

Marquette University

e-Publications@Marquette

Master's Theses (2009 -)

Dissertations, Theses, and Professional
Projects

Color Change of Commercial Resin Compositated with Different Photoinitiators

Feng Gao
Marquette University

Follow this and additional works at: https://epublications.marquette.edu/theses_open



Part of the [Dental Materials Commons](#)

Recommended Citation

Gao, Feng, "Color Change of Commercial Resin Compositated with Different Photoinitiators" (2016).
Master's Theses (2009 -). 382.
https://epublications.marquette.edu/theses_open/382

**COLOR CHANGE OF COMMERCIAL RESIN COMPOSITES WITH
DIFFERENT PHOTOINITIATORS**

by

Feng Gao, D.M.D.

**A Thesis submitted to the Faculty of the Graduate School,
Marquette University,
in Partial Fulfillment of the Requirements for
the Degree of Master of Science**

Milwaukee, Wisconsin

December 2016

ABSTRACT
COLOR CHANGE OF COMMERCIAL RESIN COMPOSITES WITH
DIFFERENT PHOTOINITIATORS

Feng Gao, D.M.D.

Marquette University, 2016

Camphorquinone (CQ) is the most commonly used photoinitiator in light-cured dental resin composites. However CQ is associated with a yellowing effect, which has led manufacturers to add alternative initiators into resin composites to reduce the amount of CQ used.

The color change upon polymerization by light and aging in artificial saliva and room air of 8 commercial traditional or bulk-fill resin composites with or without additional photoinitiator(s) beside CQ was studied. The three traditional resin composites with CQ and additional photoinitiator(s) tested were Tetric EvoCeram (Ivoclar Vivadent), AELITE LS Posterior (Bisco), and Vit-l-escence (Ultradent). The two bulk-fill resin composites with CQ and additional photoinitiator(s) tested were Tetric EvoCeram Bulk Fill (Ivoclar Vivadent) and HyperFIL (Parkell, dual cure). The control resin composites with CQ only were Heliomolar (Ivoclar Vivadent, traditional), BEAUTIFIL-Bulk (Shofu, bulk-fill) and SonicFill 2 (Kerr, bulk-fill). Sixteen specimens for each material were prepared with Teflon disc molds (7 mm diameter x 2 mm thickness) and light cured for 40 seconds with a quartz-tungsten-halogen light-curing unit. Samples were aged at 37°C in room air or artificial saliva (n=8). Color measurements were obtained with a spectrophotometer before and after polymerization and after aging for up to three months. Color change was calculated using CIELab and CIEDE2000 formulae. One way and two way ANOVA and a post-hoc SNK test was conducted for statistical analysis.

Commercial light-cured resin composites with additional photoinitiators beside CQ had greater color change upon polymerization than those with CQ only. Color changes with aging tended to be greatest within the first hour after light curing, but was not considered clinically perceptible on any resin composites tested except HyperFIL. Tetric EvoCeram Bulk Fill showed good color stability that was comparable to the traditional resin composites upon aging.

ACKNOWLEDGMENTS

Feng Gao, D.M.D.

First of all, I would like to express my deepest gratitude to my mentor Professor David Berzins, the director of the Marquette Graduate Dental Biomaterials Program, for his enormous help, enlightening guidance, constant encouragement and great support through my graduate study at Marquette University School of Dentistry. Without his continuous encouragement, guidance and support, this thesis would not have been possible.

I would like to express my sincere appreciation to Dr. Gary Stafford, Dr. Jeffrey Toth and Dr. Howard Roberts for kindly serving in my committee and their valuable suggestions and great discussion.

I would also like to thank my supervisor Dr. Meetha Medhora at Medical College of Wisconsin for supporting me to accomplish my dream of pursuing another degree in dentistry. Without her support and encouragement during the years, I would not have made my research and study in dentistry this far.

I would like to thank Dr. Liang Chen from Bisco, Inc for kindly providing AELITE LS Posterior composites as a research gift and his valuable advices in finding the resin composites of our interest.

In addition, I would like to thank Mr. Tom Silman from Marquette University's College of Engineering for making the molds used in this project.

My thanks are extended to my co-residents Drs. Anjali Mehta, Divya Mishra, Ihsan Al-Qeshtaini and Maria Rodriguez for their help and precious friendship.

Special thanks to my parents, aunt, uncle-in-law and parents-in-law for their unconditional support. I'm also grateful for the love and joy my son gives to me. Thanks to my husband for his love, patience, understanding and support over the years.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	i
LIST OF TABLES.....	iv
LIST OF FIGURES.....	v
CHAPTER	
1. INTRODUCTION.....	1
2. LITERATURE REVIEW.....	3
2.1. Background of dental resin composites.....	3
2.2. Background of photoinitiators.....	4
2.3. Bulk-fill resin composites and color change.....	6
2.4. Color measurement.....	7
2.5. Color stability.....	9
3. MATERIALS AND METHODS.....	11
3.1. Resin composites.....	11
3.2. Light curing.....	12
3.3. Aging.....	14
3.4. Color measurements.....	15
3.5. Color change.....	16
3.6. Statistics.....	17
4. RESULTS.....	18
4.1. Color change upon polymerization.....	18
4.2. Color change upon aging.....	25
4.2.1. Aging for up to 6 hours.....	25

4.2.2. Aging for up to 3 months.....	29
5. DISCUSSION.....	35
5.1. Are non-CQ dental resin composites available commercially?.....	35
5.2. Why did the resin composites with CQ+ have greater color change upon polymerization?.....	37
5.3. Color changes upon aging.....	40
5.4. Color changes of the bulk-fill resin composites.....	41
5.5. Color measurement and ΔE calculation.....	42
6. CONCLUSION.....	45
BIBLIOGRAPHY.....	46

LIST OF TABLES

Table 1. Summary of the resin composites tested.....	12
Table 2. Two way ANOVA results on color change of the traditional (A) and bulk-fill (B) resin composites after aging for 3 months.....	31

LIST OF FIGURES

Figure 1.	Molds	13
Figure 2.	Halogen light (Optilux 501).....	14
Figure 3.	Light cured dental composite resin within mold stored in artificial saliva (A) or in air (B).....	15
Figure 4.	Spectrophotometer.....	16
Figure 5.	ΔE of traditional resin composites upon polymerization calculated with the formula of CIELab (A) and CIEDE2000 formula (B).....	19
Figure 6.	ΔE of bulk-fill resin composites upon polymerization calculated with the formula of CIELab (A) and CIEDE2000 formula (B).....	21
Figure 7.	ΔL (A), Δa (B) and Δb (C) of resin composites upon polymerization calculated with the CIELab system.....	23
Figure 8.	ΔE (A), ΔL (B), Δa (C) and Δb (D) of resin composites within 6 hours of light cure calculated with the CIELab formula.....	26
Figure 9.	ΔE of resin composites after aging for 1 day, 1 month and 3 months calculated by the CIELab formula.....	30
Figure 10.	ΔE of resin composites after aging for 3 months calculated by the formula of CIELab (A) and CIEDE2000 (B)	33

CHAPTER 1

INTRODUCTION

Since the early 1970s, dental resin composites have been the material of choice for direct esthetic anterior and posterior restorations. Dental resin composites serve as a more esthetic material to use over dental amalgam. Dental resin composites, no matter traditional or bulk-fill, require the use of initiators to help initiate the polymerization process. In light-cured resin composites, photoinitiators in the soft raw material are activated by the curing light and they start the cascade reaction of polymerization, which makes the resin composites harder and stronger.

Camphorquinone (CQ) is the most commonly used photoinitiator in light-cured dental resin composites. However, this yellow agent is associated with a yellowing effect of the dental resin composites. Since color stability is a very important concern in esthetic restorative dentistry, the yellowing effect of CQ has led manufacturers to add alternative initiators into resin composites to reduce the amount of CQ used.

Experimentally, other initiators, such as trimethylbenzoyl-diphenylphosphine oxide (TPO) (1) and phenyl propanedione (PPD) (2), have been introduced as alternatives. The addition of the alternative photoinitiators as a coinitiator lowers the content of CQ and has been suggested to overcome the esthetic issue arising due to the color of CQ (3). However data on color stability of commercially available resin composites with additional photoinitiators beside CQ are insufficient to show whether or not such an approach is beneficial.

The aim of this study was to investigate the color change upon polymerization and aging in artificial saliva and room air of commercial bulk-fill and traditional dental resin composites with alternative photoinitiator systems. The null hypothesis is that the color change upon polymerization or aging on resin composites with additional photoinitiators is not different from those with CQ only.

CHAPTER 2

LITERATURE REVIEW

2.1. Background of dental resin composites

Since early 1970s, dental resin composites have been the material of choice for direct esthetic anterior restorations. Based on the dental insurance claim data in 2005, about 166 million dental restorations, which include amalgams, resin composites and crowns, are placed per year in the United States (4). Of these, 77 million are resin composites (4). In general terms, resin composites are a mixture of inorganic filler particles surrounded by a coupling agent, dispersed in an organic matrix of resin (5).

The organic monomers, which are soft in the un-cured dental resin composites, are converted into rigid polymers through a polymerization process. Some commonly used resins in dental resin composites are bisphenol A-glycidyl methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA) and ethoxylated bis-phenol A methacrylate (BisEMA) (5).

Fillers, such as silica, are reinforcing particles or fibers that are dispersed in the resin matrix. Fillers also enhance radiopacity, alter the thermal expansion behavior, and reduce the polymerization shrinkage by reducing the resin fraction (6). Resin composites with low filler contents typically exhibit low mechanical properties and show high flowability and adaptability prior to curing (7). Filler contents of 60 to 87 wt% are necessary to achieve low shrinkage and high mechanical properties (8). A coupling agent such as silane is used to enhance the bond between resins and fillers.

Initiators are added to help begin the polymerization process when external energy, such like light or heat, is applied. During the activation of the initiators, free radicals are produced and they break the double bond of the monomer and bond with them to start the reaction. As a result, a polymer forms during the polymerization process (9).

Dental resin composites can be cured through light cure or chemically without light cure or by both ways (dual cure). Reaction of the chemical cured resin composites is produced by mixing two pastes. However, the chemically cured resin composites have some disadvantages: no control over the setting time, poor color stability, and high viscosity (10). On the other hand, light-cured dental resin composites have only one paste, and do not require mixing which provide dentists full control of time. The first commercially available light-cured resin composites was NuvaFil (Dentsply) (10).

2.2. Background of photoinitiators

Initiators used in light-cured resin composites are photoinitiators. In brief, photoinitiators have the ability to absorb light, and as a result, either directly or indirectly, generate a reactive species that can then initiate the polymerization (11).

Photoinitiators have certain wavelengths for excitation/absorption. The spectral emission from the light curing unit should overlap the absorption spectrum of the photoinitiator in the resin composites (12). Four basic types of dental curing lights are quartz tungsten halogen, light-emitting diode (LED), plasma arc curing (PAC) and argon

laser (13). The light provided to cure the resin composites is in the range of the visible blue light spectrum.

Camphorquinone (CQ) is the most common photoinitiator used in light cured dental resin composites (10). This yellow agent is activated by absorbing external blue light. CQ can absorb light in the spectral range of approximately 380-500 nm, and has an absorption peak near 470 nm (3,11). CQ is relatively inefficient as a photoinitiator, thus amines, such as dimethylaminoethyl methacrylate (DMAEMA), are added as co-initiators to accelerate the initiation process during polymerization (3).

Although CQ in conjunction with a tertiary amine has traditionally been used in dental resin composites, the intensive yellow color of CQ has limited its use particularly in extra white shades of resin composites (14). Other initiators, such as trimethylbenzoyl-diphenylphosphine oxide (TPO) (1) and phenyl propanedione (PPD) (2), have been introduced as alternatives.

TPO is a well studied photoinitiator. The absorption spectrum of TPO is situated more toward the UV spectrum (380-425 nm) (15). Lucirin® TPO (Lucirin is the trade name of BASF (16)) is completely colorless after light curing (17). Currently, it is the most often used additional photoinitiator in commercial dental resin composites in the U.S. market.

PPD was suggested to be an alternative photoinitiator for resin composites in 1999 (18). Subsequent studies have evaluated the use of PPD in dental resin composites as a photoinitiator (19,20). The absorption peak of PPD is around 392 nm (2). The

commercial use of this photoinitiator is not as common as TPO. This photoinitiator was studied mainly experimentally. Beside less yellowing, PPD was suggested to reduce polymerization stress by producing a slower polymerization rate without affecting final degree of conversion, compared to CQ (2,18). However this was not conclusively proved and it is a matter of controversy that a low rate of polymerization will reduce polymerization stress development (2). Use of PPD alone or in combination with CQ was reported by Schneider *et al.* to not improve the final properties when compared to CQ alone (21). The same group also found that it was not possible to polymerize formulations containing PPD without amine using 40s of halogen light exposure (21). These disadvantages associated with PPD might be the reason for its limited use commercially.

Even though alternative photoinitiators has been suggested to overcome the esthetic issue arising due to the color of CQ (3), currently there are no non-CQ dental resin composites available commercially in the U.S. market. This may be due to the fact that most of the light curing units on the market and in dental offices are optimized for curing CQ and are not as suitable for use with alternative photoinitiators that absorb light at different wavelengths than CQ. Combining CQ with an alternative photoinitiator is a safer and more effective solution in the current situation, since the use of additional photoinitiators can reduce the amount of CQ used and the remaining CQ can ensure the initiation of polymerization by the majority of light curing units available.

