Polymerization shrinkage of UV curable dental composites containing multifunctional methacrylates

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Dental compositions containing bis-GMA as basic material, multifunctional methacrylates, inorganic filler and photoinitiator were used as a model for dental applications. The main problem in the application and UV-Vis curing process is the shrinkage of dental materials. Total shrinkage of UV-Vis curable dental composites is due to polymerization shrinkage, which is a typical behavior of multifunctional methacrylates during the polymerization process. The important factors for curing dental composites are: kind and concentration of used methacrylates, their functionality, double bond concentration, kind and concentration of added photoinitiator and UV-Vis dose. UV-curable dental compositions based on 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (bis-GMA) containing multifunctional monomers such as 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), tetraethylene glycol dimethacrylate (T3EGDMA), trimethylolpropane trimethacrylate (TMPTMA), polyethylene glycol 200 dimethacrylate (PEG200DA) were investigated. Reduction of polymerization shrinkage of dental compositions is at the moment a major problem for dental technology.

**Keywords:** dental compositions, polymerization shrinkage, multifunctional methacrylates, UV-Vis curing

INTRODUCTION

In technology of dental materials, dental compositions can be divided into clinical and technical materials. Clinical materials are mainly used in dental technology for dental surgery, whereas technical materials are mostly applied in dental technology for manufacturing of dentures. Various polymers have been widely used in dental materials for many years [1]. Polymerization shrinkage is one of dental clinicians’ main concerns when placing direct, posterior, resin-based composite restorations. Evolving improvements associated with resin-based composite materials, dental adhesives, filling techniques and light curing have improved their predictability, but shrinkage problems remained. The main motivation for the reduction of the shrinkage is the too high shrinkage phenomenon using multifunctional methacrylate monomers in dental UV curable compositions [2]. Radical photopolymerization of dental compositions is usually performed in the UV-visible area (UV-Vis) between 380 and 450 nm [3]. Polymerization shrinkage is influenced by clinical technique and manufacturing of the composite resin. This phenomenon is attributed to the formation of a three-dimensional, covalently crosslinked network during crosslinking, which reduces intermolecular distances between the monomers used to form the crosslinked network. Before cure, the molecules which form the resin are separated by their characteristic van der Waals radii. Upon cure, these intermolecular distances are reduced due to the formation of covalent bonds between monomers which produce the desired highly crosslinked polymer material [4-9]. This reduction of intermolecular distances creates internal stress throughout the polymer network, which is manifested by reduced adhesion of the polymer material to both the substrate and the object attached thereto. Shrinkage is a very important criterion in long-term performance of adhesives and inversely affects the adhesion properties. In order to control shrinkage, UV dose, kind of multifunctional methacrylates and concentration play very crucial roles. In radiation curing, free radicals are generated on the molecular chains which come closer to each other and form a crosslinked network. As the molecular chains come closer, shrinkage occurs in the dental compositions, which is detrimental for the performance of the polymer composition. There should be no or minimal shrinkage for good adhesion. Multifunctional methacrylates with the function of photoreactive crosslinkers are generally not incorporated in radiation curing but they have several benefits in improving the physical-mechanical properties of the adhesive. The shrinkage is dependent on the nature and amount of crosslinker and on radiation intensity.
It is well known that shrinkage is the main drawback of free radical photopolymerization. When photopolymerization shrinkage is constrained by adhesion to a substrate, in the case of dental compositions by adhesion to the tooth wall, shrinkage stress develops. Excessive stress results in defects such as curling and cracking which impedes the long-time application of UV-curable or UV-polymerizable materials. Besides, shrinkage also plays an important role by affecting the marginal integrity of the photo-curable system [10-16].

EXPERIMENTAL

Materials

The investigated multifunctional methacrylates: 2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane (bis-GMA), 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), tetaethylene glycol dimethacrylate (T3EGDMA), trimethylolpropane trimethacrylate (TMPTMA), and polyethylene glycol 200 dimethacrylate (PEG200DA) and bifunctional radical photoinitiator 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)benzyl]-phenyl}-2-methyl-propan-1-one (Irgacure 127) are presented in Table 1. All multifunctional methacrylates and the photoinitiator Irgacure 184 are available from BASF (Germany), and hydroxyapatite is available from Continental Chemical (USA).

Hydroxyapatite in form of white powder is the hydroxyl end member of the complex apatite group and crystallizes in the hexagonal crystal system. Thus, it is commonly used as a filler for restorative dental compositions.

