

# Studies on New Organically Modified Ceramics Based Dental Restorative Resins

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**ABSTRACT:** Novel difunctional and tetra functional organically modified ceramics with methacrylate functional groups were developed from liquid precursors using the sol-gel process. These novel inorganic-organic hybrid materials were characterized using various techniques and used for the preparation of visible light cure dental restoratives, which have good mechanical properties and excellent surface hardness. Effect of cure time on vickers hardness of cured composite was measured, and compared with that of the bisphenol A glycidyl methacrylate (Bis GMA) based composite. Statistical

evaluation using analysis of variance (single factor) showed a significant ( $P < 0.05$ ) difference in diametral tensile strength and hardness with variation in inorganic content. Also a significantly improved hardness was obtained for the new organically modified ceramic composite compared with BisGMA based composite at all exposure time. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 509–517, 2010

**Key words:** visible light cure; dental composite; organically modified ceramic; Vickers hardness number

## INTRODUCTION

The development of polymeric dental composites has revolutionized the field of dentistry over the past five decades. This development has been achieved mainly through organic monomer discovery, modifications in formulation and filler technologies, advances in light curing equipment and efficient photoinitiators. Despite these developmental advances, uses of dental composites are still limited by problems such as polymerization shrinkage and wear resistance. The post gel polymerization shrinkage causes significant stresses in the surrounding tooth structure and composite tooth bonding leading to premature restoration failure. Other problems such as uncured organic monomers leaching from the dental composites into the surrounding gum tissue have been reported to cause cytotoxic effects.<sup>1,2</sup>

Organically modified ceramic materials are new concepts,<sup>3</sup> which can be used as monomer matrix in dental restoratives to diminish their polymerization shrinkage and improve their wear resistance and biocompatibility. Inorganic-organic hybrids with tailor-made properties can be created by means of sol-gel processing of hydrolytically condensable, organically modified trialkoxysilanes, which contain radi-

cally polymerisable methacrylate groups or cyclic groups capable of ring-opening polymerization.

These organically modified ceramic materials are inorganic-organic hybrid materials with molecules containing a metal core bonded to reactive organic groups. The concept<sup>3</sup> is to combine properties of organic polymers (functionalization, ease of processing at low temperature and toughness) with properties of glass like materials (hardness, chemical and thermal stability, and transparency) to generate new/synergistic properties.<sup>3</sup>

The processing steps are based on sol-gel type reactions, which are already well known for the synthesis of ceramics.<sup>3</sup> In the case of organically modified ceramic hybrid materials, a second step, the formation of the additional organic network or cross linking follows after the build up of the inorganic network.<sup>3</sup>

These organically modified ceramic hybrid materials are used in wide range of applications such as wear resistant coating in micro electronics, micro-optics, electro-optics, and photonics, as matrices for dental composites,<sup>3</sup> and as scaffolds for tissue engineering.<sup>4</sup>

Objective of this study was to develop new organically modified ceramics based dental restorative composites consists of new inorganic-organic hybrid resins, containing alkoxides or mixtures of alkoxides of silicone, aluminum, calcium and titanium with various polymeric methacrylate group to replace the existing bisphenol A glycidyl methacrylate (Bis GMA) based composite. In this study silicone, aluminum, calcium, and titanium are selected

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because of their reported<sup>5,6</sup> osteoconductive and biocompatibility characteristics, which can enhance remineralization. Silica and alumina fillers have reinforcing effect. In dentistry, calcium hydroxide  $\text{Ca}(\text{OH})_2$  is used as dressing in paste form for antimicrobial effect during dental root canal procedure.  $\text{Ca}(\text{OH})_2$  is known to have a strong antimicrobial effect and is a bone-regeneration stimulant.  $\text{Ca}(\text{OH})_2$  has long been used to stimulate dentine bridge formation for dental regeneration, although its mechanism of action has remained largely elusive.<sup>7</sup> Tsuru et al.<sup>6</sup> reported that a kind of organically modified silica forms an apatite on its surface in a stimulated body fluid with ion concentrations nearly equal to those of the human blood plasma when it contains certain amount of calcium ions.

Effect of different inorganic materials incorporated during resin synthesis on properties of photocured composite was evaluated. These novel resins were characterized using various techniques such as refractive index, spectroscopy, and thermogravimetry and found to have excellent thermal stability<sup>8</sup> and superior shrinkage characteristics compared with BisGMA based materials. Effects of diluent concentration upon the properties of organically modified ceramics based composites was studied and reported elsewhere.<sup>9</sup> In this study, the effect of different inorganic materials incorporated in the resin on properties of cured composite was evaluated, and a comparison was made. FT-Raman spectroscopic technique was used to characterize the resin because FT-Raman spectroscopy is found to be superior to infrared spectroscopy for investigating inorganic systems as the vibrational energies of metal-ligand bonds are generally in the range of 100–700  $\text{cm}^{-1}$  a region of the infrared spectroscopy that is experimentally difficult to study.<sup>10</sup> These vibrations are frequently Raman active and peaks in this range are readily observed. These resins were used to prepare dental restorative composites, which were evaluated in terms of diametral tensile strength (DTS), flexural strength (FS), flexural modulus (FM), Vickers hardness number (VHN), water sorption (WS), and solubility(S).

