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Decomposition analysis of binary polyfunctional urethane monomer mixtures

R. PRIYAWAN, K. WAKASA*, N. A. CHOWDHURY, M. YAMAKI
Hiroshima University School of Dentistry, Department of Dental Materials, Kasumi 1-chome, Minamiku, Hiroshima City, 734 Japan

Thermal decomposition in three binary monomer mixture systems containing an experimentally synthesized monomer (EXP3) and a commercial polyfunctional urethane monomer (U–4TXA) was examined in terms of differential thermal analysis (DTA) and simultaneous thermogravimetry (TG) analysis when a sample was heated to 800 °C. The binary EXP3/U–4TXA monomer mixtures were visible light-cured (VLC) resins which included CQ (camphorquinone = 0.5 wt %) and DMAEMA (dimethylaminoethyl methacrylate = 0.5 wt %) as the photoinitiator. Their DTA curves showed that thermal decomposition initiated at around 300 °C and finished at around 500 °C. TG curves showed complete weight loss at 800 °C during thermally induced decomposition: the decomposition reaction at weight losses of 5 to 50% was calculated from the slope of the $(1/T)$ versus $\log_{10}(H_r)$ diagram, because the exothermic decomposition temperature shown on DTA curves increased with increasing heating rate from 2 to 20 °C/min. Thermal decomposition analysis showed that a decomposition with weight change had exothermic heats ranging from 0.38 to 1.07 kJ/g for the EXP U1 mixture, 1.06 to 1.76 kJ/g for EXP U2 and 1.74 to 2.02 kJ/g for EXP U3. Activation energy ranged from 1.42 to 1.89 kJ/mol at weight losses of 5 to 50% in the three binary EXP3/U–4TXA monomer mixture systems.

1. Introduction

Dental visible light-cured (VLC) resin systems have included polyfunctional monomers, which exhibit higher curing performance in resin composites than chemically cured resin composites [1–6]. A commercial dental resin composite including such a polyfunctional methacrylate monomer as triethyleneglycol dimethacrylate (TEGDMA) and bisphenol-A glycidyl dimethacrylate (bis-GMA) has usually been accepted as a restorative material [2–4]. A ternary bis-GMA/TEGDMA/urethane-based resin including polyfunctional linkages has been shown to exhibit improved thermally activated cure performance and mechanical strength [7–14]. Thermogravimetry (TG) has been used to evaluate weight changes in VLC resin composites, and response patterns have been examined using differential thermal analysis (DTA) [13–16]. Earlier reports stated that a thermally induced process occurred in multiple stages indicating the presence of different structural species in the resin matrix. Ternary resin systems showed increased strength values and higher cure performance (addition of urethane monomer to binary bis-GMA/TEGDMA monomer mixtures [14]). This study has examined the thermal decomposition of three polyfunctional urethane monomer mixtures of EXP3/U–4TXA using TG and was aimed at clarifying the effect of an added experimental urethane monomer on thermal decomposition phenomena.

2. Materials and methods

Table I details the three types of binary monomer mixtures of EXP3 and U–4TXA examined in this study. EXP U1 includes EXP3/U–4TXA (1/1; 50 wt %/50 wt %), EXP U2 has EXP3/U–4TXA(2/1; 66.6 wt %/33.3 wt %), and EXP U3 EXP3/U–4TXA (1/2; 33.3 wt %/66.6 wt %). U–4TXA is a commercial urethane polyfunctional monomer (Shin-Nakamura Chem, Wakayama, Japan). EXP3 is an experimental polyfunctional urethane monomer, which is synthesized at 40 wt % 2-HEMA/60 wt % N3500 with 2-HEMA (2-hydroxyethyl methacrylate; Tokyo Kasei Co., Tokyo, Japan) and N3500 (Isocyanurate with -NCO- content = 21.6 wt %; Sumitomo Bayer Urethane Co., Osaka, Japan) (Fig. 1). A 2-HEMA was added to N3500, which contained additionally hydroquinone monomethyl ether as a curing inhibitor (0.1 wt %; Wako Junyaku Kougyou, Osaka, Japan), for 3 to 4 h at 35 to 40 °C, and the monomer mixture was held at 20 °C for bench cooling. The synthesized EXP3 monomer was used as one urethane monomer of the binary monomer mixtures, because it was effectively mixed as one polyfunctional monomer of

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*Author to whom all correspondence should be addressed.

