

Polymerization shrinkage by investigation of uv curable dental restorative composites containing multifunctional methacrylates

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Typical commercial restorative dental compositions in the form of medical resins contain in-organic fillers, multifunctional methacrylates and photoinitiators. The currently used resins for direct composite restoratives have been mainly based on acrylic chemistry to this day. The main problem with the application and radiation curing process is the shrinkage of photoreactive dental materials during and after UV curing. Shrinkage of restorative radiation curable dental composites is a phenomenon of polymerization shrinkage, typical behavior of multifunctional methacrylates during the polymerization process. The important factors in curing of dental composites are: the kind and concentration of the used methacrylate, its functionality, double bond concentration, the kind and concentration of the added photoinitiator and UV dose emitted by the UV-lamp. They are investigated multifunctional 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA), 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (Bis-GMA), ethoxylated Bis-GMA (EBPDMA) and dodecandiol dimethacrylate (DDDMA). Reduction of polymerization shrinkage of restorative dental compositions is at the moment a major problem of dental technology. This problem can be solved through an application of photoreactive non-tacky multifunctional methacrylates in the investigated dental adhesive fillings.

Keywords: polymerization shrinkage, UV-curable, multifunctional methacrylates, dental compositions.

INTRODUCTION

Dental materials can be divided into clinical and technical materials. Clinical materials are mainly used by the dentist technology in dental surgery, whereas technical materials are mostly applied by the dental technology by manufacturing of, for example, dentures. Various polymers have been widely used in dental materials for many years¹. The main motivation for the reduction of shrinkage is an overly high shrinkage phenomenon of the curable compositions of multifunctional methacrylates monomers used in dental UV². Radical photopolymerization of dental compositions is usually performed by typical UV radiation or in UV visible area between 400 and 500 nm³. Polymerization shrinkage is influenced by the 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 the intermolecular distances between the monomers used to form the crosslinked network. Before cure, the molecules which comprise the resin are separated by their characteristic van der Waal's radii. Upon cure, these intermolecular distances are reduced due to the formation of covalent bonds between the monomers which produce the desired highly crosslinked thermoset material⁴⁻⁹. This reduction of intermolecular distances creates internal stress throughout the thermoset network, which is manifested by a reduced adhesion of the thermoset material to both the substrate and the object attached thereto. Shrinkage is a very important criterion in the long-term performance of the adhesive and affects the adhesion properties inversely. In order to control shrinkage, the UV dose and multifunctional methacrylates kind and concentration play a crucial role. In radiation curing free radicals are generated on the molecular chains which come closer to

forming a crosslinked network. Because of the molecular chains' coming closer, shrinkage occurs in the dental compositions which is detrimental for the performance of the polymer composition. There should be no shrinkage or least possible for good adhesion. Multifunctional methacrylates with the function as photoreactive crosslinkers are generally not incorporated in radiation curing but they have several benefits in improving the physic-mechanical properties of the adhesive. Shrinkage is dependent on the nature and amount of a crosslinker and also on radiation dose.

It was well known that shrinkage was the main drawback of free radical photo-polymerization. When the photo-polymerization shrinkage was constrained by adhesion to a substrate, in the case of dental compositions by adhesion to the tooth wall, shrinkage stress developed. The excessive stress resulted in defects such as curling and cracking which impeded the long-time application of the UV-curable or UV-polymerizable materials. Besides, shrinkage also played an important role in affecting the marginal integrity of the photo-curable system¹⁰⁻¹¹.

EXPERIMENTAL PART

Raw Materials

The investigated multifunctional methacrylates 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA), 2,2-bis-[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane (Bis-GMA), ethoxylated Bis-GMA (EBPDMA) and dodecandiol dimethacrylate (DDDMA) and radical photoinitiator 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184) are presented in Table 1.