The investigated UV-curable dental composition contained the following raw materials:

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Chemical structure</th>
<th>Chemical name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis-GMA</td>
<td>2,2-bis[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane</td>
<td></td>
</tr>
<tr>
<td>1,3-BDDMA</td>
<td>1,3-butanediol dimethacrylate</td>
<td></td>
</tr>
<tr>
<td>DEGDMA</td>
<td>diethylene glycol dimethacrylate</td>
<td></td>
</tr>
<tr>
<td>T3EGDMA</td>
<td>tetaethylene glycol dimethacrylate</td>
<td></td>
</tr>
<tr>
<td>TMPTMA</td>
<td>trimethylolpropane trimethacrylate</td>
<td></td>
</tr>
<tr>
<td>PEG200DA</td>
<td>polyethylene glycol 200 dimethacrylate</td>
<td></td>
</tr>
<tr>
<td>Irgacure 127</td>
<td>2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)benzyl]-phenyl}-2-methyl-propan-1-one</td>
<td></td>
</tr>
</tbody>
</table>

The thickness change of the polymer was measured with the reflective laser scanning system to determine the shrinkage. The transparent object mode of the laser displacement sensor was chosen for testing the clear liquid monomers. In this measurement mode, the laser displacement sensor detected and recorded the displacement of the upper surface of monomers caused by photopolymerization shrinkage [15]. A reflective laser scanning method based on a laser displacement sensor was used to directly measure shrinkage due to UV-curing.
The laser displacement sensor Keyence, LK-G10 (Japan) could detect the position of the upper surface of the sample (thickness of the sample). When photopolymerization occurs, the change in the sample thickness was recorded as a function of time. Percentage shrinkage (S) is defined by the dimensional change according to the following equation:

\[ S = \frac{(H_o - H_t)}{H_o} = (1 - \frac{H_t}{H_o}) \times 100 \% \]

where \( H_o \) is the initial thickness and \( H_t \) is the thickness at time t. The measured shrinkage is actually a linear shrinkage. However, as the planar dimensions are much greater than the thickness and constrain planar shrinkage, the linear shrinkage appropriately equals to the volumetric shrinkage. The photopolymerization was conducted in ambient conditions at room temperature. The plane UV source (emitting window: 25×25 mm) used was 395 nm RX Firefly SN 490454 from Phoseon Technology (USA). The radiometer from Hoeble UV Technology (Germany) was used to detect the radiation intensity on the surface of samples. The UV intensity on the sample was adjusted to 5 mW/cm².

RESULTS AND DISCUSSION

Variation of UV-Vis curing time, kind of multifunctional (meth)acrylates and functionality

To compare the UV-behaviour of multifunctional methacrylates with that of acrylates, the photopolymerization of dental compositions containing multifunctional (meth)acrylates: tetraethylene glycol dimethacrylate (T3EGDMA), diethylene glycol dimethacrylate (DEGDMA), 1,3-butanediol dimethacrylate (1,3-BDDMA), trimethylolpropane trimethacrylate (TMPTMA) and polyethylene glycol 200 dimethacrylate (PEG200DMA), was examined. As shown in Table 2 and Figure 1, the irradiation starts at 0 s and there is no shrinkage before. The shrinkage of all tested monomers significantly increased during UV exposure. In the shrinkage profiles of all tested monomers, an obvious

expansion after a very short induction time is observed (Fig. 1).

![Figure 1](image)

**Table 2** Polymerization shrinkage of multifunctional methacrylates as a function of curing time

<table>
<thead>
<tr>
<th>(Meth)acrylate</th>
<th>Polymerization shrinkage as a function of curing time [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Curing time [s]</td>
</tr>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>T3EGDMA</td>
<td>0</td>
</tr>
<tr>
<td>DEGDMA</td>
<td>0</td>
</tr>
<tr>
<td>1,3-BDDMA</td>
<td>0</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>0</td>
</tr>
<tr>
<td>PEG200DMA</td>
<td>0</td>
</tr>
</tbody>
</table>
Changing the degree of ethoxylation (1,3-BDDMA, DEGDMA or T3EGDMA) is a convenient way to alter monomer chain lengths (the segment lengths between double bonds in monomers). Two methacrylates with different degrees of ethoxylation, tri (DEGDMA) and four (T3EGDMA) moles of ethoxy groups were used to evaluate the effect of monomer chain lengths on shrinkage. Figure 1 shows that when the degree of ethoxylation is raised, shrinkage obviously decreases. Another dominant factor, the concentration of double bonds (Cdb), should be taken into consideration.

\[ \text{Cdb} [\text{mol/L}] = \text{Functionality} \times \frac{\text{Density at 25°C} [\text{kg/m}^3]}{\text{Molecular weight} [\text{kg/kmol}]} \]

The ethoxylation is an attractive way to lower shrinkage because the concentration of double bonds significantly drops with increasing the molecular weight of ethoxylated multifunctional monomers. Likewise, other ways to increase the molecular weight may be promising to solve the shrinkage problem. The influence of the concentration of double bonds in the investigated methacrylate monomers is shown in Fig. 2 (Table 3).

