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Enhanced mechanical properties are possible with urethane dimethacrylate-based experimental restorative dental composite

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Abstract

This laboratory study aimed to replace the traditional bisphenol A-glycidyl methacrylate (bisGMA) resin system with a urethane dimethacrylate (UDMA)-based resin system to enhance the physicomechanical properties of dental restorative composite (DRC). We evaluated surface roughness, porosity %, nanohardness, elastic modulus, and compressive strength (CS) in the control group (the bisGMA-resin system) and two experimental groups (UDMA-based resin systems with 20 wt.% SiO 2 or Al 2 O 3 , each 30 μm in size spherical fillers). Cylindrically shaped samples 4 mm in diameter and 6 mm in height were fabricated using light curing (n = 10). One-way analysis of variance method was used to statistically analyze the results (p ≤ 0.05). The data suggest that both UDMA-based resin systems showed increased surface roughness (R a ) and porosity % in the sample fabrication compared with the control. However, the nanohardness in both SiO 2 -based UDMA composite (0.20 ± 0.09 GPa) and Al 2 O 3 -based UDMA composite (0.22 ± 0.07 GPa) was not significantly higher compared with the control (0.19 ± 0.05 GPa). Likewise, while improved CS values were observed in both SiO 2 -based UDMA composite (15.5 ± 1.9 MPa) and Al 2 O 3 -based UDMA composite (16.2 ± 0.7 MPa) compared to the control (14.5 ± 4.5 MPa), this increase was not statistically significant. The newly developed UDMA-based resin formulation with Al 2 O 3 micro-filler showed promising physicomechanical properties and may be appropriate for use as DRC.

1. Introduction

In the practice of dentistry, composite is mostly used as an aesthetic direct restorative material for restoring a decayed tooth [1]. Modern dental restorative composite (DRC) is mainly composed of a dimethacrylate matrix system [2], and 86% of these dental composites contain one of the bisphenol A (BPA)-based monomers [3]. The derivatives of BPA, such as bisphenol A-glycidyl methacrylate (bisGMA) and bisphenol A ethoxylate dimethacrylate (bisEMA), are mostly formulated for the fabrication of DRC [4].

bisGMA is a highly viscous polymer. For reduction of the viscosity, a diluent called triethylene glycol dimethacrylate (TEGDMA) is always added in composition during fabrication [5]. The conventional bisGMA-based composite system has quite a few other disadvantages such as polymerization shrinkage, water sorption, and incomplete conversion of double bonds during the polymerization process [6, 7] These attributes make BPA-based DRC vulnerable to longterm durability. Moreover, BPA is suspected of causing estrogen-like effects [8].

DRC must possess longterm durability in dynamic oral conditions, both for patient satisfaction and to restore the mechanical functions of mastication [9]. Urethane dimethacrylate (UDMA) has been suggested as an alternative material for the formulation of dental restorative composite (DRC) [7, 10]. In contrast to bisGMA, UDMA-containing DRC demonstrate a lower viscosity, better filler loading, and higher toughness due to the
flexibility of the urethane bonds [11]. Additionally, UDMA does not contain hydroxyl groups, which reduces water sorption in the polymer chain. A higher degree of conversion and a lower residual monomer content makes this polymer a strong contender for improved mechanical properties of the resulting DRC [12, 13].

During the past few decades the advent of nano fillers has allowed the polymer industry to improve the physico-mechanical properties of new polymers well beyond past limits [14]. Nano filler based composites exhibit superior physico-mechanical properties compared with composites made by conventional fillers [14]. However, the properties of nano filler-based composites depends on the type of nano fillers, their size and shape, and also their concentration and interaction with the polymer matrix [15]. Nanoparticles of aluminum oxide (Al$_2$O$_3$) and silica dioxide (SiO$_2$) are known for their higher mechanical properties [14].

Therefore, this laboratory study sought to synthesize a new UDMA-based matrix system for DRC that could offer related or enhanced physico-mechanical properties compared with bisGMA-based commercially available DRCs on the market today. We evaluated the UEDMA-based DRC properties of surface roughness, nanohardness, elastic modulus, and compressive strength by adding nano-fillers of SiO$_2$ and Al$_2$O$_3$. Our hypothesis was that the experimental UEDMA-based DRC would have improved physico-mechanical properties.

