Effect of Urethane Dimethacrylate Diluent on the Mechanical Properties of Hybrid-filled Polymeric Dental Restorative Composites

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Abstract: Hybrid-filled polymeric dental restorative composites (PDRC) were prepared using a visible light activation system. The resin matrix system of the PDRC that we adopted in this study was 2,2'-bis-[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane diluted with triethylene glycol dimethacrylate and/or urethane dimethacrylate (UDMA). The hybrid-filler system was used as an inorganic filler component in the composite. To improve the dispersibility of the hybrid-filler in the PDRC, the filler’s surface was coupled hydrophobically with a silane compound. In the present study, we investigated the effect of UDMA diluent on the mechanical properties of the PDRC by measuring the values of the diametral tensile strength, flexural strength, and flexural modulus. A scanning electron microscopy study indicated the superior surface characteristics of the PDRC product we prepared.

Keywords: dental, restorative, urethane dimethacrylate, flexural strength, diametral tensile strength

Introduction

Many advanced polymeric materials, which consist of two or more components, are generally useful for the preparation of composite materials that exhibit synergistic effects that result from the combination of the inherent properties of the individual components. In reality, a variety of inorganic fillers are added to an organic polymer matrix to acquire the desired properties, such as enhanced mechanical and morphological properties, of the composites. In particular, polymer composites have been used in dental practices to restore teeth ever since 3M first introduced 2,2'-bis-[4-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (bis-GMA)-based composites to the dental market in 1964 [1-3]. Moreover, an increasing amount of attention has been paid toward using composites as the choice in restorative dentistry. Currently, the market for polymeric dental restorative composites (PDRC) continues to proceed through an evolutionary process fueled by a combination of factors, including the ease of processing and the superior adhesion performance to natural teeth [4,5].

PDRC is a complex material composed of inorganic filler and organic resin matrix. Since most commercial PDRC products use similar resin matrix systems, PDRC is normally divided into three categories: direct-filled (without filler), microfilled (with submicron-sized filler), and macrofilled (with micron-sized filler) [6]. In dentistry, it is important to choose the most suitable filler system for the desired purpose. To date, hybrid-filled PDRC, using a metal glass silicate macrofiller and silica microfiller, exhibits the most advanced dental properties [7,8].

The resin matrix of PDRC commonly contains bis-GMA, which is present in the majority of commercial products, but because of its extremely viscous liquid nature (1300 ~ 1500 Pa at 20°C) much research has been conducted to formulate it with diluents to achieve a more workable viscosity and to allow the sufficient incorporation of the filler [9]. In general, triethylene glycol dimethacrylate (TEGMA) has been adopted as a diluent to reduce bis-GMA’s viscosity and to smoothly fabricate the filler dispersion in the resin matrix [10]. Nevertheless, the dilution with TEGDMA increases the value of the volumetric polymerization shrinkage of PDRC [11]. Thereby, the development of new resin matrix systems that exhibit lower degree of polymerization shrinkage is one of the most essential challenges in dental science. As we reported in an earlier paper [12], PDRC containing

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a urethane dimethacrylate (UDMA) diluent, which has a segmented structure in the molecule and nearly equal molecular weight, but is less viscous than bis-GMA, exhibits superior dimensional stability and low polymerization shrinkage values.

In the present study, we prepared a hybrid-filled PDRC cured by visible light using the dimethacrylate resin matrix system containing a UDMA diluent, the composition of which established our belief that modifying the resin matrix can result in enhanced properties. The effect of UDMA on the mechanical properties of the PDRC was investigated by measuring the values of the diametral tensile strength, flexural strength, and flexural modulus. Dispersibility of the hybrid-filler in the PDRC was also evaluated by scanning electron microscopy.

**Experimental**

**Materials**
To activate the resin matrix, containing bis-GMA as a basic monomer, as well as TEGDMA and UDMA as diluents, we used a visible light system that contains a camphorquinone photo-initiator and an ethyl 4-dimethylaminobenzole photo-accelerator. The compounds were used as received from Aldrich Chem. Co. and their chemical structures, and material information of the resin matrix systems, are depicted in Figure 1 and Table 1, respectively. The hybrid-filler system used in the present study is documented in Table 2. For the hydrophobic treatment of the filler’s surface, we used γ-methacryloxypropyltrimethoxysilane (γ-MPS, Aldrich Chem. Co., 97%) as a coupling agent without any further purification.

