Monomer release from bulk-fill composite resins in different curing protocols

Gul, Pinar; Alp, Hamit H; Özcan, Mutlu

Abstract: The purpose of this study was to determine the depth of cure and the type and amount of monomers released from bulk-fill composites in different curing protocols. Five different composite resins Filtek Bulk-Fill Posterior, Filtek Bulk-Fill Flowable, SureFil SDR, X-tra Fil, and X-tra base, were used. A light-emitting diode (LED) device was used in 3 different modes (standard, high power, and extra power mode), and a halogen light device was also used as a control. Surface hardness was measured and the depth of cure was calculated. Monomer analysis was performed using high performance liquid chromatography (HPLC). The data were analyzed using Tamhane’s T2 post-hoc test (α = 0.05). The cure depth for all materials except for Filtek Bulk-Fill Posterior (extra power mode) and Filtek Bulk-Fill Flowable (high power and extra power modes) was over 80%. Under the conditions of this study, the amount of monomer released from composite resins changed according to the type of composite resin and the light mode used.

DOI: https://doi.org/10.2334/josnusd.19-0221

Posted at the Zurich Open Repository and Archive, University of Zurich
ZORA URL: https://doi.org/10.5167/uzh-197128
Journal Article
Published Version

Originally published at:
Gul, Pinar; Alp, Hamit H; Özcan, Mutlu (2020). Monomer release from bulk-fill composite resins in different curing protocols. Journal of Oral Science, 62(3):288-292.
DOI: https://doi.org/10.2334/josnusd.19-0221
Monomer release from bulk-fill composite resins in different curing protocols

Pinar Gul1, Hamit H. Alp2, and Mutlu Özcan3

1) Department of Restorative Dentistry, Faculty of Dentistry, Atatürk University, Erzurum, Turkey
2) Department of Biochemistry, Faculty of Medicine, Yüzüncü Yıl University, Van, Turkey
3) University of Zurich, Dental Materials Unit, Center for Dental and Oral Medicine, Clinic for Fixed and Removable Prosthodontics and Dental Materials Science, Zurich, Switzerland

Abstract: The purpose of this study was to determine the depth of cure and the type and amount of monomers released from bulk-fill composites in different curing protocols. Five different composite resins from Filtek Bulk-Fill Posterior, Filtek Bulk-Fill Flowable, SureFil SDR, X-tra Fil, and X-tra base, were used. A light-emitting diode (LED) device was used in 3 different modes (standard, high power, and extra power mode), and a halogen light device was also used as a control. Surface hardness was measured and the depth of cure was calculated. Monomer analysis was performed using high performance liquid chromatography (HPLC). The data were analyzed using Tamhane’s T2 post-hoc test (α = 0.05). The cure depth for all materials except for Filtek Bulk-Fill Posterior (extra power mode) and Filtek Bulk-Fill Flowable (high power and extra power modes) was over 80%. Under the conditions of this study, the amount of monomer released from composite resins changed according to the type of composite resin and the light mode used.

Keywords: bulk-fill composite resins, cure depth, curing modes, light curing units, monomer release

Introduction

Composite resins are widely used as restorative materials. These materials contain different polymer matrices, which are composed of different multifunctional methacrylates and additives. Bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA) methacrylic monomers are the main components of resin-based filler materials. In addition, the presence of additives, such as initiators, activators, inhibitors, and plasticizers, is also required for restorative materials. Studies have also reported that bisphenol A (BPA) is found in saliva that has been in contact with composite resins and fissure sealant materials [1].

Composite resins have advantages. They have excellent aesthetic properties and are easy to handle. However, they also have disadvantages, such as polymerization shrinkage and inadequate polymerization [2]. Polymerization of composite resins occurs as a result of the conversion of monomers into polymers through photo or chemical processes. However, sometimes the conversion of the monomers into polymers is not fully realized, and the unpolymerized monomers “called as residual monomer” are released into the oral environment.

It has been reported in the literature that these residual monomers released into the oral environment cause systemic or local side effects on the tissues and cells. Residual monomers also affect mechanical properties of the resins, resulting in reduced resistance and discoloration of the resin due to inadequate polymerization of the monomers. Residual monomers can also reach the pulp through dentin tubules and cause pulp irritation, leading to bacterial proliferation between dental tissues and the restorative material [3]. Moreover, these monomers can enter into the vascular system through dentine penetration and cause cytotoxic, genotoxic, mutagenic, or estrogenic effects, as well as soft tissue and allergic reactions [4]. It is therefore important to know how much monomer is released from the composite resins and to take the necessary precautions to reduce this amount.

