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Dental application of crystalline monomer with urethane linkages: a thermoanalytical study on bis-GMA-based resins

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The thermal properties of bis-GMA-based resins containing a synthesized crystalline DME–TDC which was dissolved to bis-GMA/TEGDMA base resin by 10 or 20 wt% were examined. Camphorquinone (0.5%) and a reducing agent (0.5%) were added to the base resin before the addition of DME–TDC. A thermoanalytical study using differential thermal analysis (DTA) and differential scanning calorimetry (DSC) showed that thermal change in the DTA and DSC curves depended on the composition of the bis-GMA-based resins. Heat for curing was lowest in 50/50 base resin of 40 wt% bis-GMA/60 wt% TEGDMA, 50/50 and 60/40 base resins in DTA analysis during heating. The addition of DME–TDC to each resin increased heat requirements in 50/50 resin and decreased heat requirements in 40/60 and 60/40 resins. The thermal decomposition of 50/50 bis-GMA-based resin including DME–TDC occurred at a higher temperature than that in 40/60 and 60/40 based resin. The value of activation energy for curing performance was lowest for a DME–TDC including bis-GMA-based resin.

1. Introduction

In unfilled bis-GMA-based resins the degree of polymerization is an important factor for hardness, wear resistance, mechanical strength and colour stability [1–3]. Transmission Fourier transform-infrared analysis (FT-IR) [4] and thermoanalytical methods [5–10] have shown that resin polymerization appears to be due to the monomer composition of dental resin and the concentration of camphorquinone (CQ) and reducing agents as the photo-initiator in relation to base monomers. Photopolymerization of dental composite resins was initiated by visible light in a spectrum range of 400 to 650 nm [11–13]. In this study, it was decided to analyse bis-GMA-based resins having urethane linkages by examining the thermal decomposition of the resins using DTA and to measure the curing performance in relation to activation energy for curing using DSC measurement.

2. Materials and methods

The main base monomers are given in Fig. 1 (bis-GMA; bisphenol-A diglycidyl methacrylate: Epoxylite Co, Osaka, Japan, TEGDMA; triethylene glycol dimethacrylate: Tokyo Kasei Co, Tokyo). CQ (camphorquinone, Tokyo Kasei Co) and DMAEMA (dimethylaminoethyl methacrylate, Tokyo Kasei Co) were the photo-initiators. In Table I nine DME – TDC included – bis-GMA-based resins were formulated using three kinds of comonomers (40/60, 50/50 and 60/40 as the ratio of bis-GMA/TEGDMA) at the ratio (bis-GMA/TEGDMA)/DME–TDC of 100/0(A1, B1, C1), 90/10(A2, B2, C2) and 80/20(A3, B3, C3). The ratio CQ/DMAEMA was 0.5 wt %/0.5 wt % to the resin base (see the detail concerning the synthesis of DME–TDC (dimethacryloxyethyl toluene-2,4-dicarbamate) in Fig. 2). Each bis-GMA-based resin was kept in a container at 15 °C for 24 h after adding a photo-initiator to the base resin.

The test samples were polymerized in DTA and DSC apparatus (DT-30, or -50 Shimadzu Co, Kyoto). They were heated to 800 °C with a heating rate of 10 °C min^{-1} during the DTA measurement and also cured with radiation from a visible light source (Quick Light, J. Morita Co, Kyoto) for 120 s at 37 °C during the DSC measurement (ambient temperature, N_2 gas flow). The same conditions as previously reported were used for DTA and DSC analyses [8, 9, 13].

3. Results

3.1. Synthesis of crystalline monomer DME–TDC

DME–TDC was produced by chemical reaction (Fig. 2) and clarified by analysis conditions (Table II). A monomer of 2 mol% 2-HEMA (2-hydroxyethyl methacrylate; Tokyo Kasei Co) and 1 mol% 2,4-TDI(toluene-2,4-dicarbamate; Katayama Chem) were used. The amount of di-n-butyltin dilaurate (Katayama Chem) as a catalyst was 2.5 mg to base monomer, adding additionally 5 mg hydroquinone

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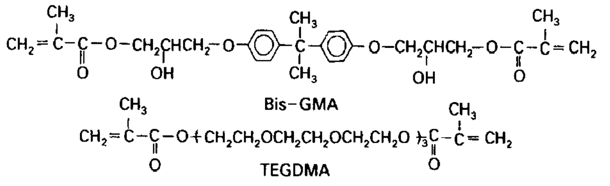

Figure 1 Base monomer structures of bis-GMA and TEGDMA.

