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Effect of diluent upon the properties of a visible-light-cured dental composite

V. KALLIYANA KRISHNAN*, K. MANJUSHA, V. YAMUNA
Biomedical Technology Wing, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Thiruvananthapuram 695 012, India

Four long-chain aliphatic organic diluents, triethylene glycol dimethacrylate (TEGDMA), ethylene glycol dimethacrylate (EDMA), triethyleneglycol diacrylate (TEGDA) and tetraethylene glycol diacrylate (TTEGDA) were used as diluents for preparing a visible-light-cured dental composite. Cured samples of pastes prepared using the above diluents were stored separately for a period of 60 days in distilled water at 37 °C and tested for changes in compressive strength, diametral tensile strength and microhardness at specific intervals of 1, 7, 14, 21, 28 and 60 days. Samples prepared using TEGDMA showed better strength values initially compared with the composite specimens prepared using the rest of the diluents although they are found to deteriorate slowly upon storage in distilled water up to 60 days. Samples prepared using EDMA showed retention in properties whereas samples prepared using TEGDA and TTEGDA showed large deviations in strength values during the first 28 days, did not deteriorate further and were found either to show improvement upon ageing or to remain constant. Sorption values seem to reach a maximum for all composites and then to decrease further after 14 days whereas solubility is found to increase with time.

1. Introduction

Dental composites based on bisphenol A–glycidyl methacrylate (BIS–GMA) have been reported [1] to contain an aliphatic diluent in order to reduce the high viscosity of BIS–GMA as well as to increase the degree of conversion. The viscosity of the BIS–GMA resin determines the quantity of filler that can be incorporated into the resin which in turn affects the final properties of the composite. Most commonly, diacrylates and dimethacrylates of various chain lengths, having unsaturated end groups have been used as diluents [2]. In this work, four different long-chain aliphatic diluents such as triethylene glycol dimethacrylate (TEGDMA), ethylene glycol dimethacrylate (EDMA), triethyleneglycol diacrylate (TEGDA) and tetraethylene glycol diacrylate (TTEGDA) have been used as diluents while preparing the composite samples. The variation in the physical properties such as the compressive strength, the diametral tensile strength and the Vickers microhardness have been measured at regular intervals with ageing of the samples stored in distilled water at 37 °C up to 60 days.

2. Experimental details

2.1. Preparation of composite paste

BIS-GMA resin (about 0.145 mol) was synthesized in the laboratory using a reported procedure [3]. TEGDMA, TEGDA and TTEGDA (all from Aldrich Chemicals, USA) and EDMA (all about 0.1 mol) (Merck Schuchardt, Germany) were used as received to dilute the resin. Their chemical structures are shown in Fig. 1.

Quartz powder, available from local sources, was used as the filler material and silanated after purification by washing with acid and subsequent heat treatment [4]. Camphorquinone photoinitiator (99% purity), dimethyl *p*-toluidine (DMPT) (synthesis grade) and 3-trimethoxysilyl propyl methacrylate (97%) used as coupling agents were all procured from Aldrich Chemicals, USA. DMPT was purified by distillation under reduced pressure before use. All other chemicals were used as received.

2.2. Studies on mechanical properties

2.2.1. Compressive strength: specimen preparation

The compressive strength (CS), diametral tensile strength (DTS) and microhardness (MH) were measured for the composite specimens before and after ageing for different periods. Specimens of 3 mm diameter and 6 mm height were prepared for CS measurement by curing the composite specimens in cavities of appropriate size in a brass mould kept between two glass plates and held using a C-clamp. Each specimen was exposed to a light source (440–480 nm wavelength; Caulk the Max, UK) for 60 s each on both sides for curing. Subsequently the samples were released from

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*Author to whom correspondence should be addressed. Fax: 91-471-341814; e-mail:bmtwing@md2.vsnl.net.in

