

Effects of Diluent's Concentration upon the Properties of Organically Modified Ceramics Based Composites for Application in Dentistry

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ABSTRACT: Organically modified ceramic resin (ormoresin) mixed with triethylene glycol dimethacrylate (TEGDMA) was used as the binder resin for the preparation of visible light cured dental composite. Three different combinations of ormoresin and TEGDMA were used for the preparation of composites, and their properties were compared in terms of depth of cure, diametral tensile strength (DTS), flexural strength (FS), flexural modulus (FM), Vickers

micro hardness (VMH), water sorption (WS), and solubility. It is found that an optimum amount of diluent is necessary for better crosslinking and properties of cured composites based on ormoresin. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 469–473, 2004

Key words: organically modified ceramics; dentistry; diluent

INTRODUCTION

The use of light cured composite for restoring cavities in teeth has increased rapidly in recent years. Composites have good esthetics and they are less expensive compared to cast gold inlays and ceramic inlays.¹

The formulation of light cured composite generally has three main components. The major component is the inorganic filler, mainly quartz or radiopaque glass along with or without fumed silica. The second and most important component is the binding resin, usually comprised of high molecular weight dimethacrylates [Bis phenol A- Glycidyl methacrylate (Bis GMA) or urethane dimethacrylate (UDMA)] mixed with low viscosity dimethacrylates (TEGDMA) together with initiator, activator, stabilizer, etc. The third component is an organo silane coupling agent (3-methacryloxypropyl-trimethoxy silane) to achieve a good bonding between the resin and the inorganic filler.

In the past 40 years after the development of Bis GMA by Bowen in 1962, it has been used as the most common monomer in composite restoratives. Though the monomer forms strong homopolymers with fair modulus and flexural strength, attempts were made by many researchers to replace Bis GMA with mono-

mers having low viscosity and more functionality. Visible light cure composite materials based on polyfunctional monomers have been found to exhibit enhanced performance with better mechanical properties and less residual monomers.²

Recently, a new family of organic-inorganic hybrid materials termed as organically modified ceramics (ormocers) has been used as substituents for BisGMA.³ The first dental restorative material based on the ormocer technology (Definite, Degussa A-G, Hanau, Germany) was put on the market in 1998.⁴ The concept of ormocer is to combine properties of organic polymer (functionalization, ease of processing at low temperatures, and toughness) with properties of glass like materials (hardness, and chemical and thermal stability) to generate new/synergistic properties. The processing steps are based on the sol-gel type reaction already well known for the synthesis of ceramics. In the case of ormocers a second step, the formation of the additional organic network or crosslinking, follows after the build up of the inorganic network. Tailoring of multifunctional ormocer precursors is the basis for their use as matrices for dental composite. Low shrinkage during curing, good mechanical properties, abrasion resistance, suitable elasticity, adhesion to teeth, and good toxicological data led to the successful development of ormocers as matrices for dental composite applications.³

The present study is on the effect of diluent concentration on various properties of a novel organically modified ceramics resin (Ormoresin).

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EXPERIMENTAL

Materials

The materials used in this study were triethylene glycol dimethacrylate (TEGDMA), 3 (trimethoxy silyl propyl methacrylate), and (–) camphorquinone (CQ), (all from Aldrich Chem. Co. Milwaukee, WI), and (4-dimethylaminophenyl) ethanol (DMAPEA, Sigma Chemicals, St. Louis, MO). Specially dried LR grade diethyl ether (S.D. fine chemicals, Mumbai, India) was used as the solvent. Purified, calcined, and silanated quartz was used as the filler material.

Synthesis of organically modified ceramics resin (Ormoresin R17)

The sol-gel technique was used to synthesize Ormoresin R17. 3-(Trimethoxy silyl propyl methacrylate) was used as obtained. Preferential hydrolysis and post condensation of the silane was carried out at lower pH. The hydrolyzed silane was neutralized with 1N sodium hydroxide solution and dissolved in diethyl ether to get 40% solution of the poly condensed 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.

The exact synthetic procedure cannot be revealed due to proprietary reasons.

Characterization of Ormoresin R17

The refractive index of Ormoresin R17 was measured using an ABBE refractometer (Model 3T Atago, Japan). The infrared spectrum was recorded using a Fourier Transform Infrared Spectrophotometer [Model FTIR, Nicolet Impact 410 (Nicolet Instruments Corporation, WI, USA)]. HPLC analysis was carried out using ethanol solution. Methanol was used as the mobile phase. For the resin C₁₈ column of high-pressure liquid chromatography equipment [Waters Associates, Model 440 (Waters Corporation, MA, USA)] was used. (Flow rate 1 mL/min, 486 tunable UV detector, 210 nm.)