## EXPERIMENTAL

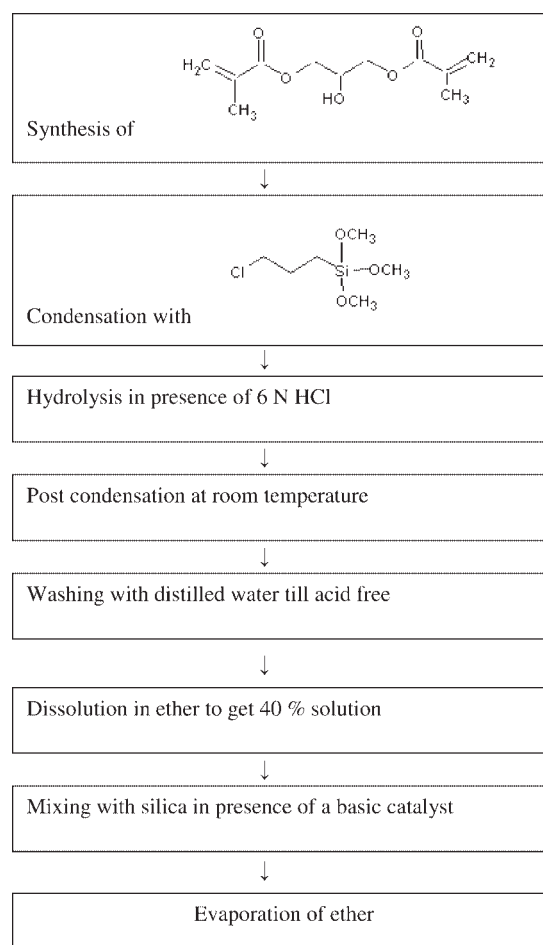
### Materials

The materials used in this study are 3(methacryloxypropyl-trimethoxy-silane), triethylene glycol dimethacrylate (TEGDMA), and 2,2 bis (4(2 hydroxy-3 methacryloxy-propoxy)phenyl)propane (BisGMA) (Aldrich Chem. Co. Milwaukee) Tetra isopropyl orthotitanate and chloropropyl trimethoxy silane (Merck Schuchardt, Germany), Laboratory Rasayan (LR) grade calcium hydroxide, LR grade aluminum

hydroxide gel, LR grade sodium hydroxide, Analytical Rasayan grade hydrochloric acid, and specially dried LR grade diethyl ether (S.D. Fine Chemicals, Mumbai, India).

### Synthesis and characterization of organically modified ceramic hybrid materials (Ormoresins)

Schematic presentation of the synthesis is as follows.



### Synthesis of Ormoresin R2

The dimethacrylate resin, 1,3-bis methacryloxy 2-(trimethoxy silyl propoxy) propane (Ormoresin R2) was synthesized by reacting 1.1 moles of glycerol dimethacrylate (which was synthesized in our lab as reported earlier)<sup>11</sup> with 1 mole of chloropropyl trimethoxy silane in presence of benzyl triethyl ammonium chloride catalyst. The mixture was allowed to react at 50–55°C under constant stirring for 6 h.

### Synthesis of Ormoresin R10

Ormoresin R10, a tetramethacrylate resin, containing silica was prepared by reacting 1 mole of Ormoresin R2 with 3 moles of distilled water in presence of 6 N HCl acid with constant stirring for 6 h at room temperature (28–30°C). The hydrolyzed product was

kept for 12 h at room temperature, extracted with diethyl ether and washed with distilled water till acid free. Ether was evaporated and added 300 ppm 4-methoxy phenol. A 40% solution of resin in ether was prepared. To the ether solution, 5% silica was added in presence of a basic catalyst and stirred at room temperature for 3 h and kept overnight to evaporate ether and dried at 37°C.

### Synthesis of Ormoresin R16

A dimethacrylate resin containing aluminum hydroxide (Ormoresin R 16) was prepared by hydrolyzing 1 mole of 3(methacryloxy propyl trimethoxy silane), with 3 moles of distilled water in presence of 6 N HCl under stirring for 6 h. The hydrolyzed silane was kept at room temperature overnight for post condensation. This was then extracted with ether, washed with distilled H<sub>2</sub>O, till acid free, and dried after evaporating ether. The hydrolyzed silane was dissolved in ether to get 40% solution. The ether solution was mixed with 1% Aluminum hydroxide and 1% silica in presence of a basic catalyst under stirring for 2 h. Ether was separated, and the resin was dried at 37°C for 48 h.

