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Dental application of polyfunctional urethane comonomers to composite resin veneering materials

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Urethane monomer/diluent monomer mixtures were used in dental composite resin veneering materials filled with various ratios of powder (filler)/liquid (comonomer), P/L. Hardness values of unfilled resins containing benzoyl peroxide only (BP0; 0.5 wt%), and filled resins (included trimethylol propane trimethacrylate (TMPT) composite filler) were tested. Significant increases in hardness were obtained with the use of TMPT composite filler in the resins. Also, their modulus values measured by bend test showed an increasing trend, compared to a commercial composite resin veneering material (a control sample; CONT) with a lower filler content (50 wt%). The DME–DPMDC/HPDM comonomer (dimethacryloxyethyl diphenylmethane-4,4′-dicarbamate/hydroxypropyl dimethacrylate), which showed a smaller fraction of surface porosity, gave greater mechanical strength values at P/L ratios of 0.55 (17.8 wt% filler content) to 1.20 (27.3 wt%) than a CONT resin. The coefficient of thermal expansion was smaller in urethane-based filling materials than a CONT resin. Also, greater activation energy of thermal decomposition was observed in the resin samples with P/L ratio 0.75 to 1.20 than in a CONT resin. Thermally-induced decomposition occurred with smaller weight loss in the experimental filled resins than in a CONT resin.

1. Introduction

Dental resin composites are available as chemically cured and visible light (VL) cured resins, classified by the polymerization method [1–5]. VL-cured resin composites for crown and bridge veneers have been used because of their ease of handling and relatively low cost [6, 7]. Their hardness and mechanical strength values increase with the degree of polymerization (curing), showing that monomer composition is very important with respect to polymerization [8, 9]. Bis-GMA/TEGDMA bases (bisphenol-A glycidyl methacrylate/triethylene glycol dimethacrylate) are typical resins used as restorative materials, as are other monomer mixtures containing urethane linkages, because the resin matrix is strengthened by the addition of a urethane comonomer to bis-GMA/TEGDMA resins [10–13]. These results suggest that the addition of a urethane comonomer to bis-GMA/TEGDMA-based resins facilitates curing of the urethane monomer at a lower activation energy. Previous studies have been of VL-cured resins containing photo-initiators and reducing agents. There have, however, been only a few reported studies of reports chemically-cured urethane dimethacrylate (UDMA)-based resins containing diluent monomer [3, 4]. The diluent monomer TEGDMA has been used with bis-GMA-based resins in commercial dental resin composites [2–13]. Also urethanes containing HPDM as a diluent monomer have been developed for dental application as resin veneering materials [14]. It was therefore deduced that the polymerization reaction was facilitated by polyfunctional urethane linkages in the resin base [10]. To study this proposition, different types of urethane linkages in the resin matrix of chemically-cured composite have been examined.

This study measured hardness and modulus values of both unfilled and filled polyfunctional urethane/diluent monomer mixtures, together with compressive strength and diametral tensile strength. The activation energy for the thermal decomposition of toughened DME-DPMDC/HPDM resin matrix was determined for various P/L ratios in the range 0.55 (17.8 wt% filler content) to 1.20 (27.3 wt% filler).

2. Materials and methods

The nine experimental resins (A0, A1, A2, B0, B1, B2, C0, C1, C2) examined in this study are listed in Table I, and the comonomers in Figs 1 and 2. The resins

TABLE I Chemical composition and Knoop hardness number of the experimental resins; results given as means (standard deviation)

Code	Chemical composition (wt %)				Hardness Hk
	DME-TDC	DME-DPMDC	HPDM	TEGDMA	
A0*	–	20	80	–	11(0.6)
A1*	–	30	70	–	21(0.7)
A2**	–	30	70	–	30(0.5)
B0*	20	–	80	–	10(0.3)
B1*	40	–	60	–	23(1.5)
B2**	40	–	60	–	32(1.2)
C0*	–	20	–	80	8(0.6)
C1*	–	40	–	60	18(0.9)
C2**	–	40	–	60	26(2.1)
CONT	UDMA + TEGDMA				18(0.7)

