Research Article / Araştırma Makalesi

INVESTIGATING THE EFFECT OF PHOTOINITIATOR RATIO ON THE POLYMERIZATION SHRINKAGE IN DENTAL COMPOSITES BY TWO COMPARATIVE METHODS

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ABSTRACT

The prupose of this study was to investigate the effects of different ratios of photoinitiator and co-initiator on the polymerization shrinkage. Thus, dental composite materials were produced. Dental composites were composed of Bisphenol A-glycidyl methacrylate (BisGMA) and hydroxyethylmethacrylate (HEMA) as monomer matrix, camphoroquinone (CQ) as photoinitiator and 2-(dimethylamino)ethyl methacrylate (DMAM) as co-initiator. Silanized hydroxyapatite (HA) was used in inorganic phase as a reinforcing material. Polymerization shrinkage was measured by Archimedes principle and laser profilometer. Also, these methods were compared with each other in this study. Statistical analysis of the data was performed with ANOVA and Tukey's post hoc test. Results of shrinkage values obtained by two methods showed that ratios of photointiator and co-initiator were affected the polymerization and, hence shrinkage rate. Also, statistically differences between the values of Archimedes principle and laser profilometer.
Keywords: Dental composite, polymerizaiton shrinkage, photoinitiators, laser profilometer, Archimedes principle.

DENTAL KOMPOZİTLERDE FOTOBAŞLATICI ORANININ POLİMERİZASYON BÜZÜLMESİNE ETKİSİNİN KARŞILAŞTIRMALI İKİ METOD İLE İNCELENMESİ

ÖZET

Bu çalışmanın amacı ticari kompozitlerde en sık kullanılan fotobaşlatıcı ve kobaşlatıcı maddelerin farklı oranlarının polimerizasyon büzülmesine etkilerini incelemektir. Bu amaçla dental kompozitler üretilmiştir. Dental kompozit içeriğinde organik matriks olarak Bisfenol A-glisidil metakrilat (BisGMA) ve Hidroksietilmetakrilat (HEMA), fotobaşlatıcı olarak kamforkuinon ve kobaşlatıcı olarak 2-(dimetilamino)etil metakrilat kullanılmıştır. İnorganik faz içinde güçlendirici madde olarak silanlanmış hidroksiapatit (HA) kullanılmıştır. Polimerizasyon büzülmesi hem Arşimet prensibi ile hem de yüzey profilometre cihazı ile ölçülmüştür. Çalışmada bu iki metodun sonuçları da kıyaslanmıştır. Verilerin istatistiki analizi ANOVA ve Tukey's post hoc testleri ile yapılmıştır. İki metod ile elde edilmiş büzülme sonuçları fotobaşlatıcı ve kobaşlatıcı miktar değişiminin polimerizasyon ve dolayısıyla büzülme oranına etkisi olduğunu göstermiştir. Arşimet prensibi ve lazer profilometre sonuçları arasında istatistiki fark olduğu bulunmuştur.
Anahtar Sözcükler: Dental kompozit, polimerizasyon büzülme, fotobaşlatıcı, lazer profilometresi, Arşimet prensibi.

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1. INTRODUCTION

Dental composites have been mostly used as restorative materials because of their good workability, esthetic appearance and improved mechanical properties since 1960s . Since 1980, light-activated composite materials are commonly used for dental restorations. Dental composites are basically composed of three main components: a continuous organic matrix (generally involving BisGMA, TEGDMA (triethyleneglycol dimethacrylate) and UDMA (urethanethyl dimethacrylate), an inorganic fillers (barium or zinc glasses, quartz, zirconia, silica, etc.) and coupling agent (generally used organosilane) to bond the filler to monomer matrix. (1-6). Champhorquinon/tertiar amin (DMAM or DMAEMA (2-(dimethylamino)ethyl methacrylate, DMPT (NN-dimethyl p-toluidine), DEPT (N,N-diethanol p-toluidine), DABE (N,N-dimethyl-p-aminobenzoic acid ethylester), and CEMA (N,N-cyanoethylmethylaniline), etc.) combination has been generally used as a photoinitiator/co-initiator system to initiate polymerization in dental composite since the photopolymerized composite were introduced [7-10]. CQ which produces free radicals on exposure to 450–500 nm radiation is usually used as photoinitiator in commercial brand due to its good interaction with light emitting diode system (LED system) [7,8,11,12].

