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Color Stability of Resin Composites Depends on The Filler and Chemical Surface Composition – an *ex Vivo* Study

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Abstract. *Purpose*: To investigate the cumulative effect of optical color dental resin composites and how this relates to bulk filler content and surface filler particle exposure and (changes) in the chemical composition of the composite surfaces. *Methods*: The 30 days oral exposure of dental composites, including wear and brushing with toothpaste, on optical color changes of two direct (Beautifil II, Filtek Z350 XT) and one indirect dental resin composite (Estenia C&B) was evaluated. The composites were inserted in an acrylic palatal appliance, and how this relates to bulk filler content, surface filler particle exposure, and (changes) in the chemical composition of the composite surfaces was investigated. Color values (ΔE) were evaluated according to the *L, a, b*, color coordinate system (International Commission on Illumination). *Results*: Significant discoloration occurred in all composites and was caused by a slightly darker, more reddish, and yellowish appearance of the composite that was in general not impacted by the absence or presence of brushing. The discoloration ΔE is related to bulk filler content, but not with filler particle exposure at the surface. Major increases in %N observed after intra-oral wear yield the conclusion that amines (i.e., photo-co-initiator) diffuse from the bulk to the composite surface to attract discolorants. In the absence of significant and systematic effects of brushing or not brushing, the causative discolorant is presumably the photoinitiator camphorquinone, known to produce a yellowish hue. *Conclusions*: Color stability of dental resin composites might be improved by changing the two-component photoinitiator/co-initiator system.

Keywords: Photoinitiator/co-initiator, Camphorquinone, X-ray photoelectron spectroscopy**,** Color stability, Biomaterials

INTRODUCTION

Degradation of resin composites during intra-oral wear limits their functional and aesthetic lifetime and is attributed to the aggressive oral environment [1, 2]. Differences in matrix viscosities and degree of C=C conversion influence the composite ability to withstand degradation in the oral cavity [3, 4, 5, 6]. A higher degree of C=C conversion increases resin density by optimizing the filler-resin matrix cure and thus yields a better filler-silane-resin matrix bond. This, in turn, decreases the diffusion rate through the resin matrix [7, 8]. Low C=C conversion will affect the structural integrity of resin composites due to the unreacted monomer, potentially initiating oxidative processes [5, 8].

Any decrease in the structural integrity of a resin composite facilitates diffusion of beverage components, food debris, salivary enzymes, and microorganisms into the resin matrix yielding further degradation [9], leaching of residual monomer [10, 11, 12], and optical color changes. Twenty-four percent of failed restorations are replaced for aesthetic reasons [13].

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Optical color change of resin composites is mostly studied *in vitro* by exposing the composite surface to a single factor, such as water, beverages, or artificial saliva [14]. *In vitro* studies have thus shown that the ratio of camphorquinone and amine, used in visible-light activated resin composites as a two-component photoinitiator/co-initiator system, impacts optical color stability. On the one hand, increased ratios of camphorquinone over amine stimulate C=C conversion, and on the other hand, an excess of amines may attract discolorations [5].

In vitro studies neglect the multifactorial nature of the *in vivo* situation. It is unknown how intra-oral wear and tooth brushing influence the optical color stability and chemical composition of resin composites. Therefore, the goal of this study was to investigate the cumulative effect of 30 days of exposure to the human oral cavity on optical color changes of two direct and one indirect dental resin composites and how this relates to bulk filler content and surface filler particle exposure.

MATERIALS AND METHODS

Resin Composites

Custom-made acrylic palatal appliances were equipped with discs (diameter 5 mm wide and 2 mm thick) of three different resin composites. They are two direct, shaped, and polymerized in the oral cavity (Beautifil II and Filtek™ Z350 XT) and one indirect, polymerized outside the oral cavity (Estenia C&B). Resin composites were selected on the basis of differences in matrix composition and filler size and content for this study:

- Beautifil II (BT, Shofu Inc. Kyoto, Japan) is a direct nano-hybrid composite Bis-GMA/TEGDMA (bisphenol-A-glycidyl dimethacrylate/triethylene glycol dimethacrylate) with glass-ionomer particles (83 wt%, based on fluorboroaluminosilicate glass particles, 0.01-4.0 µm);
- Filtek™ Z350 XT (FL, 3M ESPE, Seefeld, Germany) is a direct hybrid composite of Bis-GMA, UDMA (urethane dimethacrylate), TEGDMA, PEGDMA (polydimethacrylate), bis-EMA (ethoxylated bisphenol-A dimethacrylate), nano-filled (79 wt%, based on 20 nm silica/zirconia particles);
- Estenia C&B (ES, Kuraray Noritake Dental Inc. Okuyama, Japan) is a conventional, indirect hybrid 'ceramic' polyurethane-methacryl composite and methacrylic acid monomers (92 wt%, aluminum microfiller, 2 µm with a high proportion of nanofiller (Silica, Zirconia, Aluminum, 2 nm), which was designed and polymerized by light curing and by adding heat in a dental laboratory, indirect restoration resin composite.

