Urethane Tetramethacrylates: Novel Substitutes as Resin Matrix in Radiopaque Dental Composites

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ABSTRACT: Dental composites used in conservative and orthodontic dentistry are based on bisphenol A–glycidyl methacrylate (BIS–GMA) resin. However, certain limitations, such as high viscosity and handling difficulties, restrict the use of BIS–GMA and attempts have been made to modify the resin or to seek alternate materials. The synthesis and characterization of a urethane tetramethacrylate resin (UTMA) is reported here, which when reinforced with a silanated radiopaque glass filler, is found to provide composite pastes with superior properties. Composite pastes with formulations of varying BIS–GMA/UTMA blend ratios have been prepared and their effect on the compressive strength, diametral tensile strength, transverse strength, Vickers microhardness, water sorption, and opacity have been studied. The photoinitiator concentration has been varied for 100% urethane-based composite and its optimum concentration standardized. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 735–746, 1999

Key words: urethane tetramethacrylate; resin matrix; radiopaque; light-cured dental composite; mechanical properties

INTRODUCTION

Because of their superior properties and aesthetic quality, composites have gradually replaced conventional materials such as amalgams, silicates, and acrylics in restorative dentistry. We have reported earlier the development and evaluation of chemical-cured,[1] light-cured,[2] and light-cured-radiopaque[3] dental composites. All these composite materials had bisphenol A–glycidyl methacrylate (BIS–GMA) as the organic binder resin (20–40%) combined with purified and silanated quartz or glass (60–80%), which acted as the reinforcing filler.[4] In radiopaque composites, the filler usually contained Ba, Sr, or La atoms, which induced radiopacity to the material. BIS–GMA, however,

has certain drawbacks, the main one being its high viscosity (~ 1200 Pa/s), which inhibits its processing into a paste with good homogeneity.[5] The reason for its high viscosity is due to the presence of two bulky aromatic rings in its molecule [Fig. 1(a)]. This problem has been partly solved by incorporating low molecular weight aliphatic dimethacrylate diluents such as triethylene glycol dimethacrylate (TEGDMA), ethylene glycol dimethacrylate (EDMA), etc., to reduce the viscosity of BIS–GMA.[6] These dimethacrylate molecules [Fig. 1(b) and (c)] are expected to be incorporated into the polymer chain through their end groups when polymerization reaction takes place during curing, resulting in a hard crosslinked polymer.

However, some attempts have been made earlier to substitute BIS–GMA with alternate resin materials to overcome this difficulty.[7,8] The synthesis and evaluation of a urethane-based aliphatic tetramethacrylate resin is reported here.

(a)

(b)

(c)

Figure 1 (a) Chemical structures of Bisphenol A–glycidyl methacrylate [BIS–GMA]; (b) triethylene glycol dimethacrylate [TEGDMA]; and (c) Ethylene glycol dimethacrylate [EDMA].

This resin, when mixed with BIS–GMA in different proportions and incorporated with a radiopaque glass powder containing Ba atoms, is found to polymerize under the influence of a photoinitiator into a hard solid composite that provides more effective light curing, lower viscosity, superior physical properties, low water sorption, and greater toughness.

EXPERIMENTAL

Preparation of the Resin Matrix

BIS–GMA was synthesized in the laboratory using a reported procedure.[9] Urethane tetramethacrylate (UTMA) adduct was synthesized by a two-step process as given below.

Synthesis of MHP

As a precursor to the urethane resin preparation, 1,3-bis-(methacryloxy)-2-(hydroxy propane) (MHP)