* BPO = 0.5 wt %

** TMPT composite filler = 23 wt %

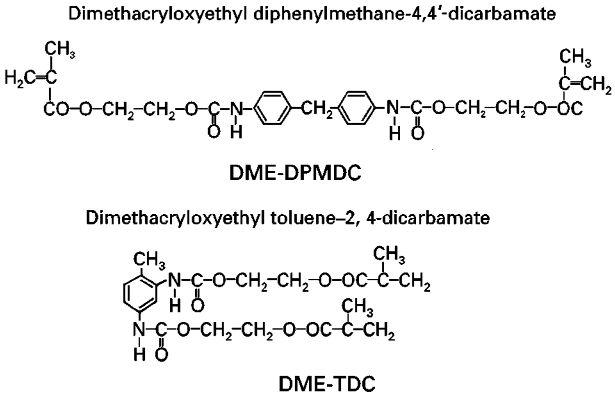

Figure 1 Urethane comonomers tested, DME-DPMDC and DME-TDC.

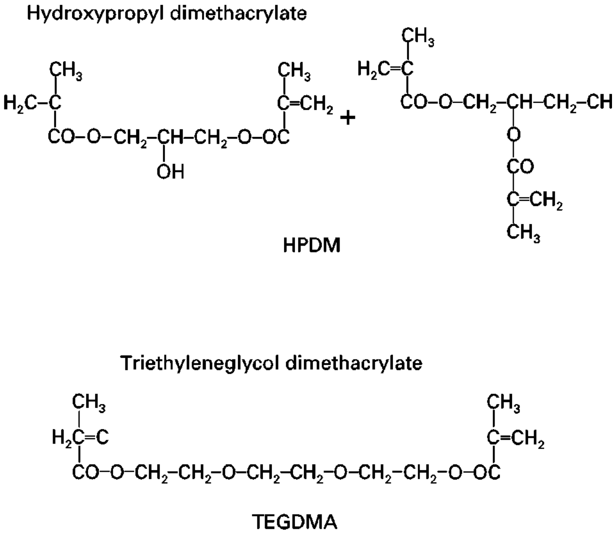

Figure 2 Diluent monomers used, HPDM and TEGDMA.

contained BPO (0.5 wt %; Katayama Kagaku Kougyou, Osaka) on the resin matrix; A2, B2 and C2 included TMPT composite filler (23.0 wt %) added to each of the resins A1, B1 and C1.

Various filler loadings were used at P (filler)/L (resin comonomer) ratios between 0.55 (17.8 wt %) and 1.20 (27.3 wt %). The filler content was lower than that in conventional posterior restorative resins, which have more than 60 wt % filler. Lower filler content was used in order to obtain a toughened resin matrix with a smaller filler content as a heat-cured composite resin veneering material. Filler contents vary from 47 to 63 wt % in commercial VL-cured veneering materials [7].

The resin materials used were urethane comonomers DME-TDC (dimethacryloxyethyl toluene-2,4-dicarbamate) and DME-DPMDC diluted by HPDM and TEGDMA, described in Figs 1 and 2. They have urethane linkages (NHCOO–) in their structures. HPDM is synthesized by methacrylic acid (0.5 mol) and glycidyl methacrylate (0.5 mol) using inhibitor (0.5 wt %; m-dinitrobenzene) and accelerator (0.01 mol; N,N-dimethyl benzylamine) at 70 °C for 10 h. The urethane monomers DME-TDC and DME-DPMDC were synthesized according to the method of Buonocore and Casciani [15].

The urethane monomers DME-TDC and DME-DPMDC were prepared by addition of 2-HEMA (1.0 mol; 2-hydroxyethyl methacrylate) to 2,4-TDC (0.45 mol; toluene-2,4-diisocyanate) as described previously [10–12]. The mixtures were heated for 2 to 3 h at 45 °C, and the catalyst and inhibitor used were, respectively, triethylenediamine (TEDA; 0.01 mol) and hydroquinone monomethyl ether (MEHQ; 0.5 wt % to the base mixture). Diluent monomers, such as HPDM (hydroxypropyl dimethacrylate) and TEGDMA (triethyleneglycol dimethacrylate, Wako Junyaku Kougyou, Wakayama) were added to the urethane monomers. TMPT composite filler was prepared using commercial inorganic silica (50 wt % colloidal silica Aerosil RM 50; Nippon Aerosil Co, Tokyo) coupled by trimethylol propane trimethacrylate (TMPT; 50 wt %). As a CONT resin, a commercial composite resin veneering material (Thermoresin, GC Co, Tokyo; 50% by weight of filler) was used. All samples tested were polymerized by heat curing at 120 °C. The curing condition in this study was selected according to the post-cured heat condition used in an earlier report [7].

