Preparation and Polymerization Behavior of Polymeric Dental Restorative Materials Containing High Molecular Weight Diluent System

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Abstract: Preparation of polymeric dental restorative materials (PDRM) showing a lower polymerization shrinkage was carried out using the hybrid-filler and 2,2'-bis-[4-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane resin matrix that is diluted with a high molecular weight dimethacrylate monomer. A visible light system was utilized to activate the resin matrix for the polymerization. In order to enhance the miscibility of the inorganic hybrid-filler with organic resin matrix and to conduct the homogeneity of the filler in the PDRM, its surface was hydrophobically treated with γ-methacryloxypropyltrimethoxysilane. The degree of conversion (DC), depth of cure, and polymerization shrinkage of the PDRM were investigated. The results revealed that PDRM prepared herein showed markedly lower polymerization shrinkage values. Besides, regardless of the filler loading, both DC and depth of cure values decreased with an increase in the amount of less flexible diluent in the resin matrix.

Keywords: dental, restorative, dimethacrylate, hybrid-filler, shrinkage

Introduction

The polymeric materials have played an important role in operative dentistry such as restoratives or pit and fissure sealants in spite of their less market size than metals or ceramics in dental application [1,24,25]. However, researches for desirable restorative dental materials have been limited to a few classes of polymers due to the strict requirement involving the adequate strength and the easiness of fabrication into a dental appliance. Since the introduction of polymethylmethacrylate for the principal denture-base in 1937, it had been widely used until the advent of 2,2'-bis-[4-(3-methacryloxy-2-hydroxy-propoxy) phenyl]propane (bis-GMA) based polymeric dental restorative material (PDRM) to the dental market by 3M Co. in 1964 [2]. Furthermore, its market has been widely expanded over other restorative materials due to their advantages that involve good handling characteristics, good adhesion to dentine or enamel component of natural teeth, and favorable esthetic properties [3].

PDRM is generally known as a complex material composed of the inorganic filler, organic resin matrix, and their interface. PDRM is normally classified by filler’s type adopted [4]: Direct-filled PDRM without filler has a good color matching and an easy polishing, however, it has a high coefficient of thermal expansion and inferior mechanical properties. Moreover, macrofilled system with micron-sized filler was unsatisfactory for some applications whereas microfilled PDRM with submicron-sized filler were unacceptable for other uses [5]. Thus, hybrid-filled PDRM was introduced using a variety of percentages and sizes of metal glass macrofiller as well as silica microfiller [6]. However, since there is no chemical bond exists between the resin matrix and filler particles, the coupling agent is mostly adopted to help the bond of the resin matrix and fillers. Commonly used coupling agents are epoxy, vinyl, or methyl silanes. In terms of silane materials, per se, γ-methacryloxypropyltrimethoxysilane (γ-MPS) must be pretty well put at the head of the list of coupling agents [7].

The resin matrix of PDRM commonly contains bis-GMA which has been marked a significant stage in the development of dental restoratives [8]. Even today, bis-GMA is still present in the majority of commercial

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Table 1. Materials Used for Preparation of Polymeric Dental Restorative Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Maker</th>
<th>Grade</th>
<th>wt%</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Resin matrix</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis-GMA(^1)</td>
<td>DAJAC Lab</td>
<td>Catalogue No. 9093</td>
<td>-</td>
<td>Monomer</td>
</tr>
<tr>
<td>TEGDMA(^2)</td>
<td>Shin-Nakamura</td>
<td>3G</td>
<td>-</td>
<td>Diluent</td>
</tr>
<tr>
<td>UDMA(^3)</td>
<td>Kyoeisha Chem. Co.</td>
<td>Lot No. 5060917</td>
<td>-</td>
<td>Diluent</td>
</tr>
<tr>
<td><strong>Photo-additives</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Camphorquinone</td>
<td>Aldrich Chem. Co.</td>
<td>A.C.S. Reagent</td>
<td>0.5(^5)</td>
<td>Photo-initiator</td>
</tr>
<tr>
<td>EDMAB(^5)</td>
<td>Aldrich Chem. Co.</td>
<td>A.C.S. Reagent</td>
<td>1.0(^6)</td>
<td>Photo-accelerator</td>
</tr>
<tr>
<td><strong>Hybrid-filler</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fumed silica microfiller</td>
<td>Degussa Co.</td>
<td>OX-50</td>
<td>25</td>
<td>Diameter=0.04 μm</td>
</tr>
<tr>
<td>Barium macrofiller</td>
<td>Hansol Chem. Co.</td>
<td>H-MAF(^7)</td>
<td>60</td>
<td>Diameter=1 μm</td>
</tr>
<tr>
<td>Fused silica macrofiller</td>
<td>Vericom Co.</td>
<td>VC-20</td>
<td>15</td>
<td>Diameter=5 μm</td>
</tr>
</tbody>
</table>