was synthesized by reacting 2,3-epoxypropyl-methacrylate (Merck-Schuchardt, Schuchardt, München, Germany; 0.9 mol) and methacrylic acid (SD Laboratories, Bombay, India; 1 mol) in the presence of a base catalyst in an inert atmosphere for 5 h at 75°C with constant stirring. Methacrylic acid was distilled under vacuum before use. The reaction profile is shown in Figure 2. The excess methacrylic acid was removed by washing repeatedly with distilled water and the resin was dried using anhydrous sodium sulfate. The refractive index of MHP was measured using an Abbe refractometer (Model 3T, Atago, Japan). The end of the reaction was indicated by the disappearance of the epoxy group of 2,3-epoxypropylmethacrylate that gave a characteristic absorption peak in the infrared region at 917 cm^{-1}, which was monitored using a Fourier transform infrared spectrophotometer (FTIR; Nicolet Impact 400D, USA). The product was further characterized by recording a NMR spectrum using a nuclear magnetic resonance spectrometer (Brooker-Avance, Switzerland; 300 MHz) and high-pressure liquid chromatography (Model 440 UV absorbance detector, Waters Associates, USA).

Synthesis of UTMA

MHP (2 mol) was inhibited with 4-methoxyphenol (500 ppm), kept overnight, and was then dissolved in chloroform (Analar grade, SD Laboratories, Bombay; 4 mol) in the presence of 1,4-di-

2,3 epoxy propyl methacrylate   methacrylic acid

↓ (base catalyst)

1,3 bis (methacryloxy) 2 hydroxy propane (MHP)

Figure 2 Reaction profile of synthesis of 1,3-bis-(methacryloxy)-2-(hydroxy propane).

Figure 3 Reaction profile of synthesis of urethane tetramethacrylate resin.

azabicyclo-[2,2,2]-octane (DABCO) used as catalyst. 1,6-hexamethylene diisocyanate (Aldrich Chemical Co., Milwaukee, WI, USA; 0.96 mol) was slowly added in an inert atmosphere at 40°C for 3 h with vigorous stirring and completed in 40 min. After the reaction was completed, the viscous resin was washed with the solvent which was subsequently removed completely from the resin under vacuum by using a flash evaporator (rotary vacuum evaporator, Buchi-type) in a water bath. The reaction mechanism is shown in Figure 3.

Refractive index of the resin was measured as before. IR spectra, NMR spectra, and HPLC of the urethane product were also recorded. The resin was stored at 20–22°C at all times.

Preparation of the Filler

Radiopaque glass powder (Schottglaswerke, Germany) was used as the filler material throughout the study. Particle size of the filler was measured using a particle size analyzer (Galai, Model CIS-1, Israel). The fine filler particles were silanated with 1% of 3-(trimethoxysilyl)propyl-methacrylate (Aldrich Chemical Co., USA) solution in acetone. The acetone was slowly evaporated by warming the mixture in a water bath at 40°C. The dried filler particles were heated at 120°C for 60 min, powdered well, and stored in a desiccator before use.

Preparation of the Composite Paste

UTMA resin was mixed with BIS–GMA in proportions of 100/0, 80/20, 60/40, 40/60, 20/80, and 0/100 by weight and thinned by using a dimethacrylate diluent to reduce the viscosity. Optimum amounts of silanated glass filler and pyrogenic silica powder along with small quantities of camphorquinone photoinitiator, tertiary amine activator, UV inhibitor, and stabilizers were incorporated into the resin mix in an agate mortar to form a homogeneous paste. Care was taken that the filler particles were mixed completely and the entire operation was carried out in dim light to prevent premature polymerization of the paste.

When light of wavelength 460–480 nm falls on the paste, the photoinitiator undergoes dissociation in the presence of tertiary amine-initiating polymerization reaction that results in the hardening of the paste into a solid mass. The mechanism of the polymerization is shown in Figure 4.

Determination of Physical Properties

Physical properties such as compressive, diametral tensile, and transverse strengths were determined for all composites prepared using UTMA/BIS–GMA in proportions stated above. A test temperature of 23–25°C was maintained during all the tests.

Compressive Strength

Samples (6-mm height × 3-mm diameter) for compressive strength (CS) measurements were prepared by light curing the composite paste packed in a split-brass mold using a visible light source (Max the Caulk, Canada) for 60 s each from both sides of the mold. The wavelength of the light varied from 460–480 nm. The surfaces

Figure 4 Polymerization initiation mechanism through camphorquinone.

of the paste were pressed flush with the mold surface using cellophane sheets before curing. After exposure, the mold was opened and the core of the composite was exposed for a further 10 s to the light source. The cured hard samples after polymerization were then stored in distilled water for 24 h at 37°C in an incubator before testing.

