Preparation and Dental Properties of Novel Functional Polymeric Restorative Materials

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Abstract: The preparation of novel polymeric dental restorative materials (PDRM) was carried out using hybrid-filler, which was consisted of fumed silica microfiller and barium glass macrofiller, resulting in the improvement of mechanical properties of PDRM. In order to enhance the miscibility of inorganic hybrid-filler with organic resin matrix in PDRM and to conduct the homogeneity of filler, its surface was hydrophobically treated with γ-methacryloxypropyl trimethoxysilane and freeze-drying method was adopted to remove the solvents. Diametral tensile strength, flexural strength, Knoop hardness, polymerization shrinkage, and abrasion resistance of PDRM prepared were investigated comparing with those of commercial PDRM products. The PDRM produced in this work showed excellent mechanical properties as well as superior polymerization shrinkage values. It was also discovered that PDRM prepared by using hybrid-filler resulted in better surface characteristics.

Keywords: dental, restorative, freeze-drying, barium, hybrid-filler

Introduction

Polymeric dental restorative materials (PDRM) were introduced commercially in the mid-1960s for the restoration of anterior teeth (Addent™ by 3M) [1,2]. Since their advent, PDRM have undergone significant development which continues to improve the longevity of dental restorations. And the present use of PDRM has expanded to include such dental restorations as inside edges, full crowns, cusp build-ups, and posterior restoratives due to its many advantages over other restorative materials that include good handling characteristics, good adhesion to dentine and enamel, easiness of rebuilding, and favorable initial esthetic properties [3-6]. Furthermore, overseas market volume of PDRM and human interest in the dental health is being greatly expanded.

PDRM, which are generally known as composite materials with distinct parts, comprise a blend of hard inorganic particles bound together by a soft organic resin matrix, and generally encompass three main components [4]: (1) the resin matrix comprising a monomer system, an initiator system, and stabilizers; (2) the inorganic filler; (3) the coupling agent that chemically bonds the reinforcing filler to the resin matrix. This provides three functions (support, form, and contour) or provides surface finish, based on filler's loading and particle size. Obviously, the properties and hence the performance of PDRM are principally dependent upon the three basic components of the material. Some of the properties are mainly related to the filler and the coupling agent, whereas other properties chiefly stem from the resin matrix [7,8].

The resin matrix commonly contains 2,2'-bis-[4-(3-methacryloxy-2-hydroxypropoxy) phenyl]propane (Bis-GMA) which is synthesized by a reaction of bisphenol-A with glycidyl methacrylate as first introduced in 1962 by Bowen [9,10]. To improve the handling qualities of highly viscous liquid nature of Bis-GMA, low viscosity monomer of triethyleneglycol dimethacrylate (TEGDMA) are commonly used to thin down restorative materials and improve its marginal edge strength but at the same time reduce its resistance to abrasion [3].

Filler particles provide dimensional stability to the unstable and soft resin matrix. Filler content and size have been shown to directly determine the physical and mechanical properties of PDRM. And more elaborate classifications of PDRM are based on the specific filler size distribution and the amount of incorporated filler as well as on the filler appearance and composition [11,12].

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Generally, the presence of filler particles decrease both the shrinkage of polymerization and the coefficient of thermal expansion but increase the hardness of PDRM. Also, filler loading is important since PDRM which are more inorganically loaded tend to be more resistant to fracture when they are used in restorations that are exposed to high stress or wear. It can be valuable that an impressive positive evolution has taken place in PDRM in the past 20 years: although the types of resin used have not changed significantly, the fillers used in resins have changed enormously. Filler size has changed from particles that approached the size of table salt (over 100 microns) to today's submicron particle size. Most of PDRM manufacturers saw that large particle-size resins were not satisfactory for some uses, and that microfilled resins were not acceptable for other uses [13]. Thus, it has been generally known that the ideal PDRM are to combine the highly filled resins with small particle resins [14,15]. However, unfortunately, it is difficult to load PDRM with large amounts of small filler since their large surface area causes significant increase in the viscosity. To have reasonable clinical handling properties, PDRM with smaller fillers should sacrifice some loading and strength compared to those with the larger fillers [16-19]. Therefore, so-called 'hybrid-filled' PDRM were introduced with various percentages and sizes of metal glass and silicon dioxide fillers. Now most companies have resins that are partially silica filled and partially radio-opaque metal glass filled to monitor the clinic operation mainly for posterior restorations through X-ray measurement.