Preparation of composite paste

Ormoresin R17 was thinned with TEGDMA in three different ratios, 70 : 30, 60 : 40, and 50 : 50. The resin mixture was mixed with 320 parts per hundred of quartz filler. The filler was silanated according to previously reported procedure⁵ to ensure strong adhesion between the resin matrix and filler. Small quantities of CQ, DMAPEA, UV inhibitor, and stabilizer were mixed in an agate mortar to form a homogenous paste.

Determination of depth of cure

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

Evaluation of mechanical properties

Preparation of samples

For diametral tensile strength (DTS) measurements, samples were prepared as per ADA specification.⁶ The same samples were used for Vickers microhardness (VMH) measurements. The paste was packed into the mold and exposed to visible light for duration of 1 min on both sides.

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

The DTS was determined as described before⁷ 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 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. A minimum of ten samples was tested in each case, and the mean of the best six values and standard deviation were calculated.

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

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

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, and 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,

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

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 = depth of the specimen in mm, and D = deflection in mm at load F from computer data.

Vickers micro hardness (VMH) 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 a 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 applied the required load upon the specimen. In all cases, a load of 100 g 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 VMH number.

$$H_v = 0.1891 F/d^2$$

where H_v = hardness number, F = test load (N), and d = mean length of the indentation diagonal length (mm).

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 till constant dry weight (W_1) was achieved. Then the samples were stored in distilled water at 37°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°C in a vacuum desiccator until 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

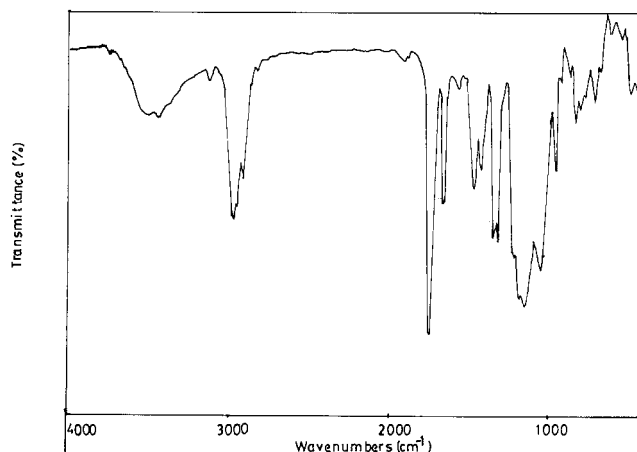


Figure 1 FTIR spectra of Ormoresin R17.

micrograms, and V is the volume of the sample in cubic millimeters.

RESULTS AND DISCUSSION

Ormoresin R17 obtained by the preferential hydrolysis and polycondensation of 3-trimethoxy silyl propyl methacrylate is a viscous resin with a refractive index of 1.4822.

FTIR spectra (Fig. 1) of Ormoresin R17 is typical for well polymerized silica as indicated by the sharpness of the strong O-Si-O asymmetric stretch at 1000–1200 cm^{-1} , symmetric Si-O-Si stretch at 786 cm^{-1} , and Si-O-Si asymmetric stretch at 1298 cm^{-1} . The other peaks obtained are 1718 cm^{-1} (C = O group), bending vibrations of the C = CH₂ at 941 cm^{-1} , stretching vibrations of the C = CH₂ at 1637 cm^{-1} , and C-H stretching at 2800–3000 cm^{-1} . The broad band at 3494 cm^{-1} is associated with Si-OH stretching vibrations and hydrogen bonded water.

In HPLC (Fig. 2) the main eluant is at a retention time of 1.322 min. The other two peaks at retention times 2.075 and 2.317 may be due to the presence of inhibitor and catalyst, both of which are supportive in nature for composite preparation.

All three formulations of composites based on Ormoresin R17 have a depth of cure of about 3 mm. As per international standards⁸ a minimum depth of cure of 1mm is sufficient for the material to be used for restorative application.