The conditioned samples were then subjected to a compressive load in a universal testing machine (Instron, Model 1011, UK) at a crosshead speed of 10 mm/min. The load at break was noted and the strength in megapascals calculated using the formula

$$\text{CS (MPa)} = \text{load/area} = P/\pi r^2$$

where P is the load in newtons and r is the diameter of the specimen in millimeters. A minimum of six samples were tested in each case and the standard deviation was calculated.

Diametral Tensile Strength

Samples (3-mm height × 6-mm diameter) for diametral tensile strength (DTS) measurements were prepared as stipulated[10] in ADA specification No. 27. The cured samples were then stored in distilled water for 24 h at 37°C and tested between the platens of a universal testing ma-

chine at a crosshead speed of 10 mm/min. Samples were placed on the platens in such a way that the longitudinal axis was parallel to the axis of the platens. Load at break was noted and the DTS in megapascals was calculated using the formula

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

where P is the load in newtons at break, D is the diameter in millimeters, and L is the height or thickness of the sample. A minimum of six samples were tested in each case and the standard deviation was calculated.

Vickers Microhardness

Specimens for surface microhardness were prepared as for DTS using the same mold. For each test, two specimens were used. The surface microhardness was measured on each side using a Vickers microhardness tester (Carl-Zeiss, Jena). At least eight measurements for each specimen were carried out and the average and standard deviation calculated. The diamond indentor is a square-based pyramid suitable for Vickers hardness measurements. The specimen was placed flat on a glass slide and mounted on a holder on the microscope stage. The specimen surface was examined microscopically and the indentor was then moved into position and the microscope stage was raised steadily until the required load was applied by the indentor on the specimen. In all cases, a load of 100 g was used. The load was held for 15 s before the microscope stage was steadily lowered. The indentor 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. The Vickers microhardness (H_V) was calculated using the following equation:

$$H_V \text{ (kg/mm}^2) = 1854.4P/d^2$$

where P is the load applied in grams and d is the length of the diagonal in microns.

Transverse Strength

Transverse strength (TS) test specimens were prepared as specified[11] in ISO specification No. 4049 (25-mm length, 2-mm depth, and 2-mm thickness). The cured bar samples were kept horizontally over two metal rods of 2-mm diameter

and 20 mm apart fixed on an aluminum platen (base plate). Load was applied at the middle of the specimen from the top using a third metal rod fixed to a second platen. A crosshead speed of 1 mm/min was maintained in the universal testing machine during the experiment. Load at break was noted and the transverse strength was determined using the formula

$$TS \ (MPa) = 3PL/2bd^2$$

where P is the load in newtons, L is the length of the specimen between two metal rods at the base plate, b is the thickness, and d is the depth in millimeters. A minimum of three specimens were tested in each case and the mean was calculated.

Water Sorption and Solubility

Water sorption of the composite samples stored in distilled water at 37°C was determined at intervals of 1, 7, and 14 days. Specimens of 10-mm diameter and 2-mm thickness were prepared by exposing composite pastes packed in stainless-steel molds to a visible light source for 60 s each on either side. The surface of the specimens were polished initially using 240-grit silicone carbide paper. They were subsequently washed with soap solution and distilled water in an ultrasonic cleaner to remove all dirt and oil. The samples were dried in a vacuum oven until dry weight was achieved (W_1). After storage in distilled water for different periods at 37°C, the samples were weighed again after removing the surface adherent water (W_2). The specimens were then stored in a vacuum oven until the final dry weight was again achieved (W_3). The solvent uptake (water sorbed) and solubility (amount of leachants) were determined using the following equations:

