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PROJECT COMPLETION REPORT

1. **Project Number** : 7025

2. **Title of the Project** : DEVELOPMENT OF A NEW PHOTOINITIATOR FOR DENTAL APP LICATIONS

3. **Funding Agency Name** : STED,Govt.of Kerala

4. **Project Reference Number provided by the Funding Agency**: No:3482/B5/2002.STED dated 14th January 2003, **Kerala State Young Scientist Award Scheme**

5. **Principal Investigator (Name & Address) : Dr.Lizymol P.P. , DEP,DBST,BMTW,SCTIMST**

6. **Co-Investigators (Name & Address): V.KalliyanaKrishnan, Scientist, DEP,DBST,BMTW,SCTIMST**

7. **Implementing Institution : SCTIMST**

8. **Collaborating Institutions** : NIL

9. **Date of Commencement** : 06.03 .2003

10. **Duration** : 1 years

11. **Date of Completion** : 05-03-2004

12. **Objectives as approved :**

To synthesize and characterize a new photoinitiator,1 phenyl 1,2 propane dione (PPD) and compare its efficiency in monomer conversion compared to (-) Camphorquinone . The comparison was made by evaluating properties like depth of cure, linear polymerization shrinkage (%), diametral tensile strength, flexural strength, flexural modulus, Vickers hardness number, water sorption and solubility of cured dental composite

13. Deviation made from original objectives if any, while implementing the project and reasons thereof :NIL

14. Field/Experimental work giving full details of summary of methods adopted, data collected supported by necessary tables, charts, diagrams and photographs :

Synthesis and characterization 1 phenyl 1, 2 propane dione

A mixture of 1 mole (19.9 gm) of alpha chloroacetophenone, 1.05 moles (9 gms) of sodium acetate, 100ml. of water and 80 ml of ethanol is heated at reflux at boiling temperature for three hours. A distillation head is attached to the reaction mixture and 67 ml of liquid is distilled. The volume of liquid in the reaction is kept approximately constant by periodic addition of water. Following this addition, 3.6 gms (1.2 moles) of paraformaldehyde and 39 ml of concentrated hydrochloric acid are added to the residue and the mixture is subjected to reflex boiling for 3 hours. The reaction product which was greenish yellow was separated from the unreacted residue. To the residue 5 ml, conc.HCl and 5 ml distilled water are added and refluxed 3 hours. Greenish yellow liquid separated out and extracted with dichloromethane and washed with distilled water four times, separated and solvent was evaporated. The resultant product was dried at 37^{o}C.

About 2 gms of greenish yellow product obtained which was found to be a diketone . It initiated the photopolymerization of Bis GMA in presence of dimethyl amino phenethyl alcohol.

For the preparation of dental composite, Bis GMA (Aldrich Chem. Co. Milwaukee, USA) was used as the resin, triethylene glycol dimethacrylate (TEGDMA) was used as the diluent monomer for the BisGMA resin and purified and silanated quartz was used as the filler. Both **1 phenyl 1, 2 propane dione (PPD) and (-) Camphorquinone (CQ)** (Aldrich Chem. Co. Milwaukee, USA) were used as the photoinitiators.

Characterization of 1 phenyl 1, 2 propane dione (PPD)

1. UV-VIS spectroscopy

PPD was dissolved in HPLC grade n-hexane and scanned in a uv-vis spectrophotometer (CARY 100 BIO UV-Visible Spectrophotometer) in the range 190 -700 nm based on ASTME

169-93. λ_{max} was noted. For comparison CQ was dissolved in HPLC grade n-hexane and characterized using UV-VIS spectrophotometer .

2. Fourier transform Infrared spectroscopy

FTIR spectra of PPD was taken using a Impact 410 FTIR Spectrometer according to ASTM E 1252-94 .

3. Preparation of filler (Purification, calcination & Silanation)

The filler is the major component in the composite. It is the filler, and its high content, imparts the distinguished features of the composite restorative material. The filler forms 30-80% of the product. 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.

One of the most popular filler used for the preparation of dental composite is crystalline quartz. (**Ref**: D.C.Smith and D.F.Williams,Ed.,Biocompatibility of Dental Materials Vol.III,Boca Raton,Florida, CRC Press Inc. P107,1982.) The popularity of crystalline quartz fillers is based on improved aesthetics because of the close match of the refractive index of quartz with the resin base and the naturally good optical clarity of raw quartz.

Commercially available quartz contains various impurities. Therefore it was washed with distilled water and stored overnight in 75% hydrochloric acid, washed with distilled water till chlorine free, dried in an air oven at 100^{o}C and calcined at 800^{o}C in a muffle furnace for 8 hours and cooled to room temperature.

