

## Polymerization shrinkage of UV curable dental composites containing multifunctional methacrylates

Z. Czech\*, A. Kowalczyk, P. Ragańska, A. Antosik

*Institute of Chemical Organic Technology, West Pomeranian University of Technology, Szczecin, Poland*

Received January 16, 2014; Revised March 5, 2014

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 Waal's 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.

\* To whom all correspondence should be sent:  
E-mail: psa\_czech@wp.pl

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-methacryloyloxypropyl)phenyl]propane (bis-GMA), 1,3-butanediol dimethacrylate (1,3-BDDMA), diethylene glycol dimethacrylate (DEGDMA), tetraethylene 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).

Hydroxylapatite 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.

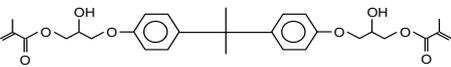
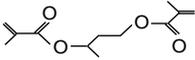
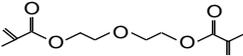
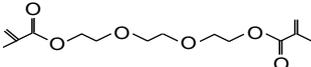
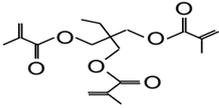
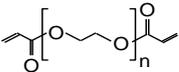
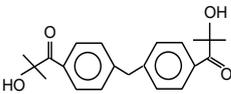
The investigated UV-curable dental composition contained the following raw materials:

Bis-GMA: basic material	40 wt.%
Multifunctional (meth)acrylate	30 wt.%
Hydroxyapatite	28 wt.%
Irgacure 127	2 wt.%

### Measurement of shrinkage

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.

**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-meth-acryloyloxypropyl)phenyl]propane
1,3-BDDMA		1,3-butanediol dimethacrylate
DEGDMA		diethylene glycol dimethacrylate
T3EGDMA		tetraethylene glycol dimethacrylate
TMPTMA		trimethylolpropane trimethacrylate
PEG200DA		polyethylene glycol 200 dimethacrylate
Irgacure 127		2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl]-2-methyl-propan-1-one

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:

$$S = (H_0 - H_t) / H_0 = (1 - H_t / H_0) \times 100 \text{ [%]}$$

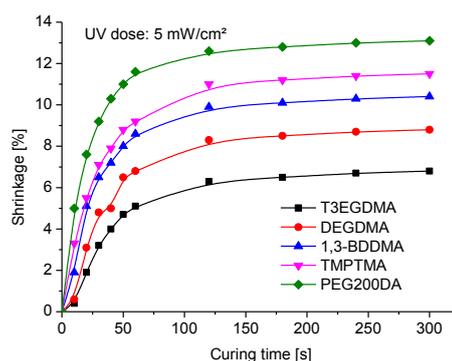
where  $H_0$  is the initial thickness and  $H_t$  is the thickness at time  $t$ . The measured shrinkage is actually a linear shrinkage. However, as the planar dimensions are much greater than the thickness and constrain planar shrinkage, the linear shrinkage appropriately equals to the volumetric shrinkage. 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 Hoenle 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/cm<sup>2</sup>.

## 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).



**Fig. 1.** Shrinkage of dental filling containing the investigated (meth)acrylates versus curing time

This expansion is induced by the accumulated curing, in this case polymerization heat, due to the higher reactivity of acrylates in comparison to methacrylates. The expansion also increases at a very early stage of curing due to auto-acceleration effect. Because of the high reactivity, the acrylate monomer PEG200DA shows much higher shrinkage than the other tested methacrylates and needs less time to reach the maximal measurable shrinkage profile. Beyond this point, the shrinkage rate decreases due to significant reduction of monomers/initiator/radicals (de-acceleration). Thus the shrinkage tends to reach the equilibrium final shrinkage.

There is no doubt that the shrinkage depends on double bonds conversion because the shrinkage phenomenon is a consequence of the polymerization process of the investigated monomers that provides curing of dental filling compositions. The double bond conversion of polymerized monomers can be assessed by comparing the shrinkage plateaus of the investigated monomers. After 240-300 s (4-5 min) shrinkage reaches a maximal level and at this moment the conversion reaction of monomers double bonds is finished.

Table 3 presents molecular weight, density, functionality of investigated monomers, concentration of double bonds in their structure, and maximal shrinkage values after UV curing.

