

Thermal Changes in Binary Polyfunctional Urethane Monomer Mixtures for Visible Light-cured Resins

Kunio Wakasa, Rachmadi Priyawan, Niaz Ahmed Chowdhury, Yasuhiro Yoshida, Nurhayaty Natsir*, Moin Jan Chowdhury*, Yasuhiko Yamasaki, Atsuharu Ikeda, Ken-ichi Shirai*, Masayuki Yoshioka* and Hideaki Shintani*

(Received for publication, October 1, 1997)

ABSTRACT

In three binary monomer mixtures containing an experimentally synthesized polyfunctional urethane monomer (code; EXP3) and a commercial one (U-4TXA), thermal analysis clarified the thermal changes with increasing test temperature to 800°C using thermally-induced process of differential thermal analysis (DTA) and simultaneously thermogravimetry (TG) analysis methods. Each monomer EXP3 or U-4TXA showed two exothermic peaks for curing and thermal decomposition, whereas U-4TXA had an endothermic reaction immediately after curing. In the case of their binary monomer systems due to binary mixtures of EXP3 and U-4TXA (CQ; camphorquinone = 0.5 wt% and DMAEMA; dimethylaminoethyl methacrylate = 0.5 wt% as the photo-initiator), their DTA curves showed that a curing occurred around 150°C, an endotherm reaction occurred around 280 to 320°C and also thermal decomposition initiated around 300°C and finished around 500°C for binary monomer mixtures. Their TG curves showed a complete weight loss at 800°C by thermally-induced decomposition. Characteristic temperatures on DTA curves increased with increasing

heating rate from 2 to 10, or 20°C/min. On DTA and TG curves, a curing started without weight change and a thermal decomposition initiated with weight change. The heat values for curing and decomposition were respectively calculated as the heat values at exothermic peaks on the DTA curves, ranging from 0.20 to 0.40 kJ/g and 0.63 to 3.36 kJ/g, respectively.

INTRODUCTION

Dental visible light-cured (VLC) resin composites have been widely accepted as a restorative material, and the compositions in resin monomers are still concerned about curing performance and residual monomers in the set resins¹⁻³. The residual monomers in the set resin composites were related to the hydrolytic degradation and discolouration of the filling materials. The resin matrix in dental resin composites was mainly composed of polyfunctional methacrylate monomers, such as triethyleneglycol dimethacrylate (TEGDMA) and bisphenol-A glycidyl dimethacrylate (bis-GMA)⁴⁻⁶. Ternary bis-GMA/TEGDMA/urethane-based resins including polyfunctional linkages exhibited the improved thermally-activated cure performance and mechanical strength⁷⁻¹², indicating a cure at 100 to 150°C. Thermo-analytical methods were used to evaluate weight changes by TG in VLC unfilled resin and also to examine DTA thermal response patterns of resin systems^{4,6,9,11-15}. It was clearly considered from their results that ternary ones exhibited increased strength values and better cure performance because of addition of urethane monomer. The results suggest that ternary monomer mixtures including polyfunctional urethane monomers are activated thermally at lower energy than in bis-GMA/TEGDMA

Hiroshima University School of Dentistry, Department of Dental Materials (Chairman: Professor Masao Yamaki)

* 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.

binary monomers.

This study was to examine thermal changes of binary monomer mixtures with two polyfunctional urethane monomers and respective constituted monomers when induced thermally in order to apply them to dental VLC unfilled resins.

MATERIALS AND METHODS

Table I indicates binary monomer mixtures of EXP3 and U-4TXA examined in this study. EXP U1 includes EXP3 (1 part) and U-4TXA (1 part), EXP U2 has EXP3 (2 part) and U-4TXA (1 part), and EXP U3 EXP3 (1 part) and U-4TXA (2 part). U-4TXA used in this study is a commercial urethane polyfunctional monomer (Shin-Nakamura Chem, Wakayama). EXP3 is an experimen-