Knoop hardness value (100 g loading for 30 s; HMV2000, Shimadzu Co, Kyoto) and surface porosity were measured. Compressive strength and diametral tensile strength were measured at 2.0 mm/min and 0.5 mm/min, respectively (AUTOGRAPH, Shimadzu Co, Kyoto). Ten cylindrical samples of 3 mm diameter and 5 mm height were used for each test.

Bend test modulus values were measured using a beam ($2.5 \times 10 \times 60$ mm) supported at each end under a static load. Flexture tests on five specimen samples were performed in the testing machine at a crosshead speed of 0.5 mm/min (AUTOGRAPH, Shimadzu Co, Kyoto). The modulus (E_B) was calculated by the formula:

$$E_B = WL^3/4bh^3d$$

where W is the proportional limit before fracture, L the distance between the supports (50 mm), b the width of the specimen (10 mm), h the thickness of the specimen (2.5 mm) and d the deflection at the centre at the proportional limit [17].

The thermal expansion coefficient and TG (thermogravimetry) of the thermal decomposition process of the resin matrix were measured using unfilled and filled samples (30 mg) with a thermal analyser (DT-50; Shimadzu Co, Kyoto), using alumina powders as a standard (30 mg). The heating rates were 2, 5 and 10 °C/min during heating to 400 °C under nitrogen gas flow (30 ml/min). The weight loss at each heating rate was analysed using an Ozawa plot [8, 9, 11, 16]. The values obtained changed with increasing heating rate. Activation energy values were calculated. For each material, seven thermal analysis measurements were taken.

3. Results

Table I lists the hardness values for the chemically-cured specimens. The 20/80 formulation gave lower values than the other formulations. The porosity percentage area in A1 resin was below 0.1%, whereas in other resins it ranged from 0.5 to 2.0%. Table II lists values of compressive strength (C) and diametral tensile strength (DT). Table III indicates modulus values obtained in the bend tests. Thermal analysis results are given as thermal expansion coefficient data (Table IV), activation energy of thermal decomposition (Table V), and TG curves (Fig. 3).

TABLE II Compressive strength (C) and diametral tensile strength (DT) in the DME-DPMDC/HPDM-based filled resins and a commercial resin (CONT). P/L ratio = 0.55 to 1.20

P/L	Mechanical strength	
	C (MPa)	DT (MPa)
0.55	343.0(52.1)	37.2(3.4)
0.65	392.0(24.5)	39.2(2.9)
0.75	416.5(20.1)	40.2(1.0)
0.85	420.4(19.4)	45.1(4.9)
0.90	422.4(15.7)	45.5(3.4)
0.95	422.9(45.1)	45.4(2.2)
1.00	401.8(29.4)	41.2(7.4)
1.10	352.8(49.0)	28.4(1.5)
1.20	350.2(55.4)	25.5(2.4)
CONT	220.5(24.5)	27.4(1.2)

Number in parenthesis are standard deviations

TABLE III Bend test modulus values in the DME-DPMDC/HPDM-based filled resins and a commercial resin (CONT). P/L ratio = 0.55 to 1.20. Mean (standard deviation)

P/L	Modulus (MPa)
0.55	2744(196)
0.65	2764(19)
0.75	2940(200)
0.85	2940(200)
0.90	2960(245)
0.95	3040(340)
1.00	2840(190)
1.10	2764(25)
1.20	2720(45)
CONT	2254(65)

TABLE IV Thermal expansion coefficient ($\times 10^{-4}$/°C) in the DME-DPMDC/HPDM-based filled resins and a commercial resin (CONT). P/L ratio = 0.55 to 1.20. Mean (standard deviation)

P/L	Temperature range (°C)			
	30–40	40–50	50–60	60–70
0.55	15.7	23.0	32.5	37.4
0.65	16.9	20.6	30.8	35.8
0.75	15.1	15.9	33.8	35.1
0.85	8.1	18.5	28.6	33.9
0.90	10.7	15.2	26.7	32.8
0.95	10.0	17.4	27.3	32.8
1.00	7.8	17.8	26.3	29.1
1.10	10.1	17.3	27.6	32.4
1.20	4.6	12.1	22.7	29.1
CONT	14.2	27.7	40.2	53.9

