

## HPLC Analysis of Residual Monomers in Ternary Bis-GMA/TEGDMA/Urethane Resin Systems

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### ABSTRACT

The monomers in ternary visible light-cured (VLC) bis-GMA/TEGDMA/urethane resins — bis-GMA (1)/TEGDMA (2)/urethane (1) and bis-GMA (1)/TEGDMA (1)/urethane (1) — were determined qualitatively and quantitatively by means of high-performance liquid chromatography (HPLC). The level of residual monomers remaining in the set resins due to visible light curing was analyzed. Both exhibited higher bis-GMA residual monomer than TEGDMA and urethane residual monomers, and urethane monomer content was fairly equivalent to TEGDMA, with the calibration curve in HPLC analysis to determine residual monomers in the set resins. Two ternary material showed lower level of residual monomer contents at longer irradiation time of 80 sec than at 40 sec during curing.

### INTRODUCTION

Dental visible light-cured (VLC) resin composites have been accepted as a restorative material which has higher curing performance than conventionally chemical-cured resin composites<sup>1-3</sup>. VLC resin composites usually exhibit a smaller unreacted monomer content than does the polymethyl methacrylate<sup>4</sup>. To extract rapidly the monomers in the hardened composite resins, acetone and

chloroform were effective solvents to examine unreacted monomers as residual monomers<sup>4</sup>. A tiny amount of residual monomers derived from the set resins was measured, and such solvents as methanol, acetone and acetonitrile were used to accelerate the extraction of unreacted residual monomers from the set resin composites in the laboratory test<sup>4-9</sup>. The residual monomer contents in the set chemically-cured samples were analyzed using HPLC technique similar to those reported by other studies, such as Fourier transform infrared spectroscopy and gas-liquid chromatography<sup>10-15</sup>. The resin matrix in dental resin composites was mainly composed of polyfunctional methacrylate monomers, such as triethylene glycol dimethacrylate (TEGDMA) and bis-phenol A glycidyl dimethacrylate (bis-GMA)<sup>7-9</sup>. Polyfunctional urethane monomers have been frequently applied to dental bis-GMA-based resins to obtain strengthened resin matrix, higher curing performance and less residual monomers<sup>3,4,16,17</sup>.

This study evaluated, using HPLC analysis, the level of residual monomer content left in photo-cured ternary bis-GMA/TEGDMA/urethane monomer mixtures, and examined their monomers as a function of radiation time at visible light curing.

### MATERIALS AND METHODS

The resins used in this study were E-1 and E-2. E-1 (bis-GMA (1)/TEGDMA (2)/Exp3 (1)) includes bis-GMA (1/4; 25 wt%), TEGDMA (1/2; 50 wt%) and Exp3 (1/4; 25 wt%) and E-2 (bis-GMA (1)/TEGDMA (1)/Exp3 (1)) has bis-GMA (1/3; 33.33 wt%), TEGDMA (1/3; 33.33 wt%) and Exp3 (1/3; 33.3 wt%). The resin monomer mixtures were bis-GMA (Shin-Nakamura Chem, Wakayama) and TEGDMA (Tokyo Kasei Co, Tokyo). Urethane monomer was added to binary bis-GMA/TEGDMA-

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**Table 3** HPLC analysis condition.

Apparatus	: Twincle, Jasco, Japan
Column	: Inertsil ODS-2 (5 mm W×250 mm L)
Mobile phase	: 75% ACN
Flow rate	: 0.5 ml/min
Column temp.:	30°C
Solvent	: Pure acetonitrile
Wavelength	: 220 nm
Range	: 0.16
Detector	: UV-100
Injection	: 5 $\mu$ l

the Exp3 content (area  $Y_0$  in 3, Table 4) to agree with  $Y_1$  (Table 4).