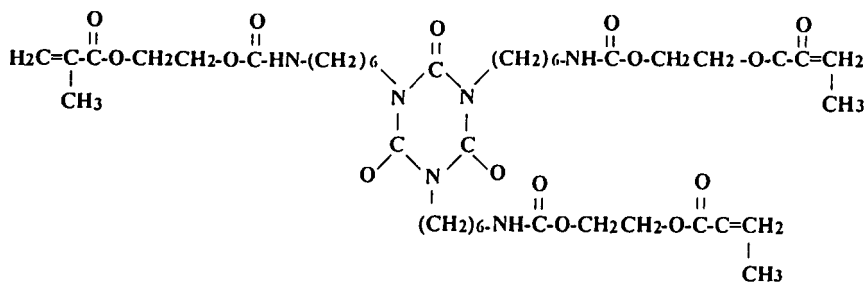
Table I The composition parts of EXP3 and U-4TXA in visible light-cured unfilled experimental resins, EXP U1, EXP U2 and EXP U3 (binary monomer mixtures) studied in this study

Code	EXP3	U-4TXA
EXP U1	1 part	1 part
EXP U2	2 part	1 part
EXP U3	1 part	2 part

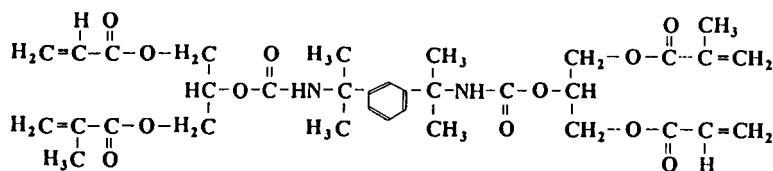
EXP 3: 2-HEMA (40)/N 3500 (60)

tal polyfunctional urethane monomer, which was synthesized at 40 wt% 2-HEMA/60 wt% N3500 with 2-HEMA (2-hydroxyethyl methacrylate; Tokyo Kasei Co, Tokyo) and N3500 (Isocyanate with —NCO— content = 21.6 wt%; Sumitomo Bayer Urethane Co, Osaka), as indicated in Fig. 1. The 2-HEMA was added to N3500, which contained additionally hydroquinone monomethyl ether as a curing inhibitor (0.1 wt%; Wako Junyaku Kougyou, Osaka), for 3 to 4 hours at 35 to 40°C, and the monomer mixture was held at room temperature (20°C) for the bench cooling. The synthesized EXP3 monomer was used as one urethane monomer of binary monomer mixtures, because it was effectively mixed as one polyfunctional monomer of ternary bis-GMA/TEGDMA/urethane based resins¹². 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 and 0.5 wt% to the binary mixtures. After the addition, they were kept in a container at 15°C for 24 hours.

The VLC samples were polymerized by heating them into 800°C with a DTA and TG analysis (DT50, Shimadzu Co, Kyoto) at heating rates of 2, 10 and 20°C/min. The sample weight was 10 mg and reference weight (alpha alumina powder) 30 mg. The test condition was as fol-



EXP 3



U - 4TXA

Figure 1 Structure formula of EXP3 and U-4TXA used in this study

lows: DTA sensitivity, 100 μV ; TG sensitivity, 20 mg; atmosphere, air under a flow of 30 mL/min N_2 . The following thermal tests were performed: DTA and TG curves, and heat values of curing performance (exotherm), endotherm reaction and thermal decomposition (exotherm) during heating.

RESULTS

Figure 2 shows schematic figure of TG and DTA curves of experimental unfilled resins when heated to 600°C with certain heating rate. Two exotherm peaks and one endotherm peak were obtained for resin mixtures. Curing performance (around 150°C) and thermal decomposition (250 to 450°C) were observed for the former, and the reaction after curing was detected as an endotherm around 280 to 320°C. Weight loss occurred with the appearance of thermal decomposition within onset and end points.

