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Dynamic DSC Analysis of Dental Visible Light-cured Polyfunctional Urethane Resins

Kunio Wakasa, Nurhayaty Natsir* and Hideaki Shintani*

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ABSTRACT

In order to apply visible light-cured (VLC) resin systems with three mixing ratios of diluent monomer/four-functional urethane monomer, newly-synthesized diluent monomer (DM) was used. The effect of DM on the thermal endothermic decomposition process showed clearly that the thermally-stable urethane matrix was given by more addition of DM (diluent monomer) to four-functional urethane monomer. Experimental monomer mixtures were resistant efficiently at higher temperatures because of improved thermal resistance of the base urethane resin, as shown by means of dynamic DSC analysis.

INTRODUCTION

Dental visible light-cured (VLC) resin composites containing polyfunctional urethanes showed high molecular weight and complicated molecular structures, because VLC resin composites exhibited higher curing and thermal resistance than chemically-cured resin composites$^{1-8)}$. Differential scanning calorimetry at isothermal temperature and differential thermal analysis and thermal expansion analysis during heating to higher test temperature have been used. To determine phase transition temperature of resin monomer, curing temperature and thermal expansion coefficient are examined and polymerization exothermicity and thermally-decomposed endotherm of resin monomers are clarified. The ternary bis-GMA (bisphenol-A glycidyl dimethacrylate)/TEGDMA (triethylene glycol dimethacrylate)/urethane-based resin systems including polyfunctional linkages exhibited the improved thermally-activated cure performance and mechanical strength$^{9-16)}$, showing that a thermally-induced process occurred in multiple stages indicating the presence of different structural species in the resin matrix$^{15-18)}$. The ternary bis-GMA/TEGDMA/urethane monomers showed the increased strength values and higher cure performance by an addition of urethane monomer to binary bis-GMA/TEGDMA monomer mixtures$^{16)}$. The monomer structures are very important in estimating thermal behaviours at higher test temperatures where thermally-decomposed phenomenon is detected. Therefore, the present study is to examine thermal properies of polymerization and thermally-induced decomposition of three polyfunctional urethanes, using dynamic differential scanning calorimetry (DSC) analysis.

MATERIALS AND METHODS

1. Monomer mixtures

Two monomers of a four-functional urethane as coded as U-4TXA and a diluent monomer (DM) were used. DM is an experimental tri-functional diluent monomer, while U-4TXA is a commercial urethane polyfunctional monomer (Shin-Nakamura Chem, Wakayama, Japan). DM was synthesized by a mixture of 40 wt% 2-HEMA and 60 wt% N3500. The 2-hydroxyethyl methacrylate (2-HEMA; Tokyo Kasei Co, Tokyo, Japan) and N3500 (Isocyanate with -NCO- content = 21.6 wt%; Sumitomo Bayer Urethane Co, Osaka, Japan) were used for the following synthesis. The 2-HEMA was added to N3500, which contained additionally hydroquinone monomethyl

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* Hiroshima University School of Dentistry, Department of Operative Dentistry (Chairman: Professor Hideaki Shintani)

A correspondence to: *Dr Kunio Wakasa*, Hiroshima University School of Dentistry, Department of Dental Materials, Kasumi 1-chome, Minamiku, Hiroshima City, 734-8553 Japan.

ether as a curing inhibitor (0.1 wt%; Wako Junyaku Kougyou, Osaka, Japan), for 3 to 4 hours at 35 to 40°C, and the synthesized one was held at 20°C for the bench cooling.

Monomer mixture code are shown as follows. A1 includes DM/U-4TXA (1/1; 50 wt%/50 wt%), A2 has DM/U-4TXA (2/1; 66.6 wt%/33.3 wt%), and A3 has DM/U-4TXA (1/2; 33.3 wt%/66.6 wt%. As VLC unfilled resins, camphorquinone (CQ; Tokyo Kasei Co, Tokyo, Japan) and dimethylaminoethyl methacrylate (DMAEMA) (Tokyo Kasei Co) were added as photosensitizer (0.5 wt%) and reducing agent (0.5 wt%) to the binary base. The monomer samples were kept in a container at 15°C for 24 hours for compositional analyses, and the powders were obtained for dynamic DSC test from polymer samples (6 mm diameter × 3 mm height) cured by visible light for 40 sec (Grip Light, Shofu Inc, Kyoto, Japan).

2. Dynamic DSC analysis

The heat of polymerization of monomers was a measure of the heat given off because of a monomer reaction and a polymer formation. The heat release of monomers has been measured by a conventional calorimetric method[9]. This isothermal calorimetric method was used to measure heats of polymerization, reaction kinetics and degree of polymerization[17,18]. Dynamic DSC analysis clarified the change of calorimetric qualities of VLC polymers with increasing test temperature on a DSC. The seven VLC samples were thermally heated during a heating from room temperature (20°C) to 600°C by dynamic DSC analysis (TA-50WSI, Shimadzu Co, Kyoto, Japan), using dynamic DSC condition, sample size, 10 mg; a reference weight of α alumina powder, 10 mg; programmed heating rate, 10°C/min; flow gas, 30 mL/min of N_2 gas; sampling time, 1 sec. The capabilities of the system included programmed instrumental calibration, keybord control of method setup and editing of the metods, programmed experimental definition and execution, realtime display of data plotting and the other analyses of printing and plotting of hard copies of data plots. After obtaining VLC powder samples, the heat values of curing performance (exotherm) and thermal decomposition (endotherm) were measured on the DSC curve (Fig. 1). The curing phenomenon was related to thermal polymerization during heating after visible light-curing. The decomposition phenomenon of dental resin composites (resin matrix and filler) was indicated, using thermogravimetry (TG) analysis with a weight loss of the resin composite[17,18]. Two endotherm reactions at two peak temperatures (peak 1 and peak 2) showed that thermal decomposition processes of VLC polymers were divided into two stages on DSC curve. The decomposition heat was defined as a heat for a thermal decomposition at peak 1 and peak 2 temperatures.

