

Residual Monomers (TEGDMA and Bis-GMA) in Three Commercial VLC Inlay Composite Resins

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Introduction

Visible-light-cured (VLC) dental composite resins have been widely accepted as anterior filling materials¹⁾. Several clinical drawbacks (e.g. limited depth of cure and insufficient wear resistance) have, however, limited their use, particularly in the load bearing posterior regions²⁾. To offset these drawbacks, recently, the so called inlay/onlay technique, including extraoral curing of the composites, have been introduced³⁾. Dental composites usually consist of an organic matrix and inorganic filler. Difunctional methacrylate such as triethyleneglycol dimethacrylate (TEGDMA) and Bis-phenol A-glycidyl dimethacrylate (Bis-GMA) are generally used as the organic matrix⁴⁾, while silica-glass or quartz are widely used as the inorganic filler⁵⁾. Although the formulations of direct-filling composites have been well published⁶⁻⁸⁾, there have been few studies, in which chemical compositions of the organic phase in the inlay composites are actually examined⁹⁾. The clinical performance of the composites is highly affected by the residual monomer contents in once set composites. In general, more residual monomers, weaker and more chemically degradable the composites¹⁰⁾. It seems necessary to identify the monomer contents of inlay composites before curing, and to measure the residual monomer contents of inlay composites after curing.

Therefore, the purpose of the present study was (1) to examine TEGDMA and Bis-GMA contents in the organic phase of three commercial VLC inlay composite resin pastes and three commercial VLC direct-filling composite

resin pastes (as control), and (2) to measure the amounts of residual TEGDMA and Bis-GMA contents in the six composite specimens cured both by VL only and by VL plus heat.

Materials and methods

Materials

Table 1 shows three commercial VLC inlay composite resins and three commercial VLC direct filling composite resins examined, with details of type, brand name, shade, batch number, manufacturer and code. The pure standards for chemical analyses were triethyleneglycol dimethacrylate (Tokyo Kasei Co., Tokyo, Japan) (TEGDMA) and Bis-phenol A-glycidyl dimethacrylate (D-GMA, Shin-Nakamura Co., Wakayama, Japan) (Bis-GMA).

Determination of inorganic filler contents in the composite

Table 1 Six commercial VLC composite resins examined, with details of type, brand name, shade, batch number, manufacturer and code.

| Type | Brand name | Shade | Batch number | Manufacturer | Code |
|----------------|--------------------------|-------|--------------|--------------------------|------|
| Inlay | CR inlay | US | 1007C | Kuraray Co., Japan | CRI |
| | Estilux Posterior CVS | A20 | Ch. B 33 | Kulzer Co., Germany | CVS |
| | Brilliant DI | D3U | 060789-19 | Coltene Co., Switzerland | BDI |
| Direct-filling | Clearfil Photo Posterior | US | 1025 | Kuraray Co., Japan | CPP |
| | P-50 | U | 9350U | 3M Co., U.S.A. | P50 |
| | Brilliant Lux | D3U | 190489-16 | Coltene Co., Switzerland | BLX |

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Specimens

The composite pastes were fired up to 575°C in a ceramic crucible in an electrically heated furnace (Accutherm II, Jelenco Co., N.Y., U.S.A.). The weight percentage of the residue in the original composite paste was regarded as the amount of inorganic fillers according to the international specification¹¹.

Monomer analyses of the composite pastes by HPLC

To examine the organic constituents of the composite specimens, small portion (0.2 g) of the composite paste was dissolved in acetonitrile (5 ml), centrifuged at 1585 g for 15 min and a small aliquot (5 μ l) was injected into a chromatographic column of a high-performance liquid chromatography (HPLC) (TWINCLE, JASCO Co., Japan). The experimental conditions of HPLC were: column-inertsil ODS-2; column temperature-30°C; mobile phase-70% acetonitrile; wavelength-254 nm; range-0.16. Quantitation of TEGDMA and Bis-GMA monomers in the composite paste was achieved by measuring the peak area of these two monomers at specific retention time in the composite and relating these to the calibration curves (between peak area and concentration) constructed on the pure monomer standards over the appropriate range. Monomer analyses were repeated nine times (i.e. three extraction x three repetition of the measurements) on each composite specimen.

