EVALUATION ON RESIDUAL MONOMER OF HDDMA MATRIX SYSTEM ON FIDER REINFORCED CONDOSITES (FRC)

(EVALUASI MONOMER RESIDU DARI SISTEM MATRIKS HDDMA PADA FIDER REINFORCED CONDOSITES (FRC))

Siti Sunarintyas*, Widowati Siswomihardjo*, Dyah Irnawati*, Jukka Pekka Matinlinna**

*Faculty of Dentistry, Gadjah Mada University, Indonesia
**University of Hong Kong, Hong Kong, China

Jl. Denta Sekip Utara, Yogyakarta 55281
E-mail: sunarintyassiti@ugm.ac.id

Abstract

Matrix system used bis-GMA was reported hazardously. An alternative monomer such as 1,6-hexanediol dimethacrylate (HDDMA) was under research. The aim of this study was to evaluate residual monomer content of HDDMA based matrix compositions on FRCs (fiber-reinforced composites). Three monomers based on bis-GMA (Sigma-Aldrich, USA), methylmethacrylate (MMA, ProSciTech, Australia), HDDMA (Esstech, USA) were used and also camphorquinone (CQ, Esstech, USA), N,N-cyanoethyl methylaniline (CEMA, Esstech, USA), E-glass fibers (StickTech, Finland). The matrix ratios (weight %) were 78.4% bis-GMA+19.6% MMA+1.0% CQ+1.0% CEMA (control-group), 78.4% HDDMA+19.6% MMA+1.0% CQ+1.0% CEMA (EXP-1group), and 49.0% HDDMA+49.0% MMA+1.0% CQ+1.0% CEMA (EXP-2group). Samples with fibers embedded in matrix were light-cured then powdered. Powder of 150mg was diluted in acetonitrile to 10ml. The solution was filtered then injected into HPLC (20µL). Residual monomer content was evaluated by mobile phase of acetonitrile and water of 7:3, flow rate 1mL/minute. The size of column was C185µ, 125mm length, 4mm diameter. UV detection used 275nm. Data were analyzed by ANOVA. The result showed the average of residual monomer content (in %) was: 0.02125±0.00018 (control-group), 0.01660±0.00016 (EXP-1group), 0.01676±0.00033 (EXP-2group). The ANOVA showed significant difference of monomer content among the groups (p<0.05). The LSD showed significant difference between EXP-1 and control-groups; also between EXP-2 and control-groups (p<0.05). There was no significant difference between EXP-1 and EXP-2 groups (p>0.05). In conclusion, a resin matrix system based on HDDMA–MMA (EXP-1 and EXP-2 groups) revealed significant difference of residual monomer content to bis-GMA–MMA (control-group) system. The HDDMA-MMA matrix system had less residual monomer content than bis-GMA-MMA.

Key words: residual-monomer, fiber-reinforced composite, 1,6-hexanediol dimethacrylate

Abstrak

Sistem matriks berbasis bis-GMA dilaporkan bersifat kurang aman bagi tubuh. Monomer alternatif 1,6-hexanediol dimethacrylate (HDDMA) sedang dalam penelitian. Tujuan penelitian ini adalah mengevaluasi jumlah kandungan monomer residu sistem matriks HDDMA pada FRC(fiber-reinforced composite). Tiga komposisi monomer digunakan dalam penelitian yaitu bis-GMA (Sigma-Aldrich, USA), methylmethacrylate (MMA, ProSciTech, Australia), HDDMA (Esstech, USA), serta camphoroquinone (CQ, Esstech, USA), N,N-cyanoethyl-methylaniline (CEMA, Esstech, USA), E-glassfibers (Sticktech, Finland). Rasio matriks resin (% berat): bis-GMA 78,4% + MMA 19,6% + CQ 1,0% + CEMA 1,0% (kelompok kontrol), HDDMA 78,4% + MMA 19,6% + CQ 1,0% + CEMA 1,0% (kelompok EXP-1), dan HDDMA 49,0%+MMA 49,0% + CQ 1,0% + CEMA 1,0% (kelompok EXP-2). Sampel dengan fiber dalam matriks disinari kemudian dilarutkan dalam acetonitrile hingga 10mL. Larutan disaring, kemudian dinjeksikan ke dalam HPLC 20µL. Jumlah monomer residu dievaluasi menggunakan mobile phase acetonitrile dan air dengan rasio 7:3, kecepatan alir 1mL/minute. Ukuran kolom adalah C 185µm, panjang 125mm, diameter 4mm. Deteksi UV menggunakan panjang gelombang 275nm. Data dianalisis menggunakan ANOVA. Hasil penelitian menunjukkan rerata kandungan monomer residu (%): 0,02125 ± 0,00018 (kelompok kontrol), 0,01660 ± 0,00016 (kelompok EXP-1), dan 0,01676 ± 0,00033 (kelompok EXP-2). Hasil Uji ANOVA menunjukkan perbedaan signifikan kandungan monomer antar kelompok (p<0,05). Uji LSD menunjukkan perbedaan signifikan antara kelompok EXP-1 dan kontrol, juga EXP-2
INTRODUCTION