Composite resins should be placed in deep cavities as layered due to the limited polymerization level and increased polymerization shrinkage risk. However, the use of this technique, called ‘incremental technique’ requires a lot of curing, which is very time consuming.

In order to alleviate this problem, resin manufacturers search for ways to reduce polymerization shrinkage and to place composite resin into larger masses. As a result, a new generation of composite resins called ‘Bulk-Fill’ has been developed. The improved translucent structure of Bulk-Fill composites and the photoactive groups placed in the methacrylate resin allow for better control of the polymerization kinetics of these composites and polymerization of the composite up to a depth of 4 mm using the bulk technique [5]. This new technology has resulted from the changes made to the monomer chemistry. Hydroxyl-free Bis-GMA, aliphatic urethane dimethacrylate, partial aromatic urethane dimethacrylate, or highly branched methacrylate was added to the resin matrix structure of the Bulk-Fill composites. This change in organic matrix and monomer structure reduces the polymer shrinkage of the composite by up to 70% and allows the necessary light for polymerization to be spread further across the composite mass by improving the translucent structure of the composite [6].

The good depth of cure may be due to the refractive index matching between the resin and filler, which enhances light transmission. Reduction in refractive index differences between resin and filler improves the degree of conversion and increases depth of cure [7]. Ilie and Stark [8] stated that greater depth of cure in bulk-fill composites could be achieved by enhancing translucency through the reduction in filler content and an increase in filler particle size.

Cure depth of resin-based materials can be evaluated using Fourier transform infrared spectroscopy or micro-Raman spectroscopy. In particular, the ratio of DC measured at the bottom to that at the top surface was found to correlate well with surface microhardness, typically measured as an indirect evaluation of the polymerization efficiency [9]. Pilo and Cardash stated that an acceptable level of cure depth should be 80% [10].

Many methods, such as gas chromatography, high performance liquid chromatography (HPLC), gas chromatography/mass spectrometry, and electrospray ionization/mass spectrometry are used to determine the type and amount of residual monomers and degradation products. However, among these, HPLC is the most commonly used method [11].

The aim of this study was to determine the depth of cure and the type and amount of monomer that is released when the different bulk-fill composite resins are polymerized using 4 different light modes for 24 h.

The hypotheses were as follows: that the depth of cure of all composite resins is at an acceptable level; that all of the monomers examined were released from all of the composite resins; and that there is no difference in the amount of monomer released from each Bulk-Fill composite resin in all light modes.

Materials and Methods

Five different bulk-fill composite resins were used in this study. Table 1 gives information about the composite resins used.

Preparation of samples and curing protocols

A total of 24 samples were obtained from each composite resin by using a

Correspondence to Dr. Pinar Gul, Department of Restorative Dentistry, Faculty of Dentistry, Atatürk University, Yakutiye, Erzurum TR-25240, Turkey
Fax: +90-442-236-0945 E-mail: opinargul@gmail.com

Color figures can be viewed in the online issue at J-STAGE.

doi.org/10.2334/josnusd.19-0221
DN/JST.JSTAGE/josnusd/19-0221

J-STAGE Advance Publication: May 31, 2020
Journal of Oral Science

(Received May 28, 2019, Accepted September 17, 2019)
After the depth of cure of samples was determined, each of the samples was stored at 4°C until the monomer analysis. The monomer analysis was performed using HPLC (Agilent 1200 series, isocratic pump, auto sampler, column frame, and Diodarray detector; Germany) and C18 RP analytical column (250 × 4.6 mm 5 μm particle size; ACE; Aberdeen, Scotland). All standards with high purity were obtained from Sigma Aldrich. For the mobile phase, acetonitrile/water with 65/35% ethanol solution for 24 h. The solutions obtained were stored at 4°C until the monomer analysis. Thus, the retention times and peak values of these monomers were defined. Accordingly, the corresponding monomer concentrations related to the calculation of the areas under the peaks obtained from the solutions in which the samples were placed were determined in μmol/L.