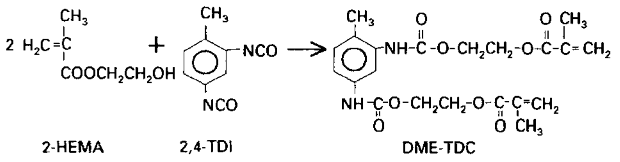

Figure 2 Chemical reaction for DME–TDC syntheses.

TABLE I Resin formulation used (see text for key)

Code	Bis-GMA/TEGDMA	(Bis-GMA/TEGDMA)/DME–TDC
A1	40/60	100/0
A2		90/10
A3		80/20
B1	50/50	100/0
B2		90/10
B3		80/20
C1	60/40	100/0
C2		90/10
C3		80/20

TABLE II FT-IR measurement conditions

Apparatus	FTIR-4200 (Shimadzu Co.)
Single beam mode	ABS
Resolution	2.0
Accumulation	250
Mirror speed	Slow
Apodization	Triangular
REC. Abscissa	4000 ~ 400 cm^{-1}
REC. Ordinate	%T 100.0 ~ 0.0 ABS 2.00 ~ 0.00

monomethyl ether(Wako Pure Chem, Osaka) in 500 ml chloroform (Wako Pure Chem) (chemical reaction time = 3–4 h, reaction temperature = 45 °C). The fundamental method used was described in the synthesis of crystalline monomers having urethane linkages [14, 15]. The finding of DME–TDC synthesis was clarified by FT-IR measurement in Fig. 3 (absorbance versus wavenumber). The trace for DME–TDC has the spectrum of an ester, showing the strong C=O(1730 cm^{-1}), C–O(1180 cm^{-1}) and also CH(930 cm^{-1}) stretching vibrations. The C=C stretching absorption band at 1600 cm^{-1} and –NH band at 1550 cm^{-1} are also seen. The peaks OH in 2-HEMA (3450 cm^{-1}) and NCO in 2,4-TDI (2250 cm^{-1}) were not detected for DME–TDC after synthesis.

3.2. Thermal characteristics

Fig. 4 shows typical DTA and TG curves of bis-GMA, TEGDMA and DME–TDC as a constituent monomer

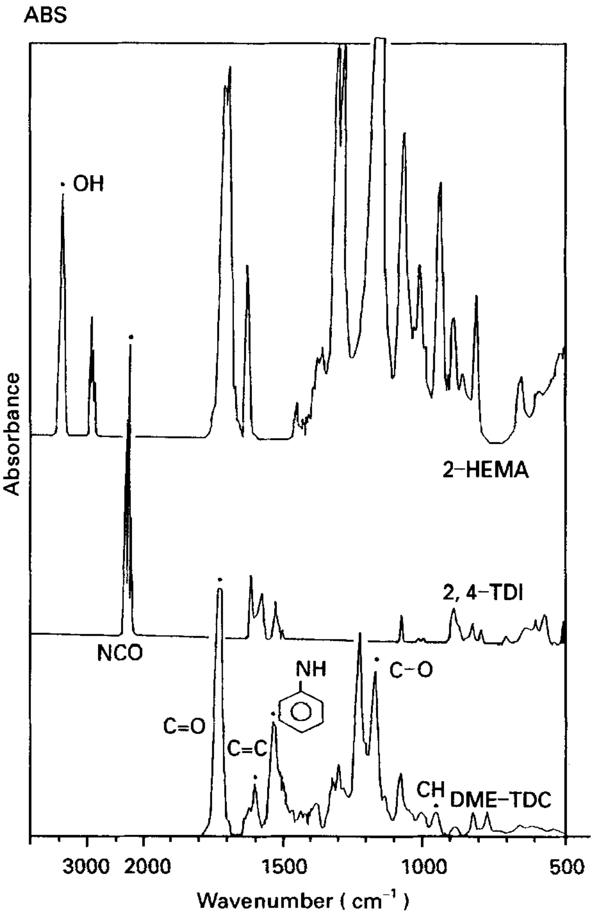

Figure 3 FT-IR analysis to clarify the syntheses of DME–TDC.