1) 2,2'-bis-[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane, 2) triethylene glycol dimethacrylate, 3) urethane dimethacrylate, 4) ethyl-4-dimethylaminobenzoate, 5) formulation: SiO\(_2\)/BaO/BaO\_2/O\(_3\) = 50/30/10/10 wt%, 6) based on resin matrix.

PDRM although it has a disadvantage of extremely high viscosity. To overcome this, research has been directed toward formulating bis-GMA with diluent to improve the filler loading and suitable handling characteristics [9]. Triethylene glycol dimethacrylate (TEGDMA) has been commonly used to thin down the restorative material and improve its marginal edge strength but simultaneously it reduces its resistance to abrasion [2]. However, the dilution with TEGDMA increases the polymerization shrinkage of PDRM [10]. Thereby, the development of new resin matrix system for PDRM showing a lower polymerization shrinkage is one of the most essential subjects in dental science. Therefore, PDRM containing a urethane dimethacrylate (UDMA) diluent, which has a segmented structure in the molecule and nearly equal molecular weight but less viscous than bis-GMA, would be expected to increase the dimensional stability of PDRM.

Therefore, the aim of the present study is to prepare the visible light-cured PDRM using the hybrid-filler and UDMA diluent system for the development of the PDRM showing a lower polymerization shrinkage. Also, to improve the wettability and dispersibility of the hybrid-filler with the resin matrix, the filler's surface was hydrophobically treated with silane coupling agent. To understand the effect of UDMA on the polymerization behavior of PDRM, various characterizations of PDRM including the polymerization shrinkage, depth of cure, and degree of conversion (DC) were investigated and discussed in detail.

### Experimental

**Materials**

As documented in Table 1, bis-GMA was used as a basic monomer. TEGDMA and UDMA were also used as diluents to achieve a more workable viscosity and allow the sufficient incorporation of the filler. The molecular structure of the resin matrix system is illustrated in Figure 1. The resin matrix was cured by a visible light system containing camphorquinone (CQ) photo-initiator and ethyl-4-dimethylaminobenzoate (EDMAB) photo-accelerator, both of which were used as received from Aldrich Chem. Co., respectively.

As a microfiller in the hybrid-filler system, Aerosil OX-50\(^8\) fused silica (primary particle size: 0.04 μm) supplied from Degussa Co. (Frankfurt, Germany) was used. Mixture of radio-opaque H-MAF\(^9\) barium silicate from Hansol Chemience Co. (primary particle size: 1 μm, Seoul, Korea) and VC-20\(^9\) amorphous fused silica obtained from Vericom Co. (primary particle size: 5 μm, Anyang, Korea) was used as a macrofiller. Based on experimental results reported by us [11], the optimum mixing ratio of hybrid-filler was Aerosil OX-50\(^8\)/H-MAF\(^9\)/VC-20\(^9\)=25/60/15 (wt/wt/wt%). γ-MPS (Aldrich Chem. Co., 97%) was used as the silane coupling agent without any further purification for the hydrophobic treatment of the filler’s surface.

