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Improvement of bis–GMA-based resins by urethane linkages: DTA and DSC thermal properties

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Experimental bis–GMA/TEGDMA/urethane resins were investigated using synthesized urethane monomers to improve thermal properties. DTA (differential thermal analysis) results show that curing temperatures were 160 and 165 °C in bis–GMA-based resins containing the synthetic 2 HEMA/N 3500 urethane monomer, 150 °C in the resin containing the 2 HEMA/HT urethane monomer, and 153 °C in the urethane monomer derived from 2 HEMA/N 3500. Also, DSC (differential scanning calorimetry) results show that the value of activation for polymerization during heating is lower in bis–GMA/TEGDMA containing synthesized urethane monomer (1.89, 2.44, 2.50 kcal/mol) than undiluted urethane monomer (7.50 kcal/mol) when these synthesized urethane monomers were diluted with bis–GMA/TEGDMA. With the use of urethane monomer as an additive to bis–GMA/TEGDMA it is possible to cure more rapidly with lower activation energy.

1. Introduction

Dental visible light-cured resins are polymerized by visible light or by heating to higher temperatures. By changing the monomer compositions and the concentration of catalyst in the resins [1–5], an increase in hardness and mechanical strength is obtained. DSC analysis of these bis–GMA-based resins was carried out at isothermal temperature to determine activation energy for visible light curing [3, 6]. The developed bis–GMA-based resins included 20 wt % as the maximum content of other urethane monomers to the base resins. However, the concentration of bis–GMA (bisphenol A glycidyl dimethacrylate)/TEGDMA (triethylene glycol dimethacrylate) was 60 wt %/40 wt % in bis–GMA-based resins [2, 3].

Thus, a newly designed range of bis–GMA/TEGDMA monomers was developed containing urethane monomers synthesized by the reaction of 2 HEMA with two commercial trifunctional isocyanates.

2. Materials and methods

Main monomers and percentages used in this study are given in Table I. E1 contains TEGDMA = 50 wt % (Tokyo Kasei Co, Tokyo), bis–GMA = 25 wt % (Shin-Nakamura Chem, Wakayama) and EXP 3 = 25 wt % and E2 contains TEGDMA = 100/3 wt %, bis–GMA = 100/3 wt % and EXP 3 = 100/3 wt %. EE is composed of TEGDMA = 100/3 wt %, bis–GMA = 100/3 wt % and EXP 4 = 100/3 wt %. Hydroxy (OH), amine (NH_2) and carboxyl (COOH) groups were needed to form urethane linkages [7]. Therefore, to synthesize urethane monomers in Fig. 1, the liquid 2 HEMA was added to N 3500 or HT, catalyzed with D–n–butyltin dilaurate (0.5 wt %) and hydroquinone (0.5 wt %) at about 60 °C for 12 h in an inert atmosphere, with continuous stirring, until the reaction was essentially completed (2 HEMA (40 wt %) and N 3500 (60 wt %) (code; EXP 3), and 2 HEMA (30 wt %) and HT (70 wt %) (code; EXP 4). 2 HEMA is 2-hydroxyethyl methacrylate (Tokyo Kasei Co), N 3500 isocyanulate (–NCO–content = 21.6%) and HT its adducts (–NCO–content = 13%) (Sumitomo Bayer Co, Osaka). Urethane linkage –NHCOO– was synthesized using 2 HEMA and N 3500, or HT as shown in Fig. 1. Camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) were used, respectively, 0.5 wt % to the base resins. Each sample was placed in a container at 15 °C for 24 h after the addition of a photo-initiator.

The samples were cured with heating rates 2, 10 and 20 °C/min to 800 °C in a DTA apparatus (DT-30, Shimadzu Co, Kyoto). Thermogravimetry (TG) curves

TABLE I Materials used for preparation of unfilled resins (E1, E2, EE). See text for key.

Code	EXP 3[a]	TEGDMA	Bis–GMA	EXP 4[b]
E 1	25	50	25	–
E 2	100/3	100/3	100/3	–
E E	–	100/3	100/3	100/3

[a] EXP 3: 2 HEMA (40)·N 3500 (60)
[b] EXP 4: 2 HEMA (30)·HT (70)