Figure 3 shows examples of TG and DTA curves of U-4TXA and EXP3 monomers at 20°C/min. U-4TXA showed low height of thermal decomposition peak with an endotherm, whereas EXP3 monomer had large peaks of thermal decomposition without endothermic peak. Figure 4 shows examples of TG and DTA curves of EXP U1, EXP U2 and EXP U3 at a heating rate of 20°C/min. The almost same shapes of DTA and TG curves were obtained for binary monomer mixtures, showing the

curves indicated as two exothermic peaks and one endothermic peak. Thus, Table II indicates curing temperature and thermal decomposition temperature of U-4TXA and EXP3 monomers. Table III (curing), IV (endothermic reaction) and V (decomposition reaction) indicate characteristic temperatures such as curing temperature (peak temperature), endothermic temperature and decomposition temperature and their heat values at each heating rate (2, 10 and 20°C/min). Lower temperature of curing in EXP3 than U-4TXA was observed, and higher decomposition onset and end temperatures in EXP3 than U-4TXA were obtained. Curing and thermal decomposition temperatures increased with increasing heating rates 2 to 10, or 20°C/min. Heat for curing ranged from 0.20 to 0.40 kJ/g, and heat for endotherm from 0.04 to 0.58 kJ/g. Decomposition heat values ranged from 0.63 to 3.36 kJ/g.

DISCUSSION

Thermoanalytical characterization of VLC unfilled resins has been determined by thermal analysis techniques of differential thermal analysis (DTA) and thermogravimetric analysis (TG). Thermal data, such as heats of cure, endotherm and thermal decomposition over selected temperature ranges was very important to evaluate thermal change of VLC unfilled resins when induced thermally^{4,7-13}. Because the thermally-heated process of

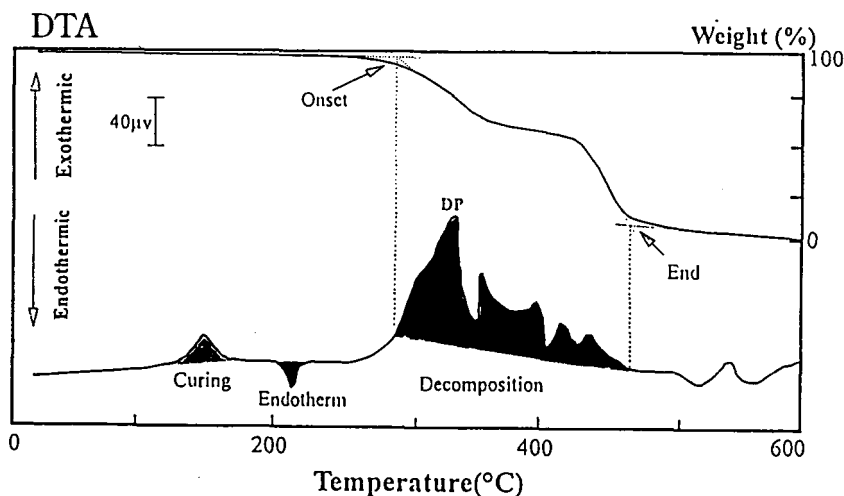


Figure 2 Schematic figure of TG and DTA curves. Onset and end points on TG curve corresponded to thermal change on DTA curve, where curing, endotherm and decomposition peaks were observed