### Synthesis of Ormoresin R17

Ormoresin R 17 is a dimethacrylate resin containing silica and calcium hydroxide. To synthesize Ormoresin R 17, 1 mole of 3(methacryloxy propyl trimethoxy silane), was hydrolyzed with 3 moles of distilled water in presence of 6 N HCl under stirring for 6 h. The hydrolyzed silane was kept at room temperature overnight for post condensation. This was then extracted with ether, washed with distilled H<sub>2</sub>O, till acid free, and dried after evaporating ether. The hydrolyzed silane was neutralized with 1 N NaOH solution and dissolved in diethyl ether to get 40% solution of the polycondensed silane in diethyl ether. The ether solution was mixed with 1% calcium hydroxide and 0.5% silica and stirred well at room temperature and dried at 37°C.

### Synthesis of Ormoresin R23

Ormoresin R23 was a tetramethacrylate resin prepared by dissolving Ormoresin R2 in diethyl ether to get a solution of 40%. To the solution 1% tetra isopropyl orthotitanate was added after making the solution alkaline by adding 1 N NaOH solution. The solution was stirred vigorously for 3 h and dried at 37°C after evaporating ether.

### Characterization of Ormoresins

Refractive indexes of all the resins were measured using an Abbey Refractometer (Model 3 T Atago,

**TABLE I**  
Different Organically Modified Ceramics Resins Prepared

Composite sample code	Inorganic material incorporated
OrmoR17C (ormo48)	Ca(OH) <sub>2</sub> + silica
OrmoR10C	Silica
OrmoR23C	Tetra isopropyl ortho titanate
OrmoR16C	Silica + Al(OH) <sub>3</sub>

Japan). The infrared spectra were recorded using a Fourier Transform Infrared Spectrometer (Model FTIR Nicolet (USA) Impact 4000 and JASCO FTIR Model 6300, Japan). Spectra of the neat resins were recorded after applying a thin coat on NaCl. FT-Raman spectra were recorded using a FT-Raman spectrometer (Model Bruker RFS 100/s) with Nd:YAG (1064 nm) laser and a liquid nitrogen cooled Ge-diode detector. The laser power used was 150 mw, and 50 scans were used for each material.

Organically modified ceramics resins were taken in liquid sample holders and irradiated with laser. All spectra were recorded at about 22°C in the spectral region 3600–3650 cm<sup>-1</sup>. Correlation of different Spectra and peak intensity ratios were then evaluated using the quick compare set up attached with the "evaluate" function of OPUS software. To compare two spectra, one was taken as reference file in the quick compare setup. All the peaks of the second spectra were compared with the reference spectra peaks use the "file limits at all region" and the data was stored.

### Dental composite paste preparation

Organically modified ceramics resin (50 parts) diluted with TEGDMA (50 parts) was used as the resin matrix and purified, silanated quartz<sup>11,12</sup> was used as the filler for the preparation of restorative paste. (-) Camphor quinone (Aldrich Chem. Co. Milwaukee) was used as the photoinitiators. Other chemicals (all from Aldrich Chem. Co. Milwaukee) used for the preparation of paste are 4-(dimethyl amino)phenethyl alcohol, 4-methoxy phenol, phenyl salicylate, 2-hydroxy-4-methoxy benzophenone, and 2,6 di-tert-butyl-4-methyl phenol (which act as inhibitors, activators and UV stabilizers).

The diluent monomer, TEGDMA, used for the organically modified ceramics resin also acts as the crosslinking agent. To 50 parts organically modified ceramics resin mixed with 50 parts of TEGDMA mixture, photoinitiator (Camphor quinone), catalyst, inhibitor, and UV stabilizer were mixed (100 ppm to 0.25% concentration with respect to the weight of organically modified ceramics resin TEGDMA mixture) to prepare the resin mixture. The prepared resin mixture was mixed with 300% of silanated quartz and 12% pyrogenic silica in an agate mortar to get a

uniform paste. The paste prepared using Ormoresins R10, R16, R17, and R23 are coded as Ormo R10C, Ormo R16C, Ormo R17C (Ormo48), and Ormo R23C (Table I), respectively.

To make a comparison of Ormoresin with the conventional BisGMA resin, restorative material was prepared using 70 parts BisGMA mixed with 30 parts of TEGDMA along with all other additives in the same proportion as above in the case of Ormoresin. Filler content (280–300%) was adjusted so as to get a paste like consistency. The prepared light cure composite was coded as BGQZ.

### Evaluation of dental composites

#### Diametral tensile strength

Stainless steel molds with 6 mm diameter and 3 mm thickness were used for the preparation of specimens for DTS measurements. Samples were prepared as per ADA specification.<sup>13</sup> The paste was packed in to the mold and exposed to visible light for duration of 60 s on both sides using Elipar, FreeLight (120 V, 3 M, ESPE) (St. Paul, MN), which is a light unit that uses focused Light-Emitting Diode (LED) technology to polymerize visible-light-activated materials. Intensity used was  $>300$  mW/cm<sup>2</sup>. The DTS was determined as described before<sup>14</sup> 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 DTS was calculated using the following equations.

$$\text{DTS (MPa)} = 2P/\pi DL$$

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 samples were calculated.