2.3. Bulk-fill resin composites and color change

Incremental filling techniques have been recommended due to a limited depth of cure in traditional resin composites as well as a way to minimize stress from polymerization shrinkage during curing (22). Unlike traditional resin composites, which typically are placed in maximum increments of 2 mm, bulk-fill resin composites are designed to be placed in 4 mm, or sometimes greater, increments (23). The manufacturers explain that the higher depth of cure of the bulk-fill resin composites is due to the more potent initiator system and/or higher translucency (24). However, few studies have examined the color changes after polymerization and aging on the bulk-fill dental resin composites with different initiators.

Most bulk-fill resin composites require an additional 2 mm occlusal layer being placed using a traditional resin composites (25). Using such a veneering layer not only improves the aesthetic quality of the translucent bulk-fill resin composites, but also overcomes the low wear resistance of bulk-fill resin composites due to their low filler content for the sake of translucency of the material (26). In the bulk-fill resin composites, such as SonicFill 2 where the occlusal layer is not required, color change is an important issue.

2.4. Color measurement

Being able to maintain its optical properties is important for resin composites, especially for those applied in the anterior teeth, since the color is always selected carefully to match the adjacent tooth for esthetic concerns in clinic. However, optical properties change as a result of polymerization (27). Resin composites become lighter and more translucent on irradiation with light (27,28).

Color differences can be quantified using either the CIELab formula (ΔE^*_{ab}) or the more recently introduced CIEDE2000 formula (ΔE_{00}) (29). The most commonly used color measuring system in dentistry is the CIELab system. This system was established by the Commission International de L'Eclairage (CIE), an international organization concerned with light and color in 1978 (29). Unlike the Munsell color system, which coordinates the hue, chroma and value on a three dimensional scale in different units, the CIELab units are evenly spaced in terms of visual perception on a numerical scale (30). The color parameters may be recorded in the $L^*a^*b^*$ coordinates using spectrophotometry. L^* in the color space represents lightness of the color on a numerical scale up to 100, with a small number representing black and a greater number representing white. The a^* color coordinate represents red (positive a^*) and green (negative a^*). The b^* color coordinate represents yellow (positive b^*) and blue (negative b^*) (30).

ΔE^*_{ab} and ΔE_{00} can be calculated based on the following equations (31):

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

$$\Delta E_{00} = \left[\left(\frac{\Delta L'}{K_L S_L} \right)^2 + \left(\frac{\Delta C'}{K_C S_C} \right)^2 + \left(\frac{\Delta H'}{K_H S_H} \right)^2 + R_T \left(\frac{\Delta C'}{K_C S_C} \right) \left(\frac{\Delta H'}{K_H S_H} \right) \right]^{1/2} \quad (2)$$

In equation (1), ΔL^* , Δa^* and Δb^* are the differences between a^* , b^* and L^* of the pair of color samples. In equation (2), R_T is the rotation function and expressed as R_T

$$= -\sin(2\Delta\theta) R_C, \text{ where } \Delta\theta = 30 \cdot \exp\left(-\frac{(\bar{h}'-275)^2}{25}\right) \text{ and } R_C = 2 \sqrt{\frac{\bar{C}'^7}{\bar{C}'^7 + 25^7}} \quad (32).$$

The weighting functions are defined as: $S_L = 1 + \frac{0.015(\bar{L}'-50)^2}{\sqrt{20 + (\bar{L}'-50)^2}}$, $S_c = 1 +$

$0.045 \bar{C}'$ and $S_H = 1 + 0.015 \bar{C}' T$ with $T = 1 - 0.17\cos(\bar{h}' - 30^\circ) + 0.24\cos(2\bar{h}') +$

$0.32\cos(3\bar{h}' + 6^\circ) - 0.2\cos(4\bar{h}' - 63^\circ)$, where for a pair of color $\bar{L}' = \frac{L_1^* + L_2^*}{2}$, $\bar{C}' =$

$$\frac{C_1^* + C_2^*}{2} \text{ and } \bar{h}' = \frac{h_1^* + h_2^*}{2} \text{ and } \Delta H = 2 \sqrt{C_1' C_2'} \sin \frac{\Delta h'}{2} \quad (32).$$

The other symbols used in equation (2) are defined as the following: $L' = L^*$, a' ,

$$= a^* (1+G), b' = b^*, C' = \sqrt{a'^2 + b'^2}, h' = \arctan \frac{b'}{a'} \text{ and } G = \frac{1}{2} \left(1 - \sqrt{\frac{C_{ab}^{*7}}{C_{ab}^{*7} + 25^7}} \right) \quad (32)$$

2.5. Color stability

Resin composites tend to discolor during long-term service in the oral cavity (33,34).

Significant color changes of resin composites have been reported after aging, even

though in most of the cases, such change in color of resin composites after aging, such as

storing in water, was found to be in the acceptable range (33). Discoloration after aging

may be due to a color change in the resin component, but also the other minor ingredients,

such as photoinitiators, may contribute to the color stability. Exposure to high

temperature and a rough composite surface are expected to affect color stability as well (33).

CHAPTER 3

MATERIALS AND METHODS

3.1. Resin composites

Eight commercial resin composites, including two bulk-fill resin composites with CQ only (BEAUTIFIL-Bulk (Shofu, San Marcos, CA) and SonicFill 2 (Kerr, Orange, CA)), two bulk-fill resin composites with CQ plus additional photoinitiator (Tetric EvoCeram Bulk Fill (Ivoclar Vivadent, Amherst, NY) and HyperFIL (Parkell, Edgewood, NY)), one traditional resin composites with CQ only (Heliomolar (Ivoclar Vivadent, Amherst, NY)) and three traditional resin composites with CQ plus additional photoinitiator (Tetric EvoCeram (Ivoclar Vivadent, Amherst, NY), AELITE LS Posterior (Bisco, Schaumburg, IL), and Vit-l-escence (Ultradent, South Jordan, UT)) were tested.

Most of the manufacturers do not disclose what the exact additional photoinitiators are because the information is considered to be proprietary. However such information can be inferred from literature. Information of the additional photoinitiators beside CQ used in the resin composites that were tested in this study are provided in Table 1. BEAUTIFIL-Bulk (35) and SonicFill 2 are the two bulk-fill with CQ only. Tetric EvoCeram Bulk Fill contains CQ, Germanium and Lucirin-TPO. HyperFIL is a bulk-fill dual cure resin composite that includes CQ and an unknown photoinitiator. Heliomolar is a traditional resin composite that uses CQ only as a photoinitiator (36). Tetric EvoCeram is a traditional resin composite with CQ and Lucirin-TPO (1). AELITE

(37) and Vit-l-escence (14) are traditional resin composites using CQ and TPO as photoinitiators.

Table 1. Summary of the resin composites tested.

Composites	Manufacturer	Photoinitiator	Reference
BEAUTIFIL-Bulk	Shofu	Bulk CQ only	(35)
SonicFill 2	Kerr	Bulk CQ only	Manufacturer
Tetric EvoCeram Bulk Fill	Ivoclar Vivadent	Bulk CQ + Germanium + Lucirin-TPO	Manufacturer
HyperFIL	Parkell	Bulk dual cure CQ + unknown	Manufacturer
Heliomolar	Ivoclar Vivadent	Regular CQ only	(36)
Tetric EvoCeram	Ivoclar Vivadent	Regular CQ + Lucirin-TPO	(1)
AELITE	Bisco	Regular CQ + TPO	(37) & Manufacturer
Vit-l-escence	Ultradent	Regular CQ + TPO	(14)

3.2. Light curing

Teflon discs of 31.75 mm x 31.75 mm x 2 mm were used. Holes of 9 mm in diameter were made in the Teflon discs. Sixteen samples for each material were prepared with the Teflon disc molds (9 mm diameter x 2 mm thickness) (Figure 1). A 5 kg weight

was kept on top of the resin composites for 3 minutes to obtain a uniform surface. A clear plastic film was used to cover the resin composites before the weight was applied and removed after light cure. Resin composites were light cured for 40 seconds with a quartz-tungsten-halogen light-curing unit (Optilux 501, sds Kerr Sybron dental specialties). The light intensity is 500 mW/cm² (Figure 2).



Figure 1. Molds

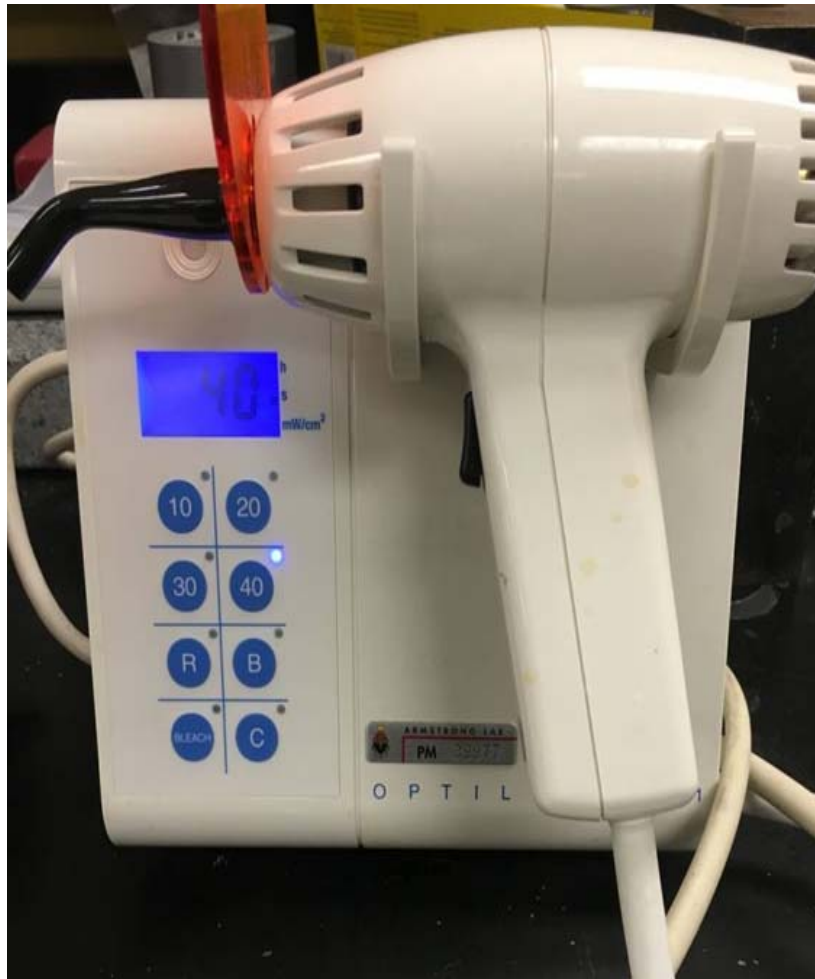


Figure 2. Halogen light (Optilux 501)

3.3. Aging

Two liters of artificial saliva were made with the following formula: 3.4 g KH_2PO_4 , 23.6 g Na_2HPO_4 , 160 g NaCl , 4 g KCl and 2 L distilled H_2O . Resin composite specimens were randomly assigned into two groups ($n=8/\text{group}$): one group was stored in artificial saliva and the other group was stored in air (Figure 3). Different storage conditions allow for differentiation of any color changes due to time versus the solution. Artificial saliva is used to simulate oral conditions, while storage in room air represents

an experimental condition upon which changes in color are solely due to the material. Both groups were kept at 37°C in an incubator with each specimen in an individual container to avoid any cross contamination.

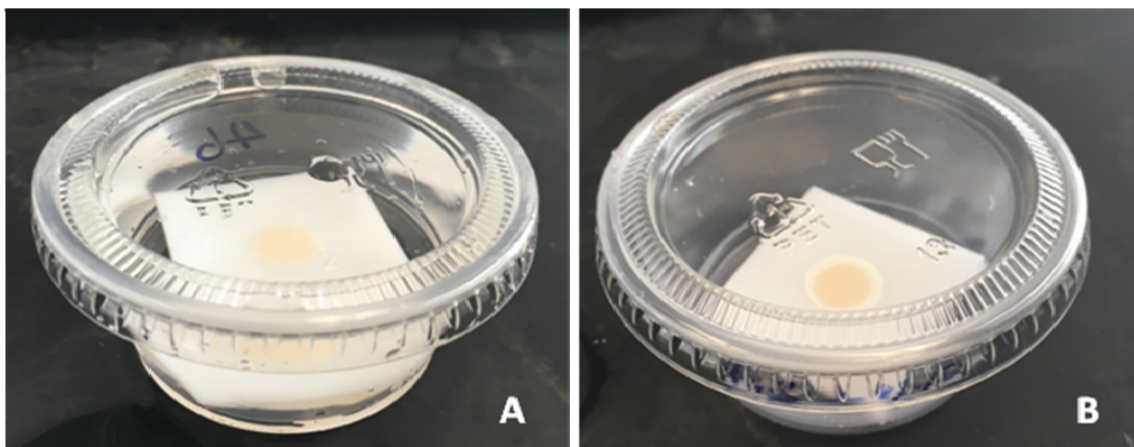


Figure 3. Light cured dental resin composites within mold stored in artificial saliva (A) or in air (B).

3.4. Color measurements

Color measurements were obtained with a spectrophotometer (Konica Minolta CM-700D, Ramsey, NJ) (Figure 4) right before light curing, soon after light curing and at different time points after aging for all specimens up to 3 months. The time points were 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours, 1 day, 1 month and 3 months. The spectrophotometer was kept in a fixed position as shown in Figure 4. L^* , a^* and b^* values were obtained and recorded for all specimens. At all time points, three measurements were taken and the average of them was used. Specimens were covered with the clear plastic film when color was measured before light curing. Two color measurements were taken soon after light curing. The first one was taken with the clear plastic film covering the resin composites as it was before light curing and within 5 seconds

after light curing. Another color measurement was taken without the film on within 5 seconds of the previous color measurement, which is the color measurement after light cure and with the plastic film.