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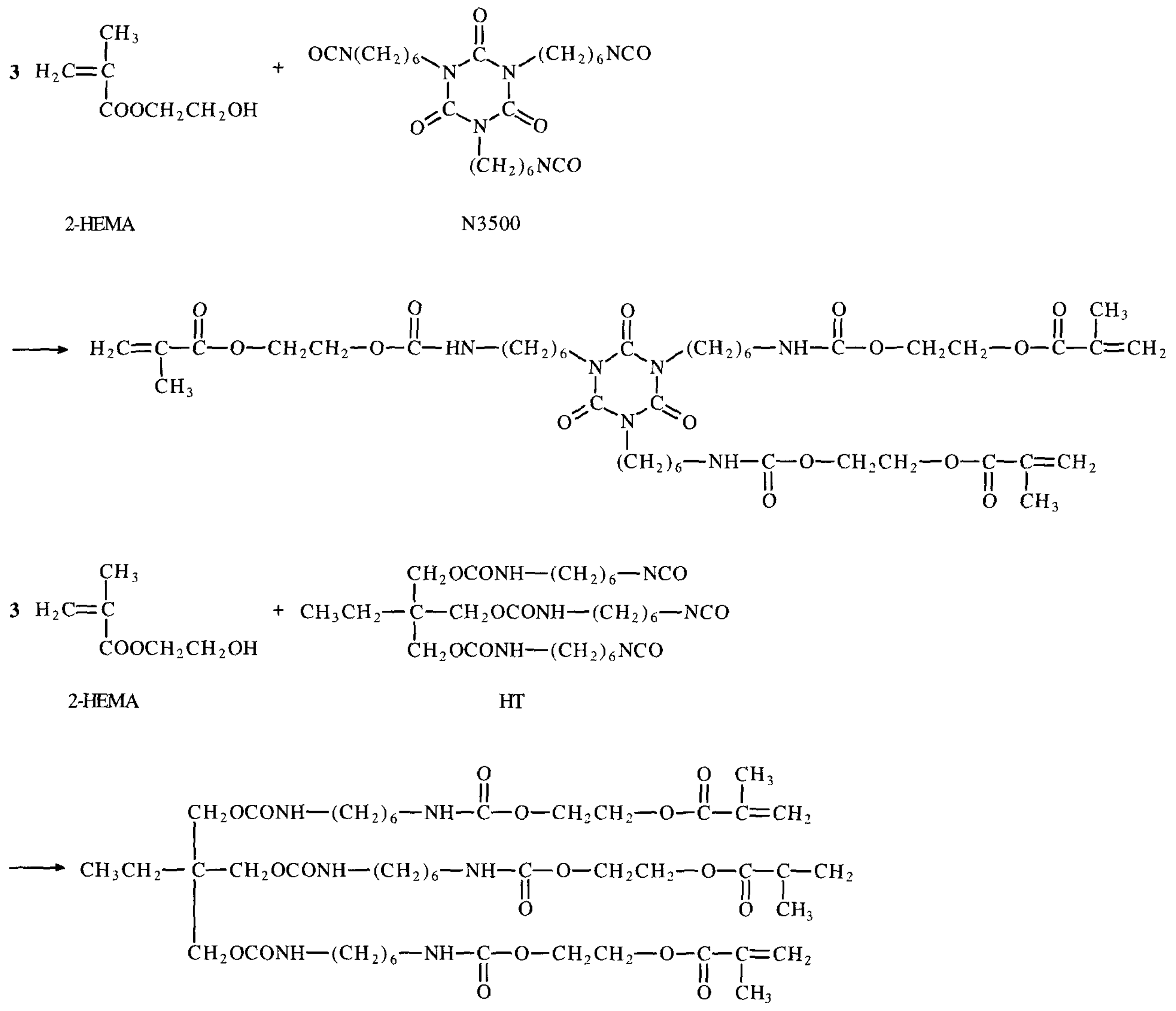

Figure 1 Synthesis of monomers containing the urethane linkage (-NHCOO-).

were measured simultaneously to obtain weight loss associated with thermal decomposition. DSC analysis was carried out by irradiation of the sample with radiation from a visible light source (Quick Light, J. Morita Co, Kyoto) for 180 s at sample temperatures of 15, 37 and 50 °C [6].

3. Results

Fig. 2 shows DTA and TG curves of experimental urethane monomer EXP 3, showing curing temperatures and thermal decomposition changes at heating rates of 2, 10 and 20 °C min. Fig. 3 (DSC curves at 15, 37 and 50 °C for experimental monomer EXP 3) shows that the both shorter peak time and larger exotherm occurred when cured at higher temperatures (Table II).

Fig. 4 shows typical DTA curves for unfilled E1, E2 and EE resins (heating mode 10 °C min). The peak

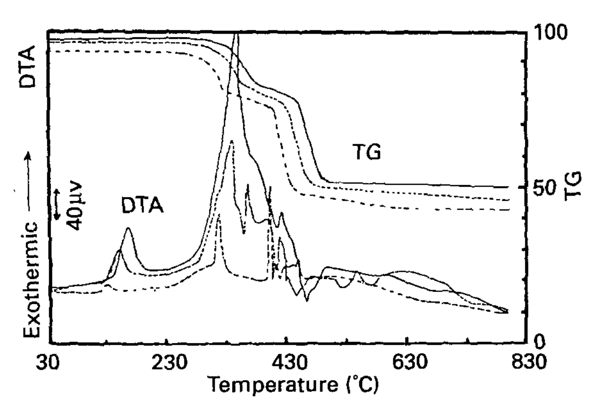

Figure 2 DTA and TG curves of EXP 3 monomer at each heating rate (—— 20 °C/min; ··· 10 °C/min; -.-. 2 °C/min).

