

POLYMERIZATION SHRINKAGE OF RESIN MIXTURES USED IN DENTAL COMPOSITES

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Abstract

Polymerization of dental composites generates shrinkage in the matrix resulting in numerous clinical problems. The influence of the most commonly used resins on the shrinkage process has not been thoroughly examined so far in the literature. The purpose of this work is to determine the effect of the resin mixture compositions on the volumetric polymerization shrinkage. The mixtures used in the tests were prepared in specific weight proportions to determine the influence of particular monomers, such as Bis-GMA, Bis-EMA, UDMA, and TEGDMA. The shrinkage measurements were performed using the self-designed video-imaging device. The studies showed that the shrinkage decreased in opposite to the Bis-GMA concentration in the mixture with the simultaneous decrease in the Bis-EMA content. The shrinkage value decreased in opposite to the molecular weight only for some monomers and compositions. Bis-EMA resin as a flexible monomer achieved the lower shrinkage values than UDMA, and the highest shrinkage values, above 6%, were achieved by compositions with the 14wt% content of Bis-GMA. Regarding the shrinkage, the most optimal composition was 56wt% Bis-GMA with the addition of Bis-EMA (24wt%) and TEGDMA (20wt%). The obtained shrinkage value was 4.73%.

Keywords: polymer blends, volumetric shrinkage, dimethacrylates, dental composite

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Introduction

Light-curable dental composites are currently the most commonly used materials for the direct reconstruction of enamel and dentin, accounting for about 70% of all dental restorations [1]. They are made of a polymer matrix reinforced with organic or inorganic, mineral, or mixed particles [2]. From the 1960's, with the invention of the Bis-GMA monomer by Bowen, they became the main direction of development in aesthetic dentistry, gradually replacing amalgams, cements and restorations made of precious metals [3]. The universality in the use of composites based on light-curable resins is primarily implied by their beneficial mechanical properties, wear resistance, durability, ease of application and aesthetic [1].

In addition to regaining the functionality of the teeth and guaranteeing their aesthetic appearance, composite restorations perform a very important function which is reducing the risk of health-threatening infections associated with the development of caries [4]. The key factor in maintaining the marginal adaptation and durability of these restorations turns out to be the polymerization shrinkage, resulting from the exchange of van der Waals intermolecular interactions to covalent bonds between monomers during polymerization. As a consequence of this phenomenon, stresses arise in the restoration-tooth interface, worsening adhesion and leading to the formation of a marginal fissure where bacteria can enter causing secondary caries [2]. Stresses exceeding the enamel strength may lead to a fracture within the bond with the material [5,6].

Most composites used in restorative dentistry shrink linearly by 0.6-1.4% [7], however, the value of volumetric contraction may be as high as 7% [8]. The polymerization shrinkage depends on the resin composition as well as the amount of filler particles and radiation intensity [9]. The size of the polymerization shrinkage depends, among others, on the molecular weight and functionality of the monomers. When comparing monomers with the same molecular weight, the polymerization shrinkage increases with functionality. Comparing monomers with the same functionality, the polymerization shrinkage increases opposite to the molecular weight, as a consequence, mixtures of Bis-GMA and other monomers will affect the polymerization shrinkage [10]. The purpose of this work is to determine the effect of resin mixture composition on the volumetric polymerization shrinkage.

Materials and Methods

In order to assess the relationship between the composition of the resins mixtures used as the matrix of dental composites and the resulting polymerization shrinkage, compositions with a suitably wide range of resin proportions were prepared, and then subjected to shrinkage tests at the designed stand and via the authors' own method.

The four most popular dimethacrylate resins: Bis-GMA (CAS 1565-94-2), Bis-EMA (CAS 41637-38-1), UDMA (CAS 72869-86-4) and TEGDMA (CAS 109-16-0) were mixed in the proportions shown in TABLE 1. The weight ratios for the mixtures and their markings are shown in TABLE 2.

TABLE 1. Physical properties of tested dimethacrylates.