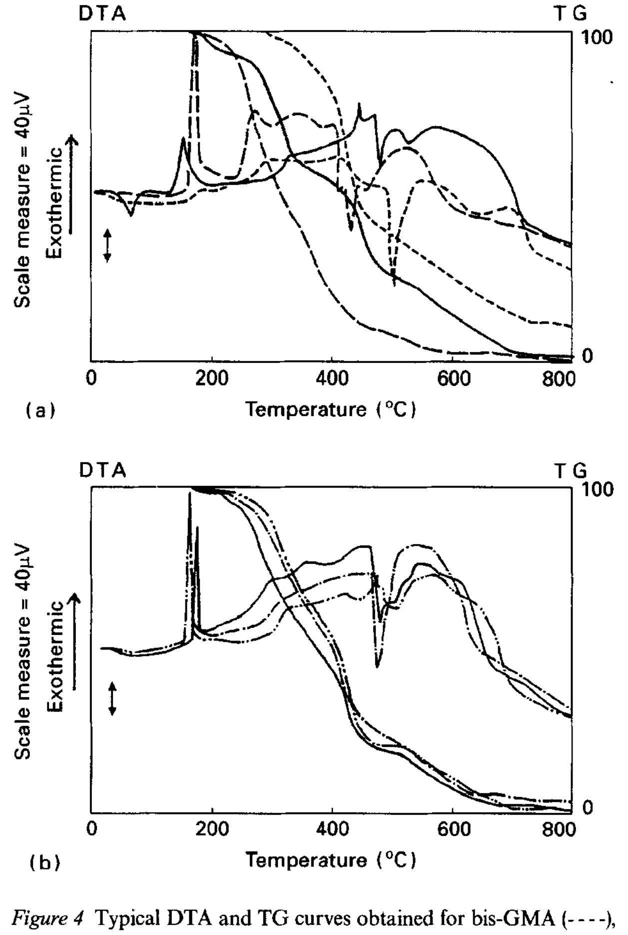

Figure 4 Typical DTA and TG curves obtained for bis-GMA (----), TEGDMA (– –) and DME–TDC (—) itself (a) and B1 (– without DME–TDC), B2(–·– 10 wt%) and B3(–··– 20 wt%) unfilled resins (b).

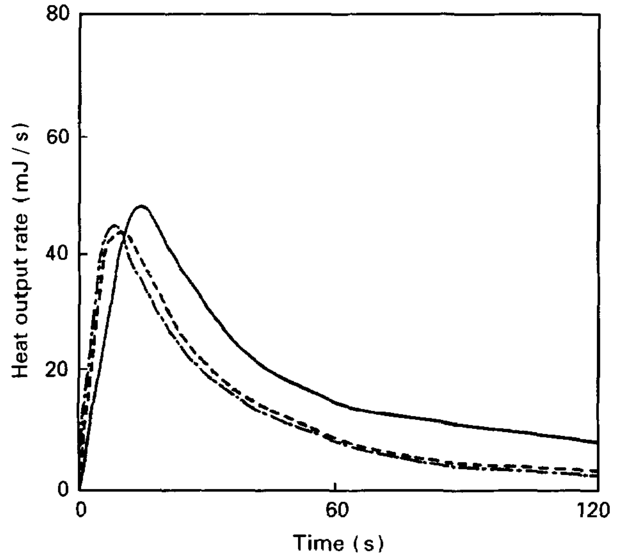

Figure 5 DSC curves for C1 (– without DME–TDC), C2(--- 10 wt%) and C3(· - 20 wt%) unfilled resins.

in bis-GMA-based resins (4a) and B1, B2 and B3 resins (4b). TG denotes weight loss (wt%) of the resin during heating to 800 °C (weight 0% = weight loss 100%). In (a) the peak temperature of pure chemicals DME–TDC and TEGDMA occurred below 200 °C for curing using the DTA curve and weight loss appeared to be associated with monomer decomposition in the range 200 to 300 °C. The decomposition temperature was measured as the temperature at 90% weight (weight loss = 10%). In Fig. 4b bis-GMA-based resin had a peak temperature (T_{pt}) and decomposition temperature (T_{dt}) showing that the heat for curing (H_t) decreased with the addition of DME–TDC to the base resin. Fig. 5 shows typical DSC curves for unfilled bis-GMA resins (C1, C2, C3), showing that they reached a peak during isothermal curing and lowered to room temperature after curing.

H_t, T_{pt} and T_{dt} values in DTA and H_s and t_{ps} values in DSC are given in Tables III and IV. The heat for curing is defined as the integrated area of DSC curves (0 to 120s). The value (kJ/g) was obtained per gram of sample from the curves. The magnitudes of H_t decreased with the addition of DME–TDC to comonomer A1 and C1 resins, whereas its magnitude increased in B1 resin. Decomposition temperature of the resin was greater in B2 and B3 resins including 10 and 20 wt% DME–TDC (268, 276 °C) than in A2 and A3 (232, 207 °C) and C2 and C3 resins (237, 224 °C). Under the isothermal temperature mode of DSC analysis curing started more rapidly in DME–TDC included resins (A2, A3, B2, B3, C2, C3) than in A1, B1 and C1 base resins (comonomers), as indicated by the t_{ps} times (Table IV). The activation energy of curing was calculated from the Arrhenius plot [13, 16];

$$K = A\exp(-\text{delta}\, E/RT)$$

$$\log_{10}K - \log_{10}A = -\text{delta}\, E/2.303R(1/T)$$

$$\text{delta}\, E = -(\text{slope}) \times 2.303R$$

TABLE III DTA thermal properties of heat for curing (H_t), peak temperature (T_{pt}) and thermal decomposition temperature (T_{dt}) when cured by heating at DTA measurement; results given as mean (standard deviation)