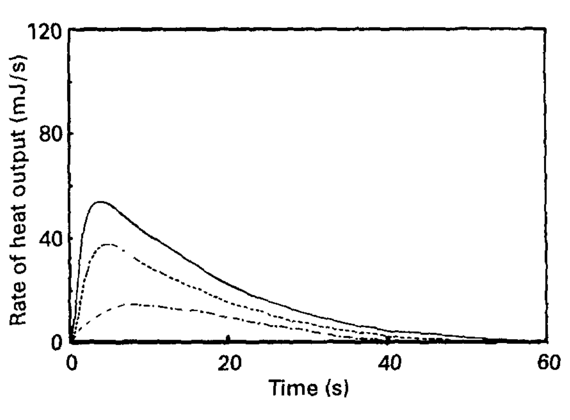

Figure 3 DSC curves of EXP 3 monomer at 15 (-.-.), 37 (···) and 50 °C (——) (isothermal temperature).

TABLE II Unfilled resins: mean value and standard deviation of thermal DTA and DSC properties. See Table I for key.

Code	DTA-TG Peak temperature (°C)	DSC Peak time (s) 15 °C	37 °C	50 °C	Activation energy (kcal/mol)
E 1	165 (4.35)	10.20 (1.59)	10.60 (2.77)	9.00 (0.00)	2.50
E 2	160 (2.08)	7.00 (0.69)	7.80 (1.20)	7.00 (0.69)	2.44
E E	150 (1.00)	10.80 (0.00)	8.60 (0.69)	8.80 (0.91)	1.89
EXP 3	153 (1.26)	12.41 (1.51)	6.20 (0.34)	4.80 (0.00)	7.50

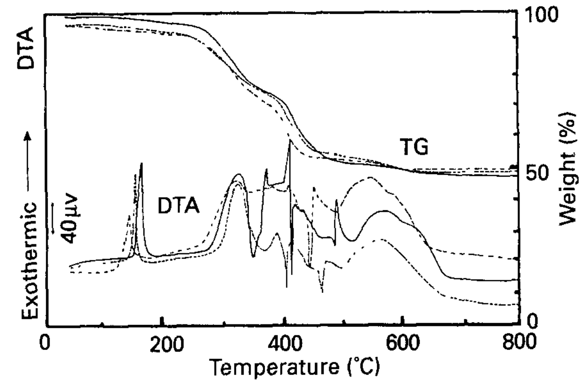

Figure 4 DTA and TG curves of E1 (——), E2 (···) and EE (–.–.) resins when heated at 10 °C/min.

temperatures were 150 °C (EE), 160 °C (E2) and 165 °C (E1), and that of EXP 3 monomer was 153 °C.

At 37 °C E2 and EE resins cured in shorter times than E1 resin (Fig. 5a). In Fig. 5b, c and d a temperature dependence of peak time and exotherm with test temperature was observed, the peak height increasing with temperature. As the relation between inverse isothermal temperature and logarithm of (heat/peak time) was obtained for E1, E2 and EE resins, activation energy for curing was calculated from the slope according to the Arrhenius plot [2, 3] (E1, 2.50; E2, 2.44; EE, 1.89 kcal/mol). The magnitude of activation energy in the EXP 3 monomer (7.50 kcal/mol) was greater than that in bis-GMA resin (Table II).