Monomer	Molecular weight (average)	Double bond concentration (mol/kg)	Viscosity (Pa·s)
Bis-GMA	510.6	3.90	1200.00
Bis-EMA	540.0	3.70	0.90
UDMA	470.0	4.25	23.10
TEGDMA	286.3	6.99	0.01

Each mixture contained camphorquinone (an initiator; CAS 10373-78-1) and N,N-dimethylaminoethyl methacrylate (CAS 2867-47-2) as a co-initiator for light-cured free-radical polymerization, as well as 20wt% of the TEGDMA, which acts as an active solvent decreasing the viscosity of the mixture and facilitating effective mixing. The amount of TEGDMA monomer was constant for all the tested mixtures. The compositions were prepared by mixing precisely weighed ingredients (± 0.1 mg) using the WAS 220 laboratory balance (Radwag). The mixing process was carried out under low energy lighting to avoid an accidental polymerization of the resins.

The shrinkage measurements were carried out on the self-designed video-imaging device which is schematically presented in FIG. 1. The specimen was deposited on the stainless steel pin of the 3 mm diameter. The top surface of the pin was placed in the optical axis of the camera to minimize the geometrical deformations of the acquired image. The pin with the resin droplet was rotated during the measurement in a full angle range with the step of 20° , realized by a stepper motor controlled by the dedicated software. In each angular position, an image (640x480 pixels) was taken until the last position of the sample was reached. The image acquisition was also controlled by the software. Yellow diffused light was used to obtain good exposure conditions (without reflections) and to avoid accidental curing.

TABLE 2. Resin compositions used to measure polymerization shrinkage. Each specimen contained 20wt% of TEGDMA.

Specimen	Bis-GMA (wt%) (G)	Bis-EMA (wt%) (E)	UDMA (wt%) (U)																											
G	80.0	-	-																											
E	-	80.0	-																											
U	-	-	80.0																											
G40E40	40.0	40.0	-																											
G56E24	56.0	24.0	-																											
G24E56	24.0	56.0	-																											
G40U40	40.0	-	40.0																											
G56U24	56.0	-	24.0																											
G24U56	24.0	- </tr <tr> <td>G27E27U27</td> <td>26.7</td> <td>26.7</td> <td>26.7</td> </tr> <tr> <td>G26E40U14</td> <td>26.0</td> <td>40.0</td> <td>14.0</td> </tr> <tr> <td>G26E14U40</td> <td>26.0</td> <td>14.0</td> <td>40.0</td> </tr> <tr> <td>G14E26U40</td> <td>14.0</td> <td>26.0</td> <td>40.0</td> </tr> <tr> <td>G40E26U14</td> <td>40.0</td> <td>26.0</td> <td>14.0</td> </tr> <tr> <td>G40E14U26</td> <td>40.0</td> <td>14.0</td> <td>26.0</td> </tr> <tr> <td>G14E40U26</td> <td>14.0</td> <td>40.0</td> <td>26.0</td> </tr>	G27E27U27	26.7	26.7	26.7	G26E40U14	26.0	40.0	14.0	G26E14U40	26.0	14.0	40.0	G14E26U40	14.0	26.0	40.0	G40E26U14	40.0	26.0	14.0	G40E14U26	40.0	14.0	26.0	G14E40U26	14.0	40.0	26.0
G27E27U27	26.7	26.7	26.7																											
G26E40U14	26.0	40.0	14.0																											
G26E14U40	26.0	14.0	40.0																											
G14E26U40	14.0	26.0	40.0																											
G40E26U14	40.0	26.0	14.0																											
G40E14U26	40.0	14.0	26.0																											
G14E40U26	14.0	40.0	26.0																											

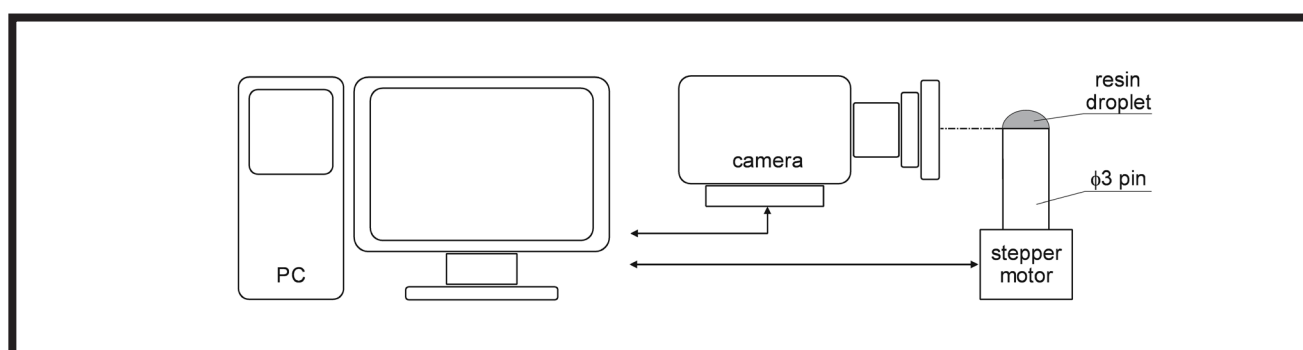


FIG. 1. The idea of the measuring system.