## RESULTS

Figure 1 shows the HPLC analysis results of the extract from the acetonitrile solvent obtained from each sample of bis-GMA/TEGDMA and Exp3 and the sample E-1 or E-2, and bis-GMA/Exp3 was needed to measure Exp3 content left in the set resin. The curves represented each peak indicating bis-GMA, TEGDMA and Exp3. Each peak of bis-GMA, TEGDMA and Exp3 in the samples was identified by comparing each peak area of monomers with standard samples. On the curves, the tracing of each peak at the retention time was marked to identify it, showing that TEGDMA peak appeared as a single strong peak and the Exp3 peak was found with bis-GMA.

Figure 2 shows calibration curves of each sample of bis-GMA, TEGDMA and Exp3 with  $r=0.9999$ . Using their calibration curves their amount of monomers were given in Table 5. Using the extracted solvent containing the residual monomers in the set resin samples at photocuring, each proportion of the residual monomers left in the resins was obtained by each calibration curve. It was clear that the quality of bis-GMA, TEGDMA and Exp3

monomers existed as detected. At each retention time, residual monomers (bis-GMA and TEGDMA) in the set E-1 and E-2 resins were less at the 80 sec irradiation than 40 sec irradiation, showing that the residue TEGDMA content was less than those bis-GMA and Exp3 urethane and also urethane monomer in E-1 than E-2 was less.