Table 1: Details of the investigated restorative materials

| Composite resins                | Manufacturer                          | Content                      | Lot No.     |
|---------------------------------|---------------------------------------|------------------------------|-------------|
| Filtek Bulk-Fill Flowable Restorative | 3M Oral Care, St. Paul, MN, USA      | Bis-GMA, UDMA, BISEMA, TEGDMA| W 65/V 42.5 | N733627    |
| Filtek Bulk-Fill Posterior Restorative | 3M Oral Care                          | Bis-GMA, BISEMA, UDMA, zirconia | W 64/V 42   | 4864       |
| SureFil SDR                     | Dentply Co., Konstanz, Germany        | polymerization modulator, dimethacrylate resin, UDMA | W 68/V 44   | 150814     |
| X-tra Fil                       | VOCO Co., Cuxhaven Germany            | Bis-GMA, UDMA, TEGDMA inorganic filler | W 86/V 70   | 1545550    |
| X-tra base                      | VOCO Co.                              | Bis-GMA, UDMA, TEGDMA inorganic filler | W 75/V 58   | 1532998    |

Table 2: Light curing units and curing protocols used in this study

| Light curing units | Type                  | Curing modes                      | Spectral range (nm) | Manufacturer                          |
|--------------------|-----------------------|-----------------------------------|---------------------|---------------------------------------|
| Hilux Ultra Plus   | Quartz-tungsten halogen | standard mode: 180 ± 67 mW/cm², 25 s | 400-520             | Benlioglu Dental Inc., Ankara, Turkey |
| VALO               | LED 3rd generation     | standard mode: 1,000 mW/cm², 10 s  | 395-480             | Ultradent Products Inc, South Jordan, UT, USA |

The samples was performed using HPLC (Agilent 1200 series, isocratic pump, auto sampler, column frame, and Diodarray detector; Germany) and C18 RP analytical column (250 × 4.6 mm 5 μm particle size; ACE; Aberdeen, Scotland). All standards with high purity were obtained from Sigma Aldrich. For the mobile phase, acetonitrile/water with 65/35% ratio was used. Flow rate and run time were set to 1 mL/min and 12 min respectively, and samples for calibration were prepared at the concentrations of 0.3, 0.6, 1.25, 2.5, 5, and 10 μg/mL. Standard substances of BPA, TEGDMA, Bis-GMA, UDMA, and 2-hydroxyethyl methacrylate (HEMA) monomers were injected into the device at appropriate rates to allow the device to fully recognize the monomer types present in the samples prior to HPLC analysis. Thus, the retention times and peak values of these monomers were defined. Accordingly, the corresponding monomer concentrations related to the calculation of the areas under the peaks obtained from the solutions in which the samples were placed were determined in μmol/L.

Statistical analysis

Statistical Package for the Social Sciences (SPSS) 18 (IBM, Chicago, IL, USA) software was used to analyze the data. Kolmogorov-Smirnov and Shaprio-Wilk tests were used to determine the distribution of the data. Additionally, data normality verification (equality of variances) was performed using Levene’s test. Tamhane’s T2 test was performed because the variances of groups were not homogeneous.

Tamhane’s T2 test was used to compare the composite resin depth of cure in different light modes for each composite resin. In addition, it was also used to compare the amount of monomers in different light modes from each composite resin. In addition, Spearman’s correlation analysis was used to compare the depth of cure of composite resins and the amount of released monomers. This analysis was performed separately for each monomer type. The value of $P < 0.05$ was considered statistically significant.

Results

Tamhane’s T2 test showed that there was a statistically significant difference among groups in terms of cure depths for Filtek Bulk-Fill Posterior and Filtek Bulk-Fill Flowable groups ($P < 0.05$). The bottom-to-top ratio of the surface-hardness for all materials except for Filtek Bulk-Fill Posterior, Mode 3 (74.94 ± 10.34) and Filtek Bulk-Fill Flowable Modes 2 and 3 (76.69 ± 9.12 and 76.40 ± 9.59) was over 80%, which indicates that the bottom surfaces were adequately cured (Fig. 1).

Chromatograms of standards and 1 of the samples are shown in Figs. 2 and 3. The retention times of the monomers were as follows: TEGDMA, 2.9 min; HEMA, 3.8 min; Bis-GMA, 6.2 min; and UDMA, 6.9 min.

The monomers released from each composite resin in different light modes and the statistical comparison results are shown in Tables 3-7. The amount of monomer released from composite resins generally changed according to the composite resin and the light mode used, and the amount of released TEGDMA and HEMA from flowable composites was less than corresponding monomer concentrations.
that from other composite resins in Modes 2 and 3 \( (P < 0.05) \). In addition, the amounts released according to monomer type were as follows, from highest to lowest: HEMA > Bis-GMA > UDMA > BPA > TEGDMA.