#### Flexural strength

Flexural strength test specimens were prepared as per ISO<sup>15</sup> specification No. 4049–2000 (E) (25 mm length, 2 mm depth, and 2 mm thickness). The paste was packed in to the mold and exposed to visible light for duration of 180 s on both sides using the same LED light source as for DTS sample preparation.

The FS 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 FS and FM were determined using the formulas

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

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

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;  $d$  = diameter of the specimen in mm;  $D$  = deflection in mm at load  $F$  from computer data. Five samples were tested and the mean value and standard deviation were calculated.

#### Vickers hardness number

The samples used for VHN measurements are similar to those used for DTS measurements. Hardness was measured without polishing the surface of the specimen. VHN was measured for each side of the sample using a Vickers Micro hardness Tester (Model HMV 2, Shimadzu, Japan) using a previously reported procedure.<sup>9</sup> Vickers 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

$$F = \text{Test load (N)}$$

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

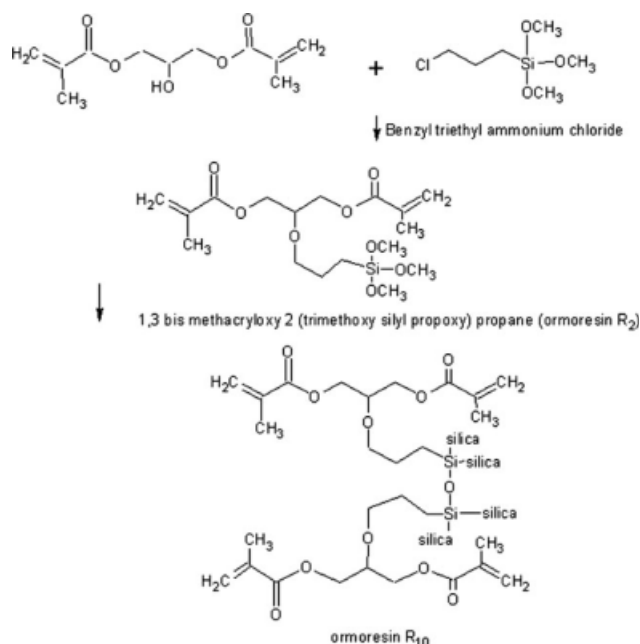
#### Effect of exposure time on VHN

Photo curable pastes were packed inside the cavity of 6 mm diameter and 3 mm height samples as those used for DTS samples. Then the upper side of the specimen was exposed to visible light from the LED source (same one used for DTS and FS) for 10, 20, 30, 40, 50, and 60 s durations, and hardness was measured on the light exposed surface. For all exposure duration, six measurements were taken. To find the effect of storage of cured samples on post polymerization, 40 s cured samples were stored at 37°C for 24 h and 7 d, and the hardness was measured as described earlier.

#### Determination of water sorption and solubility

Water sorption and water solubility were measured using cylindrical specimens of 10 mm diameter and 2 mm height. The composition of the samples and photoradiation conditions were the same as those used for DTS and FS test. The surface of the specimens was polished using 1000 grit silicon carbide paper and washed with distilled water and dried in 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





**Figure 1** Tetra methacrylate resins synthesized.

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 WS 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  $\mu\text{g}$ ;  $W_2$  is the weight in micrograms after storage of the specimen in distilled water;  $W_3$  is the final dry weight in  $\mu\text{g}$ ; and  $V$  is the volume of the sample in  $\text{mm}^3$ . Mean and standard deviation of five samples were reported.

### Statistical analysis

Statistical evaluation was done by means of one-way analysis of variance.

## RESULTS AND DISCUSSION

Table I shows the different organically modified ceramics resins prepared. The new di and tetra methacrylate organically modified ceramics monomers were synthesized by sol-gel method as exemplified by the preparation of 1,3-Bis(methacryloxy)-2(trimethoxy silyl propoxy) propane (Fig. 1)

All the resins were readily prepared in good yields and are soluble in the diluent TEGDMA. Refractive indexes of all the resins used in this study are given in Table II. A sharp interface in refractometer during refractive index measurement is an indi-

cation of purity of the resin. All the resins were characterized using FTIR<sup>8</sup> and FT-Raman Spectroscopic techniques. Figure 2 shows the FT-Raman spectra of the organically modified ceramics resins synthesized. A correlation was made between different resins using the software available with the spectrometer and shown below. The 100% correlation means both the materials are chemically identical.

Ormoresin R <sub>10</sub> and Ormoresin R <sub>16</sub>	= 72.28%
Ormoresin R <sub>10</sub> and Ormoresin R <sub>17</sub>	= 76.92%
Ormoresin R <sub>10</sub> and Ormoresin R <sub>23</sub>	= 71.58%
Ormoresin R <sub>16</sub> and Ormoresin R <sub>17</sub>	= 70.84%
Ormoresin R <sub>16</sub> and Ormoresin R <sub>23</sub>	= 84.12%
Ormoresin R <sub>17</sub> and Ormoresin R <sub>23</sub>	= 71.22%

The correlation results obtained from FT-Raman spectra showed that the different resins have drastic change in chemical structure though the change in composition of the constituents is less than 2%.