Figure 4. Color measurements were obtained with a spectrophotometer.

3.5. Color change

Color change was calculated using the CIELab formula (ΔE^*_{ab}) and the CIEDE2000 formula (ΔE_{00}) as shown in Equations 1 and 2, as described previously. Color change between the two measurements at “soon after light curing” with and

without the film was calculated to ensure no color change was registered by the use of the clear plastic film. Calculations were conducted using the time points: 1) between “before light curing” and “soon after light curing” to study the effect of polymerization and 2) between “soon after light curing” and each time point after aging to study the effect of aging.

3.6. Statistics

SigmaStat Software (Systat, San Jose, CA) was used for statistical analysis. For the color change upon polymerization and aging at 3 months, one way ANOVA with the resin composite brand as the factor was conducted for statistical analysis. When the data failed the normality test or equal variances test, ANOVA on rank test was conducted instead. For the aging at 3 months, two way ANOVA was also conducted with photoinitiators (CQ or CQ+) and aging methods (in air or in artificial saliva) as factors. In all the cases, the Student Newman Keuls (SNK) method was used as post hoc analysis. α level was set as 0.05 (significant when $p < 0.05$).

CHAPTER 4

Results

4.1. Color change upon polymerization

Color change upon polymerization was measured soon after light cure (within 10 seconds). Color at before and soon after light cure were both measured with the same plastic film in place. The plastic film was removed soon after the color measurement after the light cure (with film on), and the color was measured again to ensure there were no differences between those readings made at the same time with and without film. For the traditional resin composites, those with CQ and additional photoinitiator had greater color change than the resin composites with CQ only (Figure 5A, 5B). Evaluating the color change with polymerization via the CIELab formula (ΔE^*_{ab}) (Figure 5A) and CIEDE2000 formula (ΔE_{00}) (Figure 5B) result in the same significance groupings among resin composites, though the values of ΔE_{00} are less than ΔE^*_{ab} .

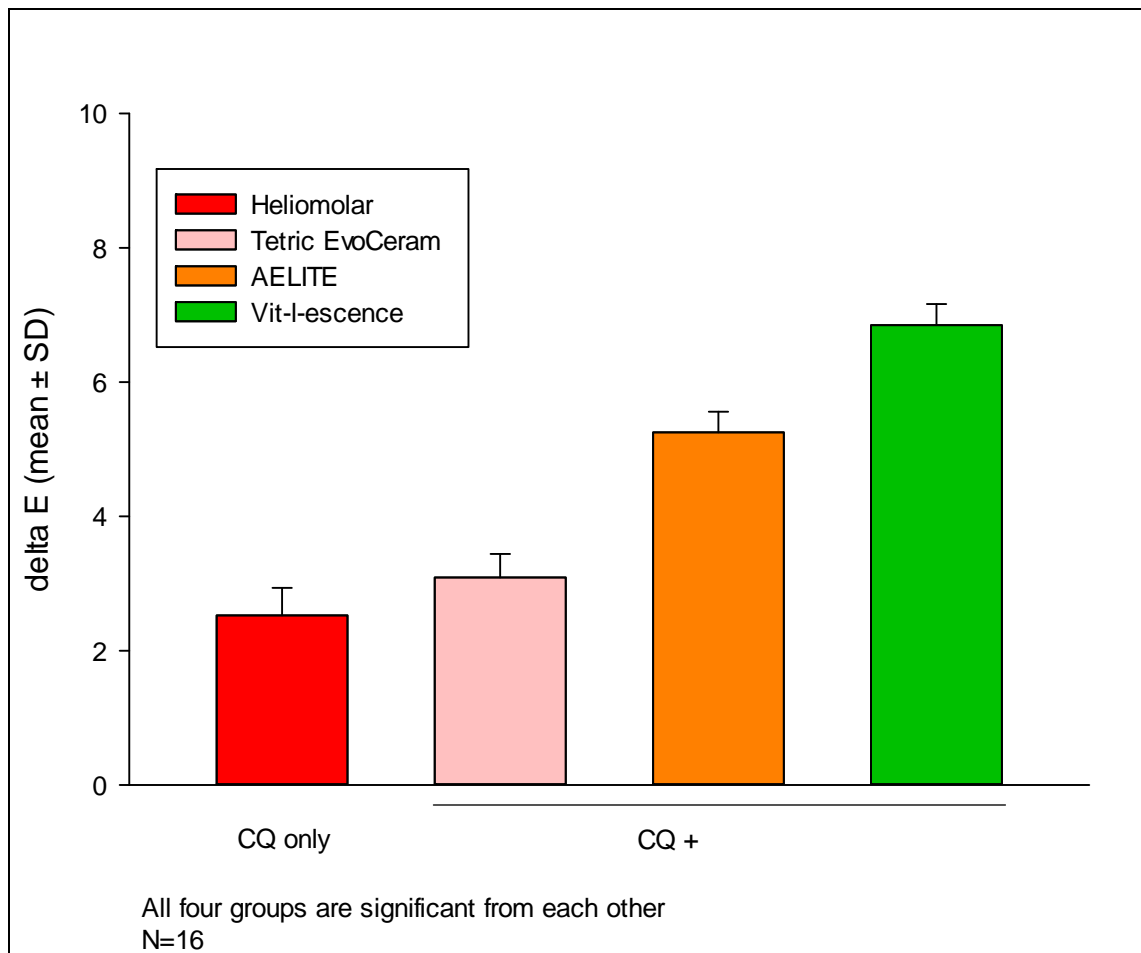


Figure 5A. Color change of traditional resin composites upon polymerization. ΔE (delta E) was calculated by the CIELab formula.

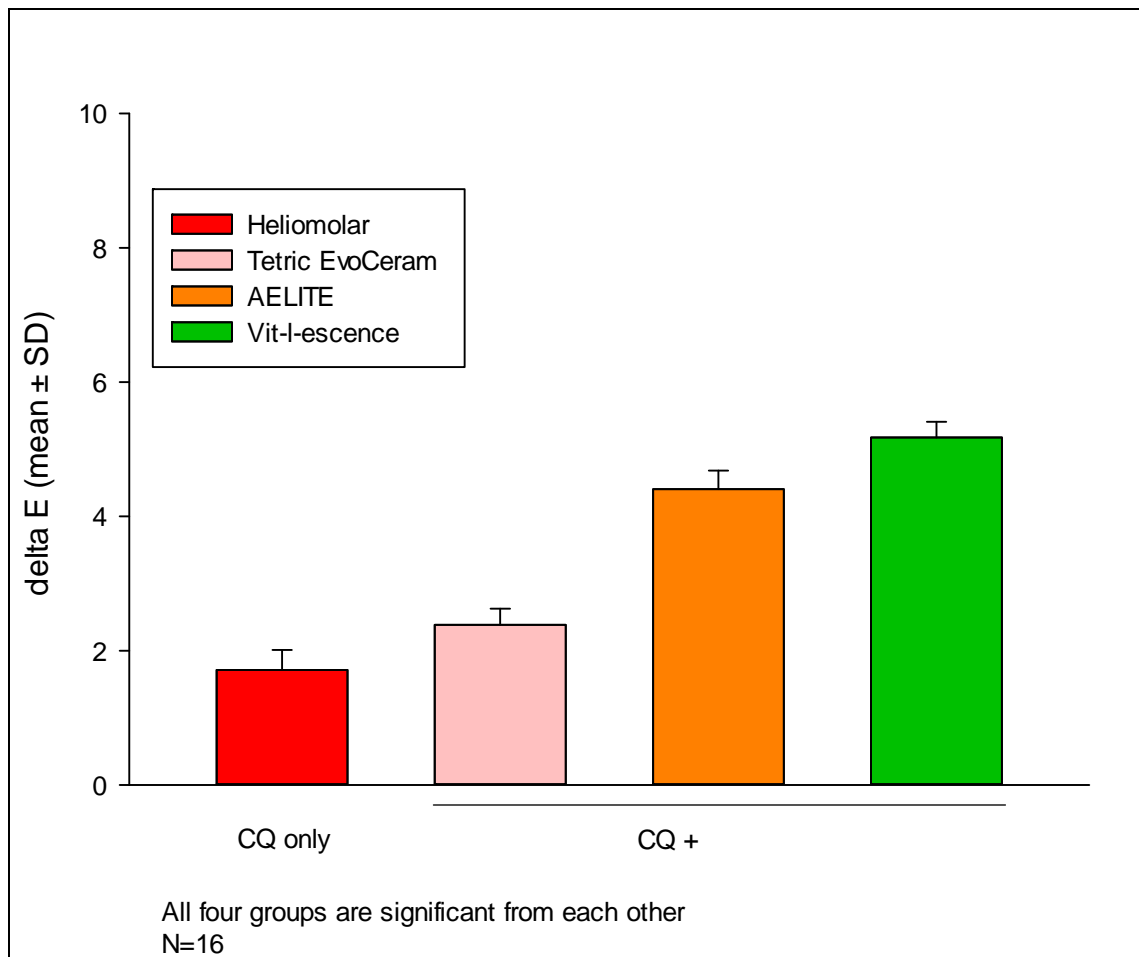


Figure 5B. Color change of traditional resin composites upon polymerization. ΔE (delta E) was calculated by the CIEDE2000 formula.

For the bulk-fill resin composites, Tetric EvoCeram (CQ with additional photoinitiator) had greater color change whereas HyperFIL (dual cure with CQ and additional photoinitiator) had less color change with polymerization compared to the two bulk-fill resin composites with only CQ (Figure 6A, 6B).

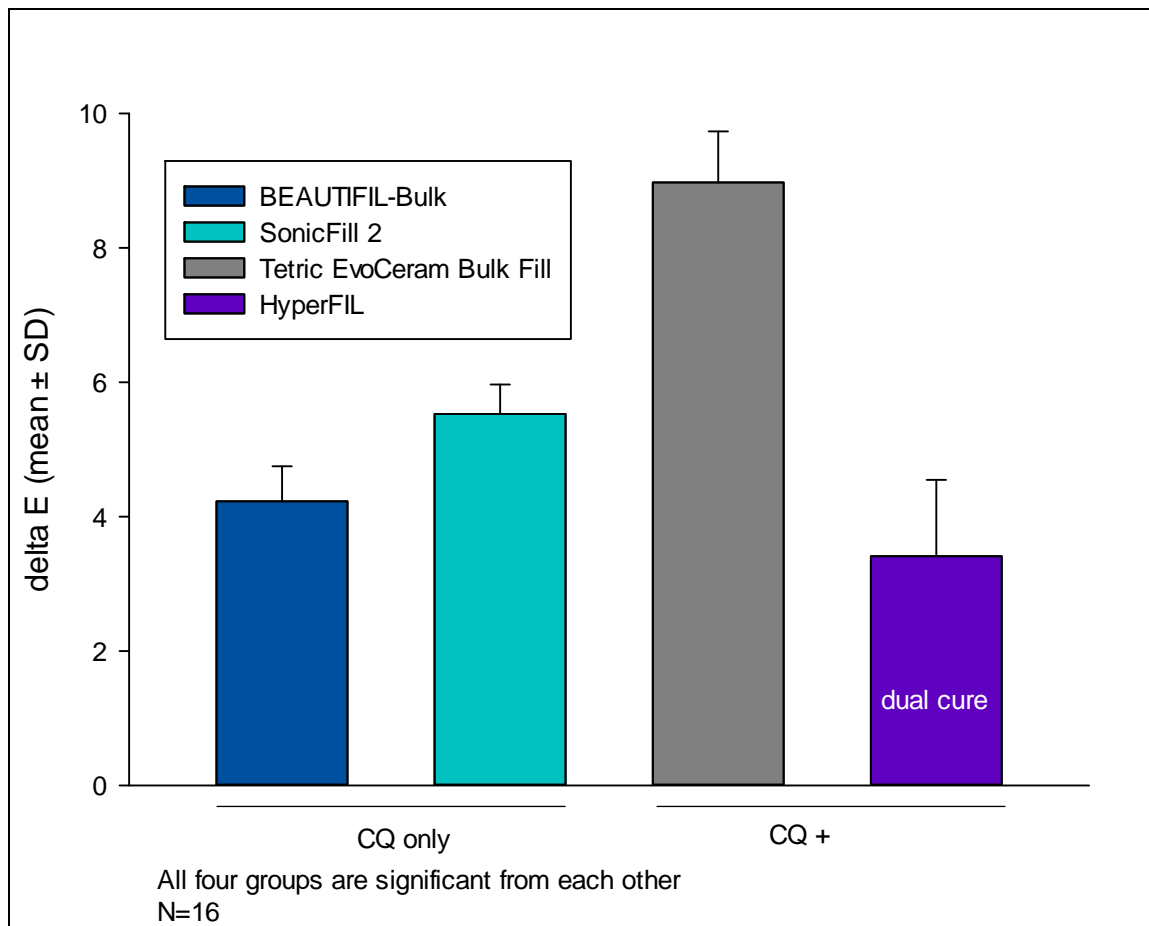


Figure 6A. Color change of bulk-fill resin composites upon polymerization. ΔE (delta E) was calculated by the CIELab formula.