However, the main problem of dental composites is shrinkage which occurs during polymerization process [13-15]. Shrinkage of composite materials occurs while van der Waals bonds of the monomers are changed into covalent bonds in the polymer network [16,17]. Shrinkage stresses during the polymerization results in internal force and deformation between the composite resin restoration and the cavity surface. Marginal stress which occurs according to the polymerization in the cavity results in deformation between the composite resin restoration and the cavity surface [18-20]. Finally, shrinkage causes marginal gaps within the tooth and leakage which could occur at the cavity interface results in recurrent caries.

Polymerization depends on the chemical composition of the composite, the intensity and mode of light irradiation, the cavity constraint. The amount of concentration and type of photoinitioator system is important issue for polymerization efficiency. Efficiency of polymerization process is generally affecting degree of conversion, depth of cure and mechanical properties [21-26] because of the increase of the rate of polymerization with increased photoinitiator concentration [27,28].

Prupose of this study was demonstrated how the amount of photoinitiator/co-initiator system would affect the polymerization shrinkage rate.

2. MATERIALS AND METHODS

2.1. Materials

Bisphenol A-glycidyl methacrylate (BisGMA, Sigma-Aldrich) and hydroxyethymethacrylate (HEMA, Sigma-Aldrich) were mixed in equal parts by weight using a mixing machine. The initiator systems, camphoroquinone (CQ) and 2-(dimethylamino)ethyl methacrylate (DMAM) were added to produce a total photoinitiator to total amine ratio of 1:1 (by weight) and then the mixture was stirred for another 12 h in a dark media. Inorganic silanated filler of hydroxyapatite was added at 70 wt.% and mixed for six hours to obtain composite resins by using PolyDrive Rheomix R600 (ThermoHaake Gebrüder Haake GmbH). Table 1 shows photoinitiator/accelator ratios of all experimental dental composites prepared throughout this study.

Table 1. Phase ratios of experimental dental materials.

	Organic phase (*Phase ratio:30%*)			Inorganic phase (*Phase ratio: 70%*)
Materials number	*BisGMA (%)*	*HEMA (%)*	*CQ /DMAM (%)*	*Silanized HA (%)*
G1	49,75	49,75	0,25	100
G2	49,5	49,5	0,5	100
G3	49	49	1	100

Each sample was prepared in the same mold with 5 mm diameter and 2 mm thickness and cured by the Elipar Freelight LED for 20 seconds under 500 mW/cm^2 light density . Four specimens were prepared for each group.

2.2. Silanization Process of Hydroxyapatite

The hydroxyapatite (5.0g±0,05), the silane (0.50±0.01 g), the solvent (100 ml cyclohexane) and n-propylamine (0.1±0.01 g) were stirred at room temperature for 30 min. Then mixture was heated to 60±5 °C temperature and stirred for additional 30 min at atmospheric pressure. The residual solvent in mixture was then removed by a rotary evaporator at 60 °C. The temperature was then increased to 95±5 °C for 1 h in a rotary evaporator. The powder was dried at 80 °C for 24 h [29,30] and was finally dried at 110 °C in a vacuum oven.

2.3. Methods

Archimedes principle

The volumetric shrinkage was measured by density measurements according to Archimedes principle as described in previous studies [31-32]. Measurements were carried out using a digital analytical balance with a density determination kit (GR-200 model, AND, MİR-Polymer-Composite Laboratory, Metallurgical Enginering Department, YTU, Turkey) To obtain stabilized readings the measurements were done in a temperature-controlled room ($T = 25\pm1$ °C) [33].

The weight of uncured specimens were carefully measured by avoiding formation of air bubbles. Since the uncured materials were rather sticky, a small mylar strip was used for measurements Thus, it was fixed on the holder of the balance and its mass was measured in air and in water. Next, each sample was placed on the myler strip film and the total mass of the composite and the film were weighed again in air and in water.

To measure the density of the polymerized resin, cylindrical specimens were made in the mold (5 mm×2 mm). Photoactivation was carried out using the established protocol described in this text before. Specimens were weighed in air and water using the same way. The density of uncured and cured specimens were calculated in g/cm according to the equation:

$$\rho = \frac{m_{air}}{m_{air} - m_{water}} X (\rho_{water} - \rho_{air}) + \rho_{air} \qquad (1)$$

ρ is the density of the material, m_{water} is the weight in grams (g) of the specimen in water, m_{air} is the weight in grams (g) of the specimen in air, ρ_{water} is the density of water at the exactly measured temperature in ◦C according to the density table for distilled water, and ρ_{air} is the density of air (0.0012 g/cm).