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TABLE I Decomposition temperatures from DTA curves of binary EXP U1, EXP U2 and EXP U3 monomer mixtures. The heating rates used were 2, 10 and 20 °C/min. See Fig. 1 for the decomposition peaks

Sample code	Heating rate (°C/min)	Decomposition peak (°C)				
		Peak I	Peak II	Peak III	Peak IV	Peak V
	2	357.7	397.0*	406.8	415.1	–
EXP U1	10	395.1	410.5*	421.3	432	–
	20	404.6*	439.9	470.6	–	–
	2	329.5	347.8	397.0*	412.4	440.0
EXP U2	10	318.5	396.3	420.9*	434.8	448.6
	20	404.6*	466.8	–	–	–
	2	340.9	351.8	387.8*	394.1	412.3
EXP U3	10	373.9	385.2	398.9	411.2*	441.8
	20	397.1*	468.5	–	–	–

* Highest decomposition peak

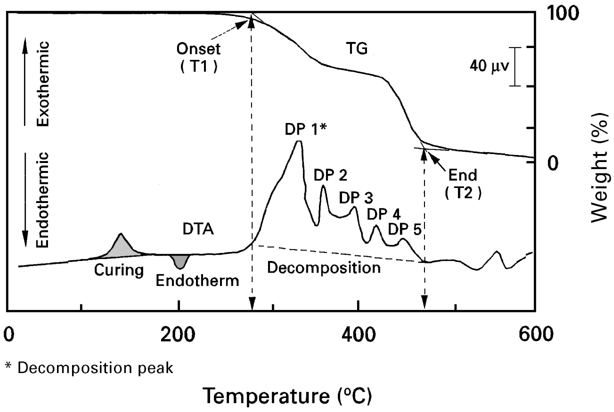

Figure 1 TG and DTA curves showing decomposition temperatures and heats of decomposition. See text for key.

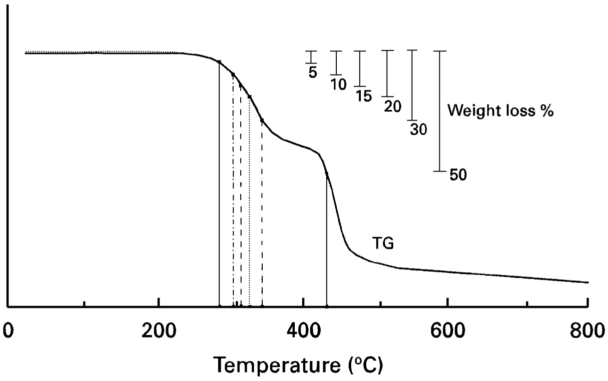

Figure 2 TG curves which represents a decomposition phenomena. At respective weight losses, decomposition temperatures were measured.

ternary bis-GMA/TEGDMA/urethane based resins [14]. To apply binary monomer mixtures to VLC unfilled resins, camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) were added as the photosensitizer and reducing agent at concentration of 0.5 wt % and 0.5 wt % to the binary mixtures. After the monomer mixture, samples were kept in a container at 15 °C for 24 h.

The VLC samples were cured thermally by heating from 20 °C to 800 °C, with DTA and TG analyses (DT50, Shimadzu Co., Kyoto, Japan) at heating rates of 2, 10 and 20 °C/min. Sample weight was 10 mg and reference weight (α alumina powder) 30 mg. The test conditions were as follows (DTA sensitivity, 100 µV; TG sensitivity, 20 mg; atmosphere, air under a flow of 30 ml/min N_2). On the DTA and TG curves, heat values of curing performance (exotherm), endotherm reaction and thermal decomposition (exotherm) during heating were measured.

The decomposition activation energy was calculated using the equation introduced by Shintani *et al.* [15]. The values were obtained from the TG curves at weight losses of 5, 10, 15, 20, 30 and 50 %, which corresponded to the thermally induced decomposition on the DTA curves. The thermal behaviour of weight loss at heating rates of 2, 10 and 20 °C/min is described in Figs 1 and 2. The change of weight loss related to the second exothermic reaction of the decomposition was as follows [15]. Activation energy for thermal decomposition was calculated based on the equation indicated originally by the Arrhenius formula [17–19].

$$\log_{10}H_r = \text{constant} - 0.4567\,(-E/RT)$$

where H_r, E, R and T are the heating rate, the activation energy for decomposition of the resin matrix, the gas constant, and the absolute temperature of the exotherm at respective weight losses (5, 10, 15, 20, 30, and 50%) on TG curves, respectively. The value of E was calculated in terms of the slope of the plot $(1/T)$ against $\log_{10}(H_r)$.