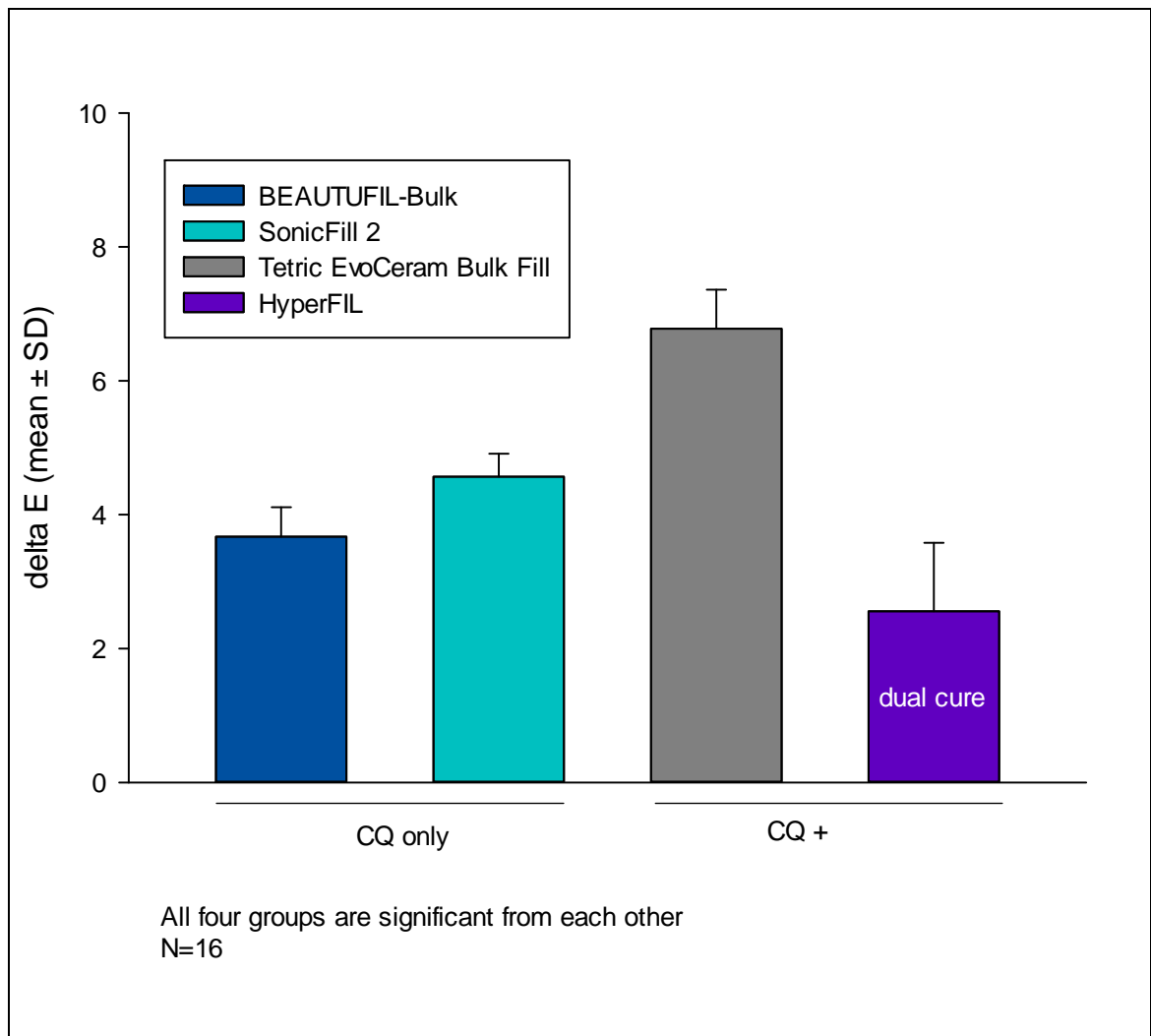


Figure 6B. Color change of bulk-fill resin composites upon polymerization. ΔE (delta E) was calculated by the CIEDE2000 formula.

ΔL between before cure and soon after cure does not show a consistent pattern (Figure 7A). However, Δb of all the resin composites are less than zero, meaning that all the resin composites tested became less yellow after light curing (Figure 7C). Δa is positive for all but one product (SonicFill 2), suggesting that the resin composites tended to become more red than green (Figure 7B).

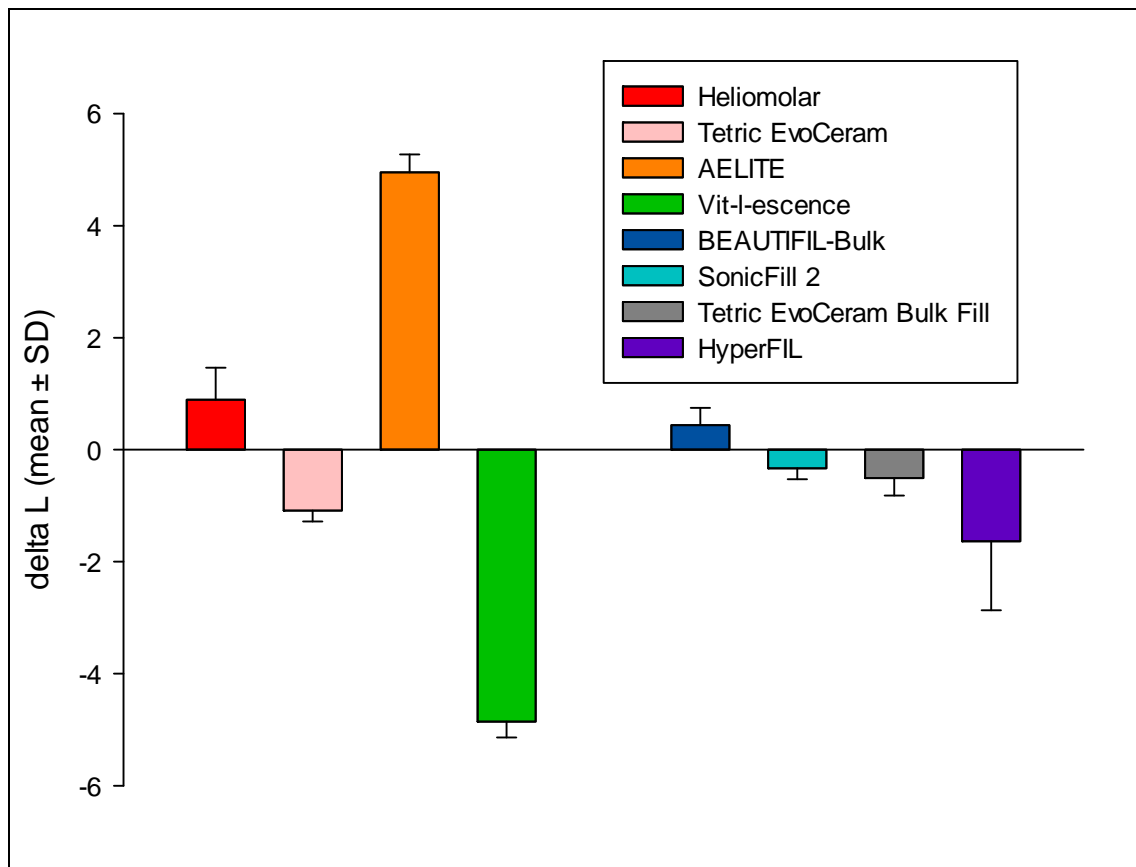


Figure 7A. ΔL of resin composites upon polymerization calculated with the CIELab formula. N is 16 for each group. ΔL (delta L) was the difference in L^* .

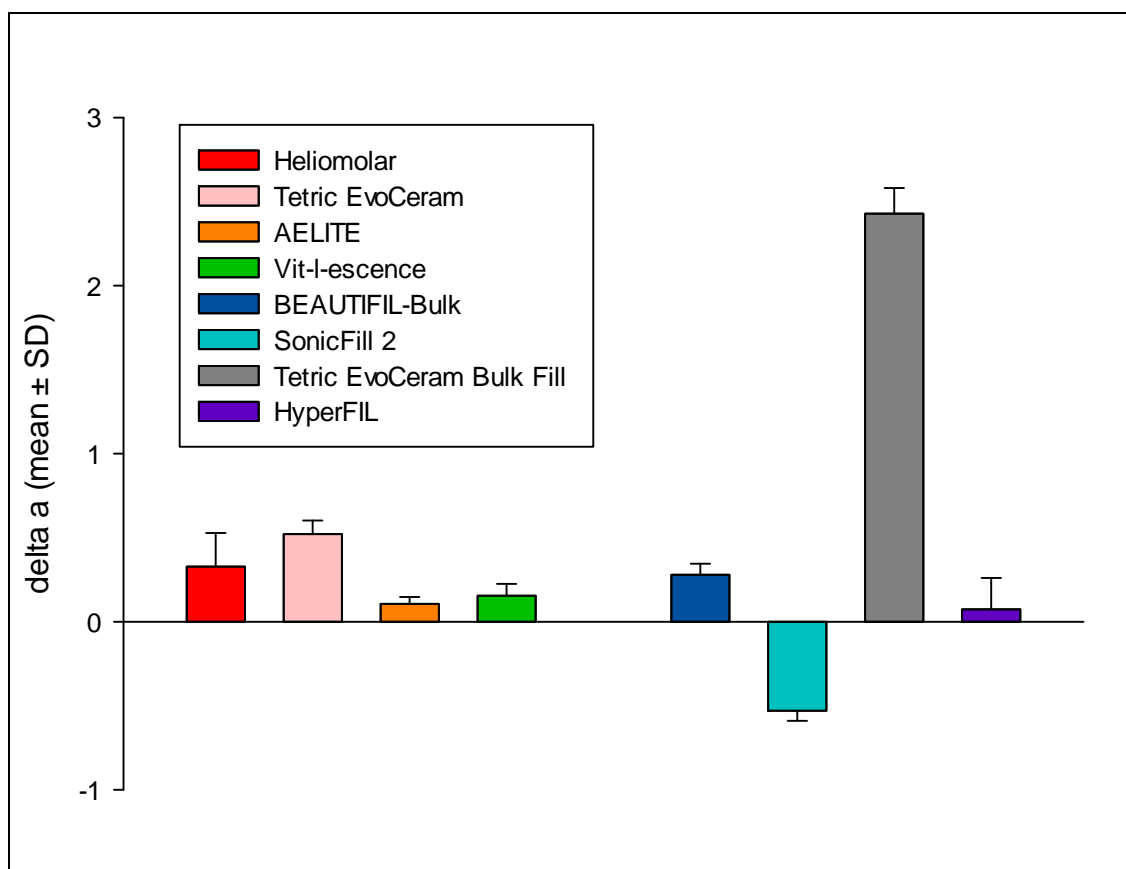


Figure 7B. Δa of resin composites upon polymerization calculated with the CIELab formula. N is 16 for each group. Δa (delta a) was the difference in a^* .

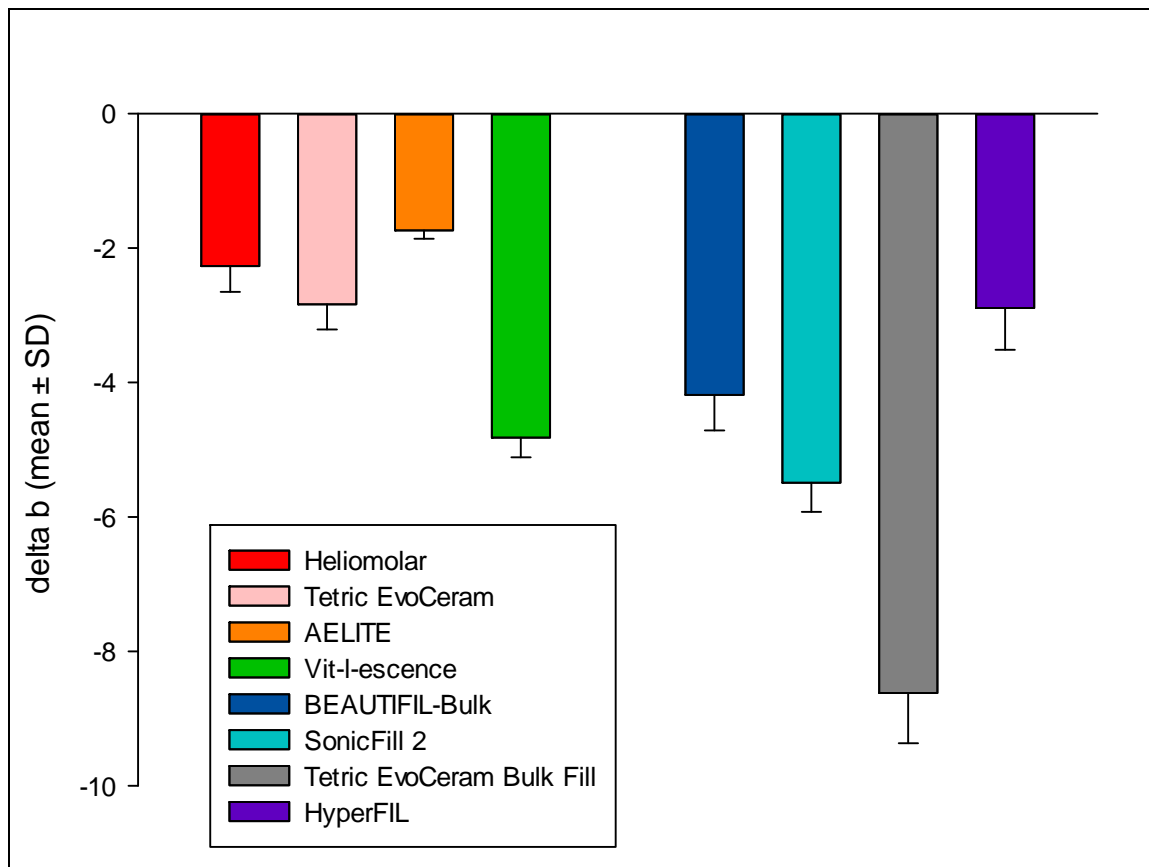


Figure 7C. Δb of resin composites upon polymerization calculated with the CIELab formula. N is 16 for each group. Δb (delta b) was the difference in b^* .