$$Water \ uptake \ (\%) = (W_2 - W_3) \times 100/W_1$$

$$Solubility \ (\%) = (W_1 - W_3) \times 100/W_1$$

Opacity

Specimens for measuring opacity were prepared[10] using a stainless-steel ring having an inside diameter of 20 ± 0.1 mm and a thickness of 1 ± 0.05 mm. The ring was placed on a flat glass and the paste was packed in the cavity. The paste was cured by exposing it to a visible light source for 4 min on each side. The mold was then kept in an incubator at 37°C for 15 min. The cured samples were removed from the mold and stored in distilled water at 37°C for 24 h. A comparison of the opacities of the specimen and two opal glass standards with $C_{0.70}$ values of 0.35 and 0.55, respectively, was made by placing the specimens and standards against a varigated black and white background. A film of distilled water covered the specimen, the standards, and also the space between them and the black and white background during observation periods.

SEM Studies

Surface morphology of the fractured composite samples were studied using a scanning electron microscope (Model 2400, Hitachi, Japan). Samples were polished and mounted on an SEM stub, coated with gold using an ion sputtering unit (E-101, Hitachi ion sputter) for 3 min under vacuum, and scanned. A magnification of ×5000– 10,000 was used during the study.

Effect of Photoinitiator Concentration on the Strength Characteristics of the 100% Urethane Composite

The effect of camphorquinone (CQ) on the strength characteristics has been studied by varying the concentration of the photoinitiator from 0.1–0.5 wt % of the resin mixture in the formulations. Pastes were prepared as described before and cured using the light source. CS, DTS, and microhardness were measured as mentioned earlier.

RESULTS AND DISCUSSION

Synthesis and Characterization of MHP

The synthesis of MHP was carried out in the presence of excess methacrylic acid to ensure that all the 2,3-epoxypropyl methacrylate [or glycidyl methacrylate (GMA)] underwent additional esterification reaction. The reaction product that is a precursor to the urethane adduct was found to be a colorless liquid having a refractive index of 1.4624. It was always stored in cold conditions to prevent premature polymerization through its dimethacrylate groups. An optimum temperature of 75°C for the reaction for 5 h ensured a yield of nearly 70% after purification with water to ensure the removal of excess methacrylic acid.

An examination of the infrared spectrum of MHP [Fig. (5a)] revealed that the characteristic

(a)

(b)

(c)

Figure 5 (a) Fourier transform infrared spectrum of 1,3-bis-(methacryloxy)-2-(hydroxy propane). (b) Nuclear magnetic resonance spectrum of 1,3-bis-(methacryloxy)-2-(hydroxy propane). (c) High pressure liquid chromatogram of 1,3-bis-(methacryloxy)-2-(hydroxy propane) [mobile phase: methanol; flow rate: 1 ml/min].

917 cm^{-1} peak of the epoxide group present in GMA has completely disappeared, thereby confirming total conversion of GMA into MHP after reaction with methacrylic acid. Important absorption peaks observed in the MHP spectra included the peaks corresponding to the carbonyl group at 1724 cm^{-1}, bending vibration of the $-C=CH_2$ peak at 947 cm^{-1}, stretching vibration of the

same group at 1637 cm^{-1}, $-O-H$ stretching vibrations at 3479 cm^{-1}, and $-C-H$ stretching at 2959 cm^{-1}.

NMR spectra [Fig. (5b)] shows four major peaks which have been characterized and shown in Table I.

Figure 5(c) shows the liquid chromatogram of MHP dissolved in spectroscopic grade methanol (mobile phase: methanol) recorded using a UV detector at 254 nm by maintaining a flow rate of 1 ml/min. A C_8 column was used, and the chromatogram indicates a major eluant after nearly 3 min with total absence of impurities. All the above data were found to support the structure of MHP as depicted in Figure 2.