Spearmann’s correlation analysis showed that there was no correlation between depth of cure of composite resins and amount of released monomers \( (P > 0.05) \).

### Table 3
The mean (standard deviation) values (μmol/L) of residual Bis-GMA released from bulk-fill composite resins 24 h after curing

| Composite resins         | Curing modes          | \( P \) |
|--------------------------|-----------------------|---------|
| Filtek Bulk-Fill Posterior | QTH LED standard LED high power LED extra power |         |
|                          | 0.67(0.11)aA         | 0.49(0.04)aA | 0.69(0.02)aA | 0.67(0.02)aA | 0.001* |
| Filtek Bulk-Fill Flowable   | 0.48(0.09)B          | 0.72(0.04)B  | 0.54(0.1)aB  | 0.94(0.05)aB | 0.001* |
| SureFil SDR              | 0.67(0.02)aA         | 0.87(0.01)C  | 0.66(0.01)B  | 0.67(0.01)aA | 0.001* |
| X-tra Fil                | 0.92(0.07)aA         | 0.86(0.02)cC | 0.66(0.05)AB | 0.81(0.06)cA | 0.001* |
| X-tra Base               | 0.45(0.00)AB         | 0.57(0.00)BD | 0.36(0.01)cC | 0.50(0.00)BD | 0.001* |

Bis-GMA, bisphenol A glycidyl methacrylate; \* \( P < 0.05 \). Different uppercase letters within the same column and different lowercase letters within the same row indicate a significant difference.

### Table 4
The mean (standard deviation) values (μmol/L) of residual TEGDMA released from bulk-fill composite resins 24 h after curing

| Composite resins       | Curing modes          | \( P \) |
|------------------------|-----------------------|---------|
| Filtek Bulk-Fill Posterior | QTH LED standard LED high power LED extra power |         |
|                        | 0.04(0.00)aA          | 0.07(0.00)aA | 0.08(0.00)aA | 0.06(0.00)A  | 0.001* |
| Filtek Bulk-Fill Flowable | 0.06(0.00)aA          | 0.08(0.01)aA | 0.02(0.00)b  | 0.02(0.00)B  | 0.001* |
| SureFil SDR           | 0.07(0.00)cA          | 0.02(0.00)b  | 0.01(0.00)BC | 0.02(0.00)cB | 0.001* |
| X-tra Fil             | 0.04(0.03)AB         | 0.07(0.01)aA | 0.03(0.04)ABCD | 0.01(0.00)BCD | 0.003* |
| X-tra Base            | 0.05(0.04)aA         | 0.06(0.04)AB | 0.03(0.00)ABD | 0.06(0.00)AB  | 0.200  |

TEGDMA, triethylene glycol dimethacrylate; \* \( P < 0.05 \). Different uppercase letters within the same column and different lowercase letters within the same row indicate a significant difference.

### Table 5
The mean (standard deviation) values (μmol/L) of residual HEMA released from bulk-fill composite resins 24 h after curing

| Composite resins       | Curing modes          | \( P \) |
|------------------------|-----------------------|---------|
| Filtek Bulk-Fill Posterior | QTH LED standard LED high power LED extra power |         |
|                        | 1.80(0.04)aA          | 1.96(0.02)aA | 1.80(0.04)aA | 1.49(0.06)A  | 0.001* |
| Filtek Bulk-Fill Flowable | 1.50(0.07)B          | 2.54(0.00)BD | 1.90(0.05)B  | 1.46(0.06)B  | 0.001* |
| SureFil SDR           | 2.56(0.02)AC         | 2.38(0.16)BC | 1.87(0.03)C  | 1.69(0.24)AC | 0.001* |
| X-tra Fil             | 3.20(0.49)AB         | 3.36(0.43)AC | 1.81(0.06)AC | 1.76(0.22)BC | 0.001* |
| X-tra Base            | 0.44(0.09)AC         | 0.99(0.02)BC | 0.68(0.27)AC | 0.92(0.17)BC | 0.001* |

HEMA, 2-hydroxyethyl methacrylate; \* \( P < 0.05 \). Different uppercase letters within the same column and different lowercase letters within the same row indicate a significant difference.