Sample code	H_t (kJ/g)	T_{pt} (°C)	T_{dt} (°C)
A1	0.14 (0.025)	191 (1.8)	243 (8.3)
A2	0.076 (0.014)	189 (0.71)	232 (4.2)
A3	0.084 (0.0074)	184 (2.7)	207 (11.8)
B1	0.099 (0.018)	173 (1.5)	253 (4.0)
B2	0.14 (0.023)	162 (4.1)	268 (6.5)
B3	0.15 (0.010)	158 (4.3)	276 (8.1)
C1	0.11 (0.020)	187 (4.7)	251 (2.1)
C2	0.060 (0.0076)	184 (0.84)	237 (5.0)
C3	0.058 (0.0055)	183 (0.16)	224 (7.0)

TABLE IV DSC thermal properties during isothermal heating; heat for curing (H_s), peak time (t_{ps}) and activation energy for curing

Sample code	H_s (kJ/g)	t_{ps} (s)	Activation energy (kcal/mol)
A1	0.33 (0.022)	14.3 (0.59)	10.9
A2	0.28 (0.022)	9.5 (0.27)	5.3
A3	0.29 (0.028)	9.0 (0.00)	6.9
B1	0.33 (0.017)	11.8 (0.54)	10.5
B2	0.27 (0.019)	7.6 (0.54)	1.5
B3	0.27 (0.017)	8.1 (0.60)	13.7
C1	0.32 (0.013)	15.6 (0.73)	12.4
C2	0.21 (0.022)	8.9 (0.88)	9.4
C3	0.25 (0.018)	9.1 (0.70)	11.9

where delta E is the activation energy for curing, K = equilibrium parameter, A = frequency factor, R = gas constant and T = absolute temperature. The magnitude was smaller in A2, B2 and C2 resins (1.5, 5.3, 9.4 kcal/mol) than in A1, B1 and C1 base resin (10.5, 10.9, 12.4 kcal/mol).

4. Discussion

In the polymerization reaction of visible light-cured resins an exothermic reaction was found, and a thermoanalytical method has been reported for commercial dental composites by two of the authors in this study [5]. Note that the thermal change and weight loss percentage were measured by DTA and TG analyses of DME–TDC including bis-GMA-based resins (Tables III, IV). DTA analysis of unfilled resins yielded a greater decomposition temperature in unfilled bis-GMA-based resin (B1; 50 wt% bis-GMA and 50 wt% TEGDMA as the base resin). Thus, under controlled formulation variations, thermal characteristics were more precisely observed (Figs. 4(DTA) and 5(DSC)).

The decomposition temperature was reduced to a lower level, nearer the decomposition temperature of TEGDMA monomer than bis-GMA monomer (Fig. 4a, b), because lower molecular weight material tended to vaporize in the sample pan (DTA analysis). The crystalline monomer DME–TDC with urethane linkage exhibited higher decomposition temperature than bis-GMA-based comonomers.

Variation of the activation energy (isothermal curing) as a function of DME–TDC content showed the difference of curing performance among the experimental resins (Table IV). As reported previously [13, 16], a plot of $\log_{10}(H_s/t_{ps})$ against inverse temperature enabled use of the slope to calculate the activation energy (delta E), showing a smaller energy value at smaller slope (see Arrhenius equation). Bis-GMA-based A1, B1 and C1 resins had almost the same activation curing energies (10.9, 10.5, 12.4 kcal/mol) and the 10 wt% addition of crystalline DME–TDC (A2, B2, C3) to each base resin exhibited a minimum value. It was known that the polymerization reaction was enhanced by DMAEMA as a reducing agent [9]. The effect of DME–TDC present within unfilled bis-GMA-based resins was determined using the thermal reaction of curing, showing that the activation energy for curing was reduced, associated with the smaller peak temperature in the DSC curve. The degree of curing performance increased with increasing ratio of DME–TDC to bis-GMA base resin. The results suggest that perfect polymerization is obtained for DME–TDC crystalline monomer as the resin base.

Bis-GMA-based resin, including DME–TDC has advantages when curing with visible-light in that the lowest values of activation energy (5.3, 1.5 and 9.4 kcal/mol) were found for these 40/60, 50/50 and 60/40 Bis-GMA base resins. Also the heat for curing in each bis-GMA-based resin looked very satisfactory clinically, with 158–191 °C as the peak temperature (DTA) and a smaller value of peak time (7.6 to 9.5 s; DSC) when DME–TDC crystalline monomer was added.

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