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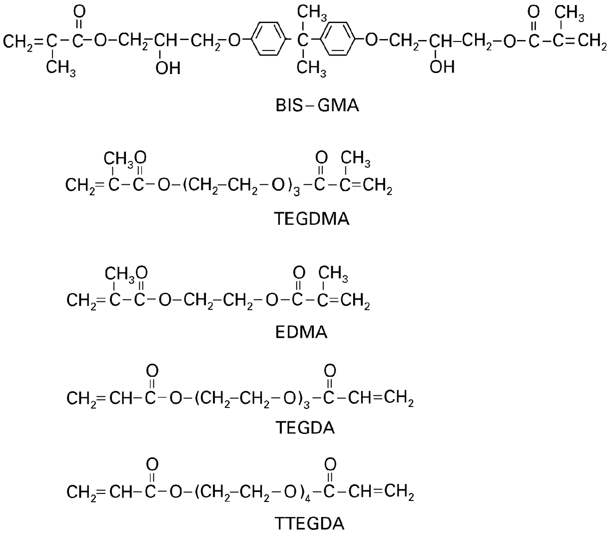

Figure 1 Chemical structures of reagents used.

the mould, and the inner surfaces of the cured composite were exposed to the light source for a further 20 s to ensure uniform curing within the core of the material. At least ten specimens of each paste were thus cured and stored at 37 °C in distilled water for different ageing periods. Care was taken to stir the media intermittently during the ageing studies.

2.2.2. Diametral tensile strength: specimen preparation

DTS specimens of 6 mm diameter and 3 mm height were prepared similarly using a stainless steel mould. Paste packed in the mould between glass slides was exposed to a light source (440–480 nm wavelength; Caulk the Max, UK) for 60 s each on both sides for curing. Curing was done as before using the visible light source. The cured specimens were taken out and stored at 37 °C in distilled water for different ageing periods.

Aged CS and DTS specimens were taken out at specific intervals of 1, 7, 14, 21, 28 and 60 days and the changes in CS and DTS values were evaluated using a universal testing machine (Instron model 1011, UK) using a reported procedure [5]. The cross-head speed of 10 mm min^{-1} was maintained for all tests. A minimum of six specimens was used for testing for each ageing period and the mean calculated. For DTS measurements a minimum of eight specimens were tested. The load at which break occurred was noted and the CS and DTS values were calculated using the equation

$$\text{CS (MPa)} = \frac{P}{\pi r^2}$$

where P is the load applied in newtons and r is the radius of the specimen in millimetres, and the equation

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

where D is the diameter of specimen in millimetres and L is the height of the specimen in millimetres.

2.2.3. Microhardness measurements

Specimens for surface microhardness were prepared as was done for DTS specimens using the same mould. For each testing, 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 taken. The diamond indenter 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 indenter was then moved into position and the microscope stage raised steadily until the required load was applied by the indenter upon 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 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. The Vickers microhardness, the H_v, was calculated using the following equation:

$$H_v\ (\text{kgf mm}^{-2}) = \frac{1854.4P}{d^2}$$

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

2.3. Water sorption and solubility studies

Water sorption of the composite samples stored in distilled water at 37 °C was determined at intervals of 1, 7, 14, 21, 28 and 60 days. Specimens of 10 mm diameter and 2 mm thickness were prepared by exposing composite pastes packed in stainless steel moulds to a visible light source for 60 s each on either side. The surface of the specimens were polished initially using 240 grit silicon carbide paper. They were subsequently washed with soapy water and distilled water in an ultrasonic cleaner to remove all dirt and oil which may be sticking to them. The samples were dried in a vacuum oven until a dry weight, W_1, was achieved. After storage in distilled water for different periods at 37 °C, the samples were weighed again after removing the surface-adherent water to give W_2. The specimens were then stored in a vacuum oven until the final dry weight, W_3 was again achieved. The solvent uptake (water sorbed) and solubility (amount of leachants) were determined using the following equations:

$$\text{water uptake (\%)} = \frac{W_2 - W_3}{W_1} \times 100$$

$$\text{solubility (\%)} = \frac{W_1 - W_3}{W_1} \times 100$$

3. Results and discussion

The efficacy of a diluent in a composite is mainly determined by the degree of conversion of the reactive species (in this case, BIS–GMA) and its efficiency as a cross-linker. It has been reported [6] that diluent monomers may increase the degree of conversion for stereochemical reasons as there is evidence to suggest that even heat-polymerized BIS–GMA is only partly polymerized. 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. This has been reported previously for BIS–GMA-based resins [7]. However, above a particular threshold value, this does not seem to be of much practical use. This is because, during the polymerization reaction of the BIS-GMA 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. It is also well known that the mechanical properties are related closely to the degree of conversion [8]. In our study we have kept the concentration of diluent at an optimum level (about 0.1 mol) in all four composite pastes. All diluents were also found to mix easily with the highly viscous organic resin binder, and incorporation of the the quartz filler into the resin mixture was found to be easy.