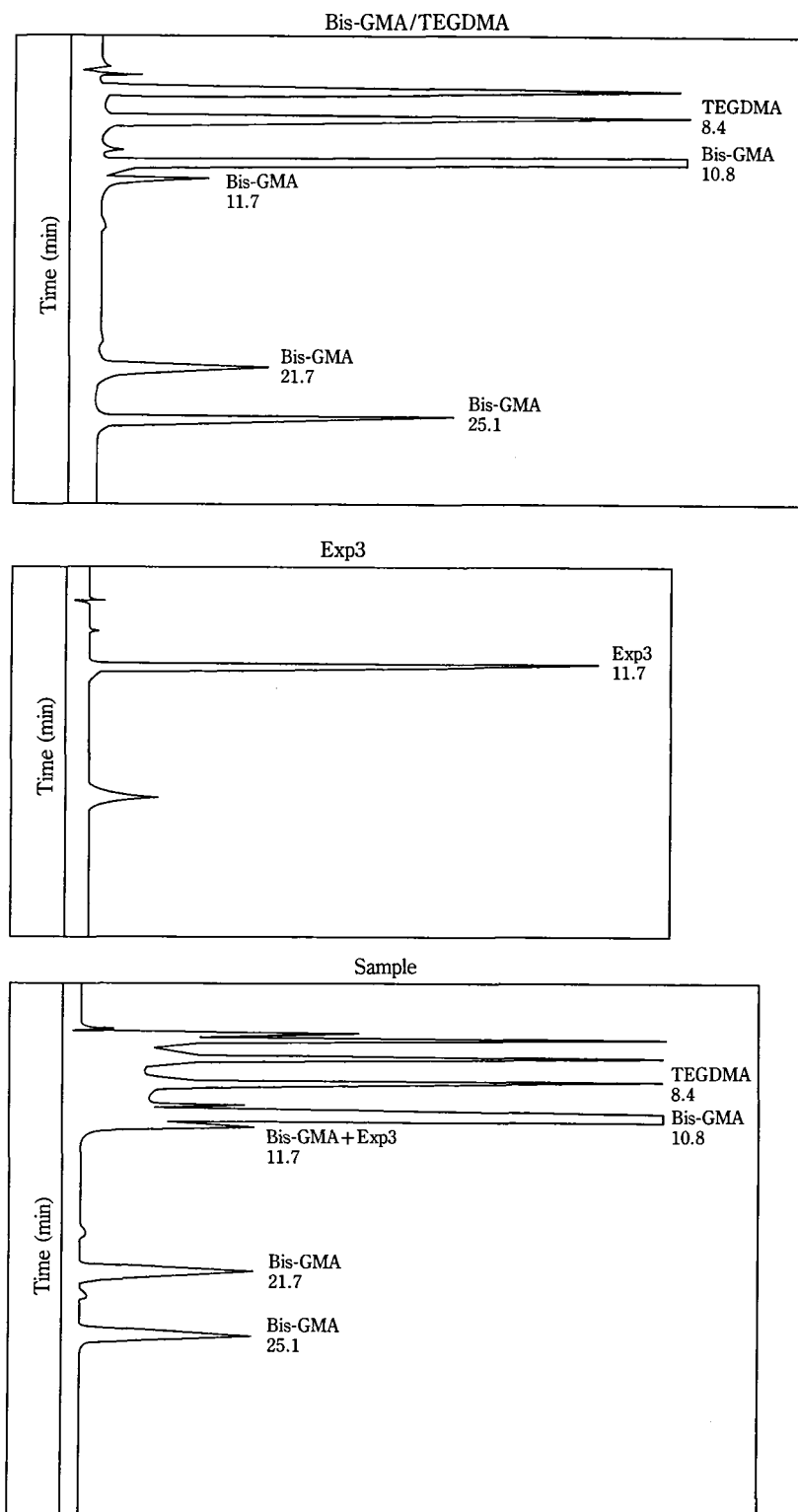
## DISCUSSION

The residual monomer contents in the set composite resins were analyzed using the solvent extraction method<sup>1-4,18,19</sup>, and their residual TEGDMA and bis-GMA monomers left in VLC bis-GMA/TEGDMA based resins were identified by acetonitrile solvent method<sup>18</sup>. Hirasawa et al reported that a long period (7 days) was required to examine the monomers fully dissolved in the solvent from the resin<sup>19</sup>. VLC resins appear to have a level of residual monomers as equal, or high as 0.22 to 0.61% (E-1) and 0.36 to 1.57% (E-2), in comparison with 0.2 to 0.5% in conventional heat-cured resins<sup>20</sup>. The percentage of residual TEGDMA monomer left in bis-GMA/TEGDMA/urethane-based resins was small as compared with bis-GMA monomer (Table 5). An approach might be needed to study the long-term serviceability to the patients of VLC composite resins, suggesting the importance of immersing the set resins in water as long as possible.

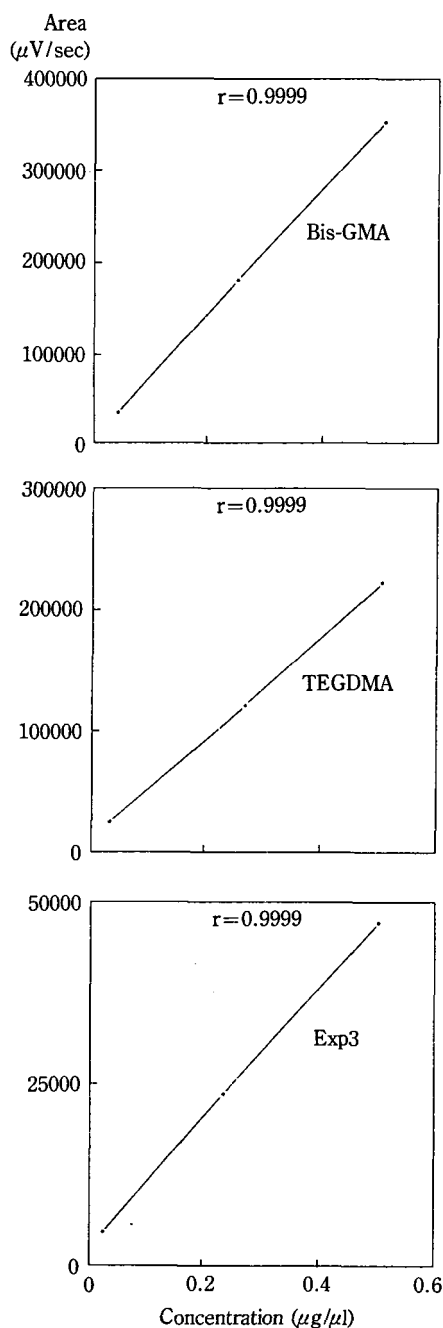
The effect of irradiation times (40 and 80 sec) on residual monomers in the set resins was tested clearly (Table 5). A small percent of residual monomers (urethane and TEGDMA) was obtained for experimental E-1 and E-2 resins. There appeared a significant difference between the samples E-1 and E-2 for urethane monomer at each irradiation of 40 and 80 sec ( $p<0.05$ ). It is noted that the urethane monomer (Exp3) gives better curing performance of the set E-1 and E-2 resins because of less residual urethane monomer than bis-GMA.