Table 1. Multifunctional methacrylates and photoinitiator used in this work

Raw material	Chemical structure	Chemical name
Bis-GMA		2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane
EBPDMA		ethoxylated Bis-GMA
1,3-BDDMA		1,3-butanediol dimethacrylate
DEGDMA		diethylene glycol dimethacrylate
TEGDMA		triethylene glycol dimethacrylate
TMPTMA		trimethylolpropane trimethacrylate
DDDMA		dodecandiol dimethacrylate
Irgacure 184		1-hydroxy-cyclohexyl-phenyl-ketone
Hydroxylapatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	mineral form of calcium apatite

The multifunctional methacrylates 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA) and photoinitiator Irgacure 184 are available from BASF (Germany), hydroxylapatite is available from Continental Chemical (USA), and 2,2-bis-[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane (Bis-GMA), ethoxylated Bis-GMA (EBPDMA) and dodecandiol dimethacrylate (DDDMA) are available from Ivoclar (Liechtenstein). Hydroxylapatite in the form of white powder is the hydroxyl end member of the complex apatite group and crystallizes in the hexagonal crystal system and in this form is commonly used as a filler for the restorative dental compositions.

Preparing of samples

The acrylic coating material with the self-adhesive properties was polymerized in ethyl acetate at 77°C in the presence of radical initiator AIBN using 2-ethylhexyl acrylate and acrylic acid (all components are available from BASF) with the 60 wt.% polymer content. The mixture of monomers containing 2-ethylhexyl acrylate and acrylic acid was added within 1 h and the post-reacted

4h. After polymerization the investigated multifunctional methacrylates were added into self-adhesive acrylic polymers.

The tested copolymers contain the following compositions:

2-Ethylhexyl acrylate:	41, 37, 32, 22, 12 wt.%
Acrylic acid:	5 wt.%
Multifunctional (meth)acrylate:	1, 5, 10, 20 and 30 wt.%
Hydroxyapatite	50 wt.%
Irgacure 127	3 wt.%

The resulted compositions are coated on the siliconized paper with the 120 g/m² coat weight and dried for 10 minutes at 105°C in the drying canal and then as adhesive layers UV cured under the UV lamp for 3 minutes.

Shrinkage measurement

The linear shrinkage studies of the prepared samples were carried out as per specification described in ASTM D 2732. The tested dried dental composition in the form of adhesive layers were cut to the size of 10 cm x 10 cm and UV cured under the UV lamp Aktiprint mini 18-2 with a transmission belt from Technigraf (Germany) (Fig. 1) with the UV dose between 10 mJ/cm² and



Figure 1. UV lamp with transmission belt

500 mJ/cm². This test method covers the determination of the degree of the unrestrained linear thermal shrinkage at the given specimen temperatures of the plastic film.

The dimensional changes in the acrylic layers after irradiation were measured and compared with the adhesive layers without the multifunctional methacrylates. The differences in the dimensions (shrinkage *S*) of the irradiated samples were determined as:

$$S[\%] = \frac{100 \cdot (A_0 - A)}{A_0}$$

where: *A*₀ is the initial and *A* is the final area of the sample after irradiation.

RESULTS AND DISCUSSIONS

Shrinkage as a function of the UV curing dose and the kind and concentration of multifunctional (meth)acrylates

To compare the shrinkage of multifunctional methacrylates 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TEGDMA), trimethylolpropane trimethacrylate (TMPTMA), 2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]propane (Bis-GMA), ethoxylated Bis-GMA (EBPDMA) and dodecandiol dimethacrylate (DDDMA) during UV curing the UV dose from 10 mJ/cm² to 500 mJ/cm² in the curing time of 3 min was chosen. The measured results are presented in Table 2, and in Figure 2 for 30 wt.% of each of investigated methacrylate monomers.