The CS values measured after storage for 60 days (Table I) in water at 37 °C in all cases were reasonable, assuming that 200–220 MPa is the minimum value required for clinical use, did not show much change with ageing and were well within the standard deviation values recorded, which was less than 10% in most cases. Statistical analysis (*t* test) indicated insignificant variation ($P > 0.05$) in CS for all populations after storage for 60 days whereas DTS values for samples containing EDMA remained fairly constant, showing significant statistical variation ($P < 0.05$) compared with other systems, which showed a decreasing trend with time. However, it should be mentioned that the values were well in excess of the minimum of 34 MPa stipulated by the American Dental Association [5]. The percentage of unreacted diluent molecules is likely to be minimal in the case of EDMA, possibly because it is a much smaller molecule. These unreacted molecules tend to leach out during ageing, resulting in considerable loss in strength, and may have adverse tissue effects [9]. At a given concentration, the mobility of the reactive species in EDMA is also likely to be enhanced, resulting in a higher degree of conversion. The degradation of filler particles at the matrix–resin interface by absorbed water [10] varies drastically in each case, resulting in various degrees of solubility (Fig. 2), which increase with time as expected. The failure may occur at the filler surface, the filler–silane interface or the silane–resin interface. The degree of water sorption (Fig. 3) may be determined to a high extent by the degree of hydrophilicity of the unreacted diluent molecules present in the composite. It is seen to reach saturation after nearly 28 days for all the composites and then to level off, which indicates that equilibrium has been established by that time. It should be emphasized that the DTS values did not deteriorate below the threshold value of 34 MPa in any of the composites.

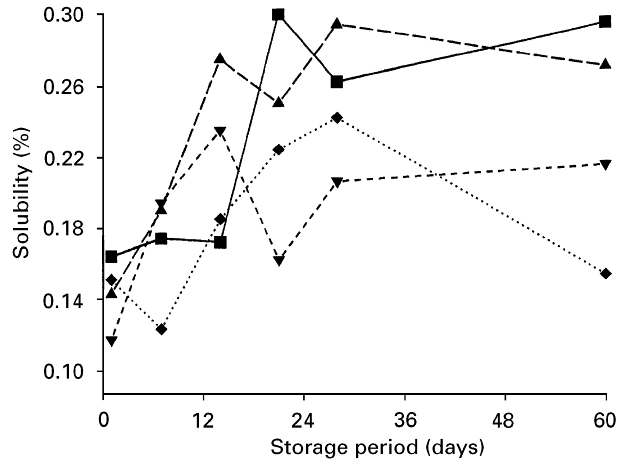

Figure 2 Solubility values at different ageing periods determined for composites prepared using TEGDMA (■), EDMA (▲), TEGDA (▼) and TTEGDA (◆).

An examination of Fig. 4 shows that the microhardness values are not much affected in the case of EDMA and the changes observed are well within the experimental error whereas, with TEGDMA, there is a noticeable decrease in hardness values, indicating that sorption of water is detrimental to the composite in the long run. The hydrolytic degradation of filler particles and the presence of a "resin-rich layer" at the surface of the composite also must have contributed to a considerable extent to the reduction in microhardness in the case of TEGDMA.