For many conventional PDRM, the resin matrix material and the filler particles are very different and there is no chemical bond existing between them. Also a good mechanical interfacial adhesion is largely essential to transfer the stress from the resin matrix to fillers and thus improve the mechanical strength of them. Therefore, to help bond the resin matrix and the filler particles together, coupling agents that reduce the gradual loss of the fillers from the PDRM surface are used. Commonly used coupling agents are epoxy, vinyl, or methyl silanes [6]. In most of commercial PDRM, the most commonly used silane is γ-methacryloxypropyltrimethoxysilane (γ-MPS) [20].

Within the past several years, PDRM utilizing visible light for activation of polymerization have become the preferred one over all direct restorative placements by most of the clinicians. Despite disadvantages of using visible lights to activate PDRM which may cause eye damage and low light penetration into PDRM, the advantages of simplicity of using them seem to outweigh the disadvantages [4,11]. The advantages of visible light activated PDRM are that the procedures are simple and the clinician can manipulate these materials for long periods while having a short curing time (40~60 seconds). Visible light curing is very efficient and it results in uniform curing of the resin matrix. Another advantage is that visible light cured PDRM are more stable in color than chemically set materials.

In this paper, visible light cured PDRM was prepared using silica/barium glass hybrid-filler whose surface was hydrophobically treated with γ-MPS. In order to improve the miscibility of hybrid-filler with Bis-GMA/TEGDM resin matrix and to increase the loading percentage of hybrid-filler in the resin matrix, freeze-drying method to remove the solvents in γ-MPS treatment was adopted. This procedure is expected to result in the enhancement of mechanical properties of PDRM. Mechanical properties including diametral tensile strength, flexural strength, and hardness of PDRM prepared were investigated comparing with those of commercial products. It was also examined to conduct the novel PDRM using hybrid-filler showing better surface characteristics. In addition, optimum workability and wear resistance with the goal in restorative dentistry to make highly wear-resistant occluding surfaces that do not cause wear on the opposing structures was investigated.

**Experimental**

**Materials**

As shown in Table 1, Bis-GMA was used as the resin matrix and TEGDMA as the diluant to reduce the viscosity of Bis-GMA, which were respectively supplied by Shin-Nakamura Chem. Co. (Wakayama, Japan). Their molecular structures are illustrated in Figure 1. The resin matrix was cured using the visible light curing system (λ =400~650 nm) containing a camphorquinone (CQ) as a photoinitiator and ethyl-4-(N,N'-dimethylamino)benzoate (EDMAB) as a photoaccelerator which were used as received from Aldrich Chem. Co. It is generally known that CQ diketone absorbs radiation energy and transfers to the excited state. At the appropriate excited state, CQ is assumed to combine with EDMAB to form a complex (exiplex), which then breaks down to give reactive free radicals. Also, to prevent any arbitrary undesired reaction in this experiment, antioxidant (butylated-hydroxy toluene, Aldrich Chem. Co.) and ultra-violet stabilizer [2-(2′-hydroxy-5-methyl-phenyl)-benzotriazole, Ciba-Geigy Co.] were adopted (see Table 1). As a microfiller in the hybrid-filler system, Aerosil OX-50 silica supplied by Degussa Co. (Frankfurt, Germany) was used which has the primary particle size of 0.04 μm and surface area of 50 m²/g. And radio-opaque H-MAF barium glass supplied by Hansol Chem. Co. (Seoul, Korea) was used as a macrofiller whose particle size was 1.0 nm and formulation was SiO₂/BaO/B₂O₃/
Table 1. Materials for the Preparation of Polymeric Dental Restorative Materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Maker</th>
<th>Grade</th>
<th>wt%</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin matrix</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bis-GMA 1)</td>
<td>Shin-Nakamura</td>
<td>EMA-1020</td>
<td>70</td>
<td>Monomer</td>
</tr>
<tr>
<td>TEGDMA 2)</td>
<td>Shin-Nakamura</td>
<td>3G</td>
<td>30</td>
<td>Monomer</td>
</tr>
<tr>
<td>Camphorquinone</td>
<td>Aldrich</td>
<td>A.C.S. reagent</td>
<td>0.5</td>
<td>Photoinitiator</td>
</tr>
<tr>
<td>EDMAB 3)</td>
<td>Aldrich</td>
<td>A.C.S. reagent</td>
<td>0.5</td>
<td>Photoaccelerator</td>
</tr>
<tr>
<td>BHT 4)</td>
<td>Aldrich</td>
<td>A.C.S. reagent</td>
<td>0.1</td>
<td>Inhibitor</td>
</tr>
<tr>
<td>Tinuvin 5)</td>
<td>Ciba-Geigy</td>
<td>Tinuvin P</td>
<td>1.0</td>
<td>UV Stabilizer</td>
</tr>
</tbody>
</table>