3. Results

Fig. 1 shows a schematic diagram of the TG and DTA curves, indicating the endothermic and exothermic reactions. The $T1$ and $T2$ points indicate the onset and end temperatures of the thermal decomposition process on the TG curve. On the DTA curve, five peaks (DP1 to DP5) were found between the $T1$ and $T2$ temperatures, and the TP point was considered as the highest of the five peaks. The decomposition heat was defined as the heat for thermal decomposition between temperatures $T1$ and $T2$. Two exotherm

TABLE II The decomposition temperatures, T1, T2, and TP, and decomposition heats on TG curves of binary EXP U1, EXP U2, and EXP U3 monomer mixtures. The heating rates used were 2, 10, and 20 °C/min. See Fig. 1 for the decomposition temperatures and its heat

Code	Heating rate (°C/min)	Decomposition			
		$T1$ (°C)	$T2$ (°C)	TP (°C)	Heat (kJ/g)
	2	269.8	438.9	397	0.38
EXP U1	10	301.4	469.7	412	1.07
	20	316.6	497.6	400.6	0.87
	2	275.4	441.2	397	1.76
EXP U2	10	296.1	479.4	426.6	1.35
	20	311.8	483.7	405	1.06
	2	266.5	438.2	397	1.74
EXP U3	10	293.2	459.9	413	2.02
	20	311.3	484.5	397.7	1.74

peaks and one endotherm peak were obtained for the three types of resin monomer mixtures. Curing performance (around 150 °C) and thermal decomposition (250 to 450 °C) were observed, and the reaction after curing was detected as an endotherm at around 280 to 320 °C. Weight loss of the monomer mixtures occurs during thermal decomposition within onset and end points. The analysis of weight decreases of 5, 10, 15, 20, 30 and 50% is indicated in Fig. 2. Table I indicates decomposition peaks I, II, III, IV and V of EXP U1, EXP U2 and EXP U3 monomers at heating rates of 2, 10 and 20 °C/min. The peak temperatures increased with increased heating rates, and then the number of peaks decreased. Thus, the peak temperature is taken to be the highest of the peaks of peak I (DP1) to peak V (DP5). Table II details the decomposition results for EXP U1, EXP U2 and EXP U3 monomers at heating rates of 2, 10 and 20 °C/min. The decomposition heats ranged from 0.38 to 2.02 kJ/g. The peak temperatures $T1$, $T2$ and TP increased slightly with increasing monomer ratio: 1/3(EXP3/(EXP3 + U−4TXA); EXP U3), 1/2 (EXP U1) and 2/3(EXP U2). The decomposition heat changed significantly with change of heating rate.

Fig. 3 shows a plot of $(1/T)$ against $\log_{10}(H_r)$ for the three types of binary EXP3/U–4TXA monomer, which were analysed using the TG curves of EXP U1 (a), EXP U2 (b) and EXP U3 (c). The curves show a linear relation at weight losses of 5 to 50%. Table III shows the values of activation energy for thermally induced decomposition at heating rates of 2, 10 and 20 °C/min. The values ranged from about 1.4 to 1.9 kcal/mol for the three test samples EXP U1, EXP U2 and EXP U3.

4. Discussion

The thermal analyses of visible light-cured (VLC) binary EXP3/U–4TXA monomer mixtures were carried out using differential thermal analysis (DTA) and thermogravimetric analysis (TG). The heats of cure, endotherm and thermal decomposition in the selected temperature ranges were important in evaluating thermal changes of thermally-induced VLC resins, as

