

Monomers Release from Dental Composites: Effect of Immersion Media and Photoactivation Light Source

¹Raquel A.B. da Silva, ¹Talita P. Prates, ¹Driely Barreiros, ²Juliana C. Biazotto, ³Patrícia H. Gatón, ¹Fábio Lourenço Romano, ²Roberto S. da Silva and ¹Léa Assed Bezerra da Silva

¹Department of Pediatric Dentistry, School of Dentistry of Ribeirão Preto, Ribeirão Preto, University of São Paulo, Brazil

²Department of Physics and Chemistry, School of Pharmaceutical Sciences of Ribeirão Preto, University of São Paulo, Brazil

³La Societat catalanad'odontostomatologia de l'Acadèmia de Ciències Mèdiques I de la Salut de Catalunya I de Balears, Barcelona, Spain

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Corresponding Author:

Léa Assed Bezerra da Silva,
Department of Pediatric
Dentistry,
School of Pharmaceutical
Sciences of Ribeirão Preto,
University of São Paulo,
SP, Brazil,
Tel: +55-16-3602-3995
Email: lea@forp.usp.br

Abstract: The present study aimed to evaluate qualitatively and quantitatively the products released by composites with different light sources when immersed in distilled water or artificial saliva. Thirty-six samples were obtained from the composites using a silicone matrix. Specimens were divided into 12 groups according to: Composite (Charisma[®], Filtek[™]Silorane or GC Kalore[®]), device used for the materials photoactivation (halogen light or LED) and immersion medium (distilled water or artificial saliva). Measurements were obtained using a UV-visible spectrophotometer. The Filtek[™]Silorane resin showed the highest absorbance and thus the highest concentration of monomers released at the maximum time assessed when immersed in artificial saliva. No significant difference was observed in the amount of monomers release when using LED (0.54 mg mL⁻¹) and halogen light (0.53 mg mL⁻¹). Release of monomers from composites can occur and is dependent on the composite formulation, immersion medium or the photoactivation unit.

Keywords: Nanoparticle Resin, Residual Monomer, Halogen Light, LED

Introduction

Composite resins have recently become the material of choice for direct restorations of dental elements because they produce satisfactory aesthetic results and minimal wear on the dental structure (Nahsan *et al.*, 2012).

Despite the evolution of their physical and chemical properties since the 1960s, no ideal composite resin has been discovered until recently; thus, research on restorative materials is important to identify material failures and to assist in improving their properties.

Developed from studies conducted by Bowen (1956; 1963), composite resins are defined as the three-dimensional combination of at least two chemically dissimilar materials with a distinct interface separating these components (Phillips, 1992).

Composite resins have four components: Resin matrix, polymerization initiators, inorganic fillers and a coverage agent of filler particles known as silane. Composite resins are classified according to the type and size of the filler particles: Macroparticles or conventional, microparticles, hybrid and nanoparticulates (Lutz and Phillips, 1983; McCabe, 1984).

The composition, size and filler particle distribution of a restorative material as well as the composition of the resin matrix can have an important effect on its clinical utility. In nanoparticulate composite resins, reduction in the size of the filler particles in addition to their shape facilitates the achievement of an excellent polish and luster. Moreover, nanoparticulate composite resins possess good mechanical properties, which increase their clinical use in the anterior and posterior teeth (Zimmerli *et al.*, 2010).

The resin matrix is composed of monomers such as Bis-GMA (bisphenol A-glycidyl methacrylate) or polyurethane (UDMA), which can be regarded as the body of the composite resin. To decrease the viscosity of the system, low viscosity diluent monomers such as TEGDMA (triethylene glycol dimethacrylate) are added. Diluent monomers allow the incorporation of high filler content and provide better handling characteristics to the final material. Other monomers found in most commercialized composites include D3MA and UTMA (Tabatabaei *et al.*, 2011).

In an effort to improve the chemical and mechanical properties of the monomers incorporated into the

composite resins, composite materials based on Silorane[®] matrix (3M España SA, Madrid, Spain) and GC Kalore[™] have become commercially available.