**Table 4** Calculation method for each amount of residual monomers left in the set resins cured by visible light. Each residual monomer content is calculated at each retention time according to the equations.

I		II		III
Bis-GMA + Exp3		Bis-GMA		Exp3
A	Bis-GMA 10.8	IB	Bis-GMA 10.8	Exp3 11.7
S	Bis-GMA + Exp3 11.7	IB*	Bis-GMA 11.7	
$Y_1 = S - \alpha\alpha$ (1)		where $Y_1$ is calculated from the area of I and II, and A and S mean area of I, and also IB* and IB area of II.		
$\alpha = IB^*/IB$ (2)		$Y_0$ is calculated from the area of III.		



**Figure 1** HPLC chromatograms of each sample of bis-GMA/TEGDMA, Exp3 and the sample. See Table 4 for each.



**Figure 2** Calibration curves of bis-GMA, TEGDMA and Exp3 for the calculation of residual monomers. See Table 4 for the calculation.

As indicated in the HPLC chart (Figure 1), the urethane monomer (Exp3) did not separate easily, showing that the isomers of bis-GMA appeared with Exp3 monomer at one retention time. Residual monomer (bis-GMA and TEGDMA) contents in the set resins found by this extract

**Table 5** The contents (wt%) of residual monomers dissolved in the solvent over a 7-day period at photo-curing, which were obtained at each retention time.

Monomers	Peak time min	E-1		E-2	
		40 s	80 s	40 s	80 s
Bis-GMA	10.8	0.61 (0.07)	0.46 (0.01)	1.51 (0.17)	1.36 (0.10)
	21.7	0.55 (0.07)	0.43 (0.02)	1.57 (0.15)	1.41 (0.10)
	25.1	0.25 (0.03)	0.22 (0)	0.54 (0.05)	0.45 (0.04)
TEGDMA	8.4	0.53 (0.15)	0.37 (0)	0.47 (0.10)	0.36 (0.08)
Exp3	11.7	0.58 (0.19)	0.43 (0.03)	0.99 (0.08)	0.99 (0.11)

analysis were comparable to those reported by other workers using different experimental techniques, such as FT-IR and GC analyses<sup>14,21</sup>. There was less residual TEGDMA than bis-GMA monomer in the E-1 and E-2 resins (Table 5). More bis-GMA residue was analyzed in the solvent from the set E-1 and E-2 samples than in TEGDMA, and bis-GMA/TEGDMA/urethane-based resins was effective as a VLC resin with less residual TEGDMA monomer than the others.

It is evident that their small contents of residual monomers are analyzed in ternary bis-GMA/TEGDMA/urethane resins by separating the superimposed peaks in HPLC chart. The synthesized urethane monomer was applicable to VLC bis-GMA-based resins, showing that urethane in bis-GMA (1)/TEGDMA (2)/urethane (1) resin possessed to residue equivalent to TEGDMA monomer, or fairly less than bis-GMA.