Figure 2 represents the effect of the UV dose in the range 10–500 mJ/cm² on the shrinkage of the multifunctional methacrylates investigated in this work. The shrinkage of all the tested monomers increases significantly during the UV exposure. It was observed that

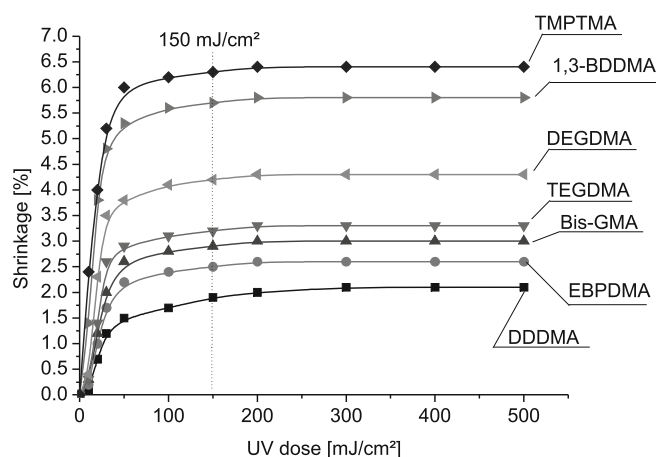


Figure 2. Influence of UV dose on polymerization shrinkage of multifunctional methacrylates

with increasing the UV dose from 0 to about 100–150 mJ/cm² shrinkage increases and remained nearly constant thereafter up to 500 mJ/cm². This indicates that 150 mJ/cm² dose is sufficient enough to crosslink the molecular chains of adhesives containing the mentioned multifunctional methacrylates.

The measured shrinkage results for the lower investigated concentrations of the multifunctional methacrylates are illustrated in Figures 3–9.

The results of shrinkage of acrylic adhesive with multifunctional methacrylates at various UV doses with variation in the concentration of different multifunctional methacrylates are presented in Figures 3–9. Figure 3 represents the effect of UV dose in the range 10–500 mJ/cm² and DDDMA concentration ranging from 1 to 30 wt.% on polymerization shrinkage of the adhesive containing DDDMA. It was observed that with increasing the UV radiation dose from 10 to 500 mJ/cm² the polymerization shrinkage values increase and between

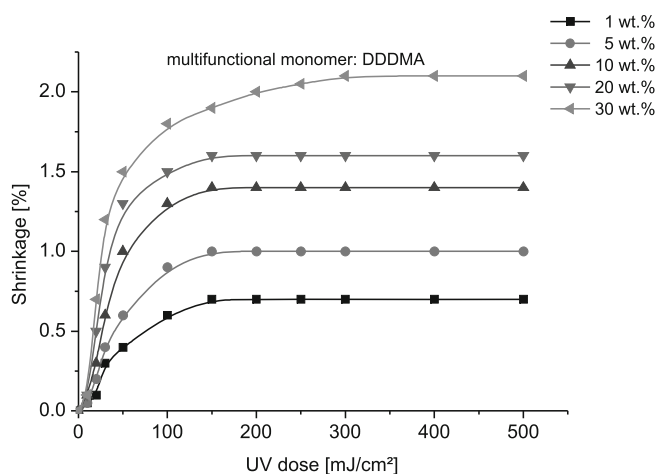


Figure 3. Shrinkage of dimethacrylate DDDMA as a function of its concentration and UV dose

Table 2. Polymerization shrinkage of multifunctional monomers as a function of UV dose

(Meth)acrylate and their shrinkage [%]	Polymerization shrinkage [%] as a function of UV dose										
	UV dose [mJ/cm ²]										
	0	10	20	30	50	100	150	200	300	400	500
DDDMA	0	0.1	0.7	1.2	1.5	1.7	1.9	2.0	2.1	2.1	2.1
EBPDMA	0	0.2	1.0	1.7	2.2	2.4	2.5	2.6	2.6	2.6	2.6
Bis-GMA	0	0.3	1.2	2.0	2.6	2.8	2.9	3.0	3.0	3.0	3.0
TEGDMA	0	0.3	1.4	2.6	2.9	3.1	3.2	3.3	3.3	3.3	3.3
DEGDMA	0	0.4	2.3	3.5	3.8	4.1	4.2	4.3	4.3	4.3	4.3
1,3-BDDMA	0	1.4	3.8	4.8	5.3	5.6	5.7	5.8	5.8	5.8	5.8
TMPTMA	0	2.4	4.0	5.2	6.0	6.2	6.3	6.4	6.4	6.4	6.4