TABLE I Variation in strength values for composites aged in distilled water for up to 60 days at 37 °C

Diluent used	CS (MPa)						DTS (MPa)					
	1 day	7 days	14 days	21 days	28 days	60 days	1 day	7 days	14 days	21 days	28 days	60 days
TEGDMA	263.23 ± 8.65	275.25 ± 14.73	258.93 ± 19.30	234.39 ± 21.66	283.49 ± 15.46	247.83 ± 14.58	51.58 ± 1.76	54.31 ± 1.01	48.46 ± 2.39	47.72 ± 4.27	49.01 ± 2.40	40.00 ± 2.30
EDMA	239.00 ± 15.94	281.29 ± 17.71	246.45 ± 16.13	314.99 ± 23.07	254.76 ± 15.72	255.37 ± 36.38	44.47 ± 2.07	49.56 ± 3.93	48.09 ± 2.90	46.23 ± 3.01	46.24 ± 2.01	46.64 ± 3.47
TEGDA	209.46 ± 12.60	224.02 ± 9.88	212.47 ± 14.90	240.59 ± 6.38	227.18 ± 10.50	240.52 ± 10.85	45.49 ± 1.13	47.15 ± 2.54	37.79 ± 1.06	38.89 ± 4.42	36.91 ± 1.44	37.60 ± 1.72
TTEGDA	234.90 ± 2.70	235.04 ± 11.62	246.47 ± 20.82	243.38 ± 9.55	240.05 ± 14.24	245.09 ± 17.21	46.20 ± 0.83	46.75 ± 2.58	47.21 ± 1.73	44.89 ± 2.20	41.05 ± 2.60	42.03 ± 3.04

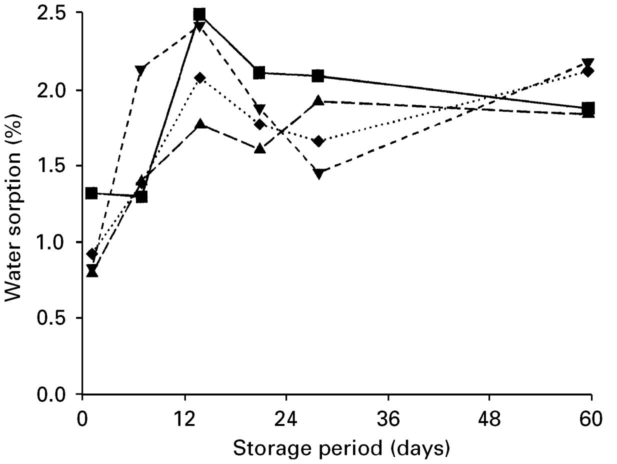

Figure 3 Solvent uptake of samples for different ageing periods determined for composites prepared using TEGDMA (■), EDMA (▲), TEGDA (▼) and TTEGDA (◆).

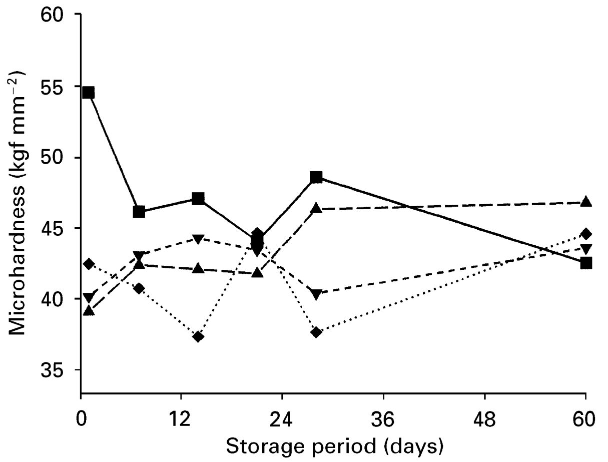

Figure 4 Variation in microhardness values with time for the composites prepared using TEGDMA (■), EDMA (▲), TEGDA (▼) and TTEGDA (◆).

4. Conclusions

Organic dimethacrylate and diacrylate diluents such as TEGDMA, EDMA, TEGDA and TTEGDA can be successfully used as thinners and cross-linkers for preparing visible-light-cured composite pastes resulting in a hard material with excellent properties upon curing. TEGDMA seems to be a better choice of the four diluents tested, providing better CS and DTS values although there is a tendency for the values to reduce with ageing. The strength characteristics are also not drastically affected by the change of diluent, although use of a low-molecular-weight thinner such as EDMA seems to favour retention of properties upon ageing.

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