

The effect of post-cure heating on residual, unreacted monomer in a commercial resin composite

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Abstract

Objectives. This paper examined the influence of post-cure temperature on the amount of unreacted monomer remaining in a commercial light-cured resin composite restoration following initial light-curing and subsequent post-cure heating.

Methods. Discs of composite were light-cured and then subjected to immediate post-cure heating (50, 75, 100, or 125°C for 7 min) or were left unheated (control). They were then placed in a solvent for two weeks at 37°C to extract the unreacted monomer. HPLC analysis was used to determine the amounts of TEGDMA, BIS-GMA, and ethoxylated BIS-GMA remaining after the different treatments. The amounts of each monomer leaching were compared using ANOVA with respect to the different curing treatments.

Results. Even the lowest post-cure heat treatment (50°C) resulted in 80% reduction in remaining, unreacted TEGDMA, 75% reduction in BIS-GMA, and 77% lower ethoxylated BIS-GMA than the light-cured only control. Post-cure heating at 75°C and above resulted in the lowest amount of each type monomer remaining uncured in the polymer and did not significantly decrease with an increase in post-cure temperature for the most part.

Significance. One of the main benefits of post-cure heating of resin composite restorations could be the enhancement of biocompatibility of these restorations as a result of the significant decrease in potentially leachable, unreacted monomer. © 2000 Academy of Dental Materials. Published by Elsevier Science Ltd. All rights reserved.

Keywords: Resin composite; Post-cure heating; Unreacted monomer

1. Introduction

Post-cure heating of resin composite materials is currently a very popular restorative technique. This method subjects a light-cured composite inlay to an immediate heat treatment for the purposes of increasing material cure, and thus enhancing clinical properties [1,2]. Many researchers have detected improved physical properties as a result of the post-cure heating process. Post-cure heating has been found to enhance surface hardness [3–5], tensile strength [3,4,6,7], flexural strength [6,8,9], color stability [10], and glass transition temperature [11].

Benefits in physical properties resulting from post-cure treatment have been found to be temporary, however. The wear resistance of light-cured only composite slowly increased when left untreated and became equivalent to the value of the post-cure heated material over time [12].

Many properties enhanced by post-cure heating (fracture toughness, flexural modulus, and flexural strength) were found to decrease to levels identical to those of the light-cured only group [13] when the specimens were subjected to water storage after curing. If post-cure heat is applied within 6 h of initial light-curing, however, one benefit that will remain unchanged in the treated restoration is an increased extent of cure over the light-cured only treatment [8]. Such a benefit in increased cure may result in a lowered amount of unreacted, potentially leachable monomer, leading to a more biocompatible restoration.

The purpose of this research was to determine the effect of different post-cure heat levels on the amount of unreacted monomer remaining in a commercial, light-cured resin composite restorative material after subjection to post-cure heating treatment. The hypothesis tested was that increased post-cure temperature would result in additional polymer cure by incorporating unreacted resin into the polymer network, leading to lower amounts of unreacted monomer remaining in the restoration.

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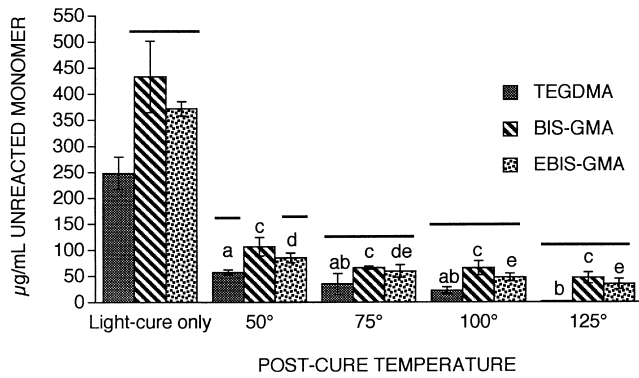


Fig. 1. Relationship between post-cure heating and monomer type and remaining, unreacted monomer in the cured composite; $n = 3$ per group, vertical bar = ± 1 standard deviation; horizontal bars connect equivalent values within each post-cure treatment; similar small case letters indicate equivalent values within a type monomer.