Silorane[®] matrix consists of a system of cationic monomers in an open-loop structure rather than in a linear structure as observed with Bis-GMA monomers. According to the manufacturer, the advantage of the Silorane[®] matrix, which is indicated for the restoration of the posterior teeth, is a lower degree of polymerization shrinkage, which is associated with satisfactory mechanical properties (Gao *et al.*, 2012; Porto *et al.*, 2013).

The composite resin GC Kalore[®] features a unique DuPont monomer technology known as single monomer, which shows decreased polymerization shrinkage and thus increased longevity of the restoration.

According to Naoum *et al.* (2012), Silorane (non methacrylate composite) and Kalore (high molecular mass methacrylate composite) have the ability to exhibit lower shrinkage rates and lower shrinkage volumes compared to conventional methacrylate composites.

According to the literature, patients subjected to restorative procedures may have residual monomers in the saliva and in the oral tissues (Reichl *et al.*, 2006). In this field, Polydorou *et al.* (2011) evaluated the influence of the light-curing source on the amount of monomers released. These authors showed that the release of substances was more material dependent and less influenced by the curing unit used. Knowing that, Van Landuyt *et al.* (2011) performed a meta-analytical study to review the literature on components release from resin-based dental materials and to determine how those components may leach out in the oral cavity. After this review, authors concluded that there is a clear need for more accurate and standardized analytical research to determine the long-term release from resin-based materials.

Therefore, the present study aimed to compare the degree of monomeric conversion of the nanoparticulate resins Filtek[™]Silorane (3M España SA, Madrid, Spain) and GC Kalore[®] (GC Corporation, Hasumuma-ChoItabashikue, JP, Tokyo, Japan) and the microhybrid composite resin Charisma[®](HeraeusKulzer GmbH, Hanau, Germany) polymerized by different photoactivation methods (halogen light and LED) and immersed in different media (water and artificial saliva) by qualitative analysis and by UV-visible absorption spectroscopy.

Material and Methods

Three photoactivated composite resins were evaluated: The nanoparticulate resins Filtek[™]Silorane (3M España SA, Madrid, Spain) and GC Kalore[®] (GC Corporation, Hasumuma-ChoItabashikue, JP, Tokyo, Japan) and the microhybrid composite resin Charisma[®](HeraeusKulzer GmbH, Hanau, Germany).

From the composite resins selected for the study, 36 samples were polymerized with the aid of a silicone matrix containing a quadrangular mold measuring 10 mm in diameter and 3 mm in thickness. Material manipulation was performed according to the manufacturer's instructions.

To obtain the samples, a spatula was used to add the composite resin in a single layer inside the silicone matrix. Next, the material was photopolymerized according to the manufacturer's instructions by different light sources (LED or halogen light). For polymerization of the composite resin specimens, halogen light (Ultralux, DabiAtlante, SP, Brazil) and LED (Bluephase, IvoclarVivadent, SP, Brazil) polymerization equipment were used.

Subsequently, the samples were removed from mold and the excess material was removed with a cutter and straight piece.

The specimens were divided into 12 groups according to the following factors: Composite resin used in the specimen preparation (Charisma[®], Filtek[™]Silorane or GC Kalore[®]), equipment used for the photoactivation of the materials (halogen light or LED) and medium in which the specimens were immersed (distilled water or artificial saliva). Thus, a total of 12 samples for each group of composite resin were obtained. Six samples were polymerized by LED and the remaining 6 samples were polymerized by halogen light. Three samples from each half were individually immersed in distilled water. The remaining 3 samples were individually immersed in artificial saliva.

The specimens were stored individually in Eppendorf tubes, each of which contained 2 ml of artificial saliva or distilled water. Samples were placed in the tubes and the analysis of the released monomers from each specimen was performed after several experimental intervals. Measurements were obtained by using a UV-visible spectrophotometer (Agilent 8453-Department of Physics and Chemistry of the School of Pharmaceutical Sciences, University of São Paulo).

For the qualitative analysis, a volume of distilled water or artificial saliva was removed from the eppendorf tube and was transferred to a 0.5 mL cuvette, which was read by the spectrophotometer. A light beam in the ultraviolet and visible range was emitted by the device, which passed through the sample and was captured by the detector. The detector recorded the reading of the samples and the absorbance versus wavelength graphs were obtained and recorded in a computer. These readings were taken 30 min, 24, 48 h, 7 and 14 days after immersion of the samples.