The resin polymerization was performed right after the first scan (of the uncured resin) followed by the second scan of the specimen. The halogen lamp Cromalux 75 (Mega-Physik) was used for curing for 20 sec. A set of 18 images of each scan was then analyzed in order to obtain the sample volume.

The sample volume was measured from the projection of the samples' visible area. The volume of such a rotational figure can be determined as the product of the half surface area A (indicated by the axis of rotation) and the radius of its rotation r . The radius of rotation r was established as the distance of the analyzed figure centroid from the axis of rotation (FIG. 2a). The area A was measured by image analysis. All the measurements were carried out in the CTAnalyser software (Bruker microCT). The measurements were taken with an accuracy of $6.6 \mu\text{m}$ for 10 samples of each resin type (each measurement for 18 + 18 images in total) and the results were statistically analyzed using the Statistica software (TIBCO Software Inc.) at the confidence level $\alpha < 0.05$. Superimposing images taken before and after curing revealed the material loss due to shrinkage (FIG. 2b).

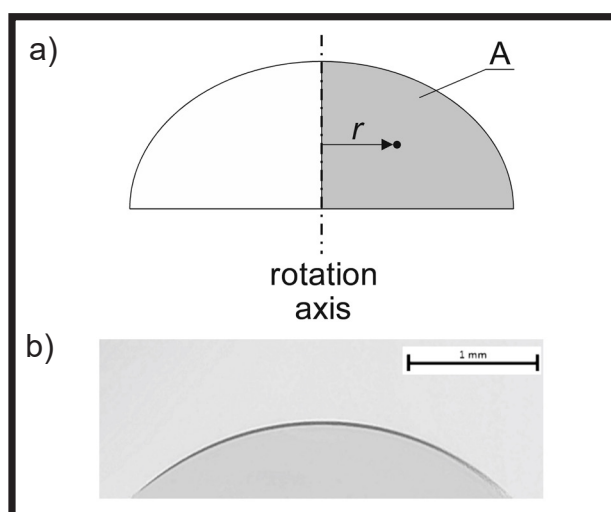


FIG. 2. a) The principle of determining data for volume calculations, b) trace of material loss after superimposing images before and after curing.

The volumetric polymerization shrinkage was calculated as follows:

$$S_V = \frac{V_1 - V_2}{V_1} \cdot 100\% \quad (1)$$

where: V_1 is the initial droplet volume and V_2 is the droplet volume of the material after polymerization.

Such a method is suitable especially for materials of relatively low viscosity, which allows them to spread freely over the pin surface and create a symmetrical drop.

Results and Discussions

The results of volumetric shrinkage for the mixtures based on Bis-GMA, Bis-EMA, UDMA, and TEGDMA are presented in FIG. 3 and TABLE 3 which also presents the standard deviation values and the variation coefficient. The material G presented the lowest shrinkage and at the same time the highest deviation. However, among all the tested samples, deviation remained low.

The varied properties of the used materials, such as viscosity, double bond concentration, and in particular the molecular weight of the monomer (TABLE 1) determine the shrinkage value generated in the polymer. Unlike UDMA and TEGDMA, the Bis-GMA as well as Bis-EMA resins have approximately the same molecular weight, and therefore a higher concentration of double bonds. According to the work [4], the main factors that affect shrinkage are: the conversion degree, the molecular weight of the monomer and the type and amount of the used reinforcement (for composites). The polymerization shrinkage increases with the conversion degree and decreases with the increasing monomer molecular weight and the decreasing double bond concentration.

According to the above statement, the G composition achieved the lowest contraction among the subjects. It contained 80% by weight Bis-GMA which has a high mass and a relatively low number of double bonds. The shrinkage value increased successively for the E and U compositions together with the decrease in the double bond concentration. Sideridou et al. [11] examined the conversion degree for dimethacrylates, such as Bis-GMA, Bis-EMA, UDMA and TEGDMA, and obtained an upward trend for the resins, respectively.

TABLE 3. Results of volumetric shrinkage measurements.