2. Materials and methods

2.1. Fabrication of experimental resin matrix

The raw materials used in the formulation of an experimental UDMA-based DRC are listed in table 1. The experimental resin was synthesized by following the methodology used by Zhang et al [10]. The constituent chemicals in experimental resin, i.e., UDMA (70.6 wt.%), hydroxypropyl methacrylate (HPMA, 27.4%), camphorquinone (CQ, 1.0 wt.%), and N,N-cyanoethyl methylaniline (CEMA, 1.0 wt.%) were mixed in a magnetic stirrer for 5 min using a 50 ml flat bottom bottle. Next, the matrix was allowed to stabilize in the dark for 48 h.

The silanated constituent fillers (i.e., SiO$_2$ and Al$_2$O$_3$) were first dispersed in an acetone solution for 5 min using a probe-type sonicator (VCX-750, Sonics & Materials, CT, USA), at a power of 350 W and frequency of 20 kHz [16], to achieve a high degree of separation and dispersion in the experimental resin. Then, the acetone was removed by evaporation. Next, 20 wt.% of each filler was added to the experimental polymer. Finally, to remove air bubbles in the polymer matrix and achieve better mixing, experimental composites were placed in an ultrasonic bath for 10 min.

2.2. Fabrication of sample

Composite cylinders 4 mm in diameter and 6 mm in height were fabricated using a polystyrene mold. A total of 10 samples were fabricated in each experimental group. The composite resin was gradually poured into the mold and the air bubbles were removed with the help of a pointed instrument. Once the mold was filled up to the brim, samples were fabricated using a dental curing light (Elipar 2500, 3M ESPE, St Paul, MN, USA) for 40 s from the top, 40 s from the side, and 40 s from the bottom. The molds were removed from the composite after polymerization. All the samples thus prepared were desiccated for 24 h before any further procedures. Similarly, control samples were fabricated using commercially available Filtek™ Z250 restorative composite material.

2.3. Micro-computed tomography testing

To study the three-dimensional structure, micro-computed tomography (Skyscan 1172, Bruker, Aartselaar, Belgium) at 100 kV voltage, 50 μA current, and 14.2 μm voxel dimensions was used to evaluate possible agglomerates and pores in the cylindrical-shaped experimental samples. Scanning was performed by 360° rotation around the vertical axis. The total porosity values were calculated with the proprietary software’s porosity tool.
2.4. Surface roughness testing
To test the mean of surface roughness ($R_a$), five samples from each study group were randomly selected and their surfaces were smoothed against 400 grit SiC paper for 15 s before testing. The surface roughness was analyzed with an optical noncontact surface profiler (ContourGT, Bruker, Campbell, CA, USA). Vision64 (v 5.30) application software was used to control the precision and the measurements of surface roughness parameters [17].

2.5. Nanohardness and elastic modulus testing
To test the nanohardness and modulus of elasticity of the experimental materials, a nanomechanical tester (UMT1, Bruker, Santa Barbara, CA, USA) was used with a Berkovich diamond nanoindenter. The samples were loaded at 30 mN under controlled ambient air temperature (26 °C ± 1 °C) and on an anti-vibration table. The loading and unloading rates were 0.5 mN/s and a dwell time of 10 s was set for the maximum load. Each specimen was indented at five different places to obtain the mean value [18].

2.6. Compressive strength (CS) testing
To test the compressive strength, samples were tested in a universal testing machine (Model no. 3369 Instron, Canton, USA) with a load cell of 5 kN and a crosshead speed of 1.0 mm min$^{-1}$. The maximum load (kgf) used and registered before debonding was converted to force (in N) and divided by the area of the bonding interface to yield the shear bond strength in MPa.

2.7. Statistical analysis
To determine significant differences ($p < 0.05$) between composite formulations (Filtek Z250, SiO$_2$-based UDMA composite, and Al$_2$O$_3$-based UDMA composite), one-way analysis of variance (ANOVA) with the post hoc Tukey’s test was used. For each parameter, a set of five samples was tested. The results were expressed as mean values with associated standard deviations (SD). Data were analyzed by SPSS software version 21.0 (SPSS®, Chicago, IL, USA).