### Surface Treatment of Hybrid-Filler and Preparation of PDRM

To improve the miscibility of the hybrid-filler with the resin matrix, the hydrophilic surface of the filler containing hydroxyl functional groups was treated using γ-MPS as illustrated in Figure 2 [11]. In details, γ-MPS of 10 wt% was pre-hydrolyzed using deionized distilled water/acetic acid (Aldrich Chemical Co., 99.7%, 1 M) (70/30 wt%) as a spreading co-solvent using a homomixer at 25°C and 8000 rpm for 2 h. Then, the hybrid-filler of 5 wt% for the total mixture was continuously added and stirred for 2 h. After removing the unreacted γ-MPS using a centrifuge, the remaining product was purified by washing with methanol followed by excess (×10) distilled water at 90°C for 25 min. Subsequent freeze-drying at -50°C for 48 h (FD5512 freeze dryer,
Figure 1. Molecular structures of resin matrix: bis-GMA basic monomer, UDMA and TEGDMA diluents.

Figure 2. Schematic diagram for hydrophobic surface treatment of the filler with silane coupling agent.

Ilshinlab Co., Korea) removed the hydrolyzed product as well as the solvent, and completed the silanol condensation reaction. To accomplish the reaction with γ-MPS, the surface-treated hybrid filler was cured at 120°C for over 2 h. Our previous experiment indicated that the hydrophobic modification of filler's surface was successfully performed [12].

To investigate the effect of the UDMA diluent on the polymerization behavior of PDRM, samples were fabricated using the γ-MPS treated hybrid-filler and the resin matrix containing a basic monomer and diluent with the corresponding ratios of resin matrix, that is, 7/3/0, 7/2/1, 7/1/2, and 7/0/3 (bis-GMA/UDMA/TEGDMA, B/U/T, wt/wt/wt%). The preparation procedure for PDRM is illustrated in Figure 3. As can be seen in Figure 3, the air trapped during kneading process was removed under reduced pressure. To ensure the optimum workability for preparing the PDRM, loading percentage of the hybrid-filler was consistently varied from 65 to 75 wt% based on the PDRM.

Measurement of Polymerization Behavior of Restorative Materials

The polymerization shrinkage of the PDRM was evaluated using a pycnometer by the measurement of the volume change before (V₁) and after (V₂) photo-curing.
according to ADA specification [13] and calculated using the equation \[100 \times (V_1 - V_2)/V_1\] and by taking the average value of triplicate measurements. Furthermore, the DC value was analyzed using a Fourier transform infra-red (FT-IR) spectroscopy (Perkin Elmer, Spectrum GX) based on a thin wafer of the PDRM specimen and calculated using a standard baseline technique [14]. The absorbance of the C=C peak at 1635 cm\(^{-1}\) originating from aliphatic groups in the dimethacrylate molecule was compared with that of the C=C peak at 1605 cm\(^{-1}\) originating from aromatic groups in the molecule. The ratio of the absorbance intensities was compared before (monomer) and after photo-polymerization (polymer) to determine the percentage of the unreacted C=C bonds remaining in the PDRM. Finally, the DC value was obtained by subtracting the residual percent of the C=C absorbance from 100\% [15], as seen in Equation (1).

\[
DC(\%) = 100 \times \frac{\text{Abs (Aliphatic C=C)/Abs (Aromatic C=C) polymer}}{\text{Abs (Aliphatic C=C)/Abs (Aromatic C=C) monomer}} - 1
\]

A major characteristic of visible light-cured dental materials is the variable depth of cure which arises from the attenuation of light transmission [16]. The intensity of the light falls within the body of the PDRM because of adsorption and scattering by the resin matrix and filler particles. Since a limited depth of cure causes inferior mechanical properties in the PDRM, it is valuable to study the factors affecting the depth of cure [17]. In this study, according to ISO 4049 specifications [18], the depth of cure was characterized by using a micrometer to an accuracy of \(\pm 0.1\) mm and by measuring the average height of three replicate of cylindrical PDRM specimens (4 mm in diameter and 20 mm in length) that all un-polymerized portions were removed with a dental spatula.