**Preparation of PDRC**
At first, to improve the dispersibility of the hybrid-filler in the PDRC, the hydrophobic surface modifications of neat hybrid-filler by γ-MPS were treated using identical procedures to those reported in previous papers [12,13]. The hydrophobicity of the surface-treated hybrid-filler was confirmed by Fourier transform infra-red (FT-IR)
Table 2. Hybrid-filler Used for Preparation of Polymeric Dental Restorative Composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Maker</th>
<th>Grade</th>
<th>wt%</th>
<th>Average diameter</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumed silica microfiller</td>
<td>Degussa</td>
<td>OX-50</td>
<td>25</td>
<td>0.04 μm</td>
<td>50</td>
</tr>
<tr>
<td>Barium silicate macrofiller</td>
<td>Hansol Chemience</td>
<td>H-MAF</td>
<td>60</td>
<td>1.0 μm</td>
<td>1.5</td>
</tr>
<tr>
<td>Fused silica macrofiller</td>
<td>Vericom</td>
<td>VC-20</td>
<td>15</td>
<td>5.0 μm</td>
<td>0.5</td>
</tr>
</tbody>
</table>

1) Formulation: SiO₂/BaO₂/B₂O₃/Al₂O₃ = 50/30/10/10 wt%.

Figure 2. Testing scheme for diametral tensile strength measurement (P: load at fracture, D: diameter of specimen, and T: thickness of specimen).

spectroscopies (Perkin Elmer, Spectrum GX) and surface contact angle measurements (SEO Co., SEO-300A). To investigate the effect of the UDMA diluent on the mechanical properties of PDRC, various samples were fabricated using the surface-treated hybrid-filler and the resin matrix system having corresponding ratios of 7/3/0, 7/2/1, 7/1/2, and 7/0/3 (bis-GMA/UDMA/TEGDM, B/U/T, wt%). The preparation of PDRC followed an identical procedure as that we proposed in a previous paper [12]. To determine the optimum workability for preparing the PDRC, the loading percentage of the hybrid-filler, the formulation of which is documented in Table 2, was consistently varied from 65 to 75 wt%, based on the PDRC.

Measurement of Mechanical Properties of PDRC

The diametral tensile strength (DTS) test was carried out using an Instron Model 4469. The cross-head speed was set at 1 mm/min. All measurements were performed using five replicate cylindrical specimens (8 mm in diameter and 4 mm in thickness) cured by visible light (XL-3000 curing unit, 3 M) for 40 sec [14]. Figure 2 represents a schematic diagram of the DTS measurement system. The reported value is the mean of those five measurements and was calculated using Equation (1).

\[ DTS = 2P/(\pi \cdot D \cdot T) \]

where \( P \) is the load at fracture, \( D \) is the diameter of the specimen, and \( T \) is the thickness of the specimen.

The FS and FM values (in MPa) were measured according to International Standard Organization specifications [15]; the system is depicted in Figure 3. As shown in Equation (2), the FS value was measured using a maximum load calculated by pressing the center of a cured rectangular specimen (25 mm × 2 mm × 2 mm) mounted between the supports (20 mm in width) of an Instron Model 4469. The FM value was determined in the same test and was calculated using Equation (3).

\[ FS = 3F \cdot L/(2 \cdot b \cdot h^2) \]

where \( F \) is the maximum load, \( L \) is the distance between supports, \( b \) is the width of the specimen, and \( h \) is the height of the specimen.

\[ FM = F_t \cdot L^3/(4 \cdot b \cdot h^2 \cdot d) \]

where \( F_t \) is the load at bending fracture, \( L \) is the distance between supports, \( b \) is the width of the specimen, \( h \) is the height of the specimen, and \( d \) is the deflection at load \( F_t \).

Scanning electron microscopy (SEM, Hitachi Co., Model S-3500N) was adopted to visualize the dispersion of filler particles and its agglomeration in the resin matrix.
from a fractured PDRC sample that was regularly coated with gold using a sputter coater, prior to test by SEM, to prevent any irregular diffraction of electron beams [16].