All the FTIR spectra<sup>8</sup> are typical for polymerized silica as indicated by the sharp peaks of the strong O—Si—O asymmetric stretch at 1000–1200  $\text{cm}^{-1}$  symmetric Si—O—Si stretch at 700–800  $\text{cm}^{-1}$  and Si—O—Si asymmetric stretch at 1298  $\text{cm}^{-1}$ . The other peaks obtained are 1716  $\text{cm}^{-1}$  (C=O group), bending vibrations of the C=CH<sub>2</sub> at 942  $\text{cm}^{-1}$ , stretching vibrations of the C=CH<sub>2</sub> at 1639  $\text{cm}^{-1}$ , and C—H stretching at 2800–3000  $\text{cm}^{-1}$ . The broad band at 3494  $\text{cm}^{-1}$  is associated with Si—OH stretching vibrations and hydrogen bonded water. FT-Raman spectra of the four synthesized resins are shown in Figure 2. Spectra of Ormo R10 indicate that Si—O—CH<sub>3</sub> stretching band of silica at 1100, which was very strong in IR was extremely weak in Raman spectra.<sup>10,16,17</sup> as the long chain aliphatics absorb at low frequency end range of CH<sub>2</sub> rocking vibrations.<sup>18</sup> The peaks of the strong O—Si—O asymmetric stretch at 1000–1200  $\text{cm}^{-1}$  symmetric Si—O—Si stretch at 700–800  $\text{cm}^{-1}$  and Si—O—Si asymmetric stretch at 1289  $\text{cm}^{-1}$  found in the FTIR spectra<sup>5</sup> were not visible in FT-Raman spectra. The other peaks obtained are 1716  $\text{cm}^{-1}$  (C=O group), bending vibrations of the C=CH<sub>2</sub> at 942  $\text{cm}^{-1}$ , stretching vibrations of the C=CH<sub>2</sub> at 1639  $\text{cm}^{-1}$  and C—H stretching at 2800–3000  $\text{cm}^{-1}$ . The peak found at 490–750  $\text{cm}^{-1}$  in the spectra of Ormo R16 is due to Al—O stretching vibration.<sup>18</sup> The peak at 781  $\text{cm}^{-1}$

**TABLE II**  
Refractive Index of Various Resins

Resin	Refractive index
Ormo R10	1.475
Ormo R16	1.483
Ormo R17	1.4822
Ormo R23	1.4864

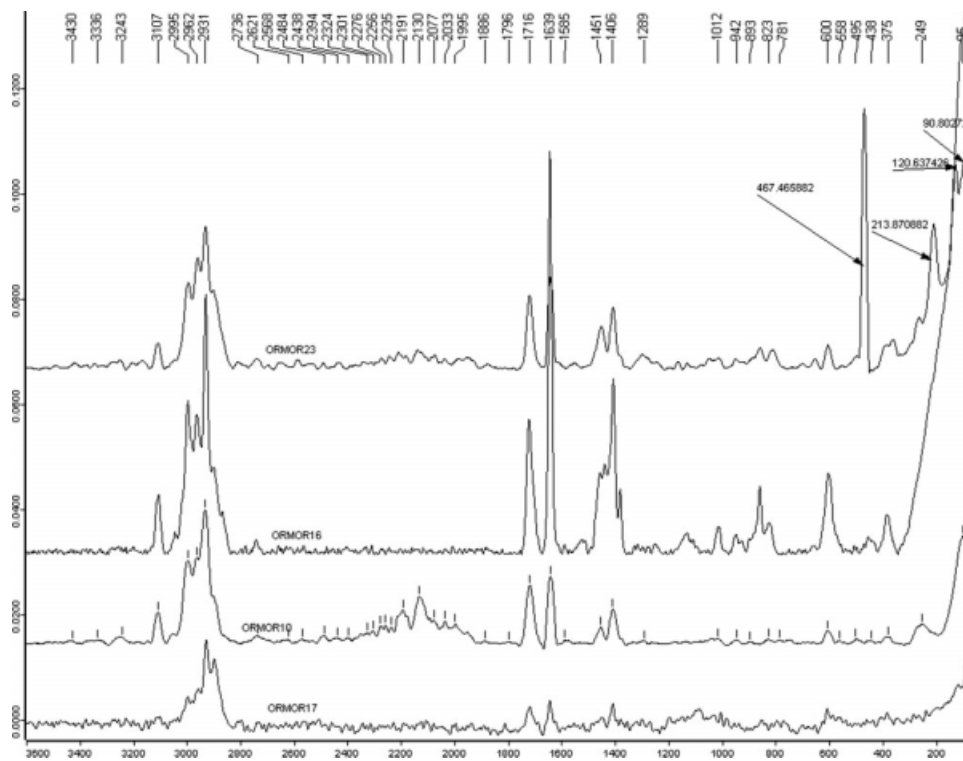


Figure 2 FT-Raman spectra of the various resins synthesized.