4.2. Color change upon aging

4.2.1. Aging for up to 6 hours

Specimens were put into either artificial saliva or kept in air after the measurements soon after light cure were obtained. Color was measured on the same day hourly up to 6 hours and L^* , a^* and b^* were recorded. ΔE , ΔL , Δa and Δb from soon after light curing to hourly after light curing up to 6 hours are shown in Figure 8 (A, B, C and D). The greatest changes were within 1 hour after light curing, though the overall color change (ΔE) within 6 hours was smaller than 2, which is not considered clinically

perceptible (Figure 8A). It is hard to determine whether or not such color change ΔE is mainly due to L^* , a^* or b^* change, since there was not a clear pattern in the change associated with L^* , a^* or b^* (Figure 8B, 8C and 8D). Note, the scales in Figure 8 A to D are different to better show differences between groups, comparatively Δa (Figure 8C) had less change.

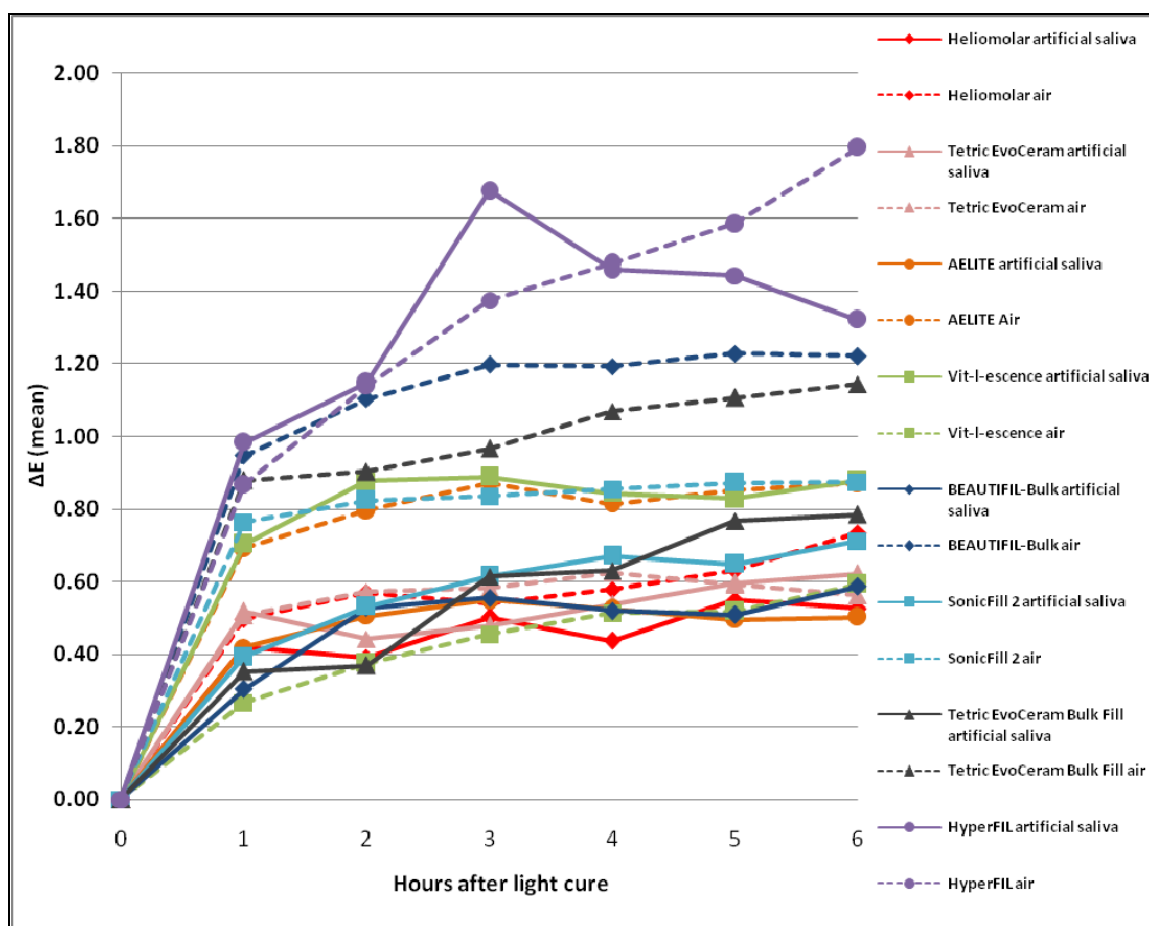


Figure 8A. Color change of resin composites within 6 hours of light cure. N is 8 for each group. ΔE was calculated by the CIELab formula.

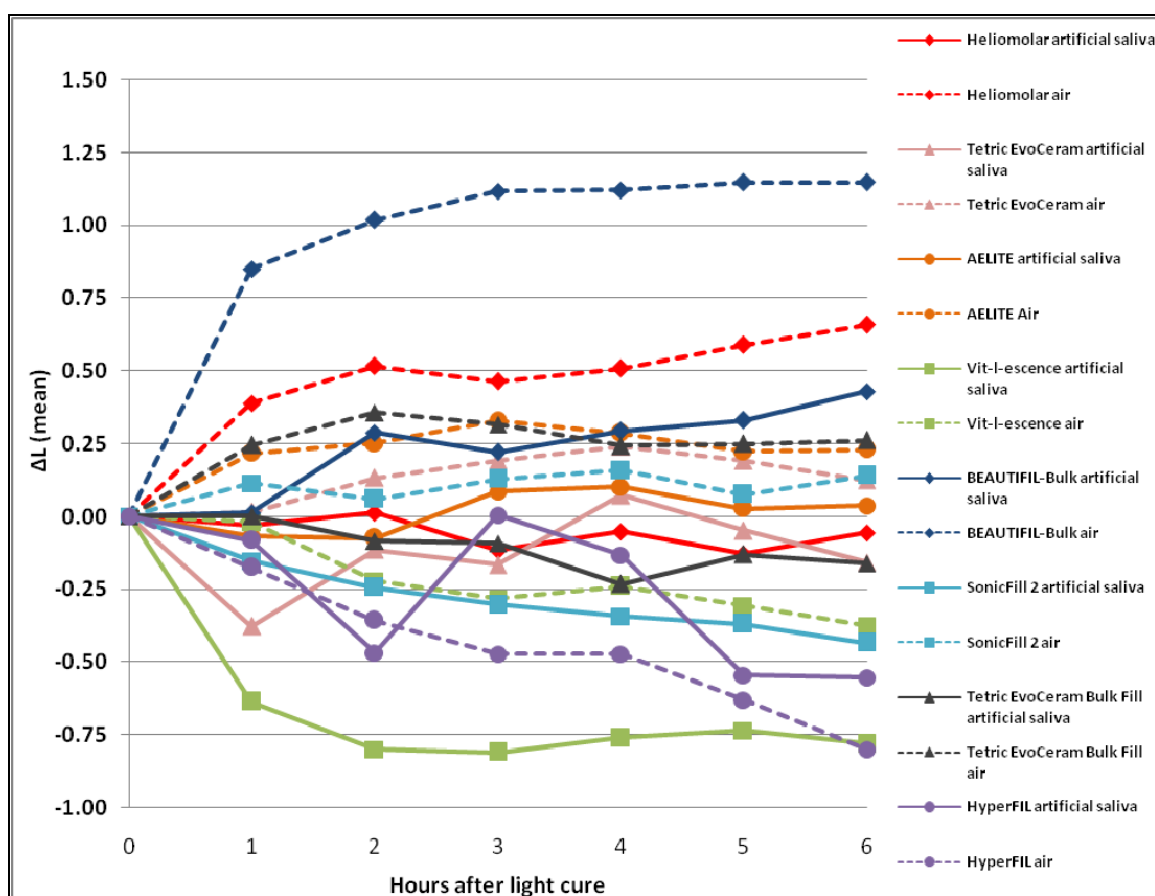


Figure 8B. ΔL of resin composites within 6 hours of light cure. N is 8 for each group. ΔL was the difference in L^* .

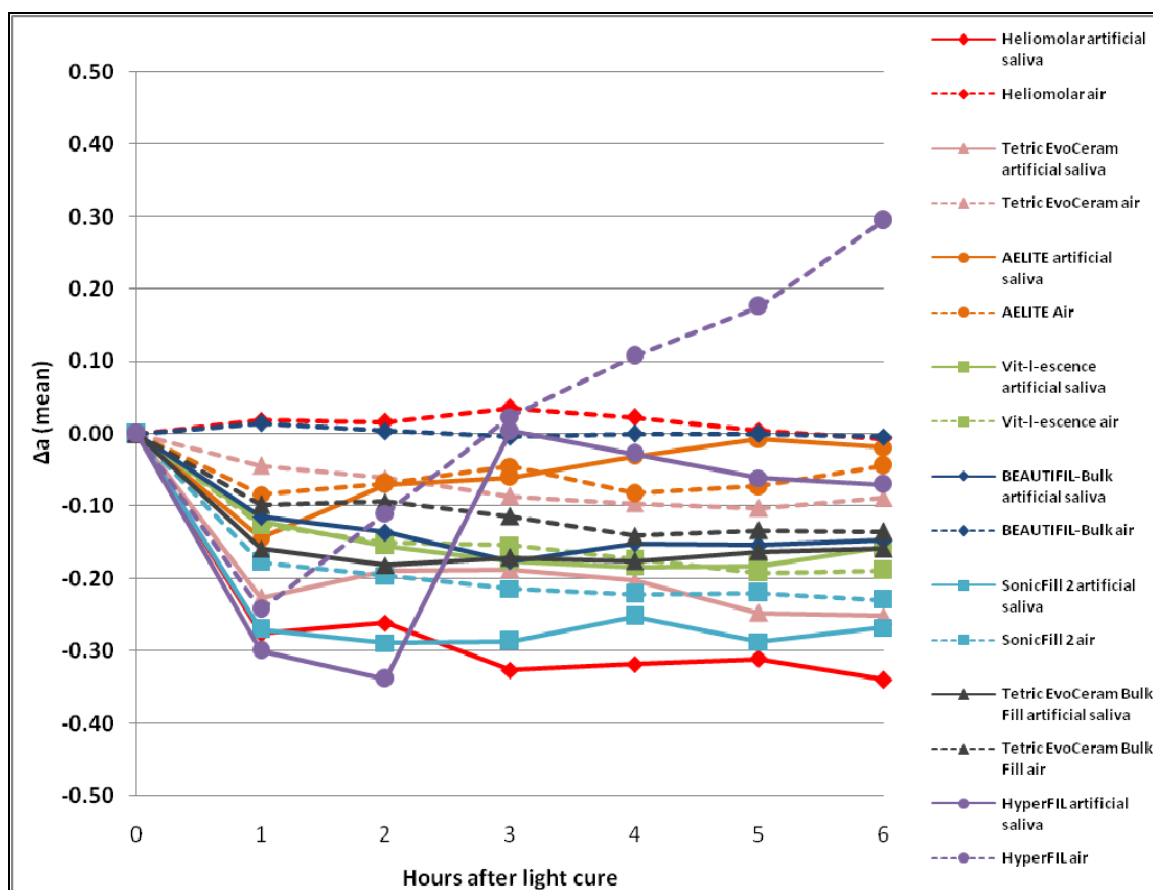


Figure 8C. Δa of resin composites within 6 hours of light cure. N is 8 for each group. Δa was the difference in a^* .

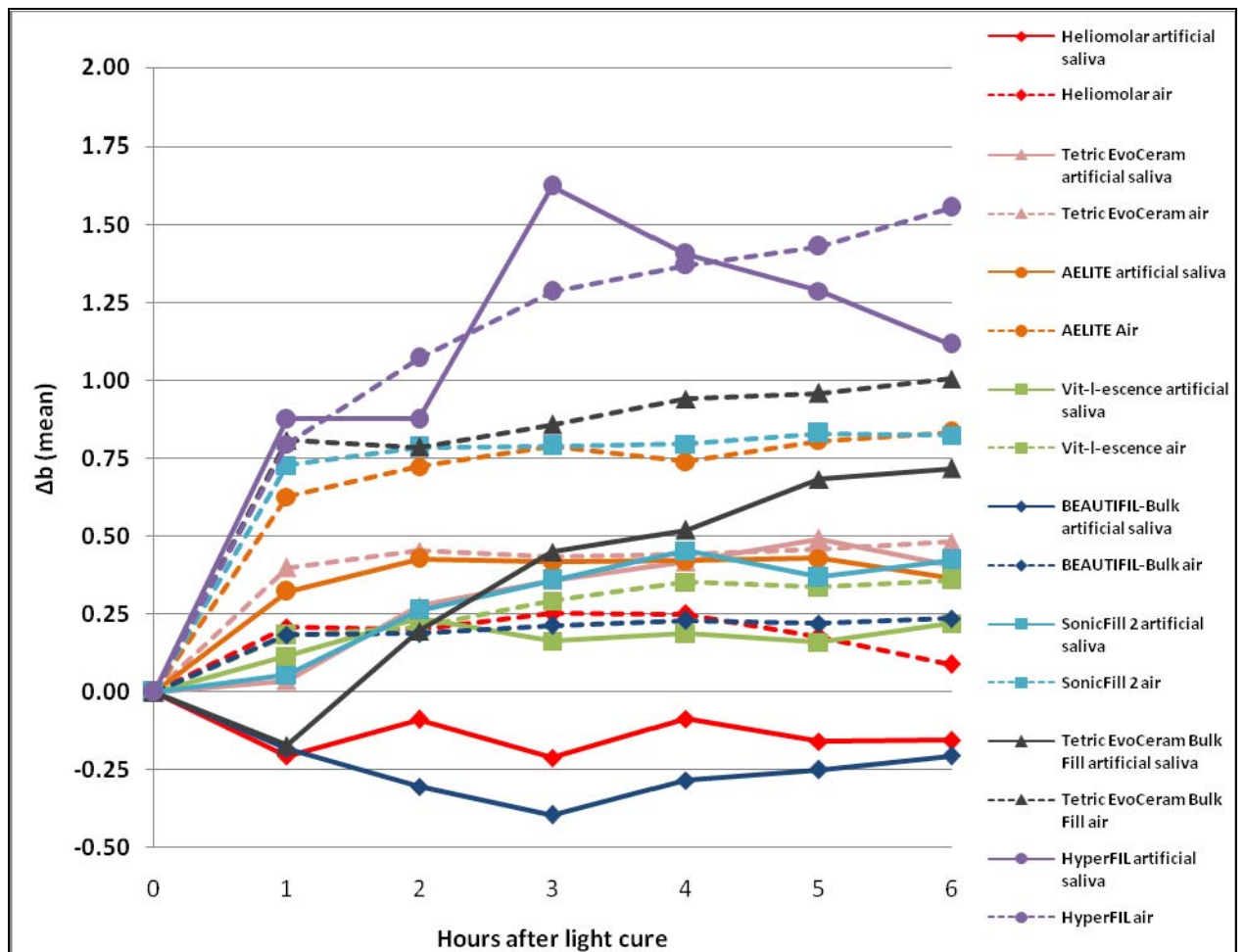


Figure 8D. Δb of resin composites within 6 hours of light cure. N is 8 for each group. Δb was the difference in b^* .