One new group of non-metallic dental biomaterials is fiber-reinforced composites (FRCs). Fiber-reinforced composites are a novel group of materials that are characterized by reinforcing fibers embedded in a polymer matrix. The reinforcing fibers prevent crack propagation by chemically bonding to the polymer matrix with covalent bonds. The use of FRCs is growing in many dental applications, such as in fixed partial dentures (FPD), periodontal splints, endodontic posts, orthodontic appliances, and some other indirect restorations. Previous research reported that some commercial FRCs had flexural moduli and strengths seven times those of composite resins with particulate fillers.

Matrix of FRC consists of polymerized monomers with the function of holding fibers together in the composite structure. It also transfers stresses between fibers and protects the fibers from the outside environment such as chemicals, moisture and mechanical shocks. Matrix may influence the compressive strength, interlaminar shear and inplane shear properties, interaction between the matrix and the fiber and defects in the composite.

There are two kinds of resin matrix which are used in dental FRCs: the crosslinked and linear polymers. The crosslinked polymer which is also called a thermostet polymer is multifunctional or dimethacrylate resins. The linear polymer is also called a thermoplastic polymer referring to monofunctional methacrylate monomers from the composite in the body has been suggested to cause adverse tissue reactions such as allergic reactions, or the monomers can even be estrogenic in nature.

It is reported that bis-GMA becomes the most cytotoxic monomer among 35 dental resin composite monomers includes bis-GMA, GMA, HDDMA, BPA, CQ, TEGDMA, HEMA, MMA, etc. Other author reported that bis-GMA had strong haemolytic potency due to the chemical structure with a high hydrolytic nature. The aromatic bis-GMA is slightly more cytotoxic than aliphatic monomer UDMA. Cell toxicity was observed at bis-GMA concentrations of 50 pg/ml and higher. In fact, recent commercial matrix system of FRCs used bis-GMA system as the basic matrix component. To reduce the harmful effect of such matrix system, it is necessary to look for a new safer matrix system for human instead of bis-GMA.

Resin matrix 1,6 hexanediol dimethacrylate (HDDMA, Figure 2) has similar reactive group to bis-GMA. The HDDMA properties are low
viscosity, fast curing monomer with low volatility, hydrophobic backbone, and good solvency for use in free radical polymerization. The HDDMA has water repellency property (hydrophobic). It is used as a functional monomer for polymers and as a cross-linking agent between molecular chains of polymers. The HDDMA has been used for adhesives and sealants, coatings, elastomer, photopolymers, electronics, improved adhesion, hardness, abrasion and heat resistance. It is reported that none of HDDMA components are listed by IARC, NTP, OSHA, ACGIH, as carcinogens. Moreover, HDDMA is reported not to produce mutagenic, embryo toxic, teratogenic, or reproductive effects in human. The objective of this current study was to evaluate residual monomer content of HDDMA matrix system on FRCs comparing to bis-GMA matrix system.

For each composition, twelve identical rectangular specimens with dimensions 2 mm x 2 mm x 25 mm were prepared. Air bubbles were removed carefully by pressing the fiber bundles with a hand instrument. The resin matrix was light cured with a halogen light curing unit on both sides of the specimens for 3 x 40 s. The average light intensity was 700mW/cm² measured with Cure Rite™ Model 8000 hand held radiometer, and the wavelength range of the curing unit was 400-500 nm. The specimen then powdered by diamond dental bur.

The residual monomer testing was adapted from ISO 3696: 1987 (E). HPLC was used to quantity the residual monomer content of the HDDMA matrix system and bis-GMA matrix system. A sample of 150 mg was diluted in ace-tonitrile to 10 ml. Magnetic stirrer was used to dissolve the solution (72 h). The supernatant of the solution was filtered through a 0.45 µm pore Millipore filter. The solution of 20 µL was injected into the HPLC. Residual monomer content was evaluated using the mobile phase of ace-tonitrile and water with 7:3 ratio, flow rate 1mL/minute. The size of column was C185µ, length 125mm, and 4mm in diameter. UV detection used 275nm.

The linear fitting of bis-GMA and HDDMA calibration curve used to calculate the concentration of each residual monomer in the sample solution, based on the area of the chromatographic peaks at the corresponding retention times. Data were analyzed by one way analysis of variance (ANOVA) followed by Post Hoc test of LSD. P-values less than 0.05 were considered to be statistically significant in all tests.