Mixture	Volumetric shrinkage [%]	S.D. [%]	Coefficient of variation [%%]
G	3.51	0.63	17.93
E	4.73	0.66	13.95
U	5.55	0.62	11.17
G40E40	5.00	0.48	9.60
G56E24	4.73	0.56	11.88
G24E56	5.65	0.63	11.15
G40U40	5.49	0.66	12.02
G56U24	5.37	0.33	6.20
G24U56	5.01	0.53	10.58
G27E27U27	5.51	0.34	6.23
G26E40U14	5.45	0.61	11.20
G26E14U40	4.84	0.44	9.09
G14E26U40	6.10	0.58	9.45
G40E26U14	5.42	0.47	8.61
G40E14U26	5.44	0.42	7.71
G14E40U26	6.22	0.54	8.74

The trend was explained by the claim that the conversion degree increases with the increasing polymerization shrinkage, as evidenced by the test results for the analogous G, E, and U materials. In the work of Yoon [12], the studies of Bis-GMA monomer shrinkage were found by the density determination. The obtained result of $3.4 \pm 0.3\%$, was approximate to the result of our work. The above results confirmed the reliability of the measuring method presented in this paper.

Only four of the sixteen compositions achieved the shrinkage level below 5%: G, E, G56E24, and G26E14U40. The mixtures containing Bis-GMA and Bis-EMA were the majority in these materials. However, the result obtained for the G26E14U40 sample, which contained only 40wt% of Bis-GMA and Bis-EMA, was unexpected. The standard deviation for this sample was 0.44% and its shrinkage value was similar to the other materials.

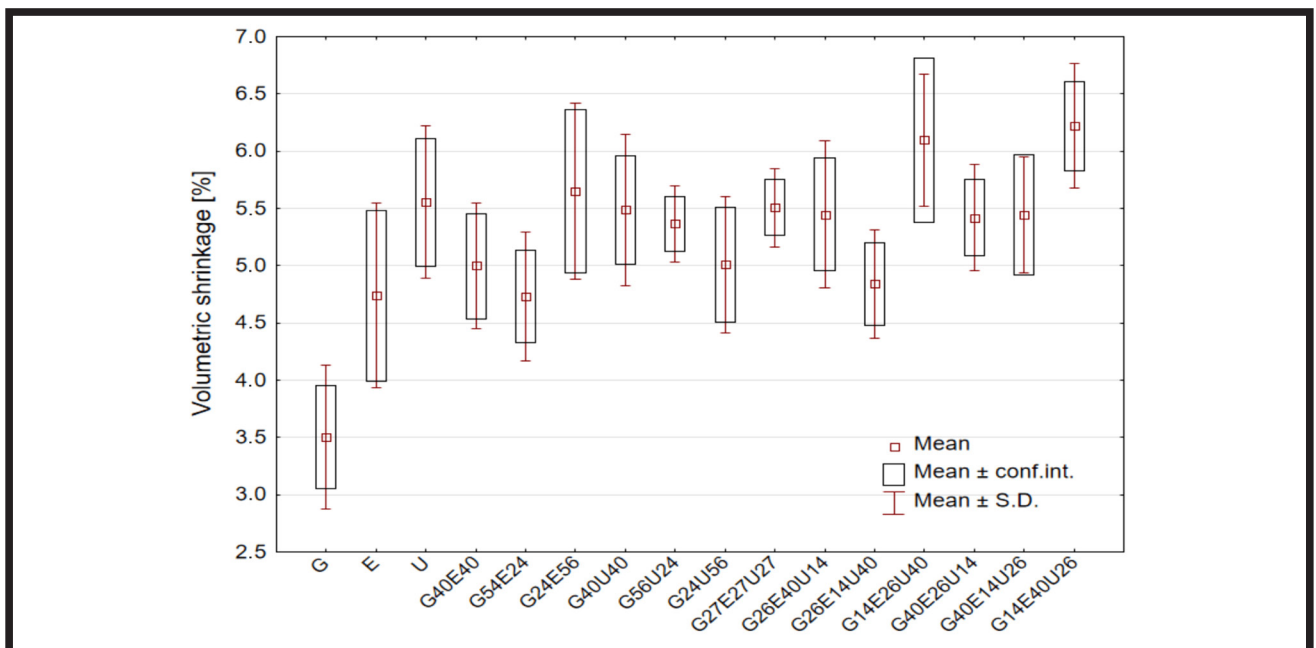


FIG. 3. Results of volumetric shrinkage measurements.