When the diluent content increased from 30 phr to 40 phr, the DTS values increased nearly to 23% and then leveled off for further increase of diluent content to 50 phr. It is well known that the mechanical properties are closely related to the degree of conversion.⁹ For composites with resin mixture 60/40 and 50/50 combinations of resin and TEGDMA, the DTS values are around 34 Mpa, which is the minimum value

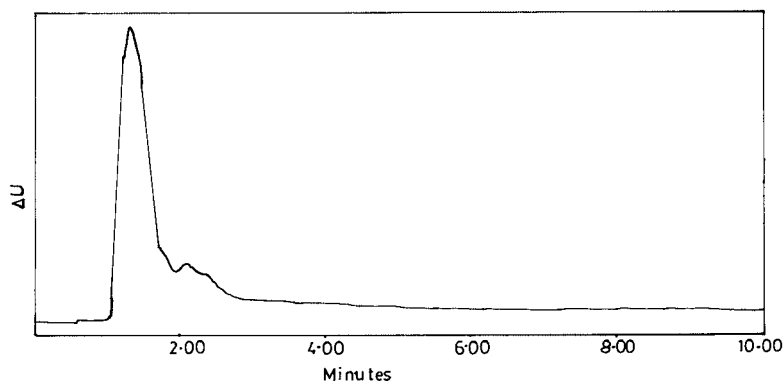


Figure 2 High-pressure liquid chromatogram of Ormoresin R17.

stipulated by the international standards⁶ for a dental composite to be used for restorative application.

The flexural strength and flexural modulus of the three formulations of composites are shown in Table I. It can be seen that as the diluent concentration increased from 30 phr to 50 phr, both flexural strength and flexural modulus were increased. Flexural strength value of the 50/50 formulation is higher than 50 Mpa, which is the minimum stipulated value for Type 2 materials for use in dentistry for application as restorative material.⁸ Flexural modulus values showed that incorporation of inorganic content to the organic resin increased the stiffness of the cured composite.

The hardness of a material is the resistance a solid shows to local deformation.¹ A positive correlation has been established between the hardness and the inorganic filler content of the restorative composite.¹ Increased filler level results in increased hardness number. In this study all three composites have the same filler content. But it is found that VMH values increased as the diluent content increased. When the diluent content increased from 30 phr to 50 phr, VMH values increased from 81 Kg/mm² to 91 Kg/mm² (Table I). This showed that when the diluent content increased, the resultant composite on curing became more resistant to indentation, which may be due to better crosslinking. The presence of inorganic content in the organic resin is contributing to

the higher hardness values of organically modified ceramic based composites.

It is found that for this particular organically modified ceramic resin, which is a very viscous resin, for a higher degree of conversion, an efficient low viscous dimethacrylate is necessary. This is because of the fact that for the degree of conversion to be higher, the mobility of the reactive species has to be enhanced, which can be achieved by increasing the diluent content up to a certain level. It is found that above a certain level of diluent concentration, the various properties leveled off, which shows that during the polymerization reaction of organically modified ceramic resin and diluent molecules, a network density has to be attained to produce resins with reasonably high strengths. Once this network forms, the strength becomes less dependent upon the degree of conversion. In this study the diluent content was increased from 30 phr to 50 phr. The diluent was found to mix with the resin easily at all combinations, and the resultant resin mixture mixed with the filler to get a uniform paste.

Water sorption and solubility values were measured for three specimens, and the mean value was taken. It was found that (Table I) when the diluent content is increased from 30 phr to 40 phr, water sorption decreased from 31 μg to 21 μg and then

TABLE I
Effects of Diluent's Concentration on Properties of Composites

Property evaluated	Material tested		
	Ormoresin 70/30	Ormoresin 60/40	Ormoresin 50/50
Depth of cure (mm)	3.03 \pm 0.03	3.1 \pm 0.04	3.1 \pm 0.06
DTS (N/mm ²)	26.4 \pm 1.8	34.22 \pm 1.6	35.63 \pm 1.56
FS (MPa)	41.29 \pm 1.8	37.27 \pm 3.08	59.63 \pm 9.54
FM (GPa)	7.06 \pm 0.78	8.3 \pm 0.62	8.7 \pm 1.9
VMH (Kg/mm ²)	81 \pm 1.29	85.2 \pm 1.02	91.6 \pm 2.14
WS ($\mu\text{g}/\text{mm}^2$)	31.01	20.91	22.26
Solubility ($\mu\text{g}/\text{mm}^2$)	8.4	4.15	7.09

slightly increased on further increase of diluent. The same trend is observed in the case of solubility also.

CONCLUSION

From the various properties evaluated, it is found that flexural modulus and VMH values of organically modified ceramic composites are good. These results showed that incorporation of inorganic content in organic resin of the organically modified ceramics improved the stiffness and hardness of the composite.

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