**RESULTS**

The concentration of bis-GMA residual monomer from E-glass FRC was obtained by calculating the peak area of the specimen using the formula of y= 0.9998 x + 6.2728 x 10⁻³ from the standard bis-GMA curve; while for HDDMA residual monomer from the formula of y= 0.9877 x + 6.0253 x 10⁻³ from the standard HDDMA curve. The average concentration of residual monomer of bis-GMA or HDDMA obtained in weight percentage was shown in Table 1.

| Matrix composition | Mean ± S.D. |
|--------------------|-------------|
| Control group      | 0.02125 ± 0.00018 |
| EXP-1 group        | 0.01660 ± 0.00016 |
| EXP-2 group        | 0.01676 ± 0.00033 |
The residual monomer evaluation revealed the control-group (bis-GMA matrix system) mean value was higher than the EXP-1 group and the EXP-2 group (HDDMA matrix system). Statistical analysis by one way ANOVA showed significant difference of residual monomer content among the groups (p<0.05) (Table 2).

Table 2. The ANOVA of residual monomer content

| Source          | F    | F      | Sig     |
|-----------------|------|--------|---------|
| Between group   | 2    | 1797.87100 | 0.00001 |
| EXP-1 group     | 15   |         |         |
| EXP-2 group     | 17   |         |         |

Further Post Hoc analysis by LSD showed significant difference between EXP-1 and control-groups; and also between EXP-2 and control-groups (p< 0.05); whilst no significant difference between EXP-1 and EXP-2 groups (p>0.05) (Table 3).

Table 3. The Post Hoc LSD of residual monomer content

| Group | (J) Group | Mean Difference (I-J) | Sig     |
|-------|-----------|-----------------------|---------|
| EXP-1 | EXP-2     | 0.00017               | 0.07800 |
|       | Control   | 0.00465*              | 0.00001 |
| EXP-2 | EXP-1     | 0.00017               | 0.07800 |
|       | Control   | 0.00448*              | 0.00001 |
| Control| EXP-1    | 0.00465*              | 0.00001 |
|       | EXP-2     | 0.00448*              | 0.00001 |

DISCUSSION

As a less invasive dental tissue saving treatment, fiber reinforced composite resins (FRCs) have gained more and more interest in dentistry. There are two main parts in FRCs, the matrix component and the fiber. Two major types of polymer matrices used in FRCs, namely cross-linked and linear polymers. The cross-linking polymer refers to multifunctional dimethacrylate resins. The linear polymer refers to a monofunctional methacrylate polymer. In FRCs with the so-called IPN structure, usually the matrix consists of a cross-linking polymer and a linear polymer.

The basic component of commercially FRCs matrix is bis-GMA. Many researches proved the negative side effect of bis-GMA. Bis-GMA is known as a highly viscous monomer, makes difficult to be handled. The current research had the objectives of replacement the matrix of bis-GMA based to HDDMA based in FRCs and evaluate their residual monomer content.

Table 1 showed that resin matrix system based on HDDMA revealed less residual monomer content than bis-GMA on FRC. It might be in-fluenced by the chemical structure characteristic of hydrophobic backbone of HDDMA and also its volatility properties. Figure 2 showed that HDDMA did not have hydroxyl groups and aromatic structures as bis-GMA. Previous research reported that removal hydroxyl groups in bis-GMA and increased the steric hindrance in the chain packing of the polymer was effective for viscosity reduction. The lower viscosity and weaker hydroxyl bonding of monomer mixtures increase the mobility of the monomer system, thereby allowing the material to reach a much higher double-bond conversion.

It was reported that the matrix system with increased mobility of monomer molecules and weaker molecular interactions possessed the highest conversion compared to bis-GMA matrix system with stonger hydrogen bonding. Besides, flexibility of monomer molecules was inhibited with increasing the size and steric hindrance of substituent especially for benzoyl group, resulting in the lowest conversion. These results suggested that viscosities of monomer mixtures and molecular structure of monomers are essential for vinyl conversion and therefore affect the properties of the matrix system.

The EXP-1 group and EXP-2 group statistically showed no significant difference in residual monomer content might be caused by the same structural characteristic of the material properties. Table 1 revealed that residual monomer content of EXP-1 group was higher than EXP-2 group. This result might cause by the higher percentage of HDDMA of EXP-1 group. By the fact that the EXP-1 group had lower mean percentage of residual monomer content than the EXP-2 group, it is recommended that the EXP-1 group to be evaluated further for the replacement alternative of bis-GMA matrix system on FRC.

This study suggested that a resin matrix system based on HDDMA-MMA (i.e. the Exp-1 and Exp-2 groups) revealed a significant difference of residual monomer content to bis-GMA-MMA (control-group) system. The HDDMA-MMA matrix system showed less residual monomer content than bis-GMA-MMA matrix system.

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