Samples for quantitative analysis were obtained by extracting the monomers from each resin selected for the study and these samples were used to obtain the calibration curves.

The methodology was based on the calibration curves obtained as follows: A total of 0.5 g of each composite

was dissolved in 5 ml of chloroform in individual Falcon tubes protected from light and incubated at room temperature. For the separation of the inorganic fillers, the samples were centrifuged for 15 min at 4000 rpm. The supernatant was transferred to a flask and was placed on a rotary evaporator until the chloroform was completely evaporated. Finally, the amount of pure monomer found in the resins Charisma[®], GC Kalore[®] and Filtek[™]Silorane were 156 mg, 115 mg and 147 mg, respectively.

After extraction of the monomers, 10 mg of monomers from each of the three resins under study was transferred to a 10 ml volumetric flask filled with methanol (polymerization inhibitor solvent) for a final monomeric resin concentration of 1 mg mL⁻¹.

The initial solution (stock) of monomers from the resins Charisma[®], GC Kalore[®] and Filtek[™]Silorane were diluted to obtain different concentrations of monomers in methanol. The following concentrations were obtained: 0.01, 0.02, 0.04, 0.08, 0.16, 0.20 and 0.25 mg mL⁻¹. The most dilute reference sample (0.01 mg/m) was discarded due to low UV-visible absorbance.

Each reference sample for the three resins was transferred to a cuvette and was analyzed by spectrophotometry. Readings in the UV-visible spectrophotometer were conducted as previously described with the specimens in the qualitative analysis.

Data interpretation was conducted by using the software Origin 5.0 to establish the calibration curves for each resin analyzed at different wavelengths and in each immersion medium (distilled water and artificial saliva).

The numerical data were statistically analyzed by using Graph Pad Software Inc. version 5.0 (La Jolla, CA, USA) by one-way ANOVA and Tukey's post-hoc test. For all analyses, a significance threshold of 5% was adopted.

Results

The present study compared the effect of the immersion media (water and artificial saliva) and the types of photoactivation equipment (LED and halogen light) for monomers release from specimens made with the resins Charisma[®], GC Kalore[®] and Filtek[™]Silorane.

When comparing the three composite resins used in the present study, we observed a higher concentration of solubilized product released from Filtek[™]Silorane incubated in saliva regardless of the photopolymerization source.

When LED light was used as the polymerization source, between 150 and 200 h of incubation, the composite Charisma[®] had the highest concentration of monomeric product when immersed in water or artificial saliva. However, within the same time interval, for the resins GC Kalore[®] and Filtek[™]Silorane, a higher concentration of monomeric products was observed

when the polymerization source was halogen light, regardless of the immersion medium.

According to the results, a higher concentration of solubilized product was observed in the first 50 h, followed by a tendency to stabilize, independent of the composite resin group, the photopolymerization equipment and the immersion medium.

When comparing the immersion media, regardless of the photopolymerization source, a greater absorbance was observed at 350 h, indicating that a higher concentration of solubilized products occurred when artificial saliva was used. In this case, the higher solubility of the products seems to be influenced by the components present in the artificial saliva.

Reregarding the UV-visible absorption spectra for the monomer of GC Kalore[®] resin immersed in water for 24 h and in saliva, for both media, we observed the presence of an absorption band in the UV region with a maximum peak at 314 nm for water and 316 nm for saliva.

Statistical analysis of the data showed no significant differences among all parameters (photopolymerization sources and immersion media) for the specimens made with the composite resin Charisma[®] and Kalore[®] ($p > 0.05$). When evaluating the composite resin Filtek[™]Silorane, no statistically significant difference was observed between the photopolymerization sources when the samples were immersed in the same medium ($p > 0.05$). In contrast, we observed a statistically significant difference when comparing the effects of different immersion media and photopolymerization sources on Filtek[™]Silorane ($p < 0.05$).