**Results and Discussion**

Mechanical properties of PDRC, including the DTS, FS, and FM values, are mainly influenced by the monomer composition and, hence, by the nature of the organic component constituting the resin matrix system [17]. Figure 4 shows the plots of DTS value of PDRC as a function of monomer composition and loading percentage of hybrid-filler. In dentistry, DTS is particularly important because of chewing forces. As depicted in Figure 2, a cylindrical specimen was made from the material and simultaneous forces are applied to the sides of the sample until fracture occurs. We found that the DTS values of PDRC prepared using the bis-GMA diluted with TEGDMA are higher than those of PDRC diluted with UDMA, irrespective of the amount of filler loading. This phenomenon may be explained by the value of the degree of conversion (DC), as indicated by Asmussen [18]; that is, the DTS value is mainly influenced by the DC value of the methacrylate double bond. As we indicated in an earlier paper [12], more flexible monomer molecules give rise to increased DC values. This finding might result from the fact that higher DC values reduce the amount of monomer that could leach out of the polymer matrix and allow the polymeric materials to have good mechanical properties.

The FS and FM values of the PDRC are plotted in

**Figure 4.** Diametral tensile strength values of various bis-GMA-based polymeric dental restorative composites containing different diluents.

**Figure 5.** Flexural strength values of various bis-GMA-based polymeric dental restorative composites containing different diluents.

**Figure 6.** Flexural modulus values of various bis-GMA-based polymeric dental restorative composites containing different diluents.

Figures 5 and 6. FM is a method of defining a material's stiffness. A low modulus indicates a flexible material. As shown in Figure 3, the FM is measured by applying a load to the material specimen that is supported at each end. The value of FS is also determined in the same test. FS is the value obtained when the sample breaks. This test combines the forces found in compression and tension. From the investigation of the solids in Figures 5 and 6, we observed that both the FS and FM values of PDRC prepared using a TEGDMA diluent are higher.
than those using UDMA; the values are similar to the DTS results (see Figure 4). The increased FM value can be explained by an increased DC value and by enhanced flexibility in the polymeric network according to the increase of the TEGDMA concentration, as we reported in a previous paper [12]. This result is due to the fact that the high concentration of the low-molecular-weight diluent, TEGDMA, results in a system that offers the following properties: a resultant high number of double bonds per unit of weight on a flexible backbone, which affords the opportunity to have a high conversion of double bonds during polymerization; a high degree of crosslinking and a compact molecule, which creates a very hard resin matrix. As such, the low molecular weight and resultant high number of double bonds per unit of weight creates a high degree of crosslinking, which creates a very rigid, stiff composite that has a relatively high amount of shrinkage; we have noted this result in our earlier paper [12]. Therefore, as observed in Figure 6, it is noteworthy that PDRC prepared using the bis-GMA diluted with the higher-molecular-weight diluent, UDMA, results in reduced FM values and a slightly softer resin matrix. On the other hand, from the concrete investigations of Figures 5 and 6, the DTS and FS values increase dramatically upon increasing the hybrid-filler content. These increases are largely due to the restricted sliding of the polymer segments relative to each other upon increasing the filler loading in the bis-GMA-based PDRC. The FM values, however, as illustrated in Figure 6, consistently decrease as the filler content in the PDRC increases. The observed decrease may be due, in large part, to the reduced tenacity of the PDRC upon decreasing the percentage of the organic resin matrix. Also, this result might be explained by the fact that the modulus of the composite depends strongly on the aspect ratio of the dispersed filler particle in the composite material [19]. That is, in the present study, assuming the same dispersibility of loaded filler in the PDRC, the aspect ratio of the filler decreases as the hybrid-filler content in the PDRC increases, which results in the decrease of the FM values.

