1995, 14, 23.
- Bibaut-Renaud, C.; Burget, D.; Fouassier, J. P.; Varelas, C. G.; Thomatos, J.; Tsagaropoulos, G.; Ryrfors, L. O.; Karlsson, O. J. *J Polym Sci Part A: Polym Chem* 2002, 40, 3171.
- American National Standard/American Dental Association. Specification No. 27. For resin based filling materials. Council on Dental Materials, Instruments and Equipment, ADA: Chicago, 1993; pp 1-36.
- Deepa, C. S.; Kalliyana Krishnan, V. *J Biomater Appl* 2000, 14, 296.
- International Standard Organization. Geneva, Switzerland. ISO 4049-2000(E).