### Table 6
The mean (standard deviation) values (μmol/L) of residual UDMA released from bulk-fill composite resins 24 h after curing

| Composite resins       | Curing modes          | \( P \) |
|------------------------|-----------------------|---------|
| Filtek Bulk-Fill Posterior | QTH LED standard LED high power LED extra power |         |
|                        | 1.60(0.04)B          | 1.96(0.02)A  | 1.80(0.04)A  | 1.49(0.06)A  | 0.001* |
| Filtek Bulk-Fill Flowable | 1.50(0.07)B          | 2.54(0.00)BD | 1.90(0.05)B  | 1.46(0.06)B  | 0.001* |
| SureFil SDR           | 2.56(0.02)AC         | 2.38(0.16)BC | 1.87(0.03)C  | 1.69(0.24)AC | 0.001* |
| X-tra Fil             | 3.20(0.49)AB         | 3.36(0.43)AC | 1.81(0.06)AC | 1.76(0.22)BC | 0.001* |
| X-tra Base            | 0.44(0.09)AC         | 0.99(0.02)BC | 0.68(0.27)AC | 0.92(0.17)BC | 0.001* |

UDMA, urethane dimethacrylate; \* \( P < 0.05 \). Different uppercase letters within the same column and different lowercase letters within the same row indicate a significant difference.

### Table 7
The mean (standard deviation) values (μmol/L) of residual BPA released from bulk-fill composite resins 24 h after curing

| Composite resins       | Curing modes          | \( P \) |
|------------------------|-----------------------|---------|
| Filtek Bulk-Fill Posterior | QTH LED standard LED high power LED extra power |         |
|                        | 0.27(0.06)aA          | 0.31(0.06)AC | 0.54(0.05)A  | 0.44(0.01)A  | 0.001* |
| Filtek Bulk-Fill Flowable | 0.30(0.01)aA          | 0.41(0.03)B  | 0.37(0.04)B  | 0.36(0.00)A  | 0.001* |
| SureFil SDR           | 0.36(0.04)B          | 0.30(0.01)BC | 0.40(0.07)AB | 0.29(0.00)B  | 0.001* |
| X-tra Fil             | 0.38(0.01)BD         | 0.42(0.10)ABD | 0.46(0.10)AB | 0.35(0.13)A  | 0.426  |
| X-tra Base            | 0.34(0.04)AB         | 0.48(0.01)BD | 0.44(0.05)B  | 0.38(0.11)AB | 0.001* |

BPA, bisphenol A; \* \( P < 0.05 \). Different uppercase letters within the same column and different lowercase letters within the same row indicate a significant difference.
Discussion

Although composite resins are considered to be stable restorative materials, their structure may deteriorate over time and their content can be released into the oral environment. In light-polymerized systems, the conversion of monomer into polymer varies between 40% and 75% [12]. Some clinical precautions may be taken to reduce the amount of residual monomer released from composite resins and to increase clinical success. Using flowable cavity liners, applying alternative light polymerization protocols, and using incremental techniques are some of those precautions. The recommended maximum layer thickness is 2 mm to ensure sufficient light penetration and polymerization. However, when the incremental technique is used, there are some risks, including time loss, cracking, and contamination between layers [13]. Bulk-fill composite resins have been produced to eliminate these risks, and there are studies in the literature indicating that these materials have better light transmittance properties and can provide sufficient polymerization depth even at thicknesses exceeding 4 mm [14].

In the present study, the thickness of composite resin samples was set to 4 mm, and depth of cure for all materials except for Filtek Bulk-Fill, Mode 3, and Filtek Bulk-Fill Flowable, Modes 2 and 3, was over 80%. Thus, the first hypothesis, that the depth of cure of all composite resins is at an acceptable level, was partially rejected.

The cure depth of the composite resins that are polymerized with light is closely related to the characteristics of the light device used in polymerization and the duration of light application. Studies suggest that increasing the power of light devices has a positive effect on the cure depth have led to the development of more powerful (>600 mW/cm²) light devices [15].

Table 2 gives radiation time, light cure intensity, and spectral range of devices. Light curing devices have a wide spectral range in terms of photo initiators. The power density of light curing devices was 800, 1,000, 1,400, and 3,200 mW/cm², and exposure time was adjusted to produce approximately the same energy densities (intensity × time about 20,000 J/cm²). However, in the present study, depth of cure for all materials except for Filtek Bulk-Fill, Mode 3, and Filtek Bulk-Fill Flowable, Modes 2 and 3, was over 80%.