3. Results
The surface roughness ($R_a$) parameter was observed to be statistically higher in both experimental groups, i.e., 5.89 ± 0.25 µm in SiO$_2$-based UDMA DRC and 5.62 ± 0.78 µm in Al$_2$O$_3$-based UDMA experimental DRC. While the control group exhibited the lowest $R_a$ among all the groups (4.11 ± 0.29 µm). Table 2 shows the surface roughness numerical values and the 2D profiler images of each corresponding group.

Both experimental UDMA-based composites were found to have a higher mean porosity % compared to the control group. Overall significant differences were observed between the SiO$_2$-based UDMA composite and the control, and also between the Al$_2$O$_3$-based UDMA composite and control ($p < 0.05$). The control group showed the lowest mean porosity % (1.25 ± 0.89) compared with experimental groups. The details are in table 3 with the micro-CT scan images of the individual groups.

Table 4 communicates the nanohardness and elastic modulus values of the study groups. Filtek Z250 (control-group) exhibited the lowest mean nanohardness value (0.19 ± 0.05 GPa). While insignificantly higher nanohardness values were observed in both the SiO$_2$-based UDMA DRC and the Al$_2$O$_3$-based UDMA DRC (i.e., 0.20 ± 0.09 GPa and 0.22 ± 0.07 GPa, respectively. On the contrary, the elastic modulus was found to be higher in the control group (3.5 ± 3.1 GPa) which suggests that the control material has a higher stiffness property compared with the experimental groups.

Table 5 presents the CS of the study groups. The control group exhibited insignificantly lower CS compared to the SiO$_2$-based UDMA DRC (15.5 ± 1.9 MPa) and the Al$_2$O$_3$-based UDMA composite (16.2 ± 0.7 MPa). The mean maximum force (in N) required to break the samples of Al$_2$O$_3$-based UDMA DRC was 50.8 ± 2.1 N.

4. Discussion
Our hypothesis could not be thoroughly realized because no statistically significant variance was observed when evaluating surface roughness and porosity %. However, nanohardness and compressive strength properties were enhanced using a UDMA-based resin system with 30 µm Al$_2$O$_3$ particles.

The surface roughness of restorative material is an important parameter. We observed higher $R_a$ values in both experimental DRC. This might be because the particle size used in the experimental DRC was ≈ 30 µm. Whereas, in the control group the particle size distribution was 0.01 µm to 3.5 µm with an average particle size of 0.6 µm [19]. Secondly, overall higher surface roughness values among all the groups might be attributed to the dry finishing of samples before testing. Surface roughness may have increased due to the abrasive particles.
Table 2. Mean surface roughness values of the study groups.

| Group               | Surface roughness ($R_a, \mu m$) | 2D profiler image |
|---------------------|----------------------------------|------------------|
| Filtek Z250 (Control) | 4.11 ± 0.29<sup>A,B</sup>       | ![Filtek Z250](image1) |
| SiO$_2$-based UDMA composite | 5.89 ± 0.25<sup>A</sup>           | ![SiO$_2$-based](image2) |
| Al$_2$O$_3$-based UDMA composite | 5.62 ± 0.78<sup>B</sup>         | ![Al$_2$O$_3$-based](image3) |

Key: Same uppercase superscript letters interpret a significant difference between the study groups.

Table 3. Mean porosity % of study samples after polymerization.

| Group               | Mean porosity % | Micro-CT scan |
|---------------------|-----------------|---------------|
| Filtek Z250 (Control) | 1.25 ± 0.89<sup>A,B</sup> | ![Filtek Z250](image4) |
| SiO$_2$-based UDMA composite | 7.89 ± 3.25<sup>A</sup> | ![SiO$_2$-based](image5) |
| Al$_2$O$_3$-based UDMA composite | 4.62 ± 1.98<sup>B</sup> | ![Al$_2$O$_3$-based](image6) |

Key: See table 2.
ceramic particles separated from the SiC paper and may have embedded into the composite surface [20]. On the other hand, the heat generated during dry finishing is high and can degrade the filler/matrix bond and result in separation of filler particles from the matrix and subsequently also increase the surface roughness [21]. The use of polishing rubbers, cups etc might have reduced the surface roughness and porosity of the samples.