TABLE 4. Probability values p from the t test. Statistically significant differences at $p < 0.05$.

	E	U	G40E40	G56E24	G24E56	G40U40	G56U24	G24U56	G27E27U27	G26E40U14	G26E14U40	G14E26U40	G40E26U14	G40E14U26	G14E40U26
G	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
E	1.000	0.051	0.471	0.981	0.051	0.052	0.041	0.467	0.016	0.070	0.755	0.009	0.043	0.090	0.000
U		1.000	0.091	0.012	0.795	0.841	0.448	0.107	0.854	0.744	0.021	0.160	0.621	0.744	0.032
G40E40			1.000	0.324	0.079	0.112	0.098	0.971	0.028	0.146	0.530	0.005	0.098	0.146	0.000
G56E24				1.000	0.012	0.013	0.006	0.323	0.002	0.019	0.651	0.001	0.008	0.023	0.000
G24E56					1.000	0.648	0.311	0.092	0.608	0.573	0.021	0.301	0.448	0.586	0.093
G40U40						1.000	0.607	0.130	0.937	0.891	0.026	0.104	0.786	0.889	0.014
G56U24							1.000	0.126	0.362	0.731	0.011	0.008	0.777	0.713	0.000
G24U56								1.000	0.040	0.168	0.523	0.008	0.121	0.175	0.000
G27E27U27									1.000	0.799	0.002	0.026	0.632	0.767	0.003
G26E40U14										1.000	0.036	0.086	0.912	0.993	0.011
G26E14U40											1.000	0.001	0.015	0.033	0.000
G14E26U40												1.000	0.028	0.075	0.691
G40E26U14													1.000	0.918	0.002
G40E14U26														1.000	0.013

The 5% shrinkage was demonstrated for the *G40E40* and *G24U56* samples. The shrinkage above 6% was achieved by two compositions: *G14E26U40* and *G14E40U26* containing the smallest amount of Bis-GMA among all the tested materials. These materials displayed the highest volumetric shrinkage. The difference in the average shrinkage value of the *G14E40U26* sample was not statistically significant only when compared to the average of the *G14E26U40* sample. The results of the t test, carried out in Statistica, for all the compositions are presented in TABLE 4.

Effect of varied two resins proportions on shrinkage

The test results confirmed the literature reports that the higher molecular weight of the monomer generated lower polymerization shrinkage. The obtained results were consistent with the literature data [7,9] regarding resins with the variable concentration of Bis-GMA and TEGDMA. In the *U* composition, 80% by weight of the Bis-GMA monomer was replaced by the same amount of UDMA monomer that had over 40% lower weight, thus obtaining the 2% higher shrinkage.

The above statement is contradictory to the analysis of the Bis-EMA shrinkage results because the resin has a higher molecular weight than Bis-GMA and the obtained shrinkage is higher. The difference between the result obtained for the *G* sample with the highest concentration of Bis-GMA and Bis-EMA as well as the other results is statistically significant, as demonstrated by the t test. The analysis of the above results is shown in FIG. 4. In addition, a significant shrinkage increase was noted with a gradual increase in the Bis-EMA monomer content and the decrease in Bis-GMA concentration. The proportions visible in the chart do not include the weight content of the TEGDMA resin. The mass concentrations are assumed relatively to the materials considered in a given context.

As for the relationship between compositions, it must be noted that the difference between the mean values of volumetric shrinkage for *G40E40* and *G56E24* was not statistically significant. The difference in the shrinkage value between the mixtures containing 30wt% Bis-EMA and the 70wt% Bis-Ema was approximately 1%. Despite the higher molecular weight (540 g/mol), the ethoxylated version of Bis-GMA did not have such strong molecular interactions occurring due to the existence of hydroxyl groups, which reduced its viscosity and resulted in the higher conversion degree and thus the higher polymerization shrinkage [13]. Therefore, the thesis cited in many papers about the dependence of the shrinkage on the molecular weight of the monomer was not confirmed for all types of resins.

In turn, the results obtained by Sideridou et al. showed the lower conversion degree for materials with a higher concentration of Bis-GMA monomer which is associated with a small number of double bonds and high system viscosity. The hydroxyl groups contained in Bis-GMA molecules are capable of forming intermolecular hydrogen bonds, which in turn limit the slip of polymer chains. Fewer double bonds are transformed, gradually increasing the system viscosity as the Bis-GMA content in the composite increases. Limiting the increasing mobility of macro-radicals and monomers affects the propagation of free radicals and thus reduces the conversion degree [11].