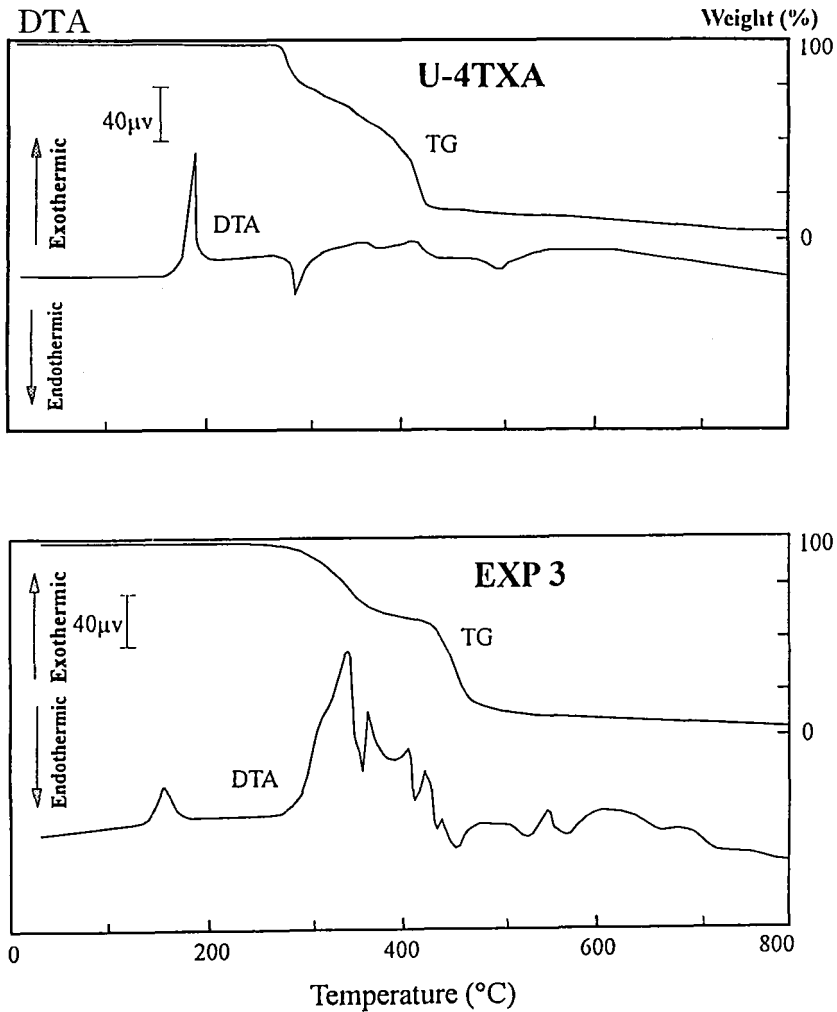


Figure 3 TG and DTA curves of U-4TXA and EXP3 monomers

resin matrix occurs in multiple stages indicating cure, endotherm and thermally-induced decomposition, an integrated thermal property can reveal an important information on VLC curing, endothermic reaction and thermally-induced decomposition phenomena.

Reducing agent is generally added with CQ to dental VLC resin composites, because the amine radicals are responsible for initiating the polymerization. The addition of CQ and reducing agent was very important with polymerization, because less polymerization occurred when CQ was added as the only photosensitizer without using a reducing agent in the resin matrix^{9,17}. Polymerization (degree of conversion) in dental resin composites was influenced by the concentration and the type of photo-

initiators in the monomer mixtures¹⁰. In VLC bis-GMA/TEGDMA based unfilled resins, the indentation hardness was affected by the content of CQ, amine and inhibitor on the mixtures¹⁶. Yoshida et al reported that the effect of photo-initiator on degree of conversion in VLC unfilled UDMA/TEGDMA resins was using CQ (photosensitizer) and DMAEMA (reducing agent), ranging from 0.25 to 5.0 wt%¹⁷. The appropriate amounts of both CQ and DMAEMA used in this investigation was 0.5 wt% for newly-designed binary urethane monomer mixtures, based on our resin monomer systems used^{9,11,12,14}.

The mixing ratio of diluent monomers such as TEGDMA, 2-HEMA, THFFMA (tetrahydrofurfuryl methacrylate) and NPGDMA (neopentylglycol dimethacrylate) with