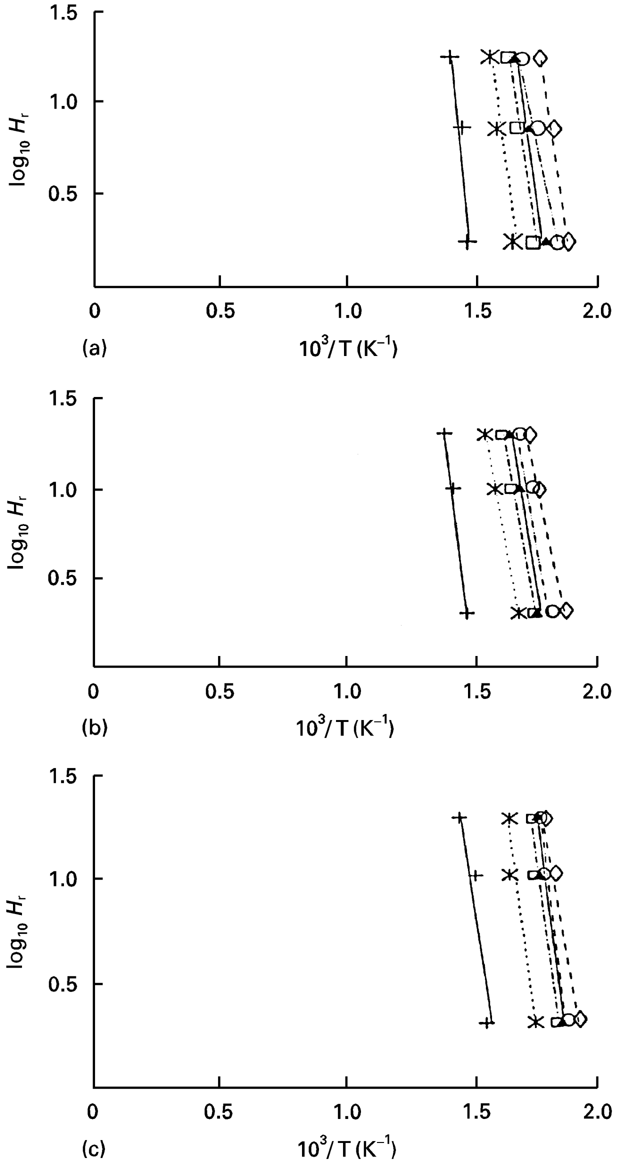

Figure 3 Plot of $(1/T)$ against $\log_{10}(H_r)$ for EXP U1 (a), EXP U2 (b) and EXP U3 (c) at various percentage weight loss values. The activation energy for decomposition of the resin matrix was calculated as described in the text. Weight loss: ◇ 5%; ○ 10%; ▲ 15%; □ 20%; × 30%; + 50%.

TABLE III Decomposition activation energy at weight decrease of 5, 10, 15, 20, 30 and 50% from TG curves of binary EXP U1, EXP U2 and EXP U3 monomer mixtures. The heating rates used were 2, 10 and 20 °C/min. See Fig. 2 for decomposition temperatures heats of decomposition

Sample code	Heating rate (°C/min)	Decomposition activation energy (kcal/mol) at weight loss (%)					
		5	10	15	20	30	50
	2	1.89	1.83	1.8	1.78	1.7	1.51
EXP U1	10	1.85	1.8	1.74	1.71	1.64	1.46
	20	1.79	1.7	1.7	1.67	1.6	1.44
	2	1.88	1.82	1.79	1.77	1.7	1.5
EXP U2	10	1.78	1.74	1.72	1.69	1.62	1.44
	20	1.73	1.7	1.68	1.65	1.58	1.42
	2	1.86	1.82	1.81	1.79	1.7	1.52
EXP U3	10	1.79	1.76	1.75	1.73	1.65	1.49
	20	1.73	1.73	1.71	1.69	1.6	1.42

shown in Fig. 1 [9–14]. Plots of $(1/T)$ against $\log_{10}(H_r)$ indicated a linear relation between them and the measured percentage weight loss was determined by TG analysis (Fig. 3). This gave a correlation coefficient of $r = 0.999$ and a negative slope. Analysis of the three experimental VLC monomer mixtures yielded different thermal results (Tables I, II, III).

DMAEMA (a reducing agent) is generally added with CQ to dental VLC resin composite, because the amine radicals are responsible for initiating the curing. The addition of CQ and reducing agent is very important in the photopolymerization of the resin matrix: less VL curing occurred when adding CQ as the only photosensitizer (i.e. no reducing agent [9, 20]). VLC binary bis-GMA/TEGDMA mixtures exhibit an indentation hardness which is affected by the content of CQ and amine in the mixtures [21]. The effect of photoinitiator on the degree of conversion in a VLC binary UDMA (a urethane monomer)/TEGDMA (a diluent monomer) resin was clarified by the content of CQ (a photosensitizer) and DMAEMA (a reducing agent) [20]. These results were based on earlier reports that 0.5 wt % CQ and DMAEMA were used for newly designed binary urethane monomer mixtures [9, 11–15, 22, 23].

In this study, binary monomer mixtures of EXP3 and U–4TXA polyfunctional monomers were applied to a VLC resin matrix. The binary monomer mixtures exhibited a decomposition temperature above 310 °C, and decomposition ceased at about 430 °C (Tables I and II), similar to the decomposition temperature (343 to 433 °C) previously reported for dental resin composites [16]. The heat of decomposition was in the range 0.38 to 2.02 kJ/g (Table II). The experimentally synthesized EXP3 monomer was used as one component of sample binary polyfunctional urethane monomers. The decomposition of bis-GMA was generally observed for separate species of the branched bis-GMA [24]. It is supposed that the separate peaks in the thermal decomposition patterns are due to the branched components of polyfunctional urethane monomers.

The binary EXP3/U–4TXA monomer systems were applied to VLC bis-GMA-based resins, including two polyfunctional urethane monomers at the monomer mixing ratios. The effect of EXP3 (an experimental synthesized monomer) with U–4TXA on the thermal exotherm and endotherm of binary monomers was examined, and thermal analysis revealed that higher decomposition temperatures occured between 310 and 430 °C and smaller decomposition heats of 0.38 to 2.02 kJ/g. The thermal decomposition phenomena were analysed from the slope of the plot of inverse temperature of exothermic decomposition temperature against logarithm of a heating rate.

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