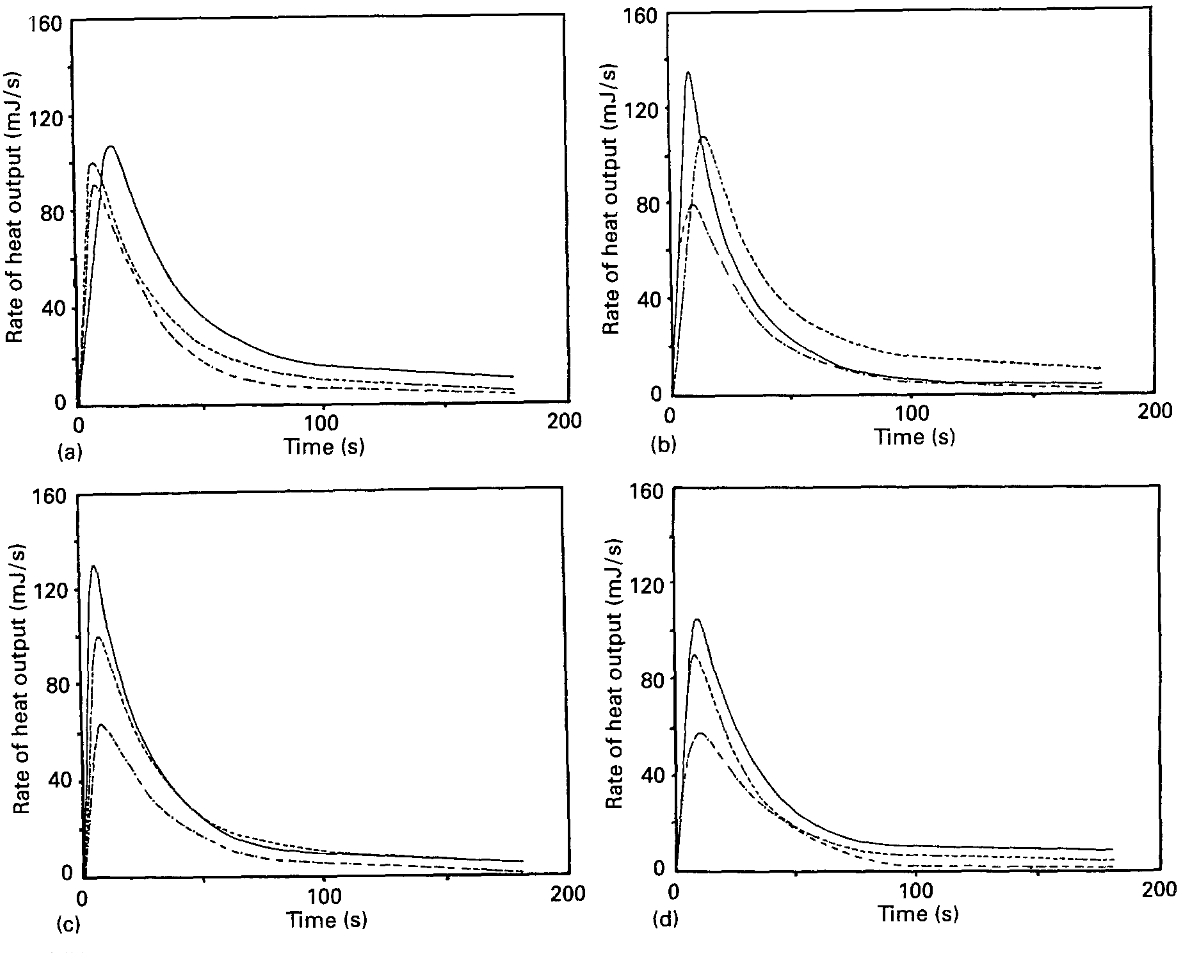

Figure 5 DSC curves: (a) E1 (——), E2 (– – –) and EE (–·–·) resins at 37 °C, and (b) E1, (c) E2, (d) EE during curing at isothermal temperatures 15 (–·–·), 37 (– – –) and 50 °C (——).

4. Discussion

The technique of DTA and DSC was an available method to study the cure behaviour of visible light-cured resins [8], and it was able to clarify the factors which affected cure performance and temperature changes simultaneously. Thus, thermoanalytical characteristics were measured for bis–GMA/TEGDMA/urethane monomer-based resins. DTA and DSC results showed that the use of urethane monomer in bis–GMA/TEGDMA comonomer exhibited a lower magnitude of activation energy when cured at isothermal temperature.

Thermal analysis determined thermal curing behaviour in relation to polymerization reaction in the base monomer [9, 10], and polymerization temperature was determined by monomer composition. The experimental urethane monomer showed weight loss of less than 50% at about 430 °C associated with thermal decomposition (Fig. 2). And also, under controlled formulation variation, DSC curves showed the cure of bis–GMA-based resins occurred at lower activation energy at isothermal temperatures (Figs 3 and 5 and Table II).

In commercial composite resins including filler (42 to 87%) the heat for curing ranged from 14.23 to 17.54 kcal/mol [11]. The result indicated that it appeared to be a strong function of filler content in the composite. It is suggested that the heat for curing is lower in unfilled than filled resins. Experimental bis–GMA-based resins containing urethane monomers (prepared by the reaction of 2HEMA with polyisocyanates) exhibit a curing temperature at about 160 °C and an isothermal curing at 7 to 11 s from DTA and DSC data. Visible light curing occurred with lower activation energy for isothermal curing using urethane monomer. With the use of urethane monomer, the possibility to develop new visible light-cured resin system based on bis–GMA exists.

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