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## REFERENCES

- 1) Wilson, T.W. and Turner, D.T.: Characterization of polydimethacrylates and their composites by dynamic mechanical analysis. *J. Dent. Res.* 66, 1032-1035, 1987.
- 2) Eliades, G.C., Vougiouklakis, G.J. and Caputo, A.A.: Degree of double bond conversion in light-cured composites. *Dent. Mater.* 3, 19-25, 1987.

- 3) 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.
- 4) Tanaka, K., Taira, M., Shintani, H., Wakasa, K. and Yamaki, M.: Residual monomers (TEGDMA and Bis-GMA) of a set visible-light-cured dental composite resin when immersed in water. *J. Oral Rehabil.* **18**, 353-362, 1991.
- 5) Cook, W.D. and Standish, P.H.: Polymerization kinetics of resin-based restorative materials. *J. Biomed. Mater. Res.* **17**, 275-282, 1983.
- 6) Stanford, G.D. and Brooks, S.C.: The loss of residual monomer from acrylic orthodontic resins. *Dent. Mater.* **1**, 135-138, 1985.
- 7) Hirose, T., Wakasa, K. and Yamaki, M.: A visible-light activating unit with experimental light-conductors - photopolymerization in bis-GMA unfilled resins for dental application. *J. Mater. Sci.* **25**, 932-935, 1990.
- 8) Urabe, H., Wakasa, K. and Yamaki, M.: Cure performance of multifunctional monomers to photoinitiators: a thermanalytical study on bis-GMA-based resins. *J. Mater. Sci.* **26**, 3185-3190, 1991.
- 9) Peutzfeldt, A. and Asmussen, E.: Influence of carboxylic anhydrides on selected mechanical properties of heat-cured resin composites. *J. Dent. Res.* **70**, 1537-1541, 1991.
- 10) Asmussen, E.: Factors affecting the quality of remaining double bonds in restorative resin polymers. *Scand. J. Dent. Res.* **90**, 490-496, 1982.
- 11) Douglas, W.H. and Bates, J.F.: The determination of residual monomer in polymethylmethacrylate denture base resins. *J. Mater. Sci.* **13**, 2600-2604, 1978.
- 12) Leung, R., Fan, P.L. and Jonston, W.M.: Exposure time and thickness on polymerization of visible-light composite. *J. Dent. Res.* **61**, Abstr. 623, 1982.
- 13) Swartz, M.L., Phillips, R.W. and Rhodes, B.F.: Visible light-activated resins. Depth of cure. *J. Dent. Res.* **61**, Abstract 823, 1982.
- 14) Antonucci, J.M. and Toth, E.E.: Extent of polymerization of dental resins by differential scanning calorimetry. *J. Dent. Res.* **62**, 121-125, 1983.
- 15) 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.
- 16) 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.
- 17) Taira, M., Khan, A.M., Tanaka, T., Shintani, H., Wakasa, K. and Yamaki, M.: Evaluation of the curing behaviours of three commercial VLC composite resins by DSC and DTA thermal analyses. *J. Mater. Sci. Mater. Med.* **6**, 167-171, 1995.
- 18) Taira, M., Khan, A.M., Ohmoto, K., Tanaka, K., Satou, N., Shintani, H., Wakasa, K. and Yamaki, M.: Residual monomers (TEGDMA and Bis-GMA) in three commercial VLC composite resins. *Hiroshima Daigaku Shigaku Zasshi* **26**, 313-317, 1994.
- 19) Hirasawa, T., Nasu, I., Hirabayashi, S. and Hirasawa, I.: The method of quantitative analysis of residual monomer in dental resin using thin film samples. *Shika Zairyou Kikai* **3**, 243-249, 1984.
- 20) McCabe, J.F.: *Applied Dental Materials*, 7th ed, Oxford, Blackwell, Scientific Publications, 1990, pp 127.
- 21) Yamaga, T., Taira, M., Sato, Y., Akagawa, Y., Wakasa, K. and Yamaki, M.: Compositional analysis of commercial light-cured composite resin veneering materials. *Shika Zairyou Kikai* **14**, 93-100, 1995.