The percentage change in volume change (V) after polymerization was calculated from the densities according to the equation:

$$\Delta V = \left(\frac{1}{\rho_{cured}} - \frac{1}{\rho_{uncured}} \right) \frac{1}{\rho_{uncured}} x \% 100 \qquad (2)$$

Laser Profilometer

Polymerization shrinkage of specimens were measured by optical surface profiling system which was described in previous study (34). The measurement of 3-dimensional surface profiles of samples before and after polymerization were carried out using OSP100A optical surface profiling system (Fig. 1) to determine polymerization shrinkage. Sample volumes before (V_b) and after (V_a) were calculated by MATLAB program using an executable software. Volumetric change ratios were obtained by using equation 1. Consequently polymerization shrinkage values of all composite samples were found by the same way.

$$shrinkage\% = \frac{V_b - V_a}{V_b} \qquad (3)$$

The mean value and standard deviation of each measured property were calculated for each group. Analysis of variance (ANOVA) was used. Statistical significance was considered at $p < 0.05$.

3. RESULTS

The volumetric shrinkage values of the experimental dental composites were ranged from 3,53 to 3,87 for laser profilometer and 4,34 to 4,76 for Arcimedes principle. These values obtained by laser profilometer and Archimedes principle are shown in Table 2 and Figure 2.
Figure 3 shows changes of shrinkage values obtained by laser profilometer and Archimedes principle depending on CQ ratio.
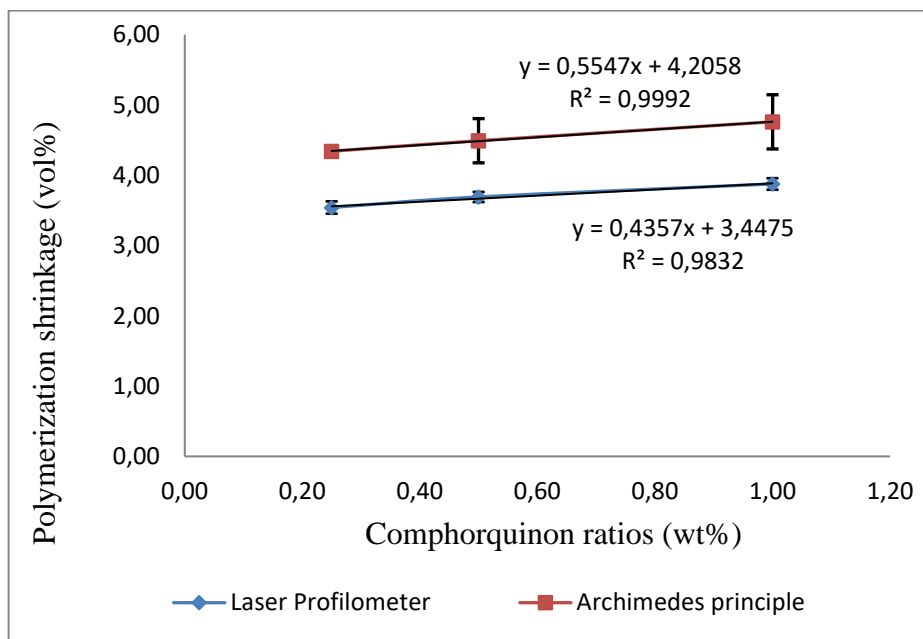
Table 2. The volumetric shrinkage values of the experimental dental composites obtained by laser profilometer and Archimedes principle.