**Results and Discussion**

When the organic resin liquid is transformed into a solid three-dimensional network, dramatic property changes are expected. In reality, the critical physical and mechanical properties associated with dental materials are influenced by the level of conversion attained during polymerization as the isolated dimethacrylate carbon-carbon double bonds of the resin matrix in PDRM are converted to an extended network of single bonds. From the viewpoint of molecular chemistry, the formation of a macromolecular chain network from discrete monomer species involves the conversion of intermolecular distance of 0.3–0.4 nm into primary covalent bond with length of about 0.15 nm resulting in the shrinkage of organic resin system [19].

Many factors, such as composition of resin matrix, specimen geometry, photo-initiator concentration, visible light intensity, and duration of irradiation, all interact to control the extent of polymerization. Thereby, the determination of DC can be critical in the interpretation of test results [20]. As previously described in Experimental Section, the DC value was analyzed using a FT-IR spectra of the PDRM before and after photo-polymerization. A characteristic FT-IR spectra of bis-GMA-based PDRM is illustrated in Figure 4. As the methacrylate monomer is converted to polymer, intensity of methacrylate C=C stretching mode absorption at 1635 cm\(^{-1}\) was decreased. These spectroscopic procedures rely on the presence of a stable band that does not change as a consequence of photo-polymerization. In the bis-GMA-based resin matrix composition, the aromatic absorption originating from
the bis-GMA monomer at 1605 cm\(^{-1}\) served as the internal standard to normalize the FT-IR spectra of the monomer and polymer specimens.

Based on the DC results obtained from samples containing different kinds of diluents, some observation can be made about the photo-polymerization of bis-GMA diluted with TEGDMA and/or UDMA (see Figure 5). Not surprisingly, the DC value decreased with an increase of less mobile UDMA content than TEGDMA in the resin matrix system regardless of loading percentage of hybrid-filler used in the current study. It is well known that the DC value of methacrylate resin depends on the nature of polymerizing monomers in such a manner that more flexible molecule give rise to an increased DC values [15]. And, with an incorporation of lower viscosity diluent (for example, TEGDMA) into the resin matrix, the strong intermolecular interaction of bis-GMA can be more easily disrupted. It has been speculated that the diffusion of initiator-generated free radicals and growing polymeric radicals is relatively faster in less viscous resin matrix system. Therefore the bis-GMA/diluent system with a lower viscosity may allow the enhanced diffusion of reactive groups during the initial stage of polymerization. Specifically, in the current study, DC values decreased from 46.6, 35.0, 26.8, and 19.1% to 27.3, 24.5, 20.9, and 14.5% as the B/U/T ratios goes from 7/0/3 to 7/3/0 wt/wt/wt% under 65, 70, 72, and 75% loading of the hybrid-filler, respectively. Further investigation of Figure 5 showed that the DC value decreased with an increase in the hybrid-filler content. This is because the filler particles tended to inhibit the free radical polymerization of the dimethacrylate resin matrix. Accordingly, higher filler loading made the PDRM to have a decreased DC value.

To evaluate the clinical restoration of the PDRM, the depth of cure value as a function of the diluent in the resin matrix is shown in Figure 6. As seen in Figure 6, the depth of cure of the PDRM dramatically decreased when TEGDMA was replaced by UDMA. The apparent reason for such behavior was, in part, explained by the DC value of the polymer matrix: that is, as previously observed in Figure 5, the DC value decreased with an increased amount of less flexible UDMA in the resin matrix over with TEGDMA. Plus, the increased filler loading resulted in a decreased DC values of the PDRM prepared herein.