Hybrid-filler and surface treatment

<table>
<thead>
<tr>
<th>Silica</th>
<th>Degussa Co.</th>
<th>Aerosil OX-50</th>
<th>10 g</th>
<th>Microfiller</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium glass</td>
<td>Hansol Chem. Co.</td>
<td>H-MAF</td>
<td>7)</td>
<td>Macrofiller</td>
</tr>
<tr>
<td>γ-MPS 6)</td>
<td>Aldrich</td>
<td>97 %</td>
<td>1 g</td>
<td>Coupling agent</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>Aldrich</td>
<td>A.C.S. reagent</td>
<td>30 g</td>
<td>Solvent</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>Aldrich</td>
<td>A.C.S. reagent</td>
<td>70 g</td>
<td>Solvent</td>
</tr>
</tbody>
</table>

1) 2,2'-Bis-[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl]propane, 2) triethylene glycol dimethacrylate, 3) ethyl-4-(N,N'-dimethylamino)benzoate, 4) butylated-hydroxytoluene, 5) 2-(2'-hydroxy-5-methylphenyl)benzotriazole, 6) γ-methacryloyloxypropyltrimethoxysilane, 7) see below.

![Bisphenol-A glycerolate dimethacrylate](image1)

![Triethylene glycol dimethacrylate](image2)

Figure 1. Molecular structures of resin matrix (Bis-GMA) and diluent (TEGDMA).

Figure 2. Schematic diagram of surface treatment of hybrid-filler with silane.

Al₂O₃ = 50/30/10 wt% [21]. Finally, γ-MPS (Aldrich Chem. Co., 97%) was used as a silane coupling agent without further purification for the surface treatment of hybrid-filler.

Surface Treatment of Hybrid-Filler and Freeze-Drying

To improve the miscibility of hybrid-filler with Bis-GMA/TEGDMA (70/30 wt%) resin matrix, the hydrophilic surface of filler containing hydroxy functional groups was hydrophobically treated with γ-MPS. This resulted in the improvement of hydrophobic characteristics in terms of mechanical and surface properties of PDRM as illustrated in Figure 2. At first, the surface of Aerosil OX-50 and H-MAF hybrid-filler was treated with γ-MPS solution which was pre-hydrolyzed with 1 wt% solution of methyl alcohol (Aldrich Chemical Co., 99.5%)/acetic acid (Aldrich Chemical Co., 99.7%, 1 M) (70/30 wt%) as the spreading cosolvent using homo-mixer at 25 °C and 8000 rpm for 2 hrs. To a 500 mL round bottom flask containing pre-hydrolyzed γ-MPS solution, 10 g of hybrid-filler [mixing ratio of Aerosil OX-50 silica/H-MAF barium glass were 20/80, 30/70, 40/60, 50/50, and 70/30 (wt/wt%)] was added continuously. This solution was stirred for 2 h. After removal of unreacted γ-MPS on a centrifuge, the remaining products were purified by washing with methyl alcohol followed by with excess (× 10) distilled water at 90 °C for 25 min. Subsequent freeze-drying at -50 °C for 48 h (Dura-Dry MP, FTS Systems) removed the hydrolyzed product as well as solvent, and completed the silanol condensation reaction. Lastly, to accomplish the reaction with γ-MPS, the surface-treated hybrid-filler was cured at 120 °C for over 2 h.
Preparation of Polymeric Dental Restorative Materials

A variety of PDRM was fabricated using hybrid-filler treated with γ-MPS and Bis-GMA/TEGDMA as the resin matrix formulated in Table 1. The preparation procedure of PDRM was illustrated in Figure 3. To investigate the effects of hybrid-filler on dental properties of PDRM, different PDRM containing various ratios of microfiller and macrofiller were prepared. As described above, corresponding ratios of hybrid-filler adopted in this experiment were 20/80, 30/70, 40/60, 50/50, and 70/30 (Aerosil OX-50 silica microfiller/ H-MAF barium glass macrofiller, wt/wt%). With consideration of optimum workability to prepare the PDRM in this study, loading percentage of hybrid-filler in the resin matrix was consistently varied from 63 to 77 wt% based on Bis-GMA/TEGDMA resin matrix.