Residual monomer measurements in the set composites by HPLC

Samples for residual monomers were prepared by packing the resin pastes in a stainless steel mold (3 mm in height and 6 mm in diameter), both ends of which were covered and pressed by two glass plates. The composite pastes were then cured by VL from one direction only, according to the manufacturers' recommended conditions (Table 2). To determine the effect of post-curing by heat on the residual monomers, the samples were divided into two groups. One group was polymerized by VL only, while the other group was heat treated following curing by VL. Post-curing by heat was carried out in a heat box (KL100, Kuraray Co., Osaka, Japan) employing an identical heating condition of 100°C for 15 min. The samples were then bench cooled. The set samples stored in a desiccator at 37°C for 24 h were milled by mortar and pestle, immersed in acetonitrile, held at 37°C for additional 24 h, centrifuged at 1585 g for 15 min, and a small aliquot

Table 2 Manufacturers' recommended conditions for VL-curing of six composite specimens

| Sample code | Light source | Irradiation period (s) |
|-------------|------------------------------------|------------------------|
| CRI | Quick Light (Morita Co., Japan) | 40 |
| CVS | Translux EC (Kulzer Co., Germany) | 40 |
| BDI | Arcus 1 (Coltene Co., Switzerland) | 120 |
| CPP | Quick Light (Morita Co., Japan) | 30 |
| P50 | Optilux (3M Co., U.S.A.) | 30 |
| BLX | Arcus 1 (Coltene Co., Switzerland) | 60 |

(5 μ l) was injected into HPLC for the determination of residual monomer concentrations of the composite specimens, employing the same experimental condition described above. This technique has been proven to be appropriate to extract most residual monomers from the set composites, as reported elsewhere¹². Residual monomer measurements were repeated nine times (i.e. three extraction x three repetition of the measurements) on each specimen.

Results

Table 3 shows inorganic filler and organic phase contents of six commercial VLC composite resin specimens. The inorganic filler content of P50 was the highest, followed by CPP, CRI, CVS and BLX, while BDI had the lowest inorganic filler content. The organic phase contents (wt%) of the composite specimens were determined by calculating 100 subtracted by the inorganic filler contents.

Fig. 1 shows the HPLC chromatogram of the acetonit-

Table 3 Concentrations of inorganic filler and organic phase of six composite resin pastes checked out (wt%), as mean values of three measurements with standard deviations

| Sample code | Inorganic filler content | Organic phase content |
|-------------|--------------------------|-----------------------|
| CRI | 87.10 \pm 0.15 | 12.90 |
| CVS | 85.60 \pm 0.25 | 14.40 |
| BDI | 76.72 \pm 1.91 | 23.28 |
| CPP | 88.00 \pm 0.35 | 12.00 |
| P50 | 88.20 \pm 0.25 | 11.80 |
| BLX | 77.10 \pm 0.88 | 22.90 |

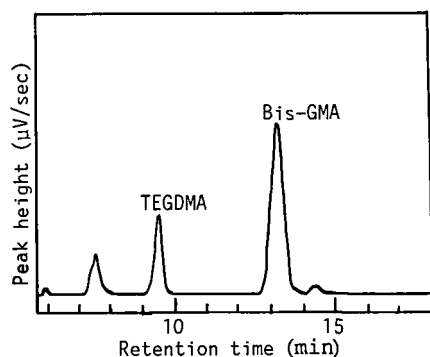


Fig. 1 HPLC chromatograph of the acetonitrile extract obtained from an inlay composite resin (CRI).

riple extract obtained from CRI. The retention time of TEGDMA and Bis-GMA were 9.4 min and 13.2 min, respectively. The concentrations of TEGDMA and Bis-GMA in the resin phase of the composite specimens are given in Fig. 2. All six composite specimens contained TEGDMA, Bis-GMA and other organic substances (others). The relative content of TEGDMA in the resin phase was the highest in BLX, followed by BDI, P50, CVS and CPP, while it was the least in CRI. The relative amount of Bis-GMA in the resin phase was the highest in CVS, followed by CPP, BLX, BDI and CRI, whilst it was the least in P50. No systematic difference was found in the amounts of TEGDMA and Bis-GMA monomers in the resin phases between inlay and direct-filling composite resin pastes.

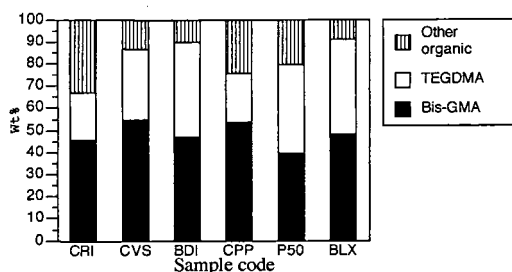


Fig. 2 TEGDMA and Bis-GMA monomer contents in the organic phases of six composite resin pastes examined, expressed as mean values of nine measurements.

Table 4 shows the results of residual TEGDMA monomer measurements. Before heat treatment, CPP showed the lowest residual TEGDMA content, followed by CRI, BLX, BDI, P50 while CVS showed the highest