2. Materials and methods

Discs (10×1 mm) of a photo-cured composite typically used for fabrication of composite inlays (lot #610292, Herculite XRV, shade A2, Kerr/Sybron, Orange, CA) were made using an aluminum mold. The uncured material was expressed into the mold between two sheets of Mylar (Type D, 0.08 mm thick, Du Pont Company, Wilmington, DE) and covered with two microscope slides. The assembly was clamped together and pressed to force the uncured paste to conform to the mold dimensions (4448 N for 10 s). The clamps and glass slides were removed and the Mylar sandwich was placed over the top surface of a 10 mm thick pre-cured composite underlay of similar lot number as the test specimen. The top surface of this pre-cured disc had been lightly coated with an unfilled, non-curable BIS-GMA/TEGDMA mixture. Such treatment provided a constant backing reflectance [14] for the curing composite as well as removing any air interface between material layers. The outer Mylar surface (and thus, the uncured composite disc) was then exposed to 500 mW/cm^2 of light energy between 400 and 520 nm for 60 s. The curing tip was maintained 1 mm from the upper glass surface. Immediately following light curing, the specimens were treated in one of two fashions. They were either subjected to a post-cure heat treatment in a digitally controlled oven (Neytronic 2000, JM Ney Company, Bloomfield, CT), or they received no additional treatment (control). Post-cure treatment consisted of 7 min exposure at 50, 75, 100, or 125°C. The discs were then placed in bottles containing 1.0 ml of methyl isobutyrate (lot 13706PQ, item #14,800-8, Aldrich Chemical Company, Milwaukee, WI), and then stored at 37°C for a period of two weeks. Seven minutes of elapsed time following light-curing was allowed for the control specimens prior to solvent immersion to provide equity among specimens with respect to their cured age, prior to extraction. The purpose of this solvent immersion was to swell the cured polymer and leach out unreacted, residual monomer.

Following this storage time, the solvent was analyzed for the presence of monomers which had leached from the cured composite. The analysis procedure consisted of high pressure liquid chromatography on an LC-18 column (cat no 5-8298, Supelco, Inc., Bellefonte, PA) using acetonitrile/water 60/40 (v/v), at a flow rate of 2.5 ml/min, and components were detected at 208 nm. Calibration graphs were made from known amounts of monomers comprising the composite: TEGDMA (lot #419-50-05, Esschem, Essington, PA), BIS-GMA (lot #307-450-1, Esschem), and ethoxylated BIS-GMA (EBIS-GMA) (lot #397-36-5, Esschem). Quantitative analysis of the monomeric components leached from the cured composite into the solvent extract discs were then made using the calibration graphs.

Three specimens were made for each testing condition, resulting in a total of 15 discs. Statistical analysis consisted of ANOVA with the Tukey–Kramer post hoc test for pairwise comparisons. All statistical significance was determined at a pre-set alpha of 0.05.

3. Results

Fig. 1 presents the amounts of leachable, unreacted monomers eluting from the differently treated discs. A general trend is noted that any post-cure treatment greatly decreased the amount of unreacted monomer remaining in the cured disc as compared to light-cure treatment only. Also, as post-cure temperature was increased, the level of unreacted monomer declined, but only significantly for two monomers: TEGDMA at 125°C and EBIS-GMA above 75°C. The statistical analysis verified visual observations of graphical data presentation. Above 75°C, there was no significant difference in the relative amount of each type monomer leaching into solution.

The two-way ANOVA indicated that both post-cure temperature ($p = 0.0001$) as well as the type of monomer ($p = 0.0001$) significantly contributed to the amount of unreacted monomer present, as well as their interaction ($p = 0.0028$). A series of one-way ANOVAs indicated that all monomer levels from the light-cure only group were significantly greater than their respective values when any post-cure heating was performed. When post-cure heated at 75°C or higher, the amount of each type monomer remaining uncured did not change. Only a slight difference was noted in unreacted components using 50°C compared to those of higher temperature levels for TEGDMA and EBIS-GMA.