One major drawbacks of conventional PDRM prepared...
Table 2. Volumetric Polymerization Shrinkage Values of Various Hybrid-Filler Based on Polymeric Dental Restorative Materials

<table>
<thead>
<tr>
<th>Loading wt%</th>
<th>B/U/T=7/0/3*</th>
<th>B/U/T=7/1/2</th>
<th>B/U/T=7/2/1</th>
<th>B/U/T=7/3/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>6.58 ± 0.62</td>
<td>5.17 ± 0.51</td>
<td>3.61 ± 0.41</td>
<td>2.09 ± 0.21</td>
</tr>
<tr>
<td>70</td>
<td>4.97 ± 0.55</td>
<td>3.82 ± 0.32</td>
<td>2.77 ± 0.39</td>
<td>1.99 ± 0.18</td>
</tr>
<tr>
<td>72</td>
<td>4.33 ± 0.52</td>
<td>3.20 ± 0.41</td>
<td>2.15 ± 0.24</td>
<td>1.83 ± 0.20</td>
</tr>
<tr>
<td>75</td>
<td>3.18 ± 0.42</td>
<td>2.73 ± 0.35</td>
<td>2.15 ± 0.22</td>
<td>1.72 ± 0.19</td>
</tr>
</tbody>
</table>

* B/U/T= 2,2’-bis-[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane/urethane dimethacrylate/triethyleneglycol dimethacrylate.

by using bis-GMA monomer combined with diluent is the volumetric shrinkage during photo-polymerization. Common organic monomers always undergo shrinkage in volume on polymerization: for example, methylethacrylate undergo 21% shrinkage [21]. The extent of polymerization shrinkage in PDRM is normally dependent, among other things, on the molecular weight and the functionality of the resin matrix used [22]. Based on the same molecular weight, the polymerization shrinkage increases with an increase of the functionality. Also, the polymerization shrinkage increases with an increased molecular weight of the monomer having an equal functionality. Consequently, the TEGDMA dilution to bis-GMA certainly increases the polymerization shrinkage that exhibits serious chemical problems in dental applications [23]. In details, the polymerization shrinkage originating from the conversion of monomer to polymeric network in PDRM certainly works against the formation of adhesive bond between PDRM and dentine component of human teeth resulting in the breakdown of PDRM itself in vivo over time. The clinical problems associated with PDRM that lack a seal at the teeth-PDRM interface include microleakage and post-operative sensitivity. Consequently, this lack of sealing may contribute to the formation of secondary caries along the interface and increase the internal stress that results in the eventual mechanical failure of PDRM. Accordingly, to overcome these defects, in the current study, it was investigated the behavior of the polymerization shrinkage of PDRM containing UDMA diluent, which has the similar molecular weight with bis-GMA monomer but less viscous, being expected to have a lower polymerization shrinkage value. In Table 2, experimental results of the polymerization shrinkage of various bis-GMA-based PDRM products prepared using various UDMA contents is depicted. With an increased UDMA content, as seen in Table 2, the observed decrease of the polymerization shrinkage values may be associated with the decreased molecular contraction of the high molecular weight dimethacrylate diluent (UDMA) than low molecular weight dimethacrylate diluent (TEGDMA) and with the possible effect of the lower DC values, as seen in Figure 5.

Conclusion

PDRM showing a lower polymerization shrinkage was prepared using a high molecular weight dimethacrylate diluent. The surface of hybrid-filler was hydrophobically treated with γ-MPS coupling agent in order to improve the miscibility with the resin matrix. A visible light was utilized to activate the resin matrix for polymerization. The DC, depth of cure, and polymerization shrinkage values of the PDRM products were investigated. The following conclusions were made from the current study:

1) In terms of the loading percentage and the dispersion of the hybrid-filler in the resin matrix and the agglomeration of the filler particles, the freeze-drying method has been shown to be optimal in the preparation of PDRM.

2) Regardless of the filler loading, the DC and depth of cure values of the PDRM decreased with an increase in the amount of less flexible UDMA diluent than TEGDMA in the resin matrix.

3) Finally, with increasing UDMA content, the observed polymerization shrinkage value considerably decreased.

References