Varied concentrations of Bis-GMA and UDMA were used in the *G40U40*, *G56U24*, and *G24U56* compositions. The shrinkage results were inconclusive for these two monomers endowed with different properties. Although both monomers are relatively large molecular structures, Bis-GMA prevails in terms of molecular weight and also has significant conversion restrictions [14] which the polymerization progress is related to. Therefore, a partial replacement of the Bis-GMA monomer in the composite may be essential to optimizing the resin composition.

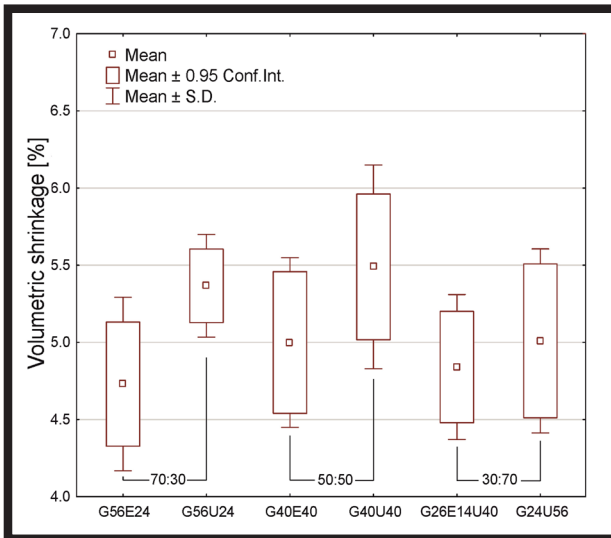


FIG. 4. Polymerization shrinkage of resins containing a constant amount of 20% TEGDMA with variable Bis-GMA:Bis-EMA and Bis-GMA:UDMA rates.

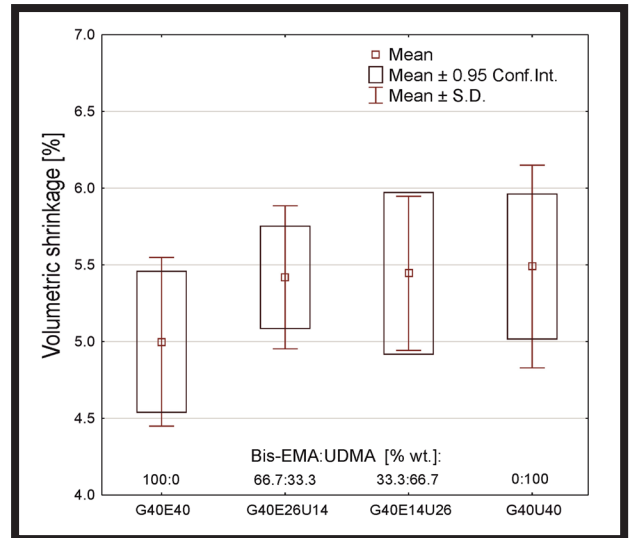


FIG. 5. Volumetric shrinkage of resins with a constant concentration of Bis-GMA (40wt%) containing a variable fraction of Bis-EMA:UDMA.

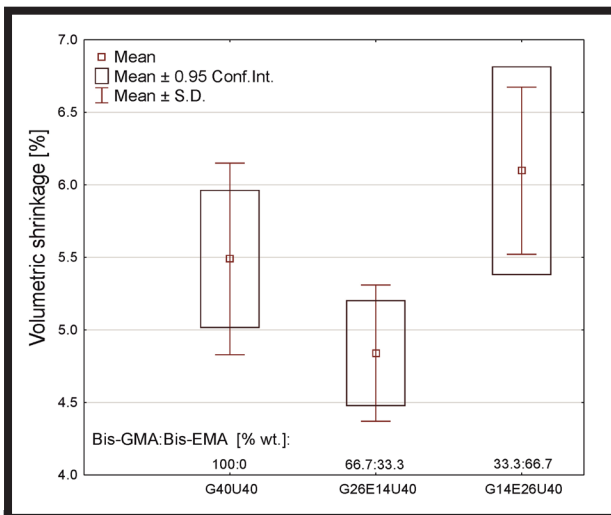


FIG. 6. Polymerization shrinkage of resins containing a constant 40% UDMA and 20% TEGDMA, with a variable rate of Bis-GMA:Bis-EMA.