Silanation

If optimum properties of the composite are to be achieved and maintained, it is important that the filler particles are bonded to the resin matrix. This allows the more plastic polymer matrix to transfer stresses to the stiffer filler particles. The bond between the two phases of the composite is provided by a coupling agent. A properly applied coupling agent can impart improved physical and mechanical properties and provide hydrolytic stability by preventing water from penetrating along the filler resin interface. The commonly used coupling agents are organo silanes. The silanol group of the silane can bond with the silanols on the filler surface and the methacrylate groups of the silane can form covalent bonds with the resin when it is polymerized, thus completing the coupling process.

3-Trimethixy silyl propyl methacrylate (Aldrich Chem. Co. Milwaukee, USA) was used as the coupling agent. It was used directly without further purification. A 1% solution of

silane with respect to filler was taken. Acetone was used as the solvent. A solution of silane in acetone was prepared and added to the filler. The mixture was stirred at room temperatute till the solvent evaporated almost completely. Then the filler was heated at 120^{o}C for 1 hour and cooled and used for the preparation of dental composite paste.

4.Preparation of Dental Composite Paste.

Imported BisGMA resin was used as the binding resin for the preparation of dental composite using purified, calcined and silanated quartz filler.

4.1.**Preparation of Resin Mixture**

Triethylene glycol dimethacrylate (TEGDMA) was used as the diluent monomer for the BisGMA resin. It also acts as the crosslinking agent. BisGMA was mixed with TEGDMA in the ratio 70/30. To this mixture 0.25 phr photoinitiator, **(Camphor quinone and/or PPD)** activator (Dimethyl amino phenethyl alcohol),inhibitor, and UV stabilizer were mixed. All the additives were mixed thoroughly to dissolve completely.

Preparation of Paste

The prepared resin mixture is mixed with 280-300 phr of silanated quartz and 12% pyrogenic silica in an agate mortar to get a uniform paste.

Determination of depth of cure and Linear shrinkage of composite

Depth of Cure

The composite paste was packed in brass mould (3mm diameter and 6 mm depth) and exposed to visible light on one side for one minute. The sample was then removed from the mould and the uncured part is removed. The depth of the cured part was measured accurately to the nearest millimeter

Shrinkage of dental composite (%)

The composite paste was packed in stainless steel mould (10mm diameter and 2 mm depth) and exposed to visible light on both side for one minute. The sample was then removed from the mould and the diameter was measured at six points on each sample. Five samples were prepared and the mean diameter (D1) for each sample was measured. Then internal diameter of the mould (D2) was accurately measured at six points using Digimatic Caliper. % shrinkage was calculated using the equation D2-D1/D2 x100.

Shrinkage

Evaluation of mechanical properties:

i**) Diametral tensile strength**

For diametral tensile strength (DTS) measurements, samples were prepared as per ADA specification. (**Ref:**New American Dental Association Specification No. 27 for direct filling resins,1993) The same samples were used for Vickers hardness (VHN) measurements. The paste was packed in to the mould and exposed to visible light for duration of 1 minute on both sides.

The diametral tensile strength was determined as described before (C.S. Deepa and V. Kalliyana Krishnan, J. Biomat. Applications. **14**(3), 296 (2000)) using 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 equations.

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

where P is the load in Newtons, r is the radius, D is the diameter and L is the thickness of the specimen in mm. A minimum of ten samples was tested in each case and the mean of the best six values and standard deviation were calculated

Flexural Strength

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

The flexural strength was determined using the same 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 at break was noted and flexural strength was determined using the formula

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

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.

A minimum of 5 samples was tested and the mean value was noted.

For flexural modulus the same equipment and samples as for the flexural strength

was used. The following formula was used to calculate flexural modulus E,

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

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.

D = deflection in mm at load F from computer data

Values are given in Table 4.

Vickers hardness number

Surface hardness number (VHN) was measured for each side of the sample using a Vickers Micro hardness Tester (Model HMV 2, Shimadzu, Japan). Hardness was measured without polishing the surface of the specimen. Vickers micro hardness tester 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 gm was applied. The load was held for 15 sec. 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. Micro hardness was calculated from the following equation. The mean value of six measurements was taken as the VHN. $H_V = 0.1891\ F/\ d^2$

Where H_V = hardness number

F = Test load (N)

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

v).Determination of Water sorption and Solubility

Cured samples of 10mm 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 desiccator which contains silica dried at 120^{o}C for 5 hours till constant dry weight (W_1) was achieved. Then the samples were stored in distilled water at 37^o C for 7 days. After storage for 7 days, the samples were again weighed (W_2) removing the surface adherent water. The specimens were then again dried at 37^{o}C in vacuum desiccator till

constant dried weight (W_3) was obtained. The water sorption and solubility were determined using the following equations,

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

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

Mean of five samples are taken and given in Table 4.