The HPLC technique is the most suitable method for eluting the nonpolar compounds forming the composite resin monomer, and it also has the advantage of separating the components according to their hydrophobic order. Also, because the monomers can be dissolved in the mobile phase in the HPLC method, the separation process is carried out at a more controlled level. The molecules of high molecular weight monomers such as Bis-GMA and UDMA can decompose with the gas chromatography technique, and only decomposition products can be detected. Therefore, the HPLC method is more suitable for determining the type and amount of monomers released from composite resins. For these reasons, in this study, HPLC was used to measure the amount of monomer released from the composite resins [11].

It has been shown that all the monomers contained in the unpolymerized composite resins are extracted into organic solutions after the resin is polymerized. The oral cavity is somewhere between water and more aggressive solutions (ethanol, methanol, acetonitrile). The United States Federal Drug Administration has recommended a 75% ethanol-water solution because it best mimics the oral environment, and this solution is used in many studies in the literature [16]. For these reasons, in the present study, the 75% ethanol/water solution was used as a storage medium.

In the present study, it was found that the monomer types examined were released from all of the composite resins, which means that the second hypothesis was not rejected. Tamhane’s T2 test, which was used to determine if there was a difference between the amount of monomer released from composite resins in different light modes, indicated that there were statistically significant differences among the groups (P < 0.05). For this reason, the third hypothesis, that there is no difference in the amount of monomer released from each Bulk-Fill composite resin in all light modes, was rejected. Spearman’s correlation analysis showed that there was no correlation between depth of cure of composite resins and amount of released monomers (P > 0.05). Similar results were obtained in other studies on the correlation between depth of cure and release of well-polymerized specimens [17].

The residual monomers can only be released from the apolymeric net-work if there is diffusion or swelling. Diffusion occurs when the solubility parameter of the storage solution is compatible with the hydrophobicity level of the polymer structure. While the aqueous solvents are drawn by the hydrophilic structures, the organic solvents are more easily dispersed into the hydrophobic structures. Diffusion into a polymeric network causes swelling and opening of existing pores. The degree of swelling depends on the stiffness and cross-link density of the polymer network, and the diffusion of the residual monomer from the polymer depends on the molecular weight and flexibility of the polymer. Monomers with low molecular weight, such as TEGDMA, are released more easily and in higher amounts than hard and high molecular weight monomers such as Bis-GMA [12]. In the present study, it was determined that the most released monomer was HEMA, which may be due to its low molecular weight. The high release level of Bis-GMA can be explained by the solubility of this monomer in ethanol, an organic solvent.

In the present study, it was found that the BPA ratios released in the modes with high total energy intensities were partially increased compared with other modes. Kwon et al. [18] found that as the polymerization time increased and the curing distance decreased, the released BPA ratio increased. The authors noted that, unlike TEGDMA and UDMA, photolysis of BPA increased when exposed to high light intensity, because of the release of BPA into the environment due to its decomposition from the BPA-based resins [18]. This may also explain the result in the present study.

It has been reported in the literature that the maximum release of monomers from composite resins occurs in the first 24 h after polymerization. Ferracane and Condon [19] stated that half of the residual monomer released into the environment within the first 3 h after the polymerization, and 85-100% of it releases within 24 h. More recent studies conducted with HPLC have shown that monomer elution continues for 24 h for the resin-based composites [20]. The amount of monomer released from the composite resins in the present study was measured after 24 h polymerization in order to ensure the majority of residual monomers was released within a few hours, and to better understand the effect of different light modes on monomer release from the composite resins.

The present study showed that the amount of monomer released changes according to the composite resin and the applied light mode. Optimal polymerization conditions are different for each monomer and each composite. For this reason, the type of monomer contained in the composite resins should be known in terms of biocompatibility and reliability of the materials, and the polymerization should be ensured according to optimal polymerization times. The composite resins should be highly polymerized in order to minimize the release of residual monomer. The properties of the light source used, such as energy density and spectral distribution, affect the final polymerization rate. The energy density (J/cm²) is the product of the light intensity (mW/cm²) and the light duration (s). Many studies report that the energy density is the main factor in determining the degree of polymerization of the composite resin. Recent studies emphasize that the light intensity, the duration of light, the type of photo initiator, and the filler content significantly affect the polymer chain length, cross-linking degree, and mechanical properties of the resin [21].

Although it has been stated that the 40 s polymerization time is satisfactory for improving the mechanical properties of the composite resin, Polydorou et al. [22] found that this was not more effective than a 20-s time period in reducing the amount of residual monomer released in a 75% ethanol solution. Furthermore, even when the polymerization time was increased to 80 s, there was no effective reduction in the amount of monomer released. In the present study, the total energy densities are set to be close enough to each other so that the light modes can be compared more easily.