A low conversion leads to the transfer of unreacted components to soft tissue and causes irritation [11,15] and such restorations have a lower clinical performance [16]. Due to the high viscosity of Bis-GMA, the addition of another more flexible monomer is recommended. For the 50/50 concentration, the highest shrinkage of 5.37% was obtained of the three samples, but no statistical significance was observed for all the results. Despite this, Ferracane [7] revealed the decreasing shrinkage with the increasing UDMA concentration in the mixture, which occurred in the results of the *G56U24* and *G24U56* samples. However, replacing Bis-GMA with 70% UDMA still did not lead to the low shrinkage values represented by sample *G* (80% by weight Bis-GMA, 20% by weight TEGDMA) but reduced it by almost 0.4% as compared to the 30wt% content.

Considering the series of samples with the same proportion variation (FIG. 4) where Bis-GMA is replaced by Bis-EMA or UDMA, two of the three samples achieved the lower shrinkage values for the Bis-EMA substitute. Moreover, in the case of the *G56E24* composition with the 70:30 Bis-GMA and Bis-EMA ratio the obtained shrinkage value was the second smallest.

Effect of the proportion variability of three resins on shrinkage

Polymerization leads to only a partial reaction of the double bonds, which is perceived as a negative phenomenon [17]. Under such conditions, only very flexible monomers undergo the complete conversion. Among the resins with the relatively low viscosity used in commercial composites are Bis-EMA and UDMA as an alternative to TEGDMA. Identification of new flexible monomers is necessary since TEGDMA contributes to the increasing polymerization shrinkage in composites [7]. The Bis-EMA monomer has a slightly higher molecular weight and the lower concentration of double bonds in the structure than the UDMA monomer, which is also reflected in the achieved value of shrinkage (FIG. 5).

The test results showed a correlation between the shrinkage and concentration of Bis-EMA and UDMA. The volumetric shrinkage slightly increased with the concentration of UDMA. There was a statistically significant difference between the average values for the *G40E40* and the *G40E14U26* samples. There were no statistically significant differences between the other tested samples. The *G40E40* sample, without UDMA, obtained a relatively low shrinkage of 5%. To summarize, Bis-EMA as a monomer of moderate viscosity was more effective than UDMA in reducing the shrinkage.

The effect on the shrinkage performed by the Bis-GMA and Bis-EMA concentrations with the constant UDMA and TEGDMA content is explained in FIG. 6. The molecular weight of the presented compositions increased together with the Bis-EMA content. It resulted in the shrinkage increase similarly to the compositions with two resins. However, the lack of Bis-EMA in the *G40U40* composition led to the even greater shrinkage than its 14wt% addition. Again, the molecular weight was not the reason for the value of generated shrinkage.

The highest 6% shrinkage was obtained for the *G14E26U40* and *G14E40U26* materials containing the smallest amount of Bis-GMA, which was replaced by Bis-EMA, UDMA and TEGDMA monomers. The most optimal composition, containing a relatively small amount of Bis-GMA, and achieving the shrinkage of less than 5% was the *G26E14U40* mixture. The same Bis-GMA content but a different UDMA and Bis-EMA monomers proportion of did not guarantee a result below 5% (*G26E40U14*).

Conclusions

The polymerization shrinkage is one of the most important properties of dental composites, but its level is still unsatisfactory in the context of generated stresses and clinical durability of restorations. The measurements of the polymerization shrinkage of the Bis-GMA, UDMA, Bis-EMA and TEGDMA resins in varying weight proportions allowed us to determine the following relationships:

The decreasing shrinkage as the molecular weight of the monomer increases was not the rule. Apart from the molecular weight of resin, other properties such as the resin viscosity, the double bond concentration and the presence of the filler, also could have an influence on the composite shrinkage.

The shrinkage decreased with the increasing Bis-GMA and simultaneous decreasing of Bis-EMA concentration in the mixture.




The compositions containing 14wt% of Bis-GMA achieved the highest shrinkage values, above the 6wt%. However, the increase in the Bis-GMA concentration to 24% and the addition of a specific amount of Bis-EMA and TEGDMA reduced the shrinkage below 5% and such compositions seem to be the optimal ones.

Considering the polymerization shrinkage, Bis-EMA is a better alternative to TEGDMA than UDMA.

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