15. Detailed analysis of results :

Characterization of PPD and CQ

The UV spectrum of PPD is given in Figure 1 and CQ is given in Figure 2. PPD has a λ max at 409 nm and CQ has a λ max at 473 nm. IR spectrum of PPD is given in Figure 3. The peak corresponding to carbonyl group obtained at 1712 cm^{-1}.

Evaluation of Dental Composites

Depth of cure of the composite which contains CQ is higher than that contains PPD. (Figure 4). As per international standard ISO 4049, a depth of cure of note less than 1mm is sufficient for a material to be used for restorative applications.

Table 1. Comparison of depth of cure of composites contain CQ and PPD

Sl.No.	sample	PI used	Resin used	Depth of cure (mm)
1.	VLC-CQ	CQ	BisGMA/TEGDMA 70/30	5.48 $\pm$ 0.039
2	VLC-PPD	PPD	BisGMA/TEGDMA 70/30	3.852 $\pm$ 0.061
3	VLC	CQ + PPD	BisGMA/TEGDMA 70/30	5.67 $\pm$ 0.09

Table 2.Mean Values of depth of cure of composites contain CQ and PPD

Sl.No.	sample	PI used	Resin used	Shrinkage (%)
1.	VLC-CQ	CQ	BisGMA/TEGDMA 70/30	1.02
2	VLC-PPD	PPD	BisGMA/TEGDMA 70/30	1.12
3	VLC	CQ + PPD	BisGMA/TEGDMA 70/30	1.12

Table 2. Comparison of shrinkage of composites containing CQ and PPD

Table 2 and Figure 5 shows that polymerization shrinkages of composites containing CQ, PPD and CQ-PPD combination as initiators are comparable. The reported value is 0.7-1.4% for all purpose composites. [**References 'Restorative Dental Materials' R.G.Craig and J.M.Powers (eds.) Mosby,Inc 2002,chapter 9, P.238**.].

Sl. No	sample code	Property evaluated	resin used	PI used	Values obtained
1	VLCPPD	DTS(MPa)	bis GMA	PPD	37.40± 0.69
2	VLCCQ	DTS(MPa)	bis GMA	CQ	36.76 ± 2.14
3	VLC	DTS(MPa)	bis GMA	PPD+CQ	44.18 ± 2.85
4	VLCPPD	FS(MPa)	bis GMA	PPD	123.4 ± 26.52
5	VLCCQ	FS(MPa)	bis GMA	CQ	97.71 ± 8.53
6	VLC	FS(MPa)	bis GMA	PPD+CQ	110.9 ± 6.0
7	VLCPPD	FM(MPa)	bis GMA	PPD	13470 ± 2669

8	VLCCQ	FM(MPa)	bis GMA	CQ	11400 ± 3254
9	VLC	FM(MPa)	bis GMA	PPD+CQ	9938 + 1029
10	VLCPPD	VHN(Kg/mm^2)	bis GMA	PPD	49.1 ± 1.98
11	VLCCQ	VHN(Kg/mm^2)	bis GMA	CQ	40.4±1.40
12	VLC	VHN(Kg/mm^2)	bis GMA	PPD +CQ	39.7 ± 2.53
13	VLCPPD	WS(μg/mm^3)	bis GMA	PPD	20.91 ± 1.92
14	VLCCQ	WS(μg/mm^3)	bis GMA	CQ	21.69 ± 2.97
15	VLC	WS(μg/mm^3)	bis GMA	PPD +CQ	20.43 ± 4.01
16	VLCPPD	S (μg/mm^3)	bis GMA	PPD	5.92 ± 1.07
17	VLCCQ	S (μg/mm^3)	bis GMA	CQ	6.03 ± 0.86
18	VLC	S (μg/mm^3)	bis GMA	PPD +CQ	3.46 ± 0.77

Table 3 Properties (Mean values) of cured dental composites containing CQ and PPD photo initiators

Diametral Tensile Strength (DTS)

Table 3 and Figure 6 shows the DTS values of composite material containing PPD or CQ initiators are comparable (within standard deviation limits) and DTS values are more than 34 MPa, which is the minimum value stipulated by international standards. But when 1:1 mixture of CQ and PPD are used together, improved DTS (statistically significant) obtained**.**

Flexural Strength and Flexural Modulus

Table 3 shows the FS (Figure 7) and FM (Figure 8) values of all the three composite formulations. We can see that all these composite materials have comparable FS values. (Statistically no significant difference) .However flexural modulus values are higher for composites contain PPD.