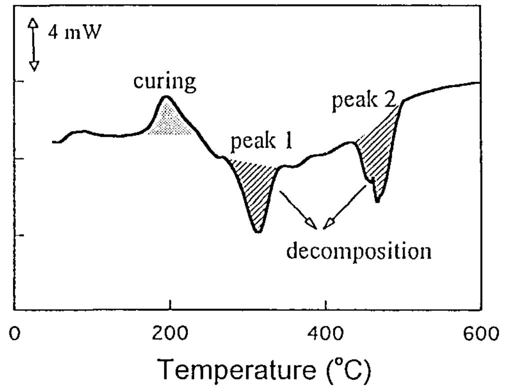

Figure 1 The schematic diagram of dynamic DSC curves, representing curing and thermal decomposition behaviours. See text for key.

RESULTS AND DISCUSSION

Table I indicates curing performance and decomposition peaks of peak 1 and peak 2 of A1, A2, and A3 samples at the heating rate of 10°C/min. The mean curing peak temperatures were 198.7 (A1), 196.67 (A2) and 205.46°C (A3), and the minimum curing heat (28.18 J/g) was obtained for A2 sample. The decomposition at peak 1 and peak 2 occurred at 314.96 (A1), 314.06 (A2), and 318.25°C (A3), and 466.83 (A1), 467.01 (A2), and 466.84°C (A3), respectively. Total heat for decomposition at peak 1 and peak 2 were 152.05 (A1), 168.65 (A2) and 155.69 J/g (A3). The thermal analyses of visible light-cured resin systems were determined in terms of dynamic DSC analysis during heating to 600°C. The heats of curing and thermal decomposition in the selected temperature ranges were important in evaluating thermal properties of newly-designed VLC resins in this study. The peak temperatures at curing and decomposition were almost the same among them, showing that there was no difference of peak temperatures among them ($p > 0.01$). The relations between diluent monomer content and heat for curing or decomposition were found clearly. The heat for curing of A2

TABLE I The curing performance and decomposition phenomena of powder materials, code A1, A2 and A3 (See text for key). The values are mean and standard deviation (parenthesis).

Code	Curing performance		Decomposition phenomena			
	Heat (J/g)	Peak temperature (°C)	Heat (J/g)		Peak temperature (°C)	
			Peak 1	Peak 2	Peak 1	Peak 2
A1	33.38	198.7	69.46	82.59	314.96	466.83
	(3.87)	(4.06)	(10.85)	(4.34)	(1.13)	(1.24)
A2	28.18	196.67	41.98	126.67	314.06	467.01
	(3.37)	(2.31)	(9.58)	(5.77)	(0.48)	(0.44)
A3	45.20	205.46	113.33	42.36	318.25	466.84
	(2.12)	(1.16)	(5.77)	(1.83)	(0.38)	(0.99)

* Irradiation time: 40 sec (from one direction)

sample had smaller values than the others, showing that A2 was cured fairly completely compared with A1 and A3 samples. This result suggests that larger heat is needed to decompose A2 sample thermally.

This study were summarized as the following results, which were effective in applying binary urethanes to dental resin matrix. Photo-initiator and reducing agent in dental urethanes were very important to give higher curing performance. Namely, DMAEMA (reducing agent) was generally added with CQ to dental VLC resin composites, because the amine radicals were responsible for initiating the curing. The addition of CQ and reducing agent activated the photopolymerization of resin matrix, because less VL curing occurred in adding CQ as the only photosensitizer with no reducing agent[22]. On the contrary, the VLC binary bis-GMA/TEGDMA mixtures exhibited the indentation hardness which was affected by the content of CQ and amine in the mixtures[23]. The earlier report exhibited that the effect of photoinitiator on the degree of conversion in a UDMA (a urethane monomer)/TEGDMA (diluent monomer) resin was controlled by the amounts of CQ (photosensitizer) and DMAEMA (reducing agent)[22], and each appropriate percentage of CQ and DMAEMA was determined to be 0.5 for newly-designed binary monomer mixtures[24,25].

In addition, to examine thermal resistance of resin matrix by dynamic DSC analysis, the initial and final decomposition temperatures were checked at higher test temperatueby 600°C. In case of VLC resin powders heated in DSC apparatus, 100% loss of weight occurred, associated with thermally-decomposed process[16], but it was difficult to measure peak temperatures in the process of decomposition clearly on their curves[18,26–28]. On dynamic DSC curves, however, the separate peaks in thermal decomposition patterns were found because of the branched components of polyfunctional urethane monomers.

CONCLUSION

The use of diluent monomer in dental urethane monomer mixtures was applied, in order to produce VLC resin systems which included three different mixing ratios of diluent monomer/four-functional urethane monomer. The effect of DM on the thermal endothermic decomposition process was examined clearly, showing that the thermally-stable urethane matrix with greater total heat of decomposition was produced by more addition of DM (diluent monomer) to four-functional urethane monomer. As explained, with the presence of DM indicating higher molecular weight, dental experimental monomer mixtures are resistant efficiently at higher temperatures, thus improving thermal resistance of the base resin. This fact suggests that the urethanes could be used as a base matrix for VLC resin. Additionally, dynamic DSC analysis clarified the decomposition behaviour of the unfilled monomers.

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