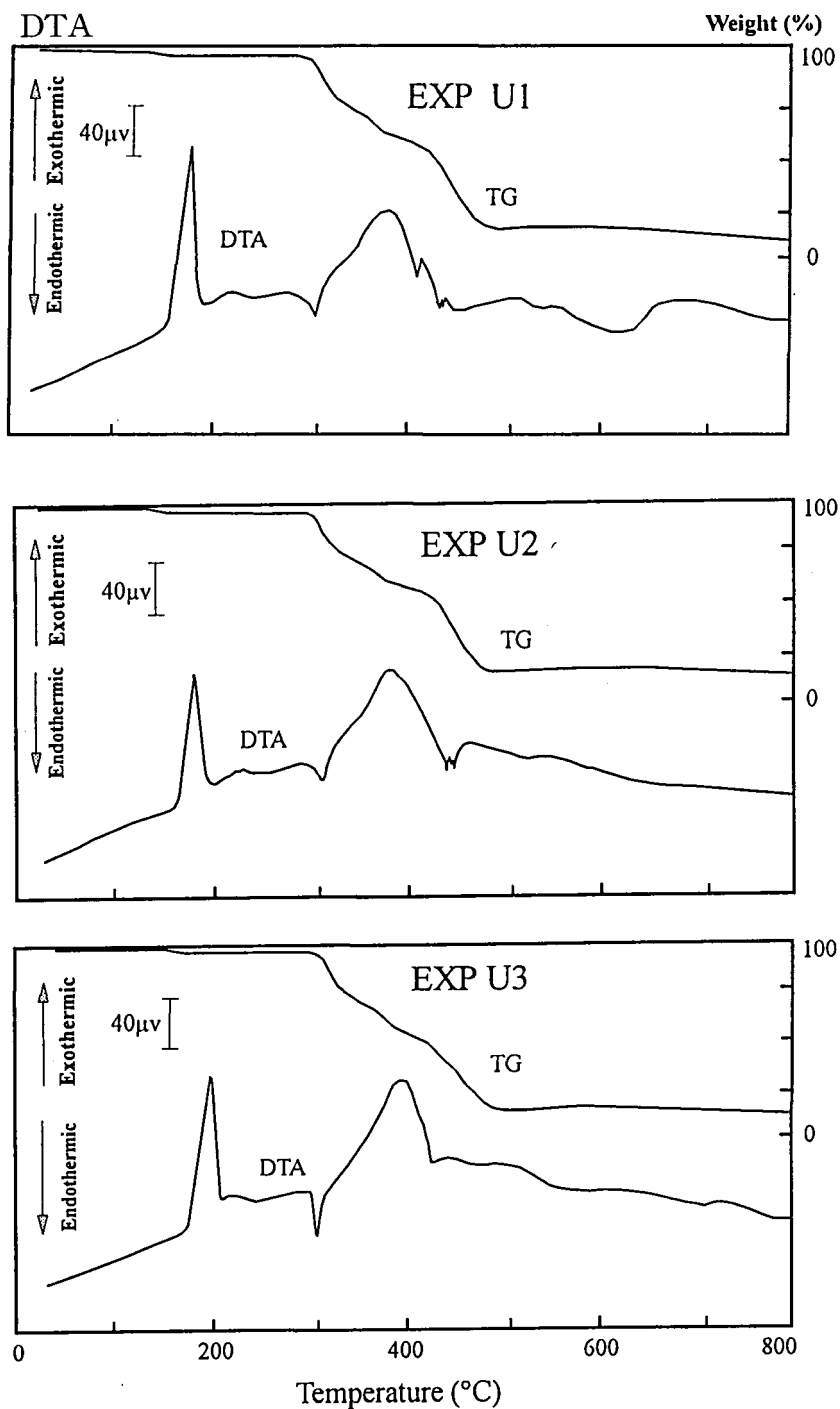


Figure 4 TG and DTA curves of EXP U1, EXP U2 and EXP U3 monomer mixtures tested

bis-GMA was important with less residual monomer amount and solubility incompatibility using 60 wt% bis-GMA/40 wt% diluent monomer¹⁸. We examined that the

mixing ratio of EXP3 and U-4TXA was effectively used for dental application of binary monomer mixtures of EXP3 and U-4TXA polyfunctional monomers to VLC un-

Table II Curing and decomposition temperatures of U-4TXA and EXP3 monomers in binary monomer mixtures

Code	Curing temperature (°C)	Decomposition temperature (°C)		
		Onset	Peak	End
U-4TXA	180	285.2	408.5	425.6
EXP 3	152	304.4	345.7 (DP 1) 367.5 (DP 2) 408.7 (DP 3) 428.3 (DP 4) 441.3 (DP 5)	469.6