Discussion

The polymerization efficacy of the composite resins is related to the degree of conversion of the monomer double bonds into single bonds. This process can be influenced by several factors, such as exposure time, intensity and the wavelength of the light source.

In the present study, the homogeneity in the polymerization of composite resins was analyzed using electron spectroscopy, a technique that allows the evaluation of the concentration of substances according to the intensity of absorbance of the absorption bands (Skoog *et al.*, 2007). This technique is unique considering the presence of unsaturated components in the resins and taking into account that compounds with these characteristics absorb UV light.

The present study explored the qualitative determination of unpolymerized monomers in the composite resins Charisma[®], GC Kalore[®] and Filtek[™]Silorane by absorption spectrum analysis according to the immersion time in water or artificial saliva.

Higher solubility of the monomers was observed in the first 50 h and it exhibited a tendency to stabilize afterwards. Moreover, the composition of the solution

strongly influenced the solubility. Higher concentration of soluble monomer was observed for all three resins when saliva was used as the immersion medium. Considering that artificial saliva is composed of various salts such as potassium and sodium chloride and paraben esters (nipagin and nipasol), the ionic strength of the solution may have affected the solubility of the resin components. These results corroborated with several studies which showed this monomers release from different types of composites maintained in human saliva (Moharamzadeh *et al.*, 2007; Tuna *et al.*, 2010; Polydorou *et al.*, 2013).

On the other hand, we observed lower solubility of the monomers when water was used as the immersion medium, regardless of the composite resin and of the photopolymerization technique used. This finding could be explained by the low polarity of all three monomers, which are organic compounds.

The use of LED or halogen as the light source does not seem to influence polymerization efficiency, as both sources have spectra with maximum emissions at 410 and 470 nm. However, the effective range is reported to be 380-500 nm for the LED and 400-500 nm for the halogen source. Thus, polymerization impairment for all resins included in our study was expected. In this field, Polydorou *et al.* (2011) evaluated the monomers released from 4 different composite materials (Ceram X, Filtek Supreme XT, Tetric Flow, Tetric EvoCeram), polymerized using either halogen or LED units. Similarly to the present study, these authors showed that the monomers release was more material dependent and less influenced by the curing unit used. Later, Randolph *et al.* (2014) also showed that composite composition had a significant influence on monomers release.

In addition, several authors showed other factors that could increase the release of monomers from the composite resin like thermal shocks, storage time and bleaching (Tabatabaee *et al.*, 2014; Tabatabaee *et al.*, 2013). Nanofilled composites released more monomer than the microfilled (Tabatabaee *et al.*, 2013).

Analyses of the absorption spectra of the products that are soluble in water and in artificial saliva for the composite GC Kalore[®] showed that the maximum absorption band occurred between 250 and 350 nm, which lies outside the light emission region of the equipment used. Thus, the polymerization quantum efficiency is inherently low and prone to incomplete polymerization; however, the extent of polymerization may depend on the material used.

The concentration (mg mL) of the monomers release after 14 days of immersion was determined based on the calibration curve. For the composite Charisma[®], a higher

concentration of monomers was detected in saliva when the LED was used for photopolymerization. For the composite Kalore[®], the highest concentration of monomers in solution was observed when the halogen source was used and the sample was immersed in saliva. Regarding the composite FiltekTMSilorane, there was a short difference in the concentration of monomers released in saliva regardless of the light source.

In general, the resin FiltekTMSilorane, whose composition is based on siloxane and oxiranes, exhibited a larger amount of free residual monomers indicating a lower polymerization efficiency using either LED or halogen light when compared with the resins Charisma (Bis-GMA and TEGDMA) and GC Kalore[®] (UDMA).

Conclusion

Regardless of the resin type, the immersion medium (distilled water and artificial saliva) or the photoactivation source (halogen or LED light), release of resin monomers occurs and reaches a peak at 300-350 h (maximum interval of analysis). The highest absorbance and, consequently, the highest concentration of released monomers was found in the composite resin FiltekTMSilorane immersed in artificial saliva at the latest time point assessed (300-350 h). Further studies should be performed to assess the possible effects of these solubilized products in direct contact with cells of the oral mucosa dental tissues.

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Author's Contributions

All authors equally contributed in this study.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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