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

(Meth)acrylate	Polymerization shrinkage as a function of curing time [%]										
	Curing time [s]										
	0	10	20	30	40	50	60	120	180	240	300
T3EGDMA	0	0.4	1.9	3.2	4	4.7	5.1	6.3	6.5	6.7	6.8
DEGDMA	0	0.6	3.1	4.8	5	6.5	6.8	8.3	8.5	8.7	8.8
1,3-BDDMA	0	1.9	5.1	6.5	7.2	8	8.6	9.9	10.1	10.3	10.4
TMPTMA	0	3.3	5.5	7.1	7.9	8.8	9.2	11	11.2	11.4	11.5
PEG200DA	0	5	7.6	9.2	10.3	11	11.6	12.6	12.8	13	13.1

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

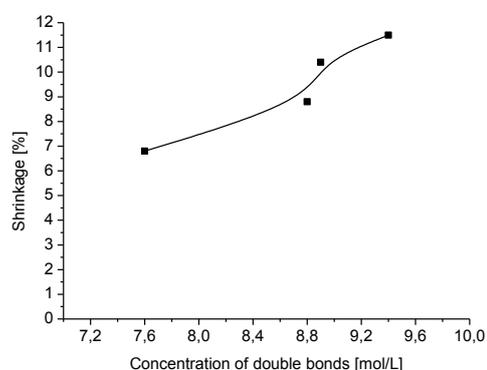
Monomer	Functionality	Molecular weight [kg/kmol]	Density at 25°C [kg/m <sup>3</sup> ]	Concentration of double bonds C <sub>db</sub> [mol/L]	Maximal shrinkage after UV curing [%]
T3EGDMA	2	286	1090	7.6	6.8
DEGDMA	2	242	1070	8.8	8.8
1,3-BDDMA	2	226	1010	8.9	10.4
TMPTMA	3	338	1060	9.4	11.5
PEG200DA	2	308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

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.

$C_{db} \text{ [mol/L]} = \text{Functionality} \times \text{Monomer density/Molecular weight}$ , where L is the monomer chain length. According to this equation, rising the degree of ethoxylation means reduction of the concentration of double bonds due to the significant increase of the molecular weight. In fact, shrinkage depends on the conversion and by full conversion, on the concentration of double bonds. Because increase of monomer chain lengths has more significant effect on decreasing the concentration of double bonds than on increasing conversion, shrinkage is low even at high conversion. It was also observed that the maximum of shrinkage decreases from 8.8 % to 6.8 % with rising the degree of ethoxylation (Table 3). Thus, the monomer chain lengths effect on the shrinkage is attributed to the change in the concentration of double bonds. Besides, the drop heat expansion shown in Fig. 1 with decreasing the degree of ethoxylation is also due to reduction of the concentration of double bonds. Thus, as shown in Table 3, the maximal 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 crosslinked networks, and the segmental diffusivity of pendant 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.

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).



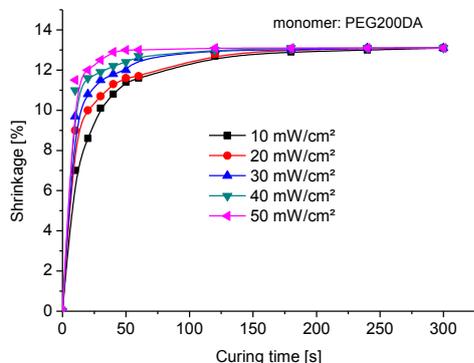
**Fig. 2.** Shrinkage of a dental composition containing multifunctional methacrylates *versus* concentration of double bonds in the methacrylates

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).

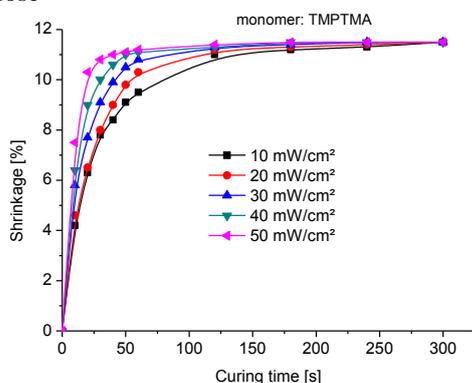
#### *Influence of the UV dose on shrinkage*

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

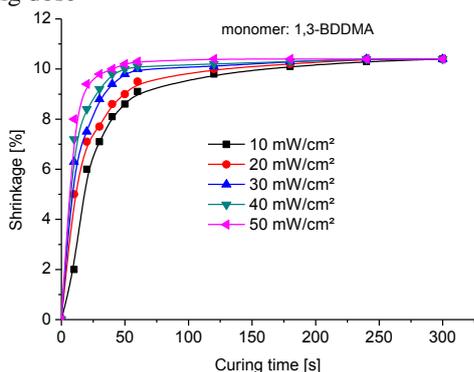
the investigated dental filler compositions containing (meth)acrylate monomers. The UV-polymerization effect on the shrinkage of the tested (meth)acrylates, evaluated for UV doses between 10 and 50 mW/cm<sup>2</sup> and for 3 min UV-crosslinking time, is shown in Table 4 and illustrated in Figs. 3-7.