Measurements of Dental Properties of Restorative Materials

In comparison with commercial PDRM, diametral tensile strength (DTS), flexural strength (FS), surface hardness, polymerization shrinkage, abrasion resistance, and dispersity of hybrid-filler (into resin matrix) were investigated. First, DTS was measured by compressive testing of cylinder type of specimen (8 mm diameter, 4 mm high) which was cured by visible light (XL-3000 Visible light curing unit, 3M Co., 400~500 nm) for 40 seconds in a teflon sheet mold. Universal testing machine (UTM, Instron Co., Model 4469, loading cell was 1000 kg) with the cross-head speed of 1 mm/min was used for DTS test [22]. Figure 4 represents the schematic diagram of DTS measurement. Reported DTS values (in MPa) was measured as the maximum force at the point of fracture as shown in following equation (1).

\[
DTS = \frac{2P}{\pi \cdot D \cdot T}
\]  \hspace{1cm} (1)

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

\[
FS = \frac{3F \cdot l}{2 \cdot b \cdot h^2}
\]  \hspace{1cm} (2)

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

FS values (in MPa) was measured according to the International Standard Organization (ISO) specification No. 4049 [23]. Figure 5 represents the schematic diagram of FS measurement. The maximum load was calculated by pressing the center of the cured rectangular specimen which had the dimensions of 25 mm × 2 mm × 2 mm, mounted between supports (20 mm of width) of UTM as shown in equation (2).

After the measurements of DTS and FS values, scanning electron microscopy (SEM, Hitachi Co., Model S-3500N) was used to investigate the surface characteristics of fractured PDRM specimen and evaluate the dispersion of hybrid-filler into Bis-GMA/TEGDMA resin matrix. The fractured surface of sample was coated...
with gold to prevent any irregular diffraction of the electron beams. The surface roughness of visible light cured PDRM, whose surface was grounded by a dental drill, was investigated by using visual observation method [24].

Knoop hardness tester (Akasi Co., Model AVK-C1, 300 g/10 sec) was used to investigate the surface hardness of PDRM prepared. Reported hardness values were obtained from the average of the tenth measurements at different sites on the same specimen. The polymerization shrinkage (in volume %) of PDRM was measured by volume change before (V1) and after (V2) photo-curing according to the American Dental Association specification No. 27 [22]. Under water bath capable of being accurately controlled at 25 ± 0.1 °C, glass dilatometer tube graduated in divisions of 1 mm with a capillary of uniform diameter approximately 0.7 mm was used for this measurement. Reported polymerization shrinkage values of PDRM herein were obtained using the equation of \[100 \times \frac{(V1-V2)}{V1}\] and the average of triplet measurements. Abrasion resistance (AR) was additionally investigated by taking the average value of triplet measurements of weight change before and after tooth brushing the rectangular PDRM specimen (20 × 20 × 2 mm) during initial 100 cycles [designated by AR(100)] and additional 100 cycles [designated by AR(200)]. Since the surface loss of a PDRM intraorally is a complex combination of physical and chemical factors such that no laboratory test satisfactorily reproduces such circumstances [22], AR of PDRM prepared was therefore relatively evaluated herein by comparing with those of other commercial products.