There are many studies in the literature related to the efficiency of LED technology in the polymerization of composite resins [23]. Although it was emphasized that LED light sources have more cure depth than QTH light sources [23], Yoon et al. [24] stated that 1 light source is not superior to another for achieving sufficient cure depth. Yap et al. [25] did not find any difference between the TEGDMA and Bis-GMA ratios released from the composite resins despite the difference in energy intensities (intensity × time) in standard LED and QTH polymerization modes. Despite the differences in the methods, there are many studies in the literature where similar results were obtained [23-25]. In the present study, it was found that the
monomer release changes according to the light modes applied and the composite resin.

Analysis of the content released from composite resins is of great importance not only to examine the mechanical and physical properties of the resin but also for the determination of the biocompatibility of these materials. Studies regarding BPA have focused on the fact that this monomer can exhibit para-hormonal activity and mimic estrogenic hormones, and thus play a role in female infertility [26]. Regarding this issue, Kita et al. [27] stated that when the BPA concentration is above 0.01 mmol/L, it may show an estrogen-like effect. Studies regarding cytotoxic doses of other monomers released from composite resins revealed that UDMA, Bis-GMA, and TEGDMA are toxic for human oral mucosa membrane cells at doses of 0.27 mmol/L, 0.11 mmol/L, and 3.7 mmol/L, respectively [28]. Toxic doses of HEMA were found to be 3 mmol/L on human gingival fibroblasts [29] and 10 mmol/L on human pulp fibroblast cells [30]. Given that the results obtained in the present study are in μmol/L, amounts of monomers released from the composite resins used in the present study were well below the toxic doses.

Therefore, the depth of cure of all composite resins is at an acceptable level, and the amount of monomer released from composite resins changed according to the type of composite resin and the light mode used, and the amount released was below the toxic dose. However, there may be differences in the amount of monomers released when considering the differences in method, light sources, storage solution, and sample sizes used in each study. For this reason, further studies are needed to provide optimal polymerization conditions for the resins and to minimize the amount of monomer released.

Acknowledgment
This work was supported by the Research Fund of Ataturk University (Project number: 2014/165) and partially 3M Turkey distributor. In addition, this study was partially presented in TDA 22nd International Dental Congress, 19-21 May 2016, Izmir, Turkey.

Conflict of interest
The authors have no potential conflict of interest to declare with respect to the authorship and/or publication of this article.