Synthesis and Characterization of Urethane Adduct

The reaction product of hexamethylene diisocyanate and MHP was devoid of any isocyanate residue as excess MHP was used during the reaction in the presence of DABCO as catalyst. Complete care was taken during the reaction to prevent any oxygen initiation by purging purified nitrogen gas throughout the reaction. Temperature was also controlled to prevent thermally initiated polymerization due to excess heating. In addition, MHP used in the reaction was inhibited with 500 ppm of 4-methoxyphenol so that the dimethacrylate groups present in MHP did not participate in the reaction and only the secondary hydroxyl group reacted with the isocyanate group. Solvent chloroform was used in excess so that the reactants stayed in the miscible state and reaction proceeded without any polymerization. A reaction time of nearly 3 h at 40°C ensured a yield of nearly 98% of a low-viscosity translucent paste having a refractive index of 1.4888. Complete removal of the solvent was ensured by flash evaporating the solvent in an evaporator under vacuum at nearly 55–60°C for 5 h.

Infrared spectrum of the paste [Fig. 6(a)] revealed the characteristic carbonyl absorption

Table I   Important NMR Spectral Peaks Indicating Specific Protons Present in MHP

No.	δ	Characteristic Proton
1	1.1–1.25(t), 1.95014(s)	$-C=C-CH_3$
2	4.16–4.26(m)	$-CH_2-CH-CH_2$
3	5.59–5.63(s, m)	$trans =CH_2$
4	6.14–6.17(s, m)	$cis =CH_2$

(a)

(b)

(c)

Figure 6 (a) Fourier transform infrared spectrum of urethane tetramethacrylate resin. (b) Nuclear magnetic resonance spectrum of urethane tetramethacrylate resin. (c) High-pressure liquid chromatogram of urethane tetramethacrylate resin [mobile phase: chloroform; flow rate: 1 ml/min].

peak at 1715–1720 cm^{-1}, —N—H stretching vibration at 3369 cm^{-1}, and bending and stretching vibrations of the —C=CH$_2$ peaks at 945 and 1637 cm^{-1}, respectively. The disappearance of the 2270-cm^{-1} peak characteristic of free —N=C=O group indicated total conversion of the isocyanate into the adduct. NMR spectrum [Fig. 6(b)] shows eight major peaks that have been characterized and shown in Table II.

Table II   Important NMR Spectra Peaks Indicating Specific Protons Present in Urethane Adduct

No.	δ	Characteristic Proton
1	1.25–1.49(t)	—CH$_2$—CH$_2$—CH$_2$—
2	1.86–1.94(d)	—C=C—CH$_3$
3	2.1648(s)	—HN—C=O
4	3.1502(s)	O=C—N—CH$_2$
5	3.70–4.40(m)	—CH$_2$—CH—CH$_2$
6	5.25–5.30(d)	—HN—C=O
7	5.5924(s)	trans =CH$_2$
8	6.10–6.14(d)	cis =CH$_2$

Liquid chromatogram of the paste in chloroform (mobile-phase chloroform) recorded using a nonbonded silica column at a flow rate of 1 ml/min indicated the presence of a number of other chemicals along with the adduct [Fig. 6(c)]. This can be attributed to the presence of inhibitor, monourethane adduct, and unreacted MHP that is present in excess. However, as all these chemicals are mandatory or supportive in nature for composite preparation, the paste was used as such and not purified further. All the above data were found to support the structure of UTMA as depicted in Figure 3.

Synthesis and Characterization of BIS-GMA

Infrared spectrum of the previously synthesized BIS–GMA is shown in Figure 7. A detailed spectral and chromatographic analysis of BIS–GMA has been reported before.[9,12] BIS–GMA has been conventionally used for all dental composites as the organic binder resin. The resin used in our

Figure 7 Fourier transform infrared spectrum of Bisphenol A–glycidyl methacrylate [BIS–GMA].

Figure 8 Bar diagram indicating changes in compressive strength values of composites with varying proportions of binder resin mixture.

experiments was a highly viscous transparent resin synthesized in our laboratory having a refractive index of 1.5508, which corresponded with reported values. As BIS–GMA contains two aromatic rings in its chain, it tends to be highly viscous, very difficult to flow, and necessitates a dimethacrylate monomer for diluting the resin. It is because of these difficulties inherent with BIS–GMA that we gradually substituted BIS–GMA with increasing amounts of the low-viscosity aliphatic UTMA adduct and studied the properties.