	Laser Profilometer Mean %(SD)	Archimedes principle Mean%(SD)
G1	3,5350(0,0874)	4,3374(0,0472)[a]
G2	3,6875(0,0718)	4,4937 (0,3144)[a]
G3	3,8750(0,0819)	4,7583(0,3856)[a]

[a] The results in the same column marked with the same letters show no statistical difference.
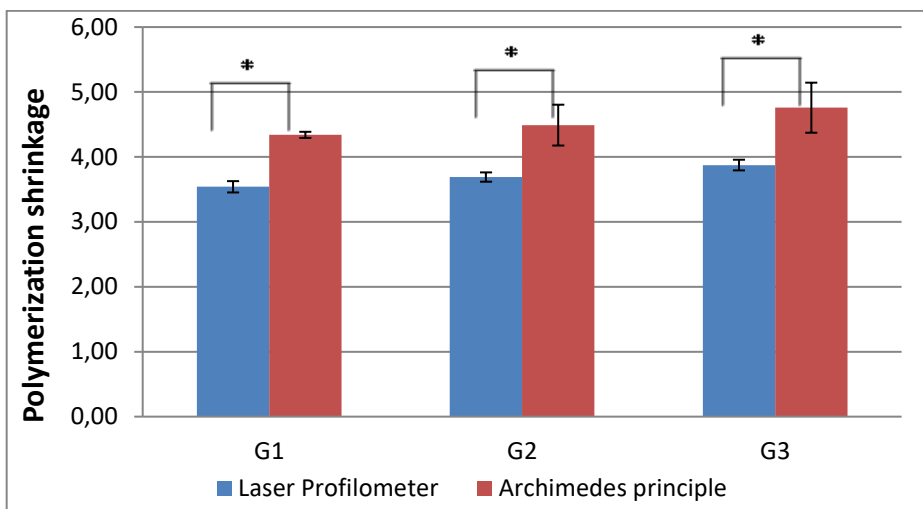
Figure 1. Values of polymerization shrinkage of experimental dental composites obtained by laser profilometer and Archimedes principle. *Significant difference between values of laser profilometer and values of Archimedes principle (p < 0.05).

Figure 2. Changes of shrinkage values obtained by laser profilometer and Archimedes principle depending on CQ ratio changing.

4. DISCUSSION

In this study the volumetric shrinkage values of Archimedes principle and laser profilometer were compared with each other. It was observed that there were statistically differences between the results of two methods (p<0,05).

However, shrinkage values represented the similar tendency for each group changed by different amount of photoinitiator system (Figure 2). Positive linear correlations between the values of laser profilometer and Archimedes principle observed ($r^2 = 0.9992$ and $r^2 = 0.9832$ for resins cured for 20 s respectively).

Shrinkage values obtained by Archimedes principle were not statistically different for each group involving different ratio of CQ/DMAM (p>0,05), since the ratio of photoinitiator system were only changed. Therefore, the density of uncured and cured material of each group were found to be close to each other. In Figure 1, it could be observed this condition from the bar graphs of Archimedes principle values.

The result of these methods were found to be different, because the magnitude of shrinkage is dependent on the methodology used. The shrinkage results obtained for any of the methods published before vary. Therefore, to compare the literature results is rather difficult, since measurements are carried out in different laboratories with different equipment and operators [35].

The values increased by ratio of CQ/DMA showed significant differences for laser profilometer method. The specimen was fixed under the laser of OSP 100A equipment for measurement before and after polymerization and cured without no displacement. Shrinkage measurement by laser was applied on the lateral side of specimen instead of the top of the sample treated with light. Thus, it was considered that a realistic measurement was obtained.

Results showed that polymerization shrinkage values increased with increased ratio of CQ/DMAM. Shrinkage values of G1 and G2 were found to be close since the ratio of CQ/DMAM were 0,25% and 0,5% respectively. However, the composite with 1.0% of CQ/DMAM was seen to be much more affected on the polymerization and, hence shrinkage. As a result, amount of CQ/DMAM was affected the polymerization efficiency.

It is known that the polymerization shrinkage of composites depends on the degree of conversion of monomer matrix during polymerization; the greater the degree of polymerization conversion the greater the shrinkage. According to the results, it could be considered that CQ/DMAM ratio had an effect on the DC of monomer.

5. CONCLUSION

In this study, dental composites involving different ratios of CQ/DMAM were produced in order to investigate the shrinkage behavior relating to the photoinitiator/co-initiator ratio. Results of the study showed that polymerization shrinkage values increased with increased ratio of CQ/DMAM. Values of Archimedes principle and laser profilometer were found to be different. However, there were linear correlations between the values of laser profilometer and Archimedes principle observed. Shrinkage values of G1 and G2 were found to be close to each other. However, the composite with 1.0% of CQ/DMAM was seen to be much more affected on the polymerization shrinkage.

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