found in Ormo R17 is the typical peak of  $\text{Ca}(\text{OH})_2$ .<sup>19</sup> The peaks observed at 495, and  $375\text{ cm}^{-1}$  in the spectra of Ormo R23 are due to the various vibrations of the  $\text{Ti}-\text{O}-\text{Ti}$ .<sup>18</sup>

### Effects of inorganic content on properties of cured dental composites prepared using Ormoresins

DTS, FS, FM, hardness, WS, and solubility of various composites are shown in Figures 3–8, which indicate that the incorporated inorganic material on organically modified ceramics resin has considerable influence on the properties of cured dental composite. The incorporation of silica resulted in increased DTS (Fig. 3) and FS (Fig. 4) values in Ormo R10 C, whereas incorporation of tetraisopropyl ortho titanate (Ormo R23 C) enhanced the FM (Fig. 5). On the

other hand, incorporation of calcium hydroxide (Ormo R17 C), increased the hardness of the composite. Calcium containing composite has excellent surface hardness (Fig. 6). The increase in DTS and FS of Ormo R10 C composite is due to the reinforcing effect of silica and also due to the tetra functionality of Ormoresin R10. As the silica particles have particle size in the nanometer range (30 nm), the particles entrapped in the net work during crosslinking of the tetramethacrylate resin. DTS and FS are bulk properties. So reinforcement has significant effect on these properties. Reinforcement in the

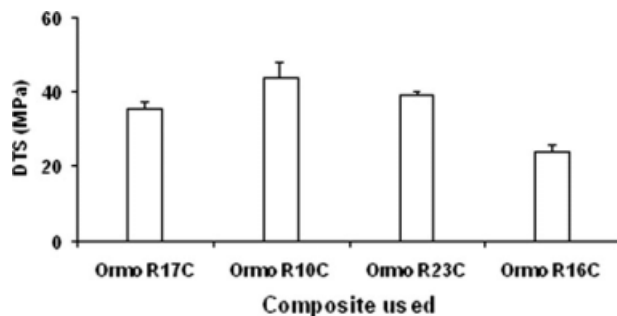


Figure 3 Diametral Tensile Strength (DTS) of various composites prepared.

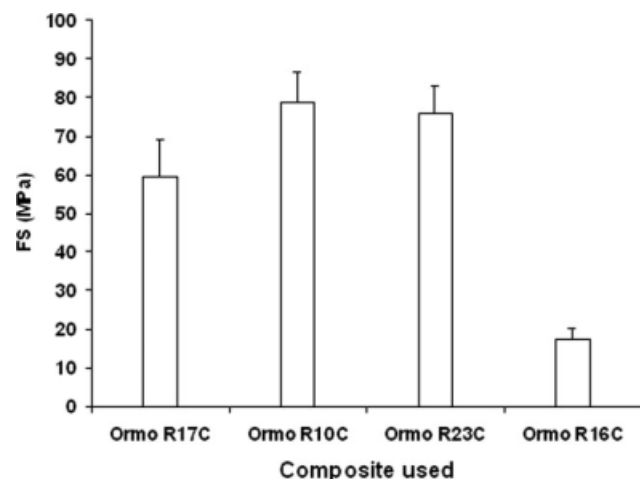
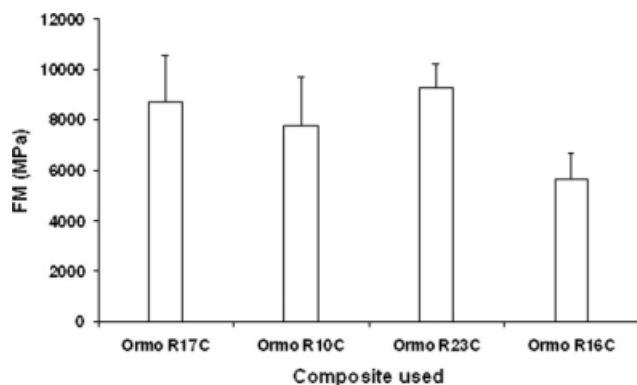


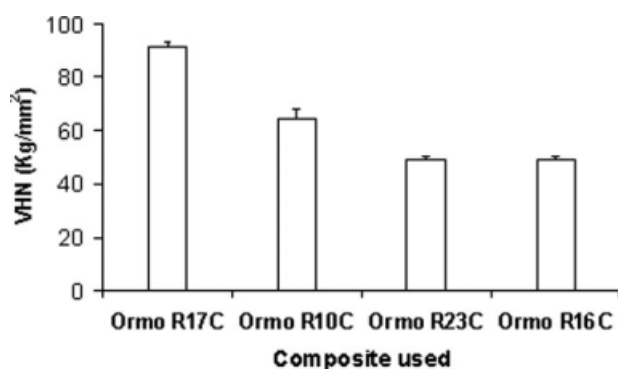
Figure 4 Flexural strength (FS) of various composites prepared.