All selected composites make use of the camphorquinone/amine two-component photoinitiator/co-initiator system.

The superficial layers of resin composites BT, FL, and ES were covered with a 100 µm thick translucent mylar strip during curing and pressed in order to create a smooth surface and prevent the formation of an oxygen inhibition layer. The direct composites were light-cured (Woodpecker, 1000-1200 mW/cm^2) in direct contact with the mylar strip for 20 s. ES was light-cured for 30 s, followed by heat curing at 100-110°C for 15 min, all according to the manufacturers' instructions.

Study Design

The study design was set up as an *ex vivo,* cross-over within-volunteer comparison, which involved 16 healthy volunteers between 18-30 years of age. Inclusion and exclusion criteria are strictly controlled only by those with full maxillary dentition, controlled oral hygiene, and able to comply with the experimental protocol that was included. Prior to enrollment, verbal and written information was provided, and all volunteers were asked to voluntary-signed written informed consent. The approval of the study design was obtained from the Medical and Health Research Ethics Committee (MHREC) Faculty of Medicine, Universitas Gadjah Mada, Yogyakarta, Indonesia (Ref: KE/FK/1125/EC).

Volunteers were equipped with a removable palatal appliance containing three sample composite discs inserted in the surface of the appliance. The three composite discs were embedded 'anterior-posterior'. The 'anterior-posterior' position of the BT, FL and ES was randomized. To monitor wearing time, each appliance was equipped with a thermosensitive chip (TheraMon®, Orthosmart, Heerhugowaard, the Netherlands). Cut off the temperature of the palatal appliance was set up at 30°C, thereby the recorded temperature exceeding 30°C was categorized as 'wearing time'.

Oral Hygiene Regime and Randomization of Volunteers

The oral hygiene regime and randomization design of the volunteers were determined as described previously [30]. Briefly, 32 removable palatal devices appliance were prepared for use during two phases of randomization of absence and presence of brushing with fluoridated toothpaste. Each phase was completed for 30 days, with a washing period in between phases for 60 days.

In each phase, a different brushing regime was evaluated, in which 16 volunteers used 16 devices during two periods of 30 days. The order of the brushing condition was randomized as well and as a consequence, for each condition and resin composite evaluated. Based on the thermosensitive chip data, one volunteer was considered non-compliant. Hence, data from 15 specimens after 30 days were available for analysis. A CONSORT flow chart explains the enrollment, intervention allocation, follow-up, and which volunteers and specimens were finally available for data analysis during the different phases of the trial (Fig. 1).