4.2.2. Aging for up to 3 months

The effect of aging in artificial saliva and air on the color change of resin composites was further studied up to 3 months. L^* , a^* and b^* were measured at 1 day, 1 month and 3 months after light curing. ΔE between different time points and soon after light curing were calculated and shown in Figure 9. Except for HyperFIL, the color change of all the resin composites tested at all the time points were less than 3 (Figure 9).

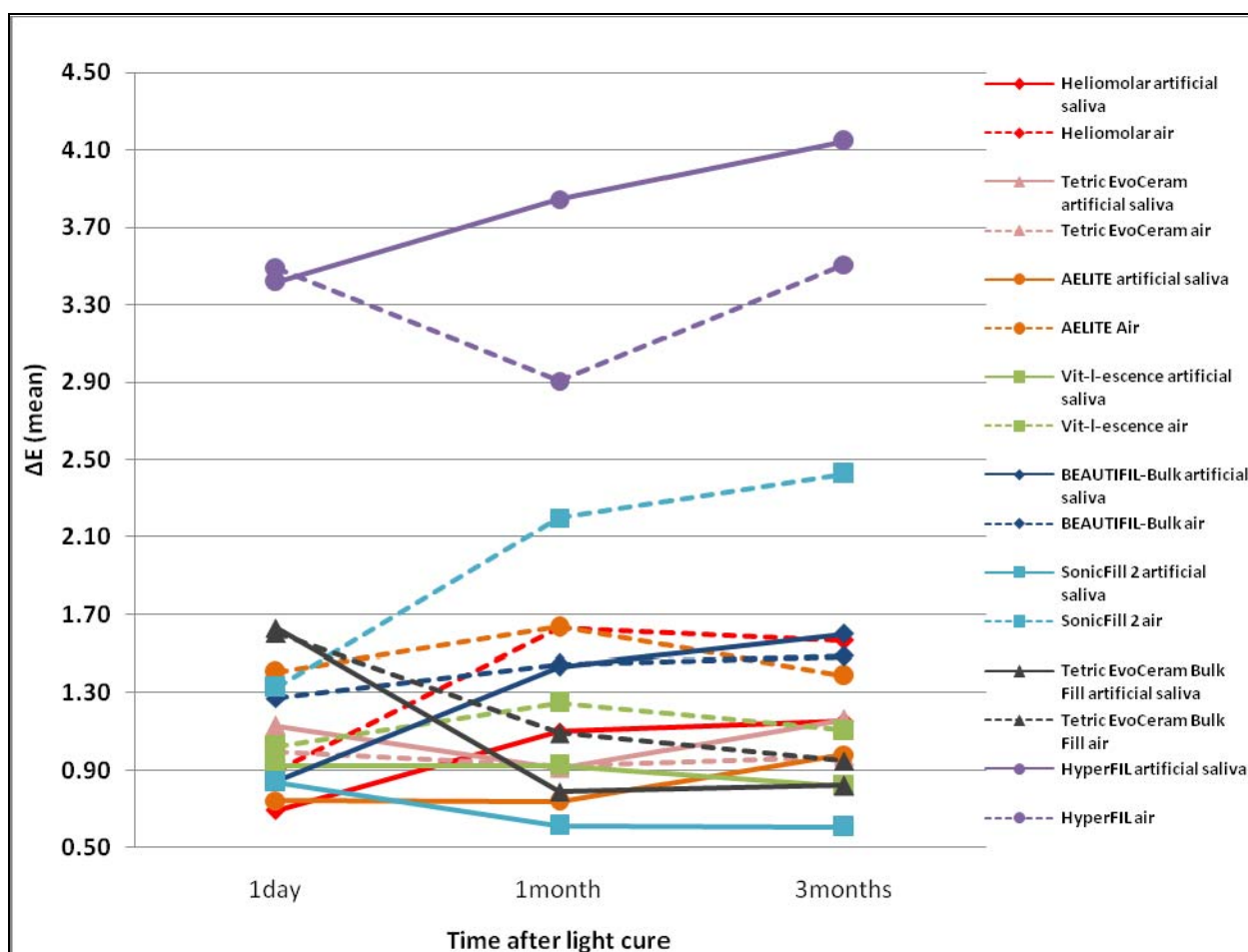


Figure 9. ΔE of resin composites after aging for 1 day, 1 month and 3 months. N is 8 for each group. ΔE was calculated by the CIELab formula.

Since 3 months is the last time point tested in this study, the data at 3 months was further statistically analyzed to study the effect of aging on the color change of the resin composites. Table 2 (A and B) shows the results of 2 way ANOVA (ΔE was calculated by the CIELab formula). In both traditional and bulk-fill resin composites, not taking into consideration the aging method, significant differences in color change were observed between resin composites with additional photoinitiators combined with CQ versus those with CQ only ($p < 0.05$ between CQ only and CQ with additional photoinitiators, Table

2A, 2B). Aging method does not affect color change differently in the bulk-fill resin composites (Table 2B), though it seems to affect the color change in the traditional resin composites after aging for 3 months (Table 2A). However, when ΔE was calculated by the CIEDE2000 formula, no significant difference ($p>0.05$) was observed by 2 way ANOVA with factors of photoinitiator or aging method in either regular or bulk-fill resin composites.

Table 2A. 2 way ANOVA on color change of the traditional resin composites at 3 months. ΔE was calculated by the CIELab formula.

Source of Variation	DF	SS	MS	F	P
photoinitiator (CQ only or CQ+)	1	1.003	1.003	7.557	0.008
aging (air or artificial saliva)	1	1.013	1.013	7.633	0.008
photoinitiator x aging	1	0.184	0.184	1.389	0.243
Residual	60	7.961	0.133		
Total	63	9.984	0.158		

DF: degrees of freedom; SS: sum of the squares; MS: mean square; F: F value; P: P value.

Table 2B. 2 way ANOVA on color change of the bulk-fill resin composites at 3 months. ΔE was calculated by the CIELab formula.

Source of Variation	DF	SS	MS	F	P
photoinitiator (CQ only or CQ+)	1	10.926	10.926	6.929	0.011
aging (air or artificial saliva)	1	1.435	1.435	0.91	0.344
photoinitiator x aging	1	4.906	4.906	3.112	0.083
Residual	60	94.609	1.577		
Total	63	111.877	1.776		

DF: degrees of freedom; SS: sum of the squares; MS: mean square; F: F value; P: P value.

In order to study the effect of the brand in more detail, ΔE of all the resin composites between soon after light cure and 3 months after light cure, which is the last time point tested in this study, are shown in Figure 10 (A and B). One way ANOVA on

rank was performed. ΔE calculated by the CIELab formula (Figure 10A) and CIEDE2000 formula (Figure 10B) show similar patterns. Again the CIEDE2000 formula seems to result in smaller values than the CIELab formula. ΔE of the resin composites Heliomolar and AELITE, both in air, are as high as that of the BEAUTIFIL-Bulk (denoted as d in Figure 10A) by the CIELab method, whereas they both are lower than BEAUTIFIL-Bulk by the CIEDE2000 method, indicating the two formula are not just merely scaled values.

It is hard to tell which aging method (in air or in artificial saliva) affects the color of the resin composites more. In most of the cases, if a difference occurs, those in artificial saliva show better stability in color (smaller ΔE). Such resin composites include SonicFill 2 (by both CIELab and CIEDE2000 methods, Figure 10A, 10B) as well as Heliomolar and AELITE (by CIELab method only, Figure 10A). However the dual cure bulk-fill resin composite HyperFIL shows the opposite effect with aging method, in which those in room air were more stable in color by both CIELab (Figure 10A) and CIEDE2000 methods (Figure 10B).

Unlike the other bulk-fill resin composites that have a greater color change after aging with both (BEAUTIFIL-Bulk and HyperFIL) or at least one (SonicFill 2) of the aging methods than the traditional resin composites after aging for 3 months, Tetric EvoCeram Bulk Fill showed good color stability that is comparable to the traditional resin composites. Such an effect is more obvious when the CIEDE2000 equation was used to calculate the color change (Figure 10B).

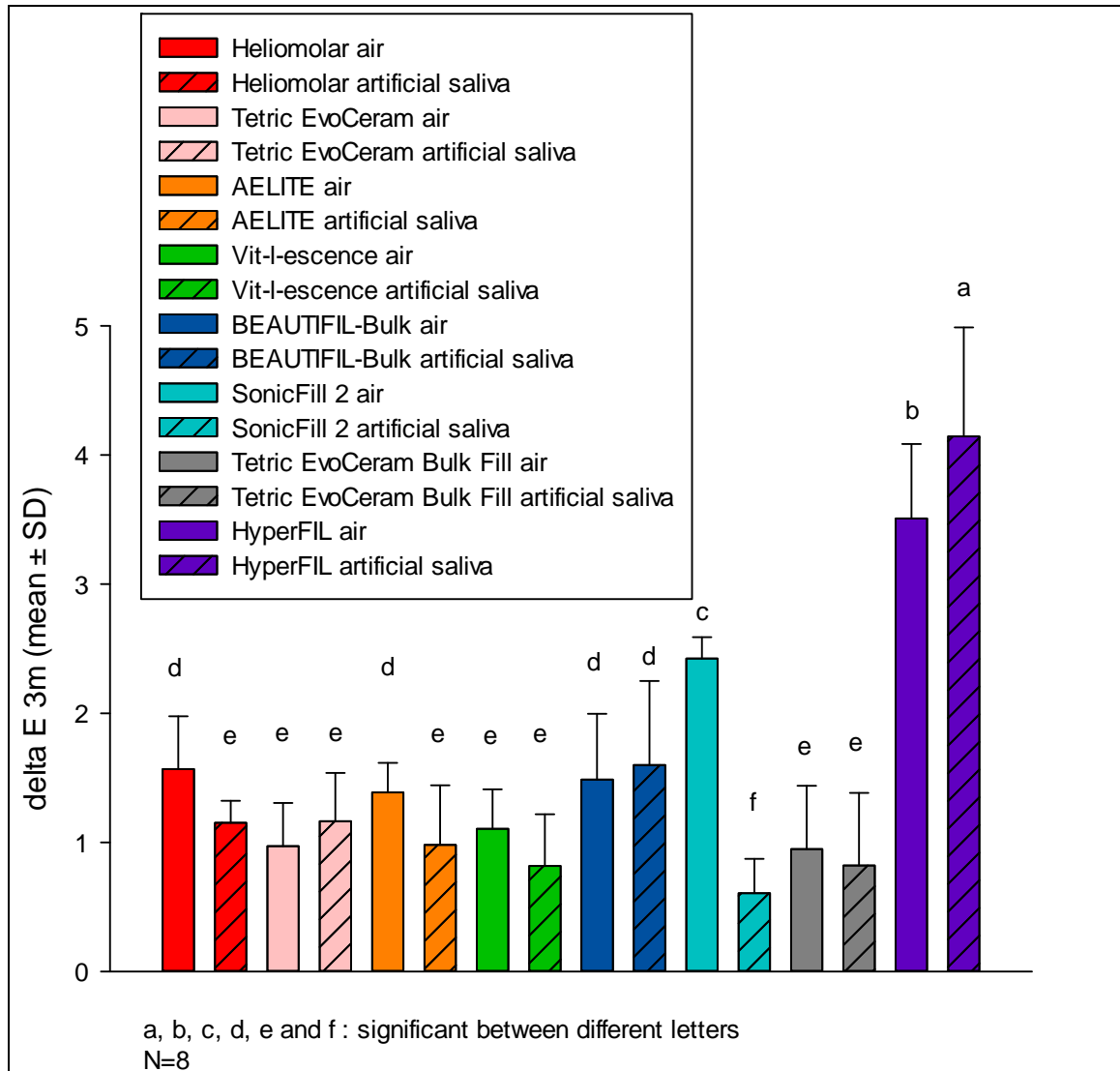


Figure 10A. ΔE of resin composites after aging for 3 months. ΔE (delta E) was calculated by CIELab formula. N is 8 for each group. Mean and standard deviation (SD) are shown.