We used micro-CT to estimate the porosity in the experimental groups. While light curing the DRC, pores might form due to air trapped during mixing, monomer contraction, or evaporation of the monomer [22]. The higher porosity % in experimental groups (i.e., 7.89 ± 3.25 and 4.62 ± 1.98 in SiO2 and Al2O3-based UDMA composites, respectively) might be attributed to chemical hand mixing. On the other hand, Filtek Z250 is a one-paste system that is homogenously mixed by the manufacturer and available in an airtight syringe.

Experimental DRCs were observed to have a higher nanohardness value compared with the control. This suggests the ability of UDMA polymers having a high degree of conversion. Moreover, the UDMA polymer is chemically and physically crosslinked and also fully aliphatic [12]. On the contrary, bisGMA is characterized by the lowest crosslink density and the lowest DC in the polymer [12]. These findings are in line with previous investigations that also suggested UDMA based copolymers have enhanced hardness properties [13, 23]. The higher nanohardness values in the Al2O3 based UDMA composite might be due to hard and tough Al2O3 ceramic particles [24]. The findings of modulus of elasticity in the experimental groups suggest that UDMA based composites have a lower modulus compared with the control group. This could be because of rigidity in the UDMA polymer due to its hydrogen bonds. The previous study also observed lower modulus of UDMA based composites compared with the bisGMA based system [25].

As expected, we observed enhanced CS in both experimental groups compared with the control group. However, this difference was found to lack significance. Although, mechanical properties are a function of the DC and the three-dimensional structure of the polymer network with a combination of stronger hydrogen bonding potential [26, 27]. However, if agglomerates or clusters form from the fillers in the matrix system it could have a detrimental effect on the material performance [28]. Prior investigators have established that physical properties mainly depend upon homogenous and uniform dispersion of nanoparticles in the polymer matrix. The influence of dispersion degree on mechanical properties is well studied. However, if the resin and the filler particle lack a chemical bond, this can negatively affect dispersion and the composite’s mechanical properties, since a strong interfacial bonding can effectively transfer the load from the matrix to the reinforcement material. The slight increase in CS among experimental groups could also be attributed to variations in filler size and distribution. The control group filled with nanoparticles showed enhanced mechanical properties due to increased surface area and uniform particle distribution (see micro-CT image of the control group in table 3) [29]. Whereas the distribution of micro-filled particles (as in case of experimental DRC) couldn’t be homogeneously obtained and agglomerations of the filler acted as stress concentration points which led to inefficient stress distribution; therefore, more stress is concentrated on adjacent particles, causing cracks in the material [30].

| Group                  | Nanohardness (GPa) | Modulus of elasticity (GPa) |
|------------------------|---------------------|----------------------------|
| Filtek Z250 (Control)  | 0.19 ± 0.05         | 5.5 ± 3.1                  |
| SiO2-based UDMA composite | 0.20 ± 0.09       | 4.6 ± 1.8                  |
| Al2O3-based UDMA composite | 0.22 ± 0.07       | 5.2 ± 3.9                  |

N.B. No statistical difference was observed between the study groups.

| Group                  | Maximum force (N) | Compressive strength (MPa) |
|------------------------|-------------------|---------------------------|
| Filtek Z250 (Control)  | 45.7 ± 3.8        | 14.5 ± 4.5                |
| SiO2-based UDMA composite | 48.8 ± 4.9      | 15.5 ± 1.9                |
| Al2O3-based UDMA composite | 50.8 ± 2.1      | 16.2 ± 0.7                |
The limitation of this laboratory study includes the filler size and weight % of the study groups. The filler size and weight % of the control group is the manufacturers’ secret. However, in experimental groups, micro-sized (30 μm) filler in 20 wt.% were incorporated. Hence, it is not rational to evaluate the properties of two different resin systems with different weight fractions and filler sizes. In the future, studies related to polymerization shrinkage, solubility, and water sorption would be helpful in further analyzing the experimental resin system.

5. Conclusion

After evaluating a few physico-mechanical properties of experimental DRC, we found evidence supporting the potential use of UDMA-based resin systems as an alternative resin system in DRC. The surface roughness of UDMA-based DRC might be lowered using nano-sized particles. The mechanical properties of UDMA-based DRC might be further improved if controlled homogenous mixing of filler particles is achieved with reduced porosity %. A UDMA-based resin system might have the potential to substitute for conventional bisGMA-based resin systems in DRC.

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