**Results and Discussion**

To improve the miscibility of hybrid-filler (Aerosil OX-50 silica microfiller/H-MAF barium marofiller) with Bis-GMA/TEGDMA resin matrix, the surface of filler was hydrophobically treated with γ-MPS followed by the freeze-drying method, which resulted in better dispersion of hybrid-filler particles and enhanced the loading percentage of filler in the resin matrix and mechanical properties of PDRM prepared. Previous work [25] showed that γ-MPS probably works by reducing the surface tension between inorganic hybrid-filler and organic Bis-GMA/TEGDMA resin matrix. In simple terms, they act as a soap to increase wetting of the filler by the resin. This allows the resin to form a better physical bond by improving its ability to adapt to the irregularities of the filler particles. Thus so, γ-MPS treatment to hybrid-filler conducts effective bond forming at the interface between the inorganic filler and organic resin matrix by introducing methacrylate functional groups on the hydrophilic filler surface (see Figure 2). Since γ-MPS reacts chemically and increases the adhesion strength through the physical bonding between the resin matrix and the filler, the wet strength is improved by the formation of hydrolytically stable siloxane bonds with hybrid-filler. This mechanism reduces the internal stress at the interface between the resin matrix and the filler providing the enhancement of mechanical properties of PDRM. To characterize the hydrophobicity of γ-MPS treated hybrid-filler qualitatively, the surface contact angle through the profile of a liquid (water) drop placed on a disc-shaped filler surface was measured by the sessile water dropping method (SEO Co., Surface and Electro Optics Model SEO 300A) [26]. To prepare highly uniform filler pellet, pressed-disc technique (4000 kg) was used. As illustrated in Figure 6, γ-MPS treated hybrid-filler with freeze-drying process (-50 °C, 48 h) in this work shows much higher contact angle values than that made by using conventional heat-drying method (60 °C, 48 h).

**Figure 6.** Photographs of surface contact angle of (A) heat-dried and (B) freeze-dried hybrid-filler.
Table 2. DTS Values and Workability of Various Hybrid-Filler Based Polymeric Dental Restorative Materials.

<table>
<thead>
<tr>
<th>Loading</th>
<th>70:30 1)</th>
<th>50:50</th>
<th>40:60</th>
<th>30:70</th>
<th>20:80</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>DTS 2)</td>
<td>Work 3)</td>
<td>DTS</td>
<td>Work</td>
<td>DTS</td>
</tr>
<tr>
<td>63</td>
<td>34 ± 3.0</td>
<td>□</td>
<td>36 ± 2.8</td>
<td>□</td>
<td>38 ± 2.0</td>
</tr>
<tr>
<td>68</td>
<td>41 ± 3.1</td>
<td>□</td>
<td>41 ± 3.0</td>
<td>□</td>
<td>38 ± 2.2</td>
</tr>
<tr>
<td>70</td>
<td>43 ± 2.7</td>
<td>□</td>
<td>43 ± 2.4</td>
<td>□</td>
<td>38 ± 2.6</td>
</tr>
<tr>
<td>72</td>
<td>46 ± 2.5</td>
<td>△</td>
<td>48 ± 3.1</td>
<td>□</td>
<td>39 ± 3.0</td>
</tr>
<tr>
<td>75</td>
<td>47 ± 2.5</td>
<td>△</td>
<td>51 ± 1.9</td>
<td>△</td>
<td>42 ± 3.1</td>
</tr>
<tr>
<td>77</td>
<td>-</td>
<td>×</td>
<td>-</td>
<td>×</td>
<td>42 ± 2.6</td>
</tr>
</tbody>
</table>

1) Microfiller/macrofiller (wt/wt%), 2) values in MPa, 3) workability; □: excellent, △: good, ×: not good.

Moreover, as shown in SEM photograph of Figure 7(A), it was observed that PDRM prepared in this work by using γ-MPS treated hybrid-filler through freeze-drying method were prevented from getting close between γ-MPS molecules which were adhered to the surface of filler. This prevention minimized the interactions between γ-MPS molecules and there was no agglomeration of filler itself so that the dispersity of filler into resin matrix was improved. Thus, from a comparison of SEM photograph of commercial product [Herculite® from Kerr Co., see Figure 7(B)], it is important to note that a better surface properties of PDRM can be obtained through γ-MPS treatment of hybrid-filler surface by freeze-drying method. The above analyses by both SEM and surface contact angle support that PDRM produced from γ-MPS treated hybrid-filler with freeze-drying process is expected to reveal the superior mechanical properties and surface characteristics.