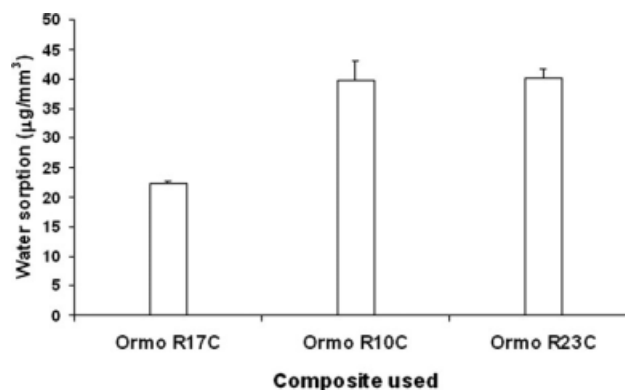
**Figure 5** Flexural modulus (FM) of various composites prepared.

nanometer size range closely approach the molecular size of the polymer, which makes for an intimate encounter between these two materials. During polymerization the filler particles and polymer interact to create constrained regions, which immobilizes a portion of the polymer chain, creating a reinforcing effect. When tetraisopropyl ortho titanate is incorporated, due to the steric hindrance of the four isopropyl groups, the mobility of the chains decreased. This resulted to low elongation. Decrease in elongation increases the modulus. Micro hardness depends on composition and surface structure. Presence of  $\text{Ca}^{++}$  ions on the surface enhances remineralization at the surface. The higher VHN is due to the relatively more mineralized surface zone.<sup>20</sup>

Spectroscopic results and enhancement in thermal stability<sup>8</sup> and other properties with different inorganic materials (Figs. 3–8) indicated the effective bonding exists between the organic and inorganic matrices. This is again conformed from the reported<sup>3</sup> studies as shown for epoxy-based ORMOCER coatings with silica being present either as nanoparticles or as molecularly dispersed Si–O–Si units, the Young's modulus increases dramatically from 2 up to 8 GPa in case of molecularly dispersed Si–O–Si units. The excellent hardness value of Ormo R17 C



**Figure 6** Vickers hardness number (VHN) of various composites prepared.



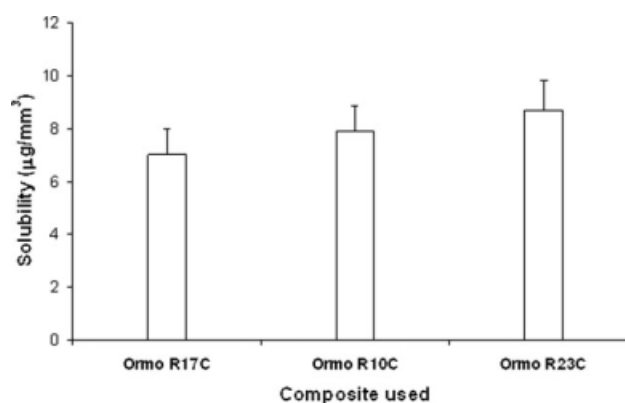
**Figure 7** Water sorption of various composites prepared.

is due to the presence of bonded  $\text{Ca}(\text{OH})_2$  in the resin during synthesis, which may also enhance surface remineralization. Further studies are required to confirm the hypothesis.

The calcium containing composite has the least WS and solubility values (Figs. 7 and 8). The higher WS and water solubility of the various organically modified ceramics composites in general are mainly due to the presence of the inorganic content in the resin, which increased the hydrophilicity. It is generally thought that the water solubility of a dental composite depends not only on the amount of components chemically unbound in the composite matrix but also on the solubility of the individual components<sup>21</sup>

#### Effect of exposure time on VHN

The effect of exposure time on VHN of Ormo R17 C is shown in Figure 9. Figure 10 is the effect of exposure time on hardness of BGQZ. As the exposure time increased, hardness was increased up to 40 s for both composites. From statistical calculations shown in Table III, it can be seen that further exposure has no significant effect on hardness. The 40 s light exposed samples of Ormo R17C again showed significant increase in hardness after 24 h storage at 37°C. During 7 days storage hardness increased significantly (Table



**Figure 8** Solubility of various composites prepared.

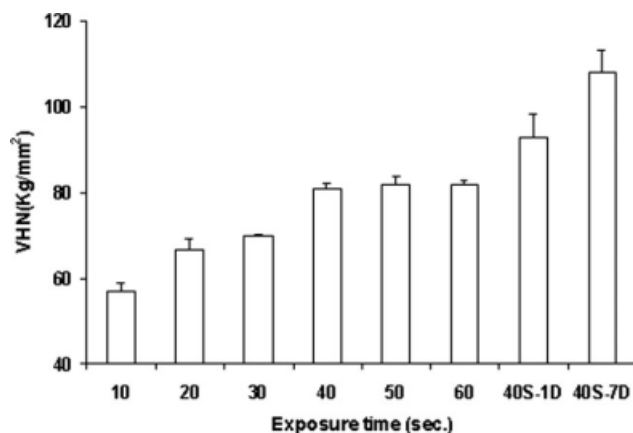


Figure 9 Effect of exposure time on VHN of Ormo R17C.