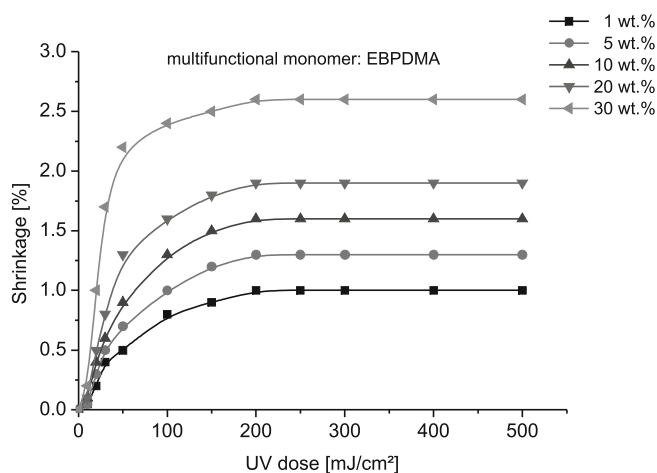


Figure 4. Shrinkage of dimethacrylate EBPDMA as a function of its concentration and UV dose

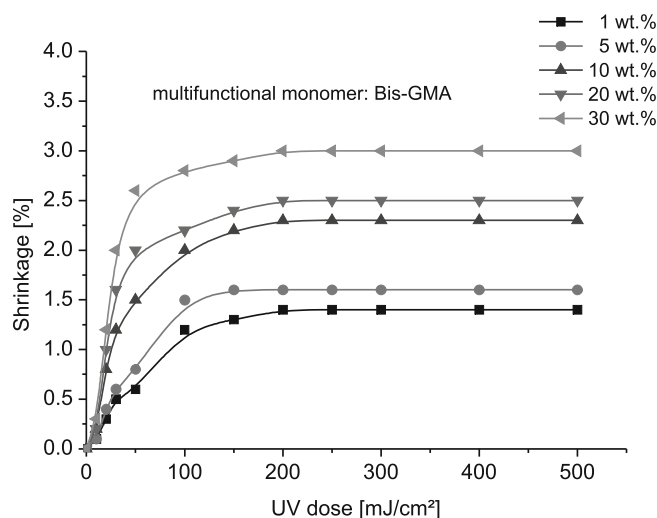


Figure 5. Shrinkage of dimethacrylate Bis-GMA as a function of its concentration and UV dose

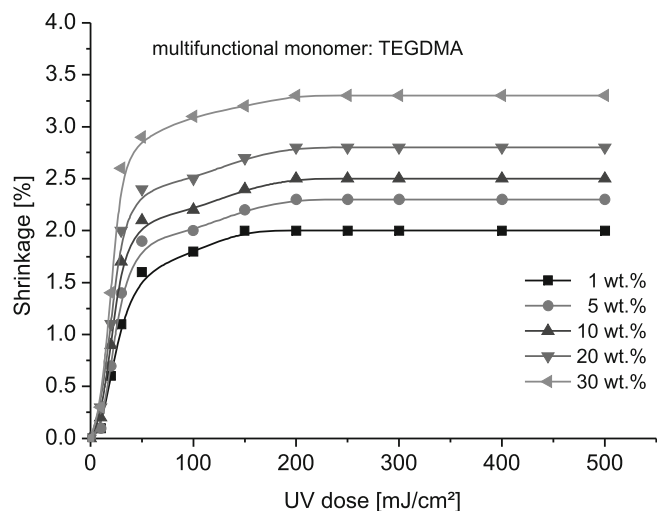


Figure 6. Shrinkage of dimethacrylate TEGDMA as a function of its concentration and UV dose