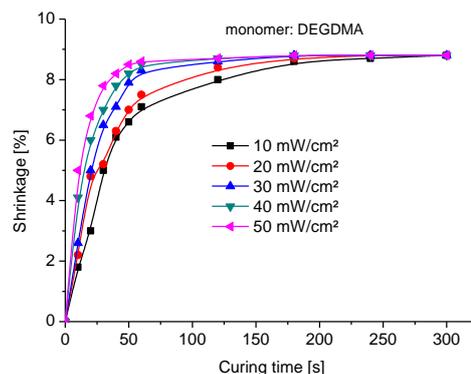
**Fig. 3.** Shrinkage of dental filling containing the monomer PEG200DA versus curing time and UV curing dose



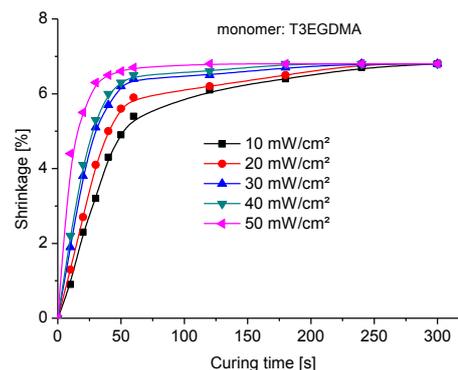
**Fig. 4.** Shrinkage of dental filling containing the monomer PTMPTMA versus curing time and UV curing dose



**Fig. 5.** Shrinkage of dental filling containing the monomer 1,3-BDDMA versus curing time and UV curing dose



**Fig. 6.** Shrinkage of dental filling containing monomer DEGDMA versus curing time and UV curing dose



**Fig. 7.** Shrinkage of dental filling containing the monomer T3EGDMA versus curing time and UV curing dose

The results of the tested dental compositions for shrinkage at different UV doses with variation of multifunctional monomers are given in Figures 3-7 which represent the effect of UV polymerization dose in the range between 10 and 50 mW/cm<sup>2</sup>. It is observed that with increasing the UV dose from 10 to 50 mW/cm<sup>2</sup> the shrinkage values during UV curing increases and remains at a constant level after 120 s, especially at higher UV doses up to 30-40 mW/cm<sup>2</sup>. This indicates that the UV dose of 50 mW/cm<sup>2</sup> is sufficient to cure the investigated dental filling compositions. The maximal shrinkage was observed for the bifunctional monomer polyethylene glycol 200 dimethacrylate (PEG200DMA).

## 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

**Table 4.** Polymerization shrinkage of monomers as a function of curing time and UV curing dose

Monomer	UV dose [mW/cm <sup>2</sup> ]	Curing shrinkage [%] as a function of curing time and UV dose										
		Curing time [s]										
		0	10	20	30	40	50	60	120	180	240	300
PEG200DA	10	0	7.0	8.6	10.1	10.8	11.4	11.6	12.7	12.9	13.0	13.1
	20	0	9.0	10.0	10.7	11.3	11.6	11.7	12.8	13.0	13.1	13.1
	30	0	9.7	10.8	11.5	11.8	12.0	12.6	13.0	13.0	13.1	13.1
	40	0	11.0	11.6	11.9	12.2	12.4	12.7	13.0	13.1	13.1	13.1
	50	0	11.5	12.0	12.5	12.9	13.0	13.0	13.1	13.1	13.1	13.1
TMPTMA	10	0	4.2	6.3	7.8	8.4	9.1	9.5	11.0	11.2	11.3	11.5
	20	0	4.6	6.5	8.0	9.0	9.8	10.3	11.2	11.3	11.4	11.5
	30	0	5.8	7.7	9.1	9.9	10.5	10.8	11.3	11.4	11.5	11.5
	40	0	6.4	9.0	10.0	10.6	11.0	11.1	11.3	11.5	11.5	11.5
	50	0	7.5	10.3	10.8	11.0	11.1	11.2	11.4	11.5	11.5	11.5
1,3-BDDMA	10	0	2.0	6.0	7.1	8.1	8.6	9.1	9.8	10.1	10.3	10.4
	20	0	5.0	7.1	7.7	8.6	9.0	9.5	10.0	10.2	10.4	10.4
	30	0	6.3	7.5	8.8	9.4	9.8	10.0	10.1	10.3	10.4	10.4
	40	0	7.2	8.4	9.2	9.8	10.0	10.1	10.2	10.3	10.4	10.4
	50	0	8.0	9.4	9.8	10.0	10.2	10.3	10.4	10.4	10.4	10.4
DEGDMA	10	0	1.8	3.0	5.0	6.1	6.6	7.1	8.0	8.6	8.7	8.8
	20	0	2.2	4.8	5.2	6.3	7.0	7.5	8.4	8.7	8.8	8.8
	30	0	2.6	5.0	6.5	7.1	7.9	8.3	8.6	8.8	8.8	8.8
	40	0	4.1	6.0	7.0	7.8	8.2	8.5	8.7	8.8	8.8	8.8
	50	0	5.0	6.8	7.8	8.2	8.5	8.6	8.7	8.8	8.8	8.8
T3EGDMA	10	0	0.9	2.3	3.2	4.3	4.9	5.4	6.1	6.4	6.7	6.8
	20	0	1.3	2.7	4.1	5.0	5.6	5.9	6.2	6.5	6.8	6.8
	30	0	1.9	3.8	5.1	5.7	6.2	6.4	6.5	6.7	6.8	6.8
	40	0	2.2	4.1	5.3	6.0	6.3	6.5	6.6	6.8	6.8	6.8
	50	0	4.4	5.5	6.3	6.5	6.6	6.7	6.8	6.8	6.8	6.8