Radiopaque glass particles were used in all the composite pastes prepared. We reported earlier on the development of light-cured dental composites using quartz as the filler[2] and the radiopaque composites using glass filler and BIS–GMA as the resin matrix.[3] Particle size analysis showed the average particle size of the filler to be less than 1 μm. The silanated filler also ensured total bonding between the filler particles and the resin.

Studies on Composite Samples Prepared at Different Urethane Adduct/BIS–GMA Proportions

Curing of the pastes prepared from various proportions of the resin binders was initiated by visible light and found to be very easy and fast. Even a small exposure time period of 10 s was enough to harden the paste. The samples were aesthetically superior (being ivory-white in color) and blended with tooth surfaces perfectly.

Figure 8 shows the variation in compressive strength values with increasing urethane content in the binder resin mixture. It can be seen that

there is a gradual increase of strength when urethane content was increased and 100% urethane samples showed a compressive strength in the range of 350–450 MPa. Considering the fact that the minimum stipulated CS value for satisfactory clinical performance is 220 MPa, the increase in CS values may be attributed to the lower viscosity of the resin and easy mixing and bonding of the filler in the resin resulting in a homogeneous paste that yielded composites with higher strength. The tetramethacrylate groups of the urethane molecules tend to polymerize and crosslink much faster than the dimethacrylate molecule of BIS–GMA. Also, it was found that the photoinitiator and other additives became easier to mix and homogenize as the urethane content increased. Another interesting feature noticed with urethane composites was their excellent color characteristics compared to BIS–GMA composites.

ADA specification No. 27 for dental materials stipulate that the DTS value of the composites should be at least 34 MPa if considered for use in dentistry. It can be seen that all the composites prepared and tested using the six different formulations had DTS values > 40 MPa (Fig. 9). However, it was noticed that there is no substantial difference in DTS values when the urethane content increased and values varied between 40 and 50 MPa and were within standard deviation limits of each other. This balance in strength, which was not observed in CS measurements, can be

Figure 9 Bar diagram indicating changes in diametral tensile strength values of composites with varying proportions of binder resin mixture.

Figure 10 Bar diagram indicating changes in microhardness (Vickers) values of composites with varying proportions of binder resin mixture.

attributed mainly to the linear aromatic rings in BIS–GMA molecules, which tends to improve the tensile strength of the composite where molecular packing was easier compared to the linear aliphatic groups of the urethane.

Vickers microhardness values show drastic improvement when the urethane content increases in the resin binder mixture. Whereas BIS–GMA-based composites were reported to have a microhardness in the range of 45–55 MPa, 100% urethane-based composites showed a microhardness

Figure 12 Bar diagram indicating changes in water sorption values of composites with time for varying proportions of binder resin mixture.

in the range of nearly 75–85 MPa. It can be clearly observed from Figure 10 that the values increase progressively when the urethane content increases from 20 to 40 to 60 to 80 and 100 wt %. One possible explanation is that the filler compatibility with the urethane resin is much better compared to BIS–GMA resin and the evidence of a resin-rich layer is almost negligible.

Although the minimum stipulated value for three-point bending or transverse strength of dental composites is 50 MPa,[11] all composites prepared from the six different formulations showed values in the range of 80 and above, although not

Figure 11 Bar diagram indicating changes in transverse strength values of composites with varying proportions of binder resin mixture.

Figure 13 Bar diagram indicating changes in solubility values of composites with time for varying proportions of binder resin mixture.

Figure 14 Scanning electron micrographs of fractured surfaces of composites prepared using binder resin proportions of BIS–GMA/UTMA (a) 100/0, (b) 80/20, (c) 60/40, (d) 40/60, (e) 20/80, and (f) 0/100.

much variation in values was observed with changes in urethane content in the case of TS (Fig. 11). It should be kept in mind that the diameter-to-height ratio of the specimens were higher than unity as in case of DTS, whereas in CS measurements, it was less than unity. Therefore, the pattern of molecular packing and orientation of the molecules in the composite is expected to contribute substantially to the strength characteristics of the composites.