Vickers Hardness Number

Table 3 and Figure 9 show the VHN of the three composites. We can see that by changing the photo initiator from CQ to PPD, composite becomes more hard resulting to a higher VHN values .VHN of composites contain CQ-PPD combination is identical with that contains CQ alone (within standard deviation limits)

Water sorption and solubility

Water sorption (Figure 10) and solubility (Figure 11) values of composites contains CQ, PPD and CQ-PPD combination have almost identical values within standard deviation limits.

16. Summary sheet of not more than 2 pages under following heads : (Title, Introduction, Rationale, Objectives, Methodology, Results, Translational Potential)

The use of light cured composite 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 esthetics and they are less expensive compared to cast gold inlays and ceramic inlays[1].

Dentistry has an ever-expanding variety of restorative materials that require curing by photoinitaiation. The formulation of light cured composite has generally three main components. The major component is the inorganic filler mainly quartz or radiopaque glass along with or without fumed silica. The second and the important component is the binding resin usually comprised of high molecular weight dimethacrylates [Bisphenol A - Glycidyl methacrylate (Bis GMA) or urethane dimethacrylate (UDMA)] mixed with low viscosity dimethacrylates (TEGDMA). Eventhough the binder does not form the major part of the composite formulation, its properties and chemistry contributing much greater proportion 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 new

photoinitiator 1 phenyl 1, 2 propane dione (PPD) was synthesized and comparison was made between CQ and PPD. PPD has a λmax at 409-nm. Synergistic effects of CQ and PPD on properties were also evaluated.

References

1.J. Manhart, K-H. Kunzelmann, H.Y.Chen and R.Hickel, J.Biomed.Mater Res (Appl Biomater)., **53**, 353(2000)

Conclusion

Depth of cure is higher for composite contains the photo initiator CQ than composite contains PPD. FM and VHN are higher for PPD containing composite.

All other properties including aesthetic appearance are comparable. Statistically no significant difference was observed in properties such as DTS, FS, WS and solubility for composites contain both photoinitiators. However statistically significant improvement is observed in DTS when CQ and PPD are used together. All other properties of cured composites contain CQ-PPD combination is comparable with that of composites contains either CQ or PPD alone.

17. Contributions made towards increasing the state of knowledge in the subject :

Lizymol, P. P*.; Krishnan, V.K.,A comparison of efficiency of two photoinitiators for polymerization of light-cure dental composite resins, Journal of Applied Polymer Science, 2008, 107; 3337-3342

Special highlight "***Data from P.P. Lizymol and colleagues advance knowledge in applied polymer science". Source: Technology Business Journal (2008-03-24)***

18. Conclusions summarising the achievements and indication of scope for future work :

A new photoinitiator 1 phenyl 1, 2 propane dione (PPD) was synthesized and comparison was made between CQ and PPD. PPD has a λmax at 409-nm. Synergistic effects of CQ and PPD on properties were also evaluated. The use of new photoinitiator for 3D printin will be a promising approach in the future.

19. Science and Technology benefits accrued :

a List of research publications with complete details :

Lizymol, P. P*.; Krishnan, V.K.,A comparison of efficiency of two photoinitiators for

polymerization of light-cure dental composite resins, Journal of Applied Polymer Science, 2008, 107; 3337-3342

Special highlight "Data from P.P. Lizymol and colleagues advance knowledge in applied polymer science". Source: Technology Business Journal (2008-03-24)

b Manpower trained on the project :

i. Research Scientists or Research Fellows : NIL

ii. No. of PhD's produced : NIL

iii. Other Technical Personnel trained : NIL

c Patents taken, if any : NIL

d Products developed, if any :

NA

20 Abstract: (In 300 words for possible publication in ..... Bulletin) NA

a Background:

b Materials:

c Results:

d Conclusion:

21 Procurement/Usage of Equipment:

a Details of Equipment: No new equipment purchased. Existing equipments were used

Sl. No.	Name of Equipment	Make/ Model	Cost (Rs.)	Date of Installation	Utilisation	Remarks regarding maintenance breakdown

b Suggestions for disposal of equipment(s):

12/12/2023

Lizymol P.P.

(Name and Signature of PIs with date)

Routing: *Signed copy of "Project completion Report" by PI → root@sctimst.ac.in, rpc@sctimst.ac.in*