4. Discussion

The amount of residual, unreacted monomer in a resin composite restoration has been implicated in causing increased potential for cytotoxicity [15]. Also, the specific type of monomer eluting has been shown to have a significant impact upon tissue culture survival [16]. Thus, the

results of this study have great clinical impact upon the use of post-cure heated resin composite materials. The extent of measured monomer released correlates well with other studies. We have measured the weight proportion of filler in an average composite disc used in this study, and determined that the volatile portion is approximately 0.03947 g. Totalling the amounts of the individual leached monomers measured in our study yields approximately 0.001055 g, that represents 2.6% of the total volatile component, which we are assuming is mostly monomeric material. When measuring total leachable materials from a micro-filled composite (Silux) on a gravimetric basis, the others determined at 2.0% of cured specimen mass was leachable [17]. However, to obtain this amount, the specimens had to be treated harshly to eliminate residual solvent: heating at 60°C under vacuum for 24 h. Using such techniques may have also eliminated some of the unreacted monomer, and lowered the actual values calculated. Thus, the values in our study agree well with other published reports, however, we have also distinguished amounts of each type monomer which remain leachable and observed the influence of post-cure heating on the leachable amounts.

The experimental hypothesis was verified, in that post-cure heating did demonstrate a dramatic decrease in the amount of unreacted monomer remaining in a resin composite. The decrease in leachable monomer arising from post-cure heating could arise from a number of mechanisms. If the extent of monomer conversion into polymer is enhanced as a result of this heating, then potentially leachable monomer is covalently bonded to the polymer network, precluding its escape upon exposure to solvent. If the additional conversion observed with heating resulted in an increase in cross-link density, unreacted monomer remaining in the polymer matrix would find it much more difficult to diffuse out as a result of the decrease in diffusion channel size. Also, unreacted monomer could have been lost as a result of volatilization during the heating process. Such a loss would also lower the measured leachable amounts. The lowered amount of leachable monomer accompanying post-cure heating measured in this study is probably the result of a combination of all of the above factors. At present, it is not possible to delineate the proportion that each factor would contribute toward the overall leachable amount.

It is of great significance to note that any degree of post-cure heating resulted in significantly lower unreacted monomer levels compared to the light-cured only control. The lowest post-cure heat treatment (50°C) demonstrated an 80% reduction in remaining, unreacted TEGDMA, 75% reduction in BIS-GMA, and 77% lower ethoxylated BIS-GMA than that seen in the light-cured only control. Only a moderate lowering of unreacted material was noted when the heat level was raised above 50°C. Most of the conventional post-curing units heat the specimens between 100 and 125°C [8]. Thus, the use of these systems, including the use of boiling water, should provide resin composite restora-

tions that have the potential to be significantly enhanced with respect to their biocompatibility. It should be noted that even using the highest recommended temperature for post-cure heating [10], potentially leachable unreacted monomer still remains in the post-cure heated material. Even with lowered amounts of leachable monomer, cell culture testing has shown that cured composites depleted of most leachable components still demonstrate a cytotoxic effect [18]. These results indicate that research efforts should be directed toward designing resin systems that have no unreacted monomer remaining after the post-cure heating treatment is performed.

However, the data do not imply that, even with no leachable monomer present, the conversion of all carbon-to-carbon double bonds is 100%. There will still be many pendent, unreacted methacrylate groups covalently bonded to the polymer chain, which still have reactive potential [19,20]. These units could be responsible for color change over time [21]. Also, measurement of unreacted monomer leaching in an organic solvent does not mimic the clinical situation, where cured resin is in an aqueous environment. Thus, data presented in this research present the potentially leachable portion of a commercial composite, not the values which would actually be detected in water, which are presumed to be much lower, owing to their hydrophobicity. Also, it should be stressed that the conditions used for light curing in the present study were those which had been found to optimize monomer conversion [22]. Clinicians using conditions other than these could expect that greater amounts of unreacted materials would be leaching from their restorations. While only a single commercial product was tested, it is felt that similar decreases in leachable components upon post-cure heating would be observed in other commercial products. Further testing needs to be performed to validate this assumption.

5. Conclusion

Based upon the limitations imposed in this research, it can be said that post-cure heating of a widely used photo-activated resin composite restorative material significantly decreases the amounts of unreacted monomer remaining after the initial light-curing stage. Even post-cure temperatures as low as 50°C greatly reduced the levels of all types of monomers present.

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