200 and 500 mJ/cm² remained constant thereafter for all the investigated DDDMA concentrations. The maximum shrinkage was thus observed for 30 wt.% DDDMA. The reason for the increased polymerization shrinkage initially from 1–5 wt.% DDDMA can be attributed to the crosslinking i.e. attraction between the intermolecular chains of the adhesive towards the crosslinker, however, once maximum crosslinking is achieved, the molecular

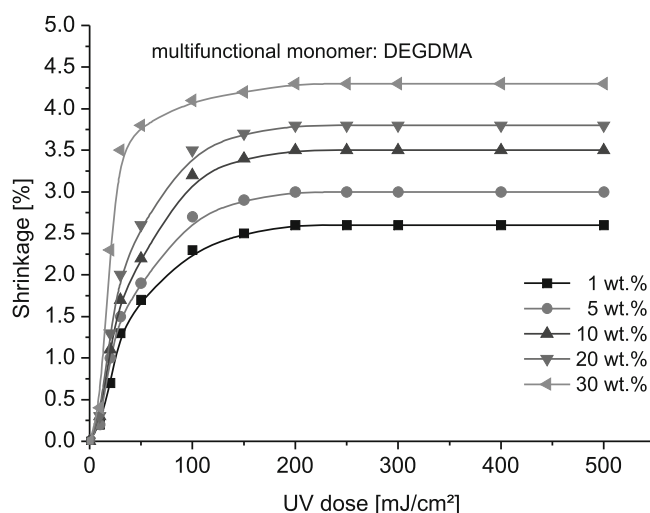


Figure 7. Shrinkage of dimethacrylate DEGDMA as a function of its concentration and UV dose

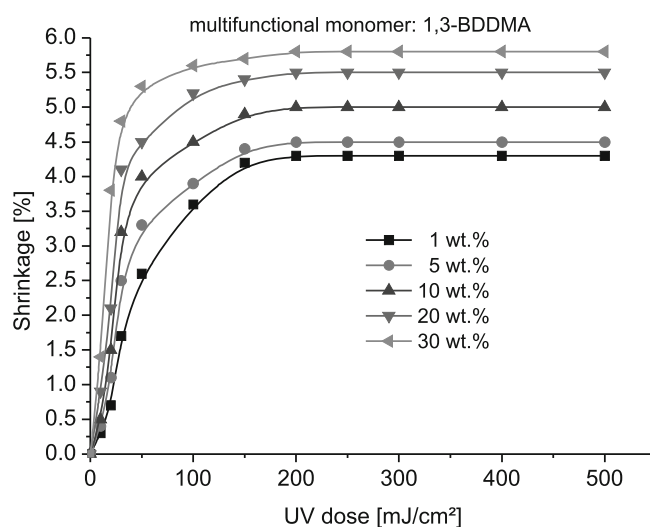


Figure 8. Shrinkage of dimethacrylate 1,3-BDDMA as a function of its concentration and UV dose

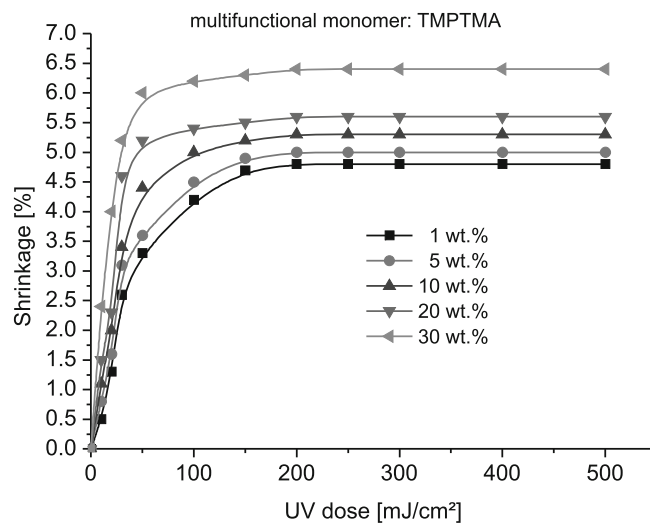


Figure 9. Shrinkage of dimethacrylate TMPTMA as a function of its concentration and UV dose

chains are dimensionally stabilized leaving no scope for further shrinkage.