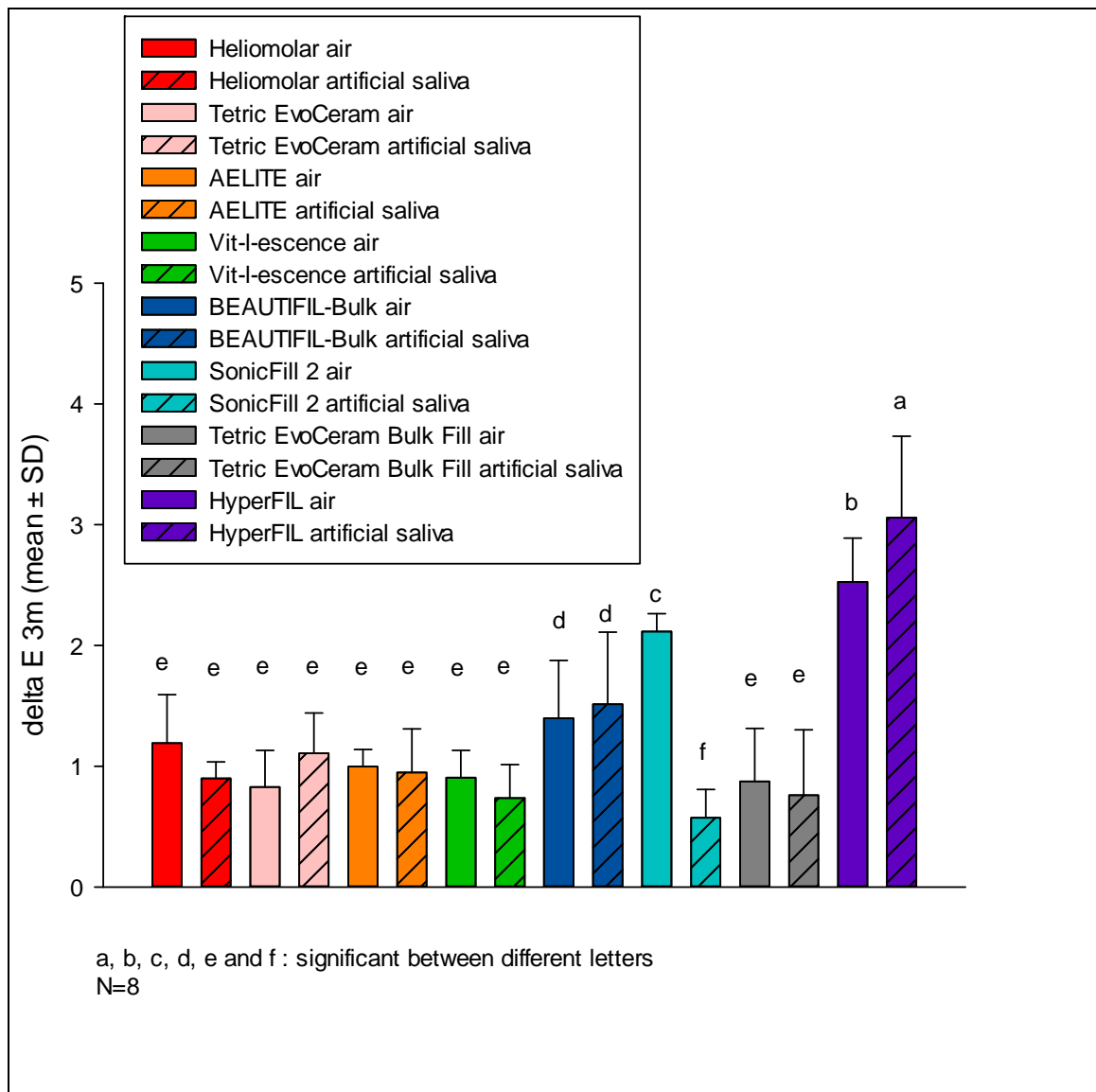


Figure 10B. ΔE of resin composites after aging for 3 months. . ΔE (delta E) was calculated by CIEDE2000 formula. N is 8 for each group. Mean and standard deviation (SD) are shown.

CHAPTER 5

Discussion

5.1. Are non-CQ dental resin composites available commercially?

As mentioned, generally, non-CQ dental resin composites are not available commercially. Even though resin composites with other photoinitiators have been studied and some were shown to be good substitutes for CQ experimentally (38,39), currently it appears there are no non-CQ dental resin composites available in the U.S. market.

The fact that most currently available light curing units on the market and in dental offices are optimized for curing CQ and may not be as suitable for exciting alternative photoinitiators that absorb light at different wavelengths may contribute to the dominant use of CQ. Even though many manufacturers are trying to substitute CQ by adding additional photoinitiators, the performance of the additional photoinitiator may be underestimated due to the use of an inappropriate light that does not provide the correct wavelength needed to cure the additional photoinitiators. The halogen light that was used in this study provides a broader irradiation spectrum, covering the absorption spectrum of both CQ and TPO (40). The first and second generations of light-emitting diode (LED) light curing units (single diode) had problems in curing photoinitiators that are sensitive to the shorter wavelengths of less than 420 nm of blue light, since they only produce a narrow irradiation spectrum with longer wavelengths of light in the 450-470 nm range that cover the absorption spectrum of CQ (37). A third generation LED light curing unit

(polywave), however, would be able to cure CQ and photoinitiators with an absorption spectrum below 430 nm (40).

Another significant disadvantage of using photoinitiators with a shorter wavelength absorption peak is that they cause a lower depth of cure compared to CQ. The shorter wavelengths of light are scattered much more than the longer wavelengths of light, and as the thickness of the restoration increases, very little of these shorter wavelengths penetrate through the resin composites and reach the bottom of the restoration (37). Price *et al.* further suggested that unless they are very translucent, resin composites that use predominantly alternative photoinitiators should be cured in small increments, by which the bottom of the resin composites could be exposed to more of the shorter wavelength (37). Depth of cure was not studied in the current study.

Considering the factors discussed, it seems reasonable for manufacturers to keep CQ as a major component photoinitiator in their resin composites, before a perfect photoinitiator is found to totally substitute for CQ in the future. However, as mentioned, to reduce the yellowing effect, different approaches have been made on selecting additional photoinitiators that can be added into the CQ/amine system to reduce the amount of CQ used.

Trimethylbenzoyl-diphenyl phosphine oxide (TPO) appears to be a very successful approach. In the 5 resin composites tested, 4 of them contain TPO (the additional photoinitiator used in the other one (HyperFIL) is unknown), and 3 of them contain only TPO, besides CQ (Table 1). In contrast to CQ, which has a broad absorption spectrum with peak absorption around 468 nm (2,15), the absorption spectrum of TPO is

situated more toward the UV spectrum (380-425 nm) (20). TPO does not require the use of the co-initiator, and in this way, TPO is more efficient as it reduces the intermediate steps required for radical production in the CQ/amine system (41). Excitation of the TPO molecule produces two molecules with free radicals that make it more efficient to initiate the polymerization process, compared to the CQ/amine system that produces only one free radical per molecule (40,41). The greater number of free radicals produced by TPO than CQ, however, may contribute to the inferior depth of cure in the resin composites containing TPO. At similar concentration, TPO absorbs many more photons than CQ, which in turn reduces the penetration of light through the resin composites (41). Nevertheless, TPO is considered a photoinitiator with high reactivity and curing efficiency (41), since TPO based resin composites have exhibited a higher degree of conversion (38,41) and rate of polymerization than those containing CQ with a tertiary amine (41). Regardless of the many advantages of TPO, one of the major concerns with this photoinitiator is that TPO based material behaves in a more toxic way than CQ/amine based materials (15). TPO reacts more efficiently with cells than CQ/amine (15).

5.2. Why did the resin composites with CQ+ have greater color change upon polymerization?

In the current study, except the dual cure HyperFIL, resin composites with CQ and additional photoinitiators showed greater color change upon polymerization (Figure 5, Figure 6). A possible reason for the greater color change in those with CQ+ may be that they have a greater degree of conversion. Additional photoinitiators may help to increase

the degree of conversion. As mentioned, resin composites with TPO show a greater degree of conversion compared to resin composites with CQ alone (38,41).

On the other hand, additional photoinitiators may also increase the speed of polymerization. As mentioned, TPO increases the rate of polymerization (41). Whether or not such a change in polymerization rate affects the polymerization shrinkage stress remains controversial (2), but the increased polymerization rate caused by additional photoinitiators could affect color change upon polymerization due to difference in the degree of conversion at the various measurement points in this study. The color change after polymerization shown in Figure 1 and Figure 2 was measured soon after light curing (within 10 seconds). The color change at 1 hour after light cure was greater than it was at 2 hours through 6 hours (Figure 8A). The relative greater color change in the first hour may reflect the ongoing polymerization process.

The exact concentration of the total photoinitiator in the different resin composites remains unknown. Although greater color changes were found in the resin composites with additional photoinitiator in this study (Figure 5, Figure 6), it is possible that resin composites showing greater color change include a greater concentration of photoinitiators, which might increase polymerization rate and therefore increase the degree of conversion soon after light cure. Concentration of the photoinitiators is critical. A good photoinitiator should have high absorption at low concentration (42). When the CQ concentration exceeds the critical level, the unreacted molecules will return to the ground state and result in yellow discoloration (43). This may further attenuate the light and result in reduced depth of cure (43). Very high TPO concentration will not increase

the degree of conversion, since TPO of less than 1 wt% already results in a maximal degree of conversion (15). However, when the concentration of photoinitiator is too low, the optimized rate of polymerization that results in optimal properties may not be able to be achieved. In the case additional photoinitiator is included in the resin composites, the ration of the amount of additional photoinitiator to CQ is important as well (37). It is not possible to know the concentration of the photoinitiators and their ratios used in the commercial resin composites because the information is considered to be proprietary. Experimental studies that control the concentrations of individual photoinitiator and their ratios are more definitive in ruling out the exact influence of the different photoinitiator system.

As mentioned, CQ requires the use of an amine as co-initiator. The rate of polymerization and degree of conversion increases as the concentration of coinitiators increases (10). In general, higher amine content leads to improved polymer properties, but it is also correlated with higher color change (21). The different co-initiator formula used could also contribute to the difference in color change. Additional photoinitiators such as TPO may also react with the co-initiator of the CQ system and therefore speed up the polymerization process.

Variables in the chemical composition of resin composites beside photoinitiator such as the types and concentrations of resin monomers and fillers may also affect color changes during polymerization, since degree of conversion can be affected by them. For instance, even though Tetric EvoCeram, which is a CQ+, is significantly different in color change from the CQ only resin composites Heliomolar, it had a smaller color

change compared to the other two regular CQ+ resin composites, AELITE and Vit-l-essence (Figure 5A, Figure 5B). According to the manufacturers, unlike AELITE and Vit-l-essence, Tetric EvoCeram does not contain any TEGDMA. This may contribute to its relatively smaller color change due to a lesser degree of conversion.

Kim and Lee stated that light curing causes a characteristic chromatic shift toward the blue region of color space in resin composites away from yellow (27). The results from the current study are in accord with this claim. In the current study, all the resin composites tested became less yellow after polymerization (Figure 7C). These results suggest that it would be beneficial to choose an initial color that is more yellow in color than the desired final color. Such a suggestion is consistent with a previous report (44). Alternatively, shade selection could be made using already polymerized resin composites color tab examples.

5.3. Color changes upon aging

Results showed a difference in color change upon aging between resin composites with CQ only and CQ combined with additional photoinitiators, when ΔE was calculated by the CIELab formula (Table 2). However such results cannot be repeated when ΔE was calculated by CIEDE2000 formula. Despite the confliction by different ΔE calculation methods, color changes in all resin composites tested except the dual cure bulk-fill resin composites HyperFIL are less than the level that can be considered as clinically perceptible (Figure 9, Figure 10). This result is consistent with previous studies (33). With regard to the clinical perceptibility in dentistry, in general a ΔE calculated by CIELab formula of less than 3.3 is considered perceptible clinically for a tooth color

restoration (45). Few studies address perceptibility calculated by the CIEDE2000 formula. ΔE of less than 1.30 was considered clinically perceptible in some studies (46, 47). The difference in color due to aging between air and artificial saliva is not clinically significant. The internal color change of the resin matrix is suggested to be a reason for the discoloration of resin composites upon aging (33).

5.4. Color changes of the bulk-fill resin composites

Many dentists have shown a preference in using bulk-fill resin composites to save time (24). Bulk-fill resin composites are designed to be filled and cured in 4 mm thickness increments in a single step, and therefore it saves time by skipping the time-consuming layering process (24). Most of the currently available bulk-fill resin composites have low hardness and elastic moduli, and therefore require a surface cap layer to overcome the low wear resistance. The three bulk-fill resin composites tested in this study were chosen because their manufacturers claim that they do not need to be covered with an outer layer of regular resin composites, because their elastic modulus and hardness are higher than the other bulk-fill resin composites (24). Thus, the color stability of these bulk-fill resin composites is an important issue with regard to their esthetic properties when used clinically.

Tetric EvoCeram Bulk Fill contains CQ, Lucirin-TPO and a newly synthesized Germanium based photoinitiator Ivocerin®. The absorption peak of this photoinitiator is around 418 nm (48). In this study, Tetric EvoCeram Bulk Fill showed a large color change after light curing (Figure 6); this may reflect its great polymerization rate and

degree of conversion. On the other hand, Tetric EvoCeram Bulk Fill showed better color stability than the other bulk-fill resin composites tested after aging (Figure 10).