Table 4 Residual TEGDMA contents, relative to original TEGDMA in the organic phase of six composite specimens (wt%), expressed as mean values of nine measurements with standard deviations

| Sample code | Residual TEGDMA in the samples cured by VL only | Residual TEGDMA in the samples cured by VL plus heat |
|-------------|---|--|
| CRI | 5.8±0.4 | 1.4±0.5 |
| CVS | 15.3±0.9 | 9.7±0.8 |
| BDI | 8.7±0.5 | 3.0±0.8 |
| CPP | 4.9±0.3 | 2.9±0.4 |
| P50 | 12.8±0.9 | 6.2±0.4 |
| BLX | 6.3±0.7 | 3.9±0.4 |

residual TEGDMA content. Following secondary cure by heat, CRI showed the least residual TEGDMA concentration, followed by CPP, BDI, BLX and P50, while CVS showed the highest TEGDMA concentration. Post-curing by heat significantly reduced the residual TEGDMA contents of all the once photo-cured composite specimens. Table 5 shows the results of residual Bis-GMA monomer measurements. Prior to heat treatment, the residual Bis-GMA content was the lowest in CPP, followed by BDI, BLX, CRI and P50, while it was the highest in CVS. Following post-curing by heat, the amount of residual Bis-GMA was the lowest in CRI, followed by CPP, BDI, BLX and CVS, while it was the highest in P50. Post-curing by heat considerably decreased the residual Bis-GMA contents of all the once VLC composite specimens.

Table 5 Residual Bis-GMA contents, relative to original Bis-GMA in the organic phase of six composite specimens (wt%), expressed as mean values of nine measurements with standard deviations

| Sample code | Residual Bis-GMA in the samples cured by VL only | Residual Bis-GMA in the samples cured by VL plus heat |
|-------------|--|---|
| CRI | 13.0±0.8 | 6.9±0.8 |
| CVS | 27.5±1.3 | 12.5±0.5 |
| BDI | 12.8±0.9 | 8.4±0.2 |
| CPP | 11.2±0.4 | 8.2±0.5 |
| P50 | 18.8±1.1 | 12.3±1.0 |
| BLX | 3.0±0.9 | 8.7±0.8 |

Discussion

It was confirmed from the results obtained here that the organic phases of all the six composite resin pastes examined contained Bis-GMA as base monomer and TEGDMA as diluent monomer, although no definite differentiation could be found in these two monomer contents between inlay and direct-filling composites. The total of these two monomer contents in six composite pastes were, however, less than 100 wt%. Other organic substances contained might be lower molecular weight substances such as polymerization initiator, inhibitor, cross-linking agent and reaction by-product of Bis-GMA, and higher molecular weight substances such as oligomers (e.g. Bis-GMA-based oligomer system¹³). TEGDMA and Bis-GMA contents of CRI and CPP were especially low. According to the manufacturer, CRI and CPP might contain other base monomer such as tetramethacryloxyethyl 2,2,4-trimethylhexamethylene diurethane (UTMA) in their organic phases. All six composite pastes might involve such variation in the monomer contents.

All six composite resin paste specimens (3 mm thick) set with first VL irradiation without any uncured portion at the bottom of the specimen. It should be, however, pre-cautioned here that more monomers could be converted at the irradiated (top) side, compared with those at the bottom side. With all such possible variation in monomer contents which depends upon the thickness of the specimen, it seems still clinically relevant to study the whole concentrations of residual monomers in the set specimens because the height of composite resin inlay restorations often exceeds 3.0 mm. Furthermore, preliminary microhardness measurements revealed that the depth of cure of these six composites set by VL far exceeded 3.0 mm, suggesting that the variation in the monomer content might be small.

In all set six composites, more Bis-GMA remained to be uncured, compared with TEGDMA (Tables 4 and 5). The reason for this might be attributed to the sluggish molecular movement of Bis-GMA monomer with high molecular weight of 512, reactivity of which with both free-radicals and the chain transfer complex limited. TEGDMA with low molecular weight of 286 could react with radicals more easily¹⁴.

It was demonstrated here that post-curing by heat significantly decreased the residual TEGDMA and Bis-GMA monomers in the once photo-cured composites. It

can be speculated that secondary cure by heat might be effective in reducing other residual monomers contained in the set composites. Due to secondary cure by heat, the mechanical strength (e.g. hardness and diametral tensile strength) of these composites were also significantly increased, as reported elsewhere¹⁵, which might be directly related to the reduction in residual monomer contents. It should be, however, noted here that post-curing by heat might also increase the molecular weight of once set polymer chains (copolymers), leading to the increment in the mechanical strength. These two factors might occur simultaneously, increasing the strength.

In the next phase of this study, it is strongly expected to investigate the relationship between residual monomer contents and clinical performance of the composites such as wear resistance, resistance to marginal fracture and resistance to discoloration.

Conclusion

We examined three commercial VLC inlay composite resins and three commercial VLC direct-filling composite resins for their organic phases in the uncured pastes, and residual monomer contents in the set composites cured both by VL and by VL plus heat, using HPLC.

(1) All six composite specimens contained TEGDMA and Bis-GMA monomers as well as other organic substances. No systematic difference was found in TEGDMA and Bis-GMA contents in the organic phases between inlay and direct-filling composite pastes.

(2) In the set composite specimens, more Bis-GMA remained to be uncured, compared with TEGDMA.

(3) It was confirmed that post-curing by heat significantly reduced residual TEGDMA and Bis-GMA monomers in once photo-cured composite specimens.

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