![Shrinkage vs Concentration of Double Bonds](image)

**Fig. 2.** Shrinkage of a dental composition containing multifunctional methacrylates versus concentration of double bonds in the methacrylates

It is widely believed that reduction of functionality lowers the shrinkage. However, the functional effect on shrinkage is very complicated. Functionality obviously affects the conversion and the concentration of double bonds. The concentration of double bonds may not decrease on reducing functionality because changing the functionality is always accompanied by changing both the molecular weight and the density. In this work the difunctional T3EGDMA, DEGDMA and 1,3-BDDMA, and the trifunctional TMPTMA were used to evaluate the functional effect. As shown in Figure 1 and Table 3, the shrinkage level decreases with the increase in monomers functionality, due to the formation of a microgel in the early step. But the shrinkage does not follow this trend. The trifunctional methacrylate TMPTMA has the highest final shrinkage of 11.5 % in comparison with other tested difunctional methacrylates (Table 3).

**Influence of the UV dose on shrinkage**

Dependencies shown in Fig. 1 point out that the UV dose during curing can influence shrinkage of

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### Table 3 Monomers parameters and shrinkage of tested dental compositions

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Functionality</th>
<th>Molecular weight [kg/kmol]</th>
<th>Density at 25°C [kg/m³]</th>
<th>Concentration of double bonds Cdb [mol/L]</th>
<th>Maximal shrinkage after UV curing [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T3EGDMA</td>
<td>2</td>
<td>286</td>
<td>1090</td>
<td>7.6</td>
<td>6.8</td>
</tr>
<tr>
<td>DEGDMA</td>
<td>2</td>
<td>242</td>
<td>1070</td>
<td>8.8</td>
<td>8.8</td>
</tr>
<tr>
<td>1,3-BDDMA</td>
<td>2</td>
<td>226</td>
<td>1010</td>
<td>8.9</td>
<td>10.4</td>
</tr>
<tr>
<td>TMPTMA</td>
<td>3</td>
<td>338</td>
<td>1060</td>
<td>9.4</td>
<td>11.5</td>
</tr>
<tr>
<td>PEG200DA</td>
<td>2</td>
<td>308</td>
<td>1110</td>
<td>7.2</td>
<td>13.1</td>
</tr>
</tbody>
</table>

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the investigated dental filler compositions containing (meth)acrylate monomers. The UV-polymerization effect on the shrinkage of the tested (meth)acrylates, evaluated for UV doses between 10 and 50 mW/cm² and for 3 min UV-crosslinking time, is shown in Table 4 and illustrated in Figs. 3-7.

**CONCLUSION**

The polymerization shrinkage of (meth)acrylate monomers was found to depend mainly on the double bonds conversion, concentration of double bonds, UV curing time and UV curing dose. Methacrylate monomers displayed lower shrinkage than acrylate monomers because the low reactivity decreases the conversion as a function of curing time. Increase in chain length of monomers
(rising the degree of ethoxylation) significantly lowered the shrinkage because the obvious rise of molecular weight decreased the concentration of double bonds. Reduction of functionality was not an attractive way to lower the final shrinkage due to the combined effect of the concentration of double bonds and conversion. The concentration of double bonds also played an important role in the shrinkage rate. When changing the degree of ethoxylation or monomer functionality, it was observed that shrinkage increased with the concentration of double bonds. Besides, heat expansion caused by curing could bring forward a maximal shrinkage rate from the shrinkage stage to the expansion stage. Thus, we believe that a promising way to decrease the shrinkage might be the increase in the molecular weights of photoreactive monomers, if other properties such as viscosity and solubility meet application requirements.

REFERENCES
Z. Czech et al.: Polymerization shrinkage of UV curable dental composites containing multifunctional methacrylates

POLIMERIZAЦИОННО СВИВАНЕ НА UV-КАТАЛИЗИРАНИ ЗЪБНИ КОМПОЗИТИ, СЪДЪРЖАЩИ МНОГОФУНКЦИОНАЛНИ МЕТАКРИЛАТИ

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(Резюме)

В статията се описват зъбни композиции, съдържащи бис-GMA като основен материал, многофункционални метакрилати, органичен пълнеж и фотоинициатор като модели за приложение за зъбни протези. Главният проблем за приложението на UV-Vis - лечебния процес е свиването на полимерния материал. Пълното свиване на UV-Vis – лечебните зъбни композиции е явление на свиване при полимеризацията, което е типично за многофункционалните метакрилати. Важни фактори за лечебната употреба на зъбните композиции са: видът и концентрацията на използвани метакрилати, тяхната функционалност, концентрацията на двойни връзки, на добавяния фотоинициатор и дозата на UV-Vis – облъчването.

Изследвани са UV-лечебни зъбни композиции, основани на 2,2-бис-[4-(2-хидрокси-3-метакрилацил-оксипропил)fenил]пропан (Bis-GMA) и съдържащи многофункционални мономери, като 1,3-бутандиол диметакрилат (1,3-BDDMA), диетилен гликол диметакрилат (DEGDMA), тетраетилен гликол диметакрилат (TEGDMA), триметилолпропан триметакрилат (TMPTMA), полиетилен гликол 200 диметакрилат (PEG200DA). Намаляването на полимеризациянното свиване при зъбните композиции в момента е главният проблем в зъболекарската технология.