References
1. Regalewicz R, Batko K, Voelkel A (2006) Identification of organic extractables from commercial resin-modified glass-ionomers using HPLC-MS. J Environ Monit 8, 750-758.
2. Lagocka R, Jakubowska K, Chlebik D, Buczakowska-Radlinska J (2015) Elution study of unreacted TEGDMA from bulk-fill composite (SDR Dentply) using HPLC. Adv Med Sci 60, 191-198.
3. Goldberg M (2008) In vitro and in vivo studies on the toxicity of dental resin components: a review. Clin Oral Investig 12, 1-8.
4. Thonemann B, Schmalz G, Hiller KA, Schweikl H (2002) Responses of L292 mouse fibroblasts, primary and immortalized bovine dental papilla-derived cell lines to dental resin components. Dent Mater 18, 318-323.
5. Cara RR, Fleming GJP, Palin WM, Walmsey AD, Burke FFT (2007) Cuspal deflection and microleakage in premolar teeth restored with resin-based composites with and without an intermediary flowable layer. J Dent 35, 482-489.
6. Tsujimoto A, Barkmeier WW, Takizawa T, Latta MA, Miyazaki M (2017) Depth of cure, flexural properties and volumetric shrinkage of low and high viscosity bulk-fill gionmers and resin composites. Dent Mater J 36, 205-213.
7. Alkhudhairy FJ (2017) The effect of curing intensity on mechanical properties of different bulk-fill composite resins. Clin Cosmet Investig Dent 9, 1-6.
8. Bie N, Stark K (2014) Curing behaviour of high-viscosity bulk-fill composites. J Dent 42, 977-987.
9. Boshchikher MR, Ruegergeeb FA, Wilson BM (2004) Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions. Oper Dent 29, 698-704.
10. Pilo R, Cardasi HS (1992) Post-irradiation polymerization of different anterior and posterior visible light-activated resin composites. Dent Mater 8, 299-304.
11. Cebe MA, Cebe F, Cenziz MF, Cotin AR, Apayog OF, Ozurtz B (2015) Elution of monomer from different bulk-fill dental composite resins. Dent Mater 31, e141-e149.
12. Alshali RZ, Salinn NA, Sung R, Satterthwaite JD, Silkin N (2015). Analysis of long-term monomer elution from bulk-fill and conventional resin-composites using high performance liquid chromatography. Dent Mater J 31, 1587-1598. J 186, 358-391.
13. El-Satry S, Silkin N, Watts DC (2012) Creep deformation of restorative resin-composites intended for bulk-fill placement. Dent Mater 28, 928-935.
14. Lempel E, Cribulya Z, Kovacs B, Szalma J, Toth A, Kunsagi-Mate S et al. (2016) Degree of conversion and Bis-GMA, TEGDMA, UDMA elution from flowable bulk-fill composites. Int J Mol Sci 17, 732.
15. Fan PL, Schumacher RM, Azzolin K, Geary R, Eichmiller FC (2002) Curing-light intensity and depth of cure of resin-based composites tested according to international standards. J Am Dent Assoc 133, 429-434.
16. Ferracane JL (1994) Elution of leachable components from composites. J Oral Rehabil 21, 441-452.
17. Polydorou O, Hammad M, König A, Hellwig E, Kimmnerer K (2009) Release of monomers from different core build-up materials. Dent Mater 25, 1090-1095.
18. Kwon JH, Oh YJ, Jung JH, Park JK, Hwang KS, Park YD (2015) The effect of polymerization conditions on the amount of unreacted monomer and bisphenol A in dental composite resins. Dent Mater J 34, 327-335.
19. Ferracane JL, Condon JR (1990) Rate of elution of leachable components from composite. Dent Mater J 6, 282-287.
20. Munksgaard EC, Peutzfeldt A, Axmussen E (2000) Elution of TEGDMA and BisGMA from a resin and a composite cured with halogen or plasma light. Eur J Oral Sci 108, 812-817.
21. Lagocka R, Jakubowska K, Chlebik D, Buczakowska-Radlinska J (2016) The influence of irradiation time and layer thickness on elution of triethylene glycol dimethacrylate from SDR (R) bulk-fill composite. Biomed Res Int 2016, doi: 10.1155/2016/3481723.
22. Polydorou O, Tritter R, Hellwig E, Kämmerer K (2007) Elution of monomers from two conventional dental composite materials. Dent Mater 23, 1535-1541.
23. Millis RW, Jandt KD, Ashworth SJH (1999) Dental composite depth of cure with halogen and blue light emitting diode technology. Brit Dent J 186, 358-391.
24. Yoon TH, Lee YK, Lim VB, Kim CW (2002) Degree of polymerization of resin composites by different light sources. J Oral Rehabil 29, 1165-1173.
25. Yap AU, Han VT, Soh MS, Soow KS (2006) Elution of leachable components from composites after LED and halogen light irradiation. Oper Dent 29, 448-453.
26. Chao HH, Zhang XF, Chen B, Pan B, Zhang LJ, Li L et al. (2012) Bisphenol A exposure modifies methylation of imprinted genes in mouse oocytes via the estrogen receptor signaling pathway. Histochim Cell Biol 137, 249-259.
27. Kita K, Jin YH, Sun Z, Chen SP, Sumiya Y, Hongu T et al. (2009) Increase in the levels of chaperone proteins by exposure to beta-estradiol, bisphenol A and 4-methoxyphenol in human cells transfected with estrogen receptor alpha cDNA. Toxicol in Vitro 23, 728-735.
28. Reichl FX, Seiss M, Marquardt W, Kleinsasser N, Schweikl H, Kehe K et al. (2008) Toxicity potentiation by H2O2 with components of dental restorative materials on human oral cells. Arch Toxicol 82, 21-28.
29. Cataldi A, Zara S, Rapino M, Patruno A, di Giacomo V (2013) Human gingival fibroblasts stress response to HEMA: A role for protein kinase C alpha. J Biomater Sci Polym Ed 24, 337-349.
30. Papageorgiou D, D’Amo V, Valletta R, Strisciuglio C, Schmalz G, Schweikl H et al. (2008) Effect of 2-hydroxyethyl methacrylate on human pulp cell survival pathways ERK and AKT. J Endodont 34, 684-688.