Table III Curing performance of binary monomer mixtures

Code	Heating rate (°C/min)	Curing	
		Peak temperature (°C)	Heat (kJ/g)
Exp U1	2	148.5 (0.71)	0.31 (0.02)
	10	178.5 (0.71)	0.36 (0.02)
	20	191.2 (0.80)	0.23 (0.07)
Exp U2	2	147.5 (0.30)	0.24 (0.05)
	10	177.6 (1.50)	0.38 (0.01)
	20	188.9 (0.31)	0.20 (0.01)
Exp U3	2	153.6 (0.60)	0.32 (0.02)
	10	184.0 (1.40)	0.40 (0.07)
	20	200.5 (0.50)	0.23 (0.01)

Table IV Endothermic reaction temperature and heat value in binary monomer mixtures

Code	Heating rate (°C/min)	Endotherm	
		Peak temperature (°C)	Heat (kJ/g)
Exp U1	2	283.8 (1.00)	0.22 (0.02)
	10	307.4 (0.14)	0.58 (0.03)
	20	322.0 (1.73)	0.05 (0.01)
Exp U2	2	283.3 (1.80)	0.17 (0.06)
	10	311.0 (0.00)	0.05 (0.02)
	20	322.2 (1.60)	0.04 (0.00)
Exp U3	2	280.9 (2.10)	0.15 (0.05)
	10	300.5 (1.40)	0.25 (0.17)
	20	312.6 (0.35)	0.13 (0.02)

filled resins. Their binary monomer mixtures exhibited that the heat for cure (a range of 0.20 to 0.40 kJ/g) was

Table V Decomposition temperature and heat of decomposition reaction of binary monomer mixtures

Code	Heating rate (°C/min)	Decomposition	
		Peak temperature (°C)	Heat (kJ/g)
Exp U1	2	395.5 (2.12)	0.63 (0.07)
	10	411.5 (0.71)	1.16 (0.14)
	20	400.8 (0.20)	0.87 (0.06)
Exp U2	2	398.5 (1.50)	2.05 (0.10)
	10	421.4 (5.10)	1.34 (0.40)
	20	401.3 (3.70)	1.11 (0.01)
Exp U3	2	391.3 (0.60)	3.36 (0.70)
	10	412.5 (0.70)	2.80 (0.00)
	20	397.1 (0.70)	1.67 (0.09)

larger ten times than dental filled resin composites (0.02 to 0.050 kJ/g) and thermally-induced decomposition occurred around 400°C. Because a small amount of residual monomers as urethane monomer (EXP3) was able to detect using the calibration curves to separate the superimposed peaks in HPLC chart¹⁹, EXP3 monomer was used as one of polyfunctional urethane monomers. This thermal result suggests that the effect of resin composition on the extent of cure is expected, because the molecular weights for UDMA, bis-GMA and TEGDMA are 968, 512 and 286. Ruyter et al reported that this phenomena was observed for separate species of the branched bis-GMA²⁰. The presence of separate peaks in thermal decomposition patterns are supposed to be due to the branched components of polyfunctional urethane monomers. Their branched components will be identified by analyzing them at their decomposed temperatures with gas-liquid chromatography (GC)/mass spectroscopy (MS).

The synthesized urethane monomer is applicable to VLC bis-GMA-based resins, because the HPLC analysis clarified a small uncured urethane residue (EXP3) as compared with residues of bis-GMA and TEGDMA in the case of bis-GMA/TEGDMA/urethane based resins. Thus, binary monomer mixtures were examined using its urethane monomer including commercial polyfunctional urethane monomer. The ratios between two polyfunctional urethane monomers were fixed at three different weight parts to clarify the effect of EXP3 (experimental synthesized monomers) to U-4TXA on thermal reactions, such

as exotherm and endotherm of binary monomers, leading to better cure performance and higher temperature decomposition.

ACKNOWLEDGMENTS

The authors would like to express deep thanks to the research facilities in Hiroshima University Graduate School for the use of *Biomaterial Combined Analysis System*, founded in 1993, from the Ministry of Education, Science, Sports and Culture, Japan.