(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

1. N. Moszner, T. Hirt, *J. Polym. Sci. Part A: Polym. Chem.* **50**, 4369 (2012).
2. A. J. Feilzer, A. J. De Gee, *J. Dent. Res.* **66**, 1636 (1987).
3. N. Moszner, U. Salz, *Macromol. Mater. Eng.* **292**, 245 (2007).
4. C. F. Liu, S. M. Collard, C. D. Armeniades, *Am. J. Dent.* **3**, 44 (1990).
5. J. Luo, J. J. Lannutti, R. R. Seghi, *Dent. Mater.* **14**, 29 (1998).
6. Z. Czech, A special report, *Adv. Polym. Techn.* **20**, 72 (2001).
7. R. Milker, Z. Czech, Removable and Repositionable Pressure-Sensitive Adhesive Products, STICK, 3rd European Congress of Adhesive and Sealant Raw Materials, Nürnberg, Germany, 2003, p. 23
8. R. Labella, P. Lambrechts, B. Van Meerbeek, *Dent. Mater.* **15**, 128 (1999).
9. Z. Czech, *Polish J. Chem. Technol.* **45** (2004).
10. J. R. Condon, J. L. Ferracane, *J. Am Dent. Assoc.* **131**, 497 (2000).
11. Z. Czech, A. Kowalczyk, J. Kabatc, J. Świdarska, *Eur. Polym. J.* **48**, 1446 (2012).
12. C. M. Kemp-Scholte, C. L. Davidson, *J. Dent. Res.* **69**, 1240 (1990).
13. Z. Czech, A. Butwin, J. Kabatc, J. Świdarska, *Polym. Bull.* **69**, 71 (2012).
14. C. L. Davidson, A. J. De Gee, *J. Dent. Res.* **63**, 1396 (1984).
15. Y. Jian, Y. He, T. Jiang et al., *J. Polym. Sci. Part B: Polym. Phys.* **50**, 923 (2012).
16. A. K. Singh, D. S. Mehra, U. K. Niyogi et al. *J. Polym. Mater.* **28**, 525 (2011).

## ПОЛИМЕРИЗАЦИОННО СВИВАНЕ НА UV-КАТАЛИЗИРАНИ ЗЪБНИ КОМПОЗИТИ, СЪДЪРЖАЩИ МНОГОФУНКЦИОНАЛНИ МЕТАКРИЛАТИ

З. Чех\*, А. Ковалчик, П. Раганска, А. Антошик

*Институт по органична химична технология, Западно-поморански технологичен университет, Шчечин 70322,  
Полша*

Постъпила на 15 януари 2014 г.; коригирана на 5 март, 2014 г.

(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 и UV-Vis - лечебния процес е свиването на полимерния материал. Пълното свиване на UV-Vis – лечебните зъбни композиции е явлението на свиване при полимеризацията, което е типично за многофункционалните метакрилати. Важни фактори за лечебната употреба на зъбните композиции са: видът и концентрацията на използваните метакрилати, тяхната функционалност, концентрацията на двойни връзки, на добавения фотоинициатор и дозата на UV-Vis – облъчването.

Изследвани са UV-лечебни зъбни композиции, основани на 2,2-бис-[4-(2-хидрокси-3-метакрилоил-оксипропил)фенил]пропан (Bis-GMA) и съдържащи многофункционални мономери, като 1,3-бутандиол диметакрилат (1,3-BDDMA), диетилен гликол диметакрилат (DEGDMA), тетраетилен гликол диметакрилат (T3EGDMA), триметилпропан триметакрилат (TMPTMA), полиетилен гликол 200 диметакрилат (PEG200DA). Намаляването на полимеризационното свиване при зъбните композиции в момента е главният проблем в зъболекарската технология.