To observe the effect of mixing ratios of hybrid-filler on the dental properties of PDRM, DTS values and workability were investigated at various filler loading onto resin matrix and at a variety of mixing ratios of silica microfiller and barium macrofiller in hybrid-filler that was hydrophobically treated with γ-MPS as previously described. From the results presented in Table 2, it was found that PDRM containing 30/70 (wt%/wt%) of microfiller/macrofiller (designated by Mi/Ma) with 75 wt% filler loading percent into resin matrix and 50/50 (wt%/wt%) of Mi/Ma with 72 wt% filler loading percent showed superior DTS values and workability. In addition, interestingly, further inspection of Table 2 showed that DTS value of PDRM containing 50/50 (wt%/wt%) of Mi/Ma with 75 wt% filler loading percent was the highest one (50 MPa). However, that was not enough to have a sufficient workability to formulate

Figure 7. SEM photographs of the fractured surface of (A) polymeric dental restorative material prepared by using silane-treated hybrid-filler and (B) Herculite® from Kerr Co. (×30000).
PDRM despite of excellent mechanical properties. This is understood by us that the loading percentage of silica microfiller whose surface area is relatively larger than that of barium macrofiller was too high to load enough fillers into resin matrix resulted in inferior flow characteristics to fabricate PDRM specimen. Thus so, from the above results, DTS, FS, surface hardness, polymerization shrinkage, and AR values of PDRM containing 30/70 of Mi/Ma (wt%/wt%) with 75 wt% hybrid-filler loading into resin matrix (referred to as DKU 1) and 50/50 with 72 wt% (referred to as DKU 2) were investigated by comparing with those of other current commercial PDRM products (for instance, Z-100® from 3M Co., Aeelitefil® from BISCO Co., Herculite® from Kerr Co., Charisma® from Kulzer Co., and Prismafil® from Caulk Co.).

In our previous study [27], it was found that most of commercial PDRM products have been using Bis-GMA as a resin matrix and hybrid-filler (referred to as hybrid-filled PDRM) with the exception of Z-100® produced from zirconium silicate single microfiller (referred to as microfilled PDRM, average filler diameter=1.0 μm). And the loading percentage of filler in commercial hybrid-filled PDRM was 70~76 wt% (based on resin matrix, see Table 3) which was calculated by the weight fraction of residual filler after complete extracting the resin matrix of PDRM samples with chloroform/tetrahydrofuran cosolvent (50/50 vol%). Therefore, in Figure 8, DTS and FS values of DKU 1 and DKU 2 prepared in this work were compared with those of commercial PDRM products which filler type is hybrid one.

Observation of Figure 8 shows that DKU 1 and DKU 2 samples showed more enhanced and narrower deviations of DTS and FS values than commercial hybrid-filled PDRM products, for instance Aeelitefil® from BISCO Co. or Herculite® from Kerr Co. Also, the level of these values achieved herein was sufficiently favorable relative to ISO specification (DTS and FS values in specification should be larger than 25 and 50 MPa, respectively) [24]. Nevertheless, more interestingly, comparing with Z-100®, manufactured by using zirconium silicate homomicrofiller, it was found that DTS and FS values of DKU 1 and DKU 2 was slightly lower than those values of Z-100® (as reported in a previous study [27], DTS and FS values of Z-100® were 56 ± 5, 186 ± 9 MPa, respectively). However, DKU 1 and DKU 2 specimens prepared in this study have a competitive narrower deviations and reproducibility in DTS and FS values than Z-100® (corresponding standard DTS deviation of DKU samples and Z-100® were 6.5 ~ 7.1 and 8.9% and corresponding standard FS deviation were 2.6 ~ 3.5 and 4.8%, respectively). These phenomena were understood by us that, as previously mentioned in SEM studies of Figure 7, such striking increases in absolute DTS and FS values and their narrower deviations in values would be anticipated upon the improved filler’s dispersion into resin matrix, that is believed to result from the prevention the agglomeration of filler itself that was mainly attributed to the freeze-drying treatment of hybrid-filler’s surface. From these experimental results, it was concluded that mechanical properties of PDRM can indeed mainly attributed to the dispersity of filler into resin matrix if the resin matrix system and loading percentage of filler into resin matrix are same. The identical strategy was used to characterize the Knoop hardness, polymerization shrinkage, and abrasion resistance of DKU 1, DKU 2, and other commercial hybrid-filled PDRM samples and the results are presented in Table 3. As seen in Table 3, the results of these efforts clearly showed that DKU 1 and DKU 2 samples prepared in this work showed superior values in Knoop hardness and abrasion resistance relative to other commercial hybrid-filled PDRM products even micro-