REFERENCES

- 1) Lee, H. and Colby, C.: Heat of polymerization of nine, mono, di-, trimethacrylate esters tested neat and with low levels of peroxide by dynamic differential scanning calorimetry. *Dent. Mater.* **2**, 175–178, 1986.
- 2) Wilson, T.W. and Turner, D.T.: Characterization of polydimethacrylate and their composite by dynamic mechanical analysis. *J. Dent. Res.* **66**, 1032–1035, 1987.
- 3) Abadie, M.J.M. and Appelt, B.K.: Photocalorimetry of light-cured dental composite. *Dent. Mater.* **5**, 6–9, 1989.
- 4) Lutz, F. and Phillips, R.W.: A classification and evaluation of composite resin system. *J. Prosthet. Dent.* **50**, 480–488, 1983.
- 5) Cook, W.D. and Standish, P.H.: Cure of resin based restorative materials II. White light photopolymerized resins. *Aust. Dent. J.* **28**, 307–311, 1983.
- 6) Stafford, G.D. and Brooks, S.C.: The loss of residual monomer from acrylic orthodontic resins. *Dent. Mater.* **1**, 135–138, 1985.
- 7) Ferracane, J.L. and Greener, E.H.: The effect of resin formulation on degree of conversion and mechanical properties of dental restorative resins. *J. Biomed. Mater. Res.* **20**, 121–131, 1986.
- 8) Asmussen, E. and Peutzfeldt, A.: Mechanical properties of heat treated restorative resins for use in the inlay/onlay technique. *Scand. J. Dent. Res.* **98**, 564–567, 1990.
- 9) Hirose, T., Wakasa, K. and Yamaki, M.: A visible-light activating unit with experimental light-conductor-photopolymerization in bis-GMA unfilled resins for dental application. *J. Mater. Sci.* **25**, 932–935, 1990.
- 10) Peutzfeldt, A. and Asmussen, E.A.: Influence of carboxylic anhydrides on selected mechanical properties of heat-cured resin composites. *J. Dent. Res.* **70**, 1537–1541, 1991.
- 11) Urabe, H., Wakasa, K. and Yamaki, M.: Cure performance of multifunctional monomer to photo-initiator: a thermoanalytical study on bis-GMA based resins. *J. Mater. Sci.* **25**, 3185–3190, 1991.
- 12) Priyawan, R., Wakasa, K., Chowdhury, N.A. and Yamaki, M.: Improvement of bis-GMA-based resins by urethane linkages: DTA and DSC thermal properties. *J. Mater. Sci. Mater. Med.* **6**, 1–4, 1995.
- 13) Ban, S. and Hasegawa, J.: Heat of polymerization of dimethacrylate monomer investigated by isothermal DSC measurement. *Dent. Mater. J.* **3**, 85–92, 1984.
- 14) Shintani, H., Wakasa, K. and Yamaki, M.: Thermoanalytical evaluation of visible light-cured composites. *J. Mater. Sci.* **22**, 1295–1298, 1987.
- 15) Vaidyanathan, J., Vaidyanathan, T.K., Wang, Y. and Viswanadhan, T.: Thermoanalytical characterization of visible light cure dental composite. *J. Oral Rehabil.* **19**, 49–64, 1992.
- 16) Peutzfeldt, A. and Asmussen, E.: Mechanical properties of three composite resins for the inlay/onlay technique. *J. Prosthet. Dent.* **66**, 322–324, 1991.
- 17) Yoshida, K. and Greener, E.H.: Effect of photo-initiator on degree of conversion of unfilled light cured resin. *J. Dent.* **22**, 296–299, 1994.
- 18) Taira, M., Khan, A.M., Ohmoto, K., Satou, N., Shintani, H., Wakasa, K. and Yamaki, M.: Curing performance of four experimental bis-GMA based binary monomer mixtures for dental visible-light-cured composite resin inlays. *J. Mater. Sci. Letters* **13**, 1229–1231, 1994.
- 19) Chowdhury, N.A., Wakasa, K., Priyawan, R. and Yamaki, M.: Effect of filler content on mechanical strength in bis-GMA based resins with urethane linkages. *J. Mater. Sci. Mater. Med.* **6**, 400–403, 1995.
- 20) Ruyter, I.E. and Øysaød, H.: Composite for use in posterior teeth: composition and conversion. *J. Biomed. Mater. Res.* **21**, 10–24, 1987.