As there are no chemical bonds existing between the resin matrix and the filler particles, the coupling agent is mostly adopted to help bond the resin matrix and fillers. Commonly used coupling agents are epoxy, vinyl, and methyl silanes. In terms of silane materials, per se, $\gamma$-MPS is positioned at the head of the list of coupling agents [20]. Hydrophilic hybrid-filler can be chemically modified readily to become a hydrophobic one and this modification promotes the strong physical contact between the filler and polymer matrix [21]. In addition, the particle-particle interactions of the hybrid-filler lead to the formation of agglomerates and particle networks that are related to the shear thinning effect [22]. Thus, if the hybrid-filler has similar hydrophobic characteristics to the polymer matrix, it would be more effectively dispersed and wetted with dimethacrylate resin matrix, and it is expected that the hybrid-filler would act as a new suitable reinforcement to improve the mechanical properties of the PDRC.

To confirm the results of the mechanical property measurements and to investigate the dispersibility of the hybrid-filler in PDRC, we performed FT-IR spectroscopy and surface contact angle measurements. Figure 7 shows the FT-IR spectra of hybrid-fillers whose surfaces have either been treated with $\gamma$-MPS or not. The broad OH stretching absorption peak at 3650~3000 cm$^{-1}$, which arises from the silanol group (Si-OH), definitely disappeared in the spectrum of the $\gamma$-MPS-treated hybrid-filler. Therefore, this FT-IR spectroscopy study indicates that surface modification of the hybrid-filler has occurred. Also, as shown in Figure 8, we see that the surface contact angle of water on the surface of the $\gamma$-MPS-treated hybrid-filler is $87^\circ$, but on the other hand, that of the neat hybrid-filler is $10^\circ$, which indicates the hydrophilic surface of the filler. As such, we infer that the dispersibility or wettability between the hybrid-filler and the resin matrix in the PDRC is remarkably improved by the hydrophobic surface treatment.

The SEM photographs presented in Figure 9 show that there is a dense interfacial space between the filler particles and the resin matrix. Additionally, the hydrophobic treatment of the hybrid-filler's surface provides good wetting and the absence of holes around the fillers. Since $\gamma$-MPS increases adhesion strength, the wet strength between the resin matrix and the filler particles can be improved by the formation of hydrolytically stable siloxane bonds as observed in the FT-IR spectra of the hybrid-filler in the range 1110~1000 cm$^{-1}$ (Figure 7). Moreover, it might be deduced that PDRC prepared by using the $\gamma$-MPS-treated hybrid-filler through the freeze-drying method prevented it from getting close between the $\gamma$-MPS molecules, which were adhered to the surface.
of the filler particles. In reality, as we mentioned earlier, the surface contact angle shown in Figure 8 is 85°, which indicates the superior hydrophobic characteristic of the filler used in this work. This prevention minimizes the interactions between the γ-MPS molecules and no agglomeration of the filler itself occurs and, hence, the dispersion of the hybrid-filler in the resin matrix was improved. In simple terms, γ-MPS acts as a soap to increase the wetting ability of the filler particles by the resin matrix [23]. This effect allows the resin to form a better physical bond by improving the ability to adapt to the irregularities of the filler particles and, thus, strong interfacial adhesion occurs between them. This mechanism reduces the internal stress at the interface between the resin matrix and the filler particles and provides an enhancement of the mechanical properties of PDRC.

**Figure 8.** Real-time photographs of the surface contact angle measurement of (A) neat and (B) silane treated hybrid-filler.

**Figure 9.** SEM photographs of the fractured surface of polymeric dental restorative composites using (A) bis-GMA/UDMA/TEGDMA = 7/1/2 and (B) bis-GMA/UDMA/TEGDMA = 7/2/1 (filler loading was 70 wt%, ×30000).

**Conclusion**

Visible light-activated polymeric dental restorative composites containing a urethane dimethacrylate diluent were prepared using a hybrid-filler whose surface was hydrophobically treated with γ-MPS coupling agent to improve the dispersion of filler in the resin matrix. The DTS, FS, and FM values of the PDRC products were investigated and SEM analysis was executed to visualize the surface characteristics of the product. We make the following conclusions:

1) There was no agglomeration of the filler itself and so the dispersibility and wettability of the hybrid-filler in the resin matrix was improved.

2) The mechanical properties of the PDRC were more enhanced for the PDRC prepared using bis-GMA diluted
with TEGDMA than with UDMA. In addition, the DTS and FS values significantly increased upon increasing the hybrid-filler content. The FM value consistently decreased, however, upon increasing the content of the filler particles.

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References