Figure 8. (A) Diametral tensile and (B) flexural strengths of various hybrid-filled polymeric dental restorative materials.
Table 3. Dental Properties of Various Polymeric Dental Restorative Materials

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Product name</th>
<th>Loading %1)</th>
<th>Hardness (HK)</th>
<th>Polymerization shrinkage, %</th>
<th>AR(100) (mg/cm²)2)</th>
<th>AR(200) (mg/cm²)2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKU12)</td>
<td>-</td>
<td>75</td>
<td>60 ± 2</td>
<td>2.5 ± 0.3</td>
<td>1.8 ± 0.1</td>
<td>1.6 ± 0.2</td>
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<tr>
<td>DKU22)</td>
<td>-</td>
<td>72</td>
<td>61 ± 3</td>
<td>2.3 ± 0.2</td>
<td>1.5 ± 0.2</td>
<td>0.8 ± 0.2</td>
</tr>
<tr>
<td>BISCO</td>
<td>Aelitefil</td>
<td>75</td>
<td>51 ± 4</td>
<td>2.5 ± 0.4</td>
<td>1.1 ± 0.2</td>
<td>0.8 ± 0.3</td>
</tr>
<tr>
<td>KERR</td>
<td>Herculite</td>
<td>76</td>
<td>48 ± 3</td>
<td>2.6 ± 0.3</td>
<td>2.3 ± 0.3</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>Kulzer</td>
<td>Charisma</td>
<td>75</td>
<td>36 ± 5</td>
<td>2.1 ± 0.4</td>
<td>1.8 ± 0.2</td>
<td>0.9 ± 0.2</td>
</tr>
<tr>
<td>Caulk</td>
<td>Prismafil</td>
<td>74</td>
<td>48 ± 4</td>
<td>1.8 ± 0.3</td>
<td>2.0 ± 0.3</td>
<td>1.1 ± 0.2</td>
</tr>
<tr>
<td>3M</td>
<td>Z-100</td>
<td>79</td>
<td>66 ± 5</td>
<td>2.1 ± 0.3</td>
<td>1.8 ± 0.2</td>
<td>1.3 ± 0.2</td>
</tr>
</tbody>
</table>

1) Microfiller/macrosfiller=30/70 (wt/wt%), 2) microfiller/macrosfiller=50/50 (wt/wt%), 3) the percentage of filler loading was a weight ratio after separation filler from resin matrix using chloroform and tetrahydrofuran, 4) AR(100): abrasion resistance from 0 to 100 cycles, 5) AR(200): abrasion resistance from 100 to 200 cycles.

filled Z-100®. In addition, specifically, polymerization shrinkage which is one of the clinically important factor was remarkably similar to that observed in the commercial products. In this way, future work will consider the preparation of PDRM that have a biocompatibility and long-term weatherability. It is hoped that these efforts will lead to novel functional PDRM that have an enhanced dental properties which will meet or exceed current commercial PDRM products.

Conclusion

Novel functional visible light cured PDRM was prepared using silica/barium glass hybrid-filler whose surface was hydrophobically treated with γ-MPS via freeze-drying process in order to improve the miscibility of hybrid-filler with Bis-GMA/TEGDMA resin matrix and to increase the loading percentage of hybrid-filler in the resin matrix. The mechanical properties, polymerization shrinkage, and workability of PDRM were investigated and optimized. The followings are concluded from the this study:

1) To increase the loading percentage and dispersity of silica/barium glass hybrid-filler into Bis-GMA/TEGDMA resin matrix and diminish the agglomeration of hybrid-filler, the freeze-drying method has shown to be the optimal in the preparation of PDRM with excellent DTS, FS, polymerization shrinkage, and AR properties.

2) DKU 1 and DKU 2 PDRM samples prepared in this work showed superior values in DTS, FS, Knoop hardness, polymerization shrinkage, and abrasion resistance relative to other commercial hybrid-filled PDRM products even microfilled Z-100®.

3) Thus, to achieve the enhanced dental properties which will meet or exceed current commercial PDRM products, work is currently in progress to develop suitable methods to prepare the novel functional PDRM by which substantially superior biocompatibility and long-term weatherability can be achieved.

References

15. S. C. Bayne, H. O. Heymann, and E. J. Swift, Jr., J.