HyperFIL behaved differently from all the other bulk-fill resin composites. It showed a small color change upon polymerization (Figure 6) but a large color change upon aging (Figure 10). HyperFIL is a dual cure resin composite. At the time that light was applied, the polymerization process had already started, since in order to produce smooth surfaces, a 5 kg weight was applied and kept on all the samples for three minutes before light curing, and in the case of HyperFIL, after mixing. The color change upon polymerization in the current study was actually reflecting the color change upon light curing after three minutes of chemical cure. This explains the small value of ΔE shown in Figure 6A and Figure 6B. However, HyperFIL also showed a great color change after aging, which is around 3 by the CIEDE2000 calculation (Figure 10B) and over 4 by the CIELab calculation (Figure 10A). In both methods, it is considered as clinically perceptible. Post-irradiation polymerization has been assumed to happen in cured resin composites as observed by a change in hardness over a period of time, which could be on the scale of minutes to months (38). This theory may explain the great color change in HyperFIL upon aging. This dual cure resin composite may experience a longer post-irradiation polymerization.

5.5. Color measurement and ΔE calculation

Change in light scattering and absorption properties, like light reflectivity and translucency, may affect the color measurement (21). In this study, the color measurement was based on reflective light. Translucency was not considered. Some

manufacturers believe the high translucency of resin composites will result in higher depth of cure (24). A study by Kim *et al.* determined translucency parameter values of a few commercial resin composites, including SonicFill 2, Tetric EvoCeram Bulk Fill and Tetric EvoCeram, by calculation of the color difference between readings over black and white backgrounds for the same sample using the CIELab formula (24). They found that Tetric EvoCeram Bulk Fill had the highest translucency parameter, followed by SonicFill 2 and then Tetric EvoCeram. The finding in this study is in agreement with their findings. The color change upon polymerization (Figure 5, Figure 6) on these three resin composites (Tetric EvoCeram Bulk Fill > SonicFill 2 > Tetric EvoCeram) may be caused by the difference in depth of cure that positively related with the translucency property of the resin composites.

Using CIEDE2000 and CIELab equations, the color change was calculated and the values were comparable, although the CIEDE2000 values were always smaller. The CIELab formula is more known and accepted in the field of dentistry. In addition to color change (ΔE), CIELab calculations also provide ΔL^* , Δa^* and Δb^* values, which indicate more detailed information on the lightness/darkness, changes toward red/green and yellow/blue, respectively. Therefore, using CIELab not only provided more information on color properties, but also made comparison with many other studies possible. However, the newly developed CIEDE2000 formula is getting more and more attention. This formula corrects the nonuniformity of the CIELab color space, especially for small color differences (47). Despite the equation being more complicated, the CIEDE2000 formula has been shown to provide a better fit for evaluating the color difference for dental ceramics (47,49) and reflects the color difference of resin composites better than

CIELab formula (46). Therefore it is rational to expect CIEDE2000 to be used more extensively in dentistry in the future. Thus, having the color change calculated by the CIEDE2000 formula will be beneficial for future studies.

CHAPTER 6

Conclusion

Color change upon polymerization and aging in air and artificial saliva was tested on eight commercial resin composites with either CQ only or CQ and additional photoinitiators.

Resin composites with additional photoinitiator(s) beside CQ showed greater color change upon polymerization, not taking into consideration the dual cure resin composite HyperFIL, whose curing process included a 3 minute gap between the start of light and chemical cure under the current experimental condition.

Color change with aging tended to be greatest within the first hour after light curing, but was not considered clinically perceptible on any resin composites tested except HyperFIL. Tetric EvoCeram Bulk Fill showed good color stability that is comparable to the traditional resin composites upon aging.

Bibliography

1. Palin WM, Senyilmaz DP, Marquis PM, Shortall AC. Cure width potential for MOD resin composite molar restorations. *Dent Mater*. 2008 Aug;24(8):1083-94.
2. Schneider LF, Pfeifer CS, Consani S, Prahl SA, Ferracane JL. Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites. *Dent Mater*. 2008 Sep;24(9):1169-77.
3. Sim JS, Seol HJ, Park JK, Garcia-Godoy F, Kim HI, Kwon YH. Interaction of LED light with coinitiator-containing composite resins: effect of dual peaks. *J Dent*. 2012 Oct;40(10):836-42.
4. Beazoglou T, Eklund S, Heffley D, Meiers J, Brown LJ, Bailit H. Economic impact of regulating the use of amalgam restorations. *Public Health Rep*. 2007 Sep-Oct;122(5):657-63.
5. Schneider LF, Cavalcante LM, Silikas N. Shrinkage stresses generated during resin-composite applications: A review. *J Dent Biomech*. 2010; 2010.
6. Cramer NB, Stansbury JW, Bowman CN. Recent advances and developments in composite dental restorative materials. *J Dent Res*. 2011 Apr;90(4):402-16.
7. Shah PK, Stansbury JW. Role of filler and functional group conversion in the evolution of properties in polymeric dental restoratives. *Dent Mater*. 2014 May;30(5):586-93.
8. Lohbauer U, Frankenberger R, Krämer N, Petschelt A. Strength and fatigue performance versus filler fraction of different types of direct dental restoratives. *J Biomed Mater Res B Appl Biomater*. 2006 Jan;76(1):114-20.
9. Brandt WC, Schneider LF, Frollini E, Correr-Sobrinho L, Sinhoreti MA. Effect of different photo-initiators and light curing units on degree of conversion of composites. *Braz Oral Res*. 2010 Jul-Sep;24(3):263-70.
10. Bittencourt BF, Dominguez JA, Farago PV, Pinheiro LA, Gomes OM. Alternative coinitiators applicable to photocurable resin composites. *Oral Health Dent Manag*. 2014 Sep;13(3):568-72.
11. Stansbury JW. Curing dental resins and composites by photopolymerization. *J Esthet Dent*. 2000;12(6):300-8.

12. Lee DS, Jeong TS, Kim S, Kim HI, Kwon YH. Effect of dual-peak LED unit on the polymerization of coinitiator-containing composite resins. *Dent Mater J*. 2012;31(4):656-61.
13. Voltarelli FR, dos Santos-Daroz CB, Alves MC, Peris AR, Marchi GM. Effect of different light-curing devices and aging procedures on composite knoop microhardness. *Braz Oral Res*. 2009 Oct-Dec;23(4):473-9.
14. Santini A, Miletic V, Swift MD, Bradley M. Degree of conversion and microhardness of TPO-containing resin-based composites cured by polywave and monowave LED units. *J Dent*. 2012 Jul;40(7):577-84.
15. Van Landuyt KL, Krifka S, Hiller KA, Bolay C, Waha C, Van Meerbeek B, Schmalz G, Schweikl H. Evaluation of cell responses toward adhesives with different photoinitiating systems. *Dent Mater*. 2015 Aug;31(8):916-27.
16. <https://www.b2bcomposites.com/msds/chriscraft/580664.pdf>
17. Porto IC, Soares LE, Martin AA, Cavalli V, Liporoni PC. Influence of the photoinitiator system and light photoactivation units on the degree of conversion of dental composites. *Braz Oral Res*. 2010 Oct-Dec;24(4):475-81.
18. Park YJ, Chae KH, Rawls HR. Development of a new photoinitiation system for dental light-cure composite resins. *Dent Mater*. 1999 Mar;15(2):120-7. Erratum in: *Dent Mater* 1999 Jul;15(4):301.
19. Emami N, Söderholm KJ. Influence of light-curing procedures and photoinitiator/co-initiator composition on the degree of conversion of light-curing resins. *J Mater Sci Mater Med*. 2005 Jan;16(1):47-52.
20. Schroeder WF, Cook WD, Vallo CI. Photopolymerization of N,N-dimethylaminobenzyl alcohol as amine co-initiator for light-cured dental resins. *Dent Mater*. 2008 May;24(5):686-93.
21. Schneider LF, Cavalcante LM, Consani S, Ferracane JL. Effect of co-initiator ratio on the polymer properties of experimental resin composites formulated with camphorquinone and phenyl-propanedione. *Dent Mater*. 2009 Mar;25(3):369-75.
22. Park J, Chang J, Ferracane J, Lee IB. How should composite be layered to reduce shrinkage stress: incremental or bulk filling? *Dent Mater*. 2008 Nov;24(11):1501-5.

23. Tiba A, Zeller GG, Estrich CG, Hong A. A laboratory evaluation of bulk-fill versus traditional multi-increment-fill resin-based composites. *J Am Dent Assoc*. 2013 Oct;144(10):1182-3.
24. Kim EH, Jung KH, Son SA, Hur B, Kwon YH, Park JK. Effect of resin thickness on the microhardness and optical properties of bulk-fill resin composites. *Restor Dent Endod*. 2015 May;40(2):128-35.
25. Van Dijken JW, Pallesen U. A randomized controlled three year evaluation of "bulk-filled" posterior resin restorations based on stress decreasing resin technology. *Dent Mater*. 2014 Sep;30(9):e245-51.
26. Leprince JG, Hadis M, Shortall AC, Ferracane JL, Devaux J, Leloup G, Palin WM. Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins. *Dent Mater*. 2011 Feb;27(2):157-64.
27. Kim IJ, Lee YK. Changes in color and color parameters of dental resin composites after polymerization. *J Biomed Mater Res B Appl Biomater*. 2007 Feb;80(2):541-6.
28. Makinson OF. Colour changes on curing light-activated anterior restorative resins. *Aust Dent J*. 1989 Apr;34(2):154-9.
29. Gómez-Polo C, Portillo Muñoz M, Lorenzo Luengo MC, Vicente P, Galindo P, Martín Casado AM. Comparison of the CIELab and CIEDE2000 color difference formulas. *J Prosthet Dent*. 2016 Jan;115(1):65-70.
30. Karaagaclioglu L, Yilmaz B. Influence of cement shade and water storage on the final color of leucite-reinforced ceramics. *Oper Dent*. 2008 Jul-Aug;33(4):386-91.
31. Pecho OE, Ghinea R, Alessandretti R, Pérez MM, Della Bona A. Visual and instrumental shade matching using CIELAB and CIEDE2000 color difference formulas. *Dent Mater*. 2016 Jan;32(1):82-92.
32. Pant DR, Farup I. Riemannian Formulation of the CIEDE2000 Color Difference Formula. *Society for Imaging Science and Technology*. 2010; 103-108.
33. Çelik EU, Aladağ A, Türkün LŞ, Yilmaz G. Color changes of dental resin composites before and after polymerization and storage in water. *J Esthet Restor Dent*. 2011 Jun;23(3):179-88.
34. Ameye C, Lambrechts P, Vanherle G. Conventional and microfilled composite resins. Part I: Color stability and marginal adaptation. *J Prosthet Dent*. 1981 Dec;46(6):623-30.

35. Abdel-Karim UM, El-Eraky M, Etman WM. Three-year clinical evaluation of two nano-hybrid giomer restorative composites. *Tanta Dent J.* 2014 Dec; 11(3):213-22.
36. Guiraldo RD, Consani S, Consani RL, Berger SB, Mendes WB, Sinhoreti MA, Correr-Sobrinho L. Comparison of silorane and methacrylate-based composite resins on the curing light transmission. *Braz Dent J.* 2010;21(6):538-42.
37. Price RB, Felix CA. Effect of delivering light in specific narrow bandwidths from 394 to 515nm on the micro-hardness of resin composites. *Dent Mater.* 2009 Jul;25(7):899-908.
38. Miletic V, Santini A. Micro-Raman spectroscopic analysis of the degree of conversion of composite resins containing different initiators cured by polywave or monowave LED units. *J Dent.* 2012 Feb;40(2):106-13.
39. Ilie N, Hickel R. Can CQ be completely replaced by alternative initiators in dental adhesives? *Dent Mater J.* 2008 Mar;27(2):221-8.
40. Randolph LD, Palin WM, Bebelman S, Devaux J, Gallez B, Leloup G, Leprince JG. Ultra-fast light-curing resin composite with increased conversion and reduced monomer elution. *Dent Mater.* 2014 May;30(5):594-604.
41. Leprince JG, Palin WM, Vanacker J, Sabbagh J, Devaux J, Leloup G. Physico-mechanical characteristics of commercially available bulk-fill composites. *J Dent.* 2014 Aug;42(8):993-1000.
42. Stansbury JW. Curing dental resins and composites by photopolymerization. *J Esthet Dent.* 2000;12(6):300-8.
43. Ogunyinka A, Palin WM, Shortall AC, Marquis PM. Photoinitiation chemistry affects light transmission and degree of conversion of curing experimental dental resin composites. *Dent Mater.* 2007 Jul;23(7):807-13.
44. Seghi RR, Gritz MD, Kim J. Colorimetric changes in composites resulting from visible-light-initiated polymerization. *Dent Mater.* 1990 Apr;6(2):133-7.
45. Doray PG, Li D, Powers JM. Color stability of provisional restorative materials after accelerated aging. *J Prosthodont.* 2001 Dec;10(4):212-6.
46. Gómez-Polo C, Portillo Muñoz M, Lorenzo Luengo MC, Vicente P, Galindo P, Martín Casado AM. Comparison of the CIELab and CIEDE2000 color difference formulas. *J Prosthet Dent.* 2016 Jan;115(1):65-70.

47. Acar O, Yilmaz B, Altintas SH, Chandrasekaran I, Johnston WM. Color stainability of CAD/CAM and nanocomposite resin materials. J Prosthet Dent. 2016 Jan;115(1):71-5.
48. <http://radtech.org/2014proceedings/papers/technical-conference/Medical%20&%20Dental/Gorsche%20-%20Recent%20advances%20in%20monomers%20and%20photoinitiators%20for%20dental%20restoratives.pdf>
49. Ghinea R, Pérez MM, Herrera LJ, Rivas MJ, Yebra A, Paravina RD. Color difference thresholds in dental ceramics. J Dent. 2010;38 Suppl 2:e57-64.