III). Hardness has been shown to be a good indicator of conversion of double bonds.<sup>22,23</sup> The greater the monomer conversion, the more will be the hardness. Therefore, hardness values can be used as an indirect measure of degree of conversion. The gradual increase of hardness (VHN) with exposure time up to 40 s indicates increase in monomer conversion for both composites. Further exposure up to 60s has no significant effect on hardness. However, storage at 37°C after 40 s exposure increased the hardness, which indicates the onset of post polymerization during storage. Comparison between BGQZ and R17C shows that at all exposure time Ormo R17C has significantly higher VHN. The VHN value for Ormo R17C at 10s curing is 56.8, whereas that for BGQZ is 28.1. For Ormo R17C VHN was 108 after 7 day storage (Fig. 9), whereas for BGQZ was 60.5 (Fig. 10). The results indicate that in spite of the exposure time, curing completes only by post polymerization, which occurs in the oral cavity in real clinical conditions.

### CONCLUSIONS

The synthesis and characterization of different organically modified ceramics resins were success-

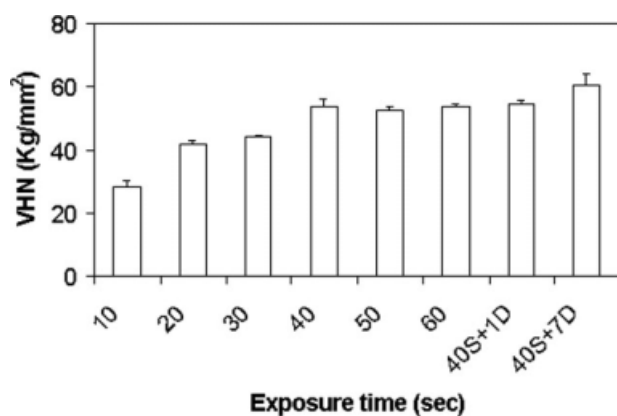


Figure 10 Effect of exposure time on VHN of BGQZ.

TABLE III  
Statistical Analysis (ANOVA Single factor) for Effect of Curing on VHN

GROUP I	GROUP II	P value
BGQZ-10S	BGQZ-20S	7.95 E <sup>-08</sup>
BGQZ-20S	BGQZ-30S	0.00032
BGQZ-30S	BGQZ-40S	2.29 E <sup>-06</sup>
BGQZ-40S	BGQZ-50S	0.4535
BGQZ-50S	BGQZ-60S	0.1284
BGQZ-40S	BGQZ-40S + 1D curing	0.2855
BGQZ-40S	BGQZ-40S + 7D curing	0.0019
+ 1D curing		
Ormo-10S	Ormo-20S	3.17 E <sup>-05</sup>
Ormo-20S	Ormo-30S	0.0188
Ormo-30S	Ormo-40S	5.498E <sup>-09</sup>
Ormo-40S	Ormo-50S	0.219
Ormo-50S	Ormo-60S	0.8849
Ormo-40S	Ormo-40S + 1D curing	0.00039
Ormo-40S	Ormo-40S + 7D curing	0.00065
+ 1D curing		
BGQZ-10S	Ormo-10S	4.14 E <sup>-10</sup>
BGQZ-20S	Ormo-20S	1.466 E <sup>-9</sup>
BGQZ-30S	Ormo-30S	1.17 E <sup>-16</sup>
BGQZ-40S	Ormo-40S	2.99 E <sup>-10</sup>
BGQZ-50S	Ormo-50S	1.28 E <sup>-11</sup>
BGQZ-60S	Ormo-60S	3.28 E <sup>-13</sup>
BGQZ-40S	Ormo-40S+ 1D curing	1.4 E <sup>-08</sup>
BGQZ-40S + 1D curing	Ormo-40S + 7D curing	3.99 E <sup>-09</sup>

fully completed by simple techniques. Visible light cure composite pastes for restorative applications were developed. Composite samples were prepared from the above pastes and characterized. Different resins have been found to have a correlation of only 70–80% even at less than 2% variation of inorganic content. The amount of inorganic content in the resin has a direct impact on the structural variation of organically modified ceramic resins. The results showed that both organic and inorganic contents of the resin have contribution to physico chemical properties of cured composite. The selection of alkoxide and specific organic monomers having functional groups responsible for effective chemical bond formation and enhanced properties of the inorganic-organic hybrid materials are important. The incorporated silica increased the DTS and FS, whereas tetra isopropyl ortho titanate increased the modulus and Ca(OH)<sub>2</sub> increased the surface hardness significantly. The maximum *in situ* polymerization occurred at 40 s exposure time as indicated by the VHN data. Further post polymerization occurs on storage at 37°C. Comparison with Bis GMA based composite showed that the new organically modified ceramics based composite has significantly better hardness value, which shows a better surface ion concentration of calcium on the surface of organically modified ceramic composite.

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