Similarly the effect of multifunctional methacrylates ethoxylated Bis-GMA (EBPDMA), 2,2-bis-[4-(2-hydroxy-3-methacryloyloxy-propyl)phenyl]propane (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), diethylene

glycol dimethacrylate (DEGDMA), 1,3-butanediol dimethacrylate (1,3-BDDMA) and trimethylolpropane trimethacrylate (TMPTMA) on shrinkage is given in Figures 4–9 whereas the results of comparative polymerization shrinkage for different multifunctional methacrylates in the concentrations of 30 wt.% have been summarized in Figure 2. For all the multifunctional methacrylates a similar trend of shrinkage was observed as with DDDMA i.e. the shrinkage is initially increased from 10 to 150 mJ/cm² UV dose and remained unaffected thereafter. Similarly with increasing the concentration of EBPDMA, Bis-GMA, TEGDMA, DEGDMA, 1,3-BDDMA and TMPTMA and resultant molecular attraction among the acrylic adhesive acrylic chains towards a crosslinker resulted in the increased polymerization shrinkage. However, once the maximum crosslinking is achieved the adhesive becomes dimensionally stable and further shrinkage is arrested. The order of shrinkage for all the multifunctional methacrylates is represented in Figure 2 and Table 2. The order of polymerization shrinkage for various methacrylates is given as: TMPTMA > 1,3-BDDMA > DEGDMA > TEGDMA > Bis-GMA > EBPDMA > DDDMA.

From the structure of the multifunctional methacrylates and the polymerization shrinkage behavior can be explained. DDDMA is characterized by a very long organic spacer between two reactive end methacrylate groups and this effect reduces polymerization shrinkage after the UV exposure.

There is no doubt that shrinkage depends on the double bonds conversion because the shrinkage phenomenon is the consequence of the polymerization process of the investigated monomers what contributes to polymerization and curing of adhesive compositions.

Changing the degree of ethoxylation in the case of 1,3-BDDMA, DEGDMA or TEGDMA is a convenient way to alter the monomer chain lengths according to the segment lengths between the double bonds in monomers. Two methacrylates with a different degree of ethoxylation, tri (DEGDMA) and four (TEGDMA) mol ethoxy groups to evaluate the effect of monomer chain lengths on shrinkage were used. Thus, the monomer chain lengths effect on the shrinkage is attributed to the change of the concentration of the double bonds. Besides, decreasing the degree of ethoxylation is also due to the reduction of the concentration of the double bonds.

Thus, as shown in Table 2, the maximum of the shrinkage level moved from the expansion stage to the shrinkage stage when the degree of ethoxylation was increased. The mobility of free radicals and monomeric and pendant double bonds rises due to the formation of less highly cross-link networks, and the segmental diffusivity of pendent double bonds rises due to the more flexible pendant double bonds. Thus, the propagation is less diffusion-controlled when the degree of ethoxylation is up.

CONCLUSIONS

From the above study the following conclusion can be drawn that the polymerization shrinkage of the adhesive containing multifunctional (meth)acrylate monomers mainly depended on the kind and concentration of the

used methacrylates, UV curing dose and of course on the relative concentration of the photoreactive double bonds. With increasing the UV dose and the raise of multifunctional methacrylates concentration the shrinkage in acrylic adhesive rose from 10 to 500 mJ/cm² and after the 150 mJ/cm² UV dose shows a constant level. The increase of the chain length of monomers through raising the degree of ethoxylation can significantly lower the shrinkage. While changing the degree of ethoxylation or monomer functionality, it was observed that shrinkage increased with the concentration of the double bonds.

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