Figure 12 clearly illustrates the water sorption characteristics of the composite. It can be seen that the adsorbed water content increases progressively with time (1, 7, and 14 days). Urethane composites tend to show a slightly higher sorption value compared to BIS–GMA composites, which is expected because of the presence of aliphatic and urethane linkages in the molecule where permeability is easier compared to the bulky nature of BIS–GMA in the aromatic composites. The diffusion seems Fickian in nature, although not of the first order.

The amount of leachable components from the composite during sorption process also is found to increase with time as well as with urethane content in the molecule (Fig. 13). The solubility is due to the migration of degraded filler ion particles, unreacted monomers, and silane, if any. The explanation given in the sorption process holds true here also as the movement of degraded filler and residual monomer molecules is facilitated among aliphatic molecules.

The opacity values of all the composites ($C_{0.70}$) under study were found to lie between 0.35 and 0.55 and be acceptable as per the stipulated ADA specification.[10] It was observed that the samples

(e)

(f)

Figure 14 (*Continued from the previous page*)

Figure 15 Bar diagram indicating changes in compressive strength values with increase in photoinitiator concentration for urethane based composites.

tended to become more translucent with an increase in urethane content. In fact, one of the disadvantages observed for the BIS–GMA composite was its excess transparency. This problem can be remedied by incorporating urethane into the resin binder.

The SEMs [Fig. 14(a–f)] were taken from fractured surfaces of the different composites prepared. It can be seen that the filler/resin interface is highly homogenous in urethane-rich composites compared to BIS–GMA-rich composites, explaining their higher strength and hardness due to excellent resin/filler bonding characteristics. Also, the porosity is highly reduced.

It has been previously reported that the content of photoinitiator and time of exposure has a significant effect on the properties of dental light-cured composites.[13] In this study, the amount of photoinitiator varied from 0.1 to 0.5 wt % for 100% UTMA-based composites and determined

the variation in compressive, DTS and microhardness. It can be seen from Figure 15 that the compressive strength improves considerably with photoinitiator concentration, the values reaching nearly 450 MPa at 0.5%. This can be attributed to a higher free-radical concentration, thereby leading to a faster polymerization rate and crosslinking. However, DTS values do not show appreciable change (Fig. 16), but all the values were > 40 MPa, the required minimum limit being 34 MPa. Microhardness values, on the other hand, were found to improve drastically with CQ concentration (Fig. 17). The linear aliphatic UTMA chain

Figure 16 Bar diagram indicating changes in diametral tensile strength values with increase in photoinitiator concentration for urethane-based composites.

Figure 17 Bar diagram indicating changes in micro-hardness (Vickers) values with an increase in photoinitiator concentration for urethane-based composites.

tends to induce more hardness on the surface than the bulky BIS–GMA molecules. As the photoinitiator tends to impart yellow coloration to the composite, a maximum limit of 0.5 wt % of the resin mixture was maintained and not increased further.

CONCLUSIONS

MHP, a dimethacrylatehydroxy resin, can be synthesized by reacting 2,3-epoxypropylmethacrylate with methacrylic acid in the presence of a base catalyst. MHP, when reacted with hexamethylene diisocyanate under inert atmosphere at 40°C, tends to produce a UTMA adduct. This adduct can be treated with a silanated radiopaque glass filler and other additives to provide a paste of high viscosity that, when exposed to a visible light source at 440–480 nm, tends to harden within 10–20 s. The compressive strength and microhardness of the urethane adduct-based composites are found to increase with urethane content in the resin binder mixture and to be highly superior to conventional BIS–GMA-based composites, whereas the DTS and TS are comparable. Water sorption and solubility values tend to increase with time and urethane content in the

composite samples. Increase in photoinitiator concentration is found to improve the compressive strength and microhardness of urethane composites appreciably. The aesthetic characteristics such as opacity, improved strength, and hardness of urethane composites makes it an ideal substitute for BIS–GMA-based composites in dentistry.

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