TABLE V Activation energy of thermal decomposition in the DME-DPMDC/HPDM-based filled resins and a commercial resin (CONT). P/L ratio = 0.55 to 1.20. Mean (standard deviation)

P/L	Activation energy (kJ/mol)
0.55	83.7(2.1)
0.65	76.1(1.6)
0.75	211.3(6.3)
0.85	267.8(8.4)
0.90	286.2(10.0)
0.95	285.3(14.6)
1.00	328.4(9.2)
1.10	277.8(8.8)
1.20	219.2(3.8)
CONT	126.4(6.3)

4. Discussion

Addition of either HPDM or TEGDMA as a diluent monomer to the resin component resulted in a progressive increase in the hardness. Higher mechanical strength values were obtained for the DME-DPMDC/HPDM copolymers containing various filler contents than for the CONT resin sample, associated with the increased modulus values in the experimental resin veneering materials. The urethanes

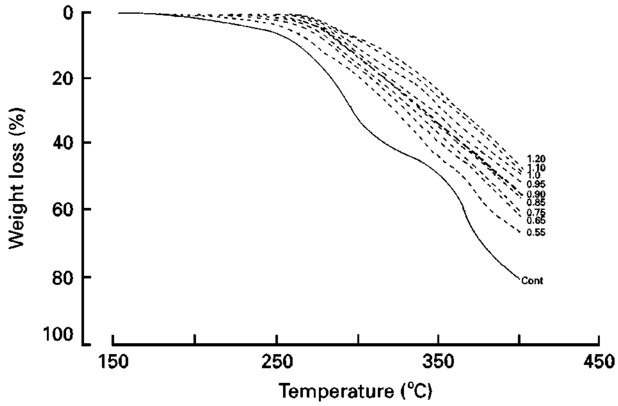

Figure 3 TG curves for the DME-DPMDC/HPDM-based filled resins and a commercial resin (CONT) at a heating rate of 2 °C/min. P/L ratio = 0.55 to 1.20.

containing HPDM showed almost the same water uptake (67.8 mg over 14 days at 37 °C) as a commercial resin (about 70 mg) [14], and urethane-based resin veneering materials remained stable for a longer immersion period in distilled water [7]. Within the copolymer samples tested, there appeared to be a significant difference between A1 and A2, B1 and B2, or C1 and C2 ($p < 0.05$). However, there is no significant difference between the unfilled resins and filled resins (Table I). Addition of filler to A1, B1 or C1 resin matrix (TMPT filler content = 23.0 wt %) resulted in improved hardness values. The average bend test modulus values ranged from 2720 to 3040 MPa (Table III), showing greater values than that in the UDMA-based CONT sample (2254 MPa). The resin veneering materials were toughened by the experimental comonomers, so that their modulus values approached that of acrylic resin (2940 MPa) [18].

The resin surface was examined because it is related to curing performance and monomer viscosity (3.5 to 7.2 N s/m^2), whereas a commercial resin sample showed 7.1 N s/m^2) [19–22]. Because its surface porosity was less than 0.1%, the resin matrix selected in this study was DME-DPMDC/HPDM. In B1 resin (DME-TDC/HPDM), higher surface porosity (about 2.0%) was observed, because the viscosity of B1 resin was higher than that of the others resins, as judged by mechanical mixing. The resin matrix of the experimental materials exhibited enhanced thermal stability compared to the CONT resin (Fig. 3). In each test temperature range, the coefficient of thermal expansion of DME-DPMDC/HPDM based filled resins had smaller values than a CONT resin (a composite resin veneering material). These values were relatively greater than that of acrylic resin material (0.81×10^{-4} per degree) [23].

Statistical analysis of activation energy (Table V) showed that the filled resins had a significantly higher energy than a CONT resin sample ($p < 0.05$). In the 30(bis-GMA)/70(TEGDMA) formulation [9], rapid decomposition occurred at about 180 °C. The formulation of 30(urethane)/70(diluent monomer) decomposed at a higher temperature than the formulation reported in [9].

It may be summarized that DME-DPMDC/HPDM resins demonstrated significantly higher values of compressive strength and diametral tensile strength, associated with increased modulus values, when 0.85, 0.90 and 0.95 (P/L) ratios were used. This increased strength was obtained for the DME-DPMDC/HPDM matrix with TMPT composite filler. The results suggest that these resin composites may be applied as a resin veneering material in the dental field.

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