CONSORT
TRANSPARENT REPORTING of TRIALS

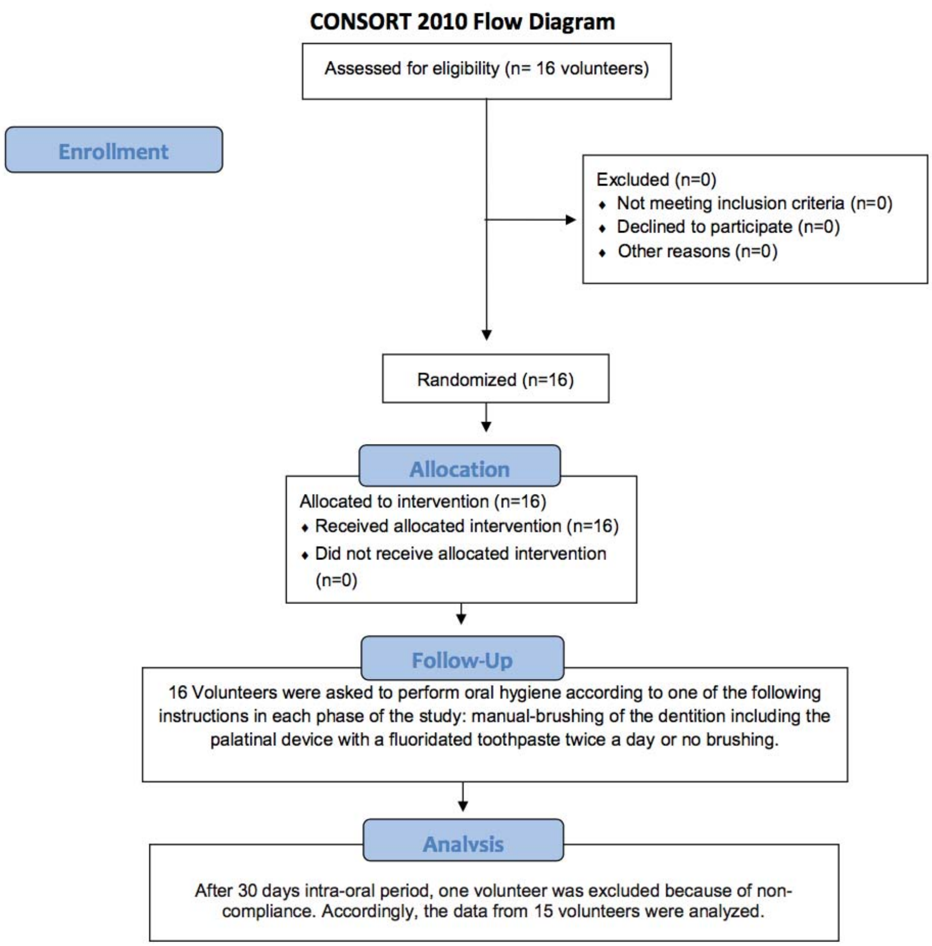


FIGURE 1. Consolidated Standards of Reporting Trials (CONSORT) 2010 flow diagram explaining enrollment, intervention allocation, follow-up, and data analysis.

Color Analysis

After 30 days of wear and brushing, the resin composites were carefully removed from the palatal appliance. Prior to color measurement, the biofilm was gently scraped off with a pocket probe from the composite surfaces and cleaned further by sonication five times for 1 min in demineralized water and dried in air. Composite sample surfaces were microscopically examined to confirm complete biofilm removal. The color of each composite was measured and compared to the color of the corresponding fresh composite using a customized, dark mini box studio connected to a digital camera (Canon Digital Ixus, Japan, 8 Mega Pixels). In order to standardize the capturing of the images of each specimen, the aperture size was set (F=2.8); capturing speed = 1/500 s; the intensity of light = 1/32; timer = 2 s. The camera was directed perpendicularly to the center of the resin composite disc, and the setting of the camera parameters was standardized for each specimen image captured. The color values were evaluated according to the International Commission on Illumination (CIE) by *L, a, b,* color coordinates system using the digital color meter application available on a Macintosh computer. The color difference between a fresh composite disc (t = 0) and 30 days old disc after wear and brushing (ΔE) was obtained using the following equation:

$$\Delta E = ((L_2\text{-}L_1)^2 + (a_2\text{-}a_1)^2 + (b_2\text{-}b_1)^2)^{1/2} \qquad (1)$$

The values of ΔL, Δa, Δb represent the change in *L, a, b,* respectively. Here, *L* represents the degree of grey (L = 0 is black, and L = 100 is white), the *a* scale runs from red (+*a*) to green (-*a*), and the *b* scale runs from yellow (+*b*) to blue (-*b*). ΔE accounts for the numerical distance between *L, a*, and *b* coordinates before and after exposure to the oral cavity. Note that ΔL, the greyscale is the absorption of light in the composite, which is a bulk property [15].

X-Ray Photoelectron Spectroscopy

To determine filler exposure prior to and after intra-oral wear and the chemical composition of the composites, X-ray photoelectron spectroscopy was carried out as described previously [30]. Scanning was made with a 1000 x 250 µm spot at a resolution of 150 eV in the range of 1-1200 eV, after which narrow scans were made of the C_{1s} (280-300 eV) electron binding peak. The C_{1s} peak was decomposed in 4 components (1: C-C at 284.8 eV, 2: C-N/C-O at 286.3 eV, 3: C=O/O-C-O at 288.1 eV, and 4: O-C=O at 289.5 eV) with a full width at half maximum set at 1.4 eV, whereas the O_{1s} was decomposed in 2 components (C=O at 531.5 eV and C-O/C-O-C at 532.7 eV) with a full width at half maximum setting voltage at 1.7 eV.
SiO_2 was the most predominant component in all filler particles and was used for calculation of the surface filler exposure at the surface, using the following approach:

$$\%O_{filler} = 2 \text{ x } \%Si_{measured} \qquad (2)$$

hence:

$$\{O_{matrix}/C_{matrix}\}_{experimental} = (\%O_{measured} - 2 \text{ x } \%Si_{measured})/\%C_{measured} \qquad (3)$$

$$\{O_{matrix}/C_{matrix}\}_{experimental} = \%matrix_{exposed} \text{ x } \{O_{matrix}/C_{matrix}\}_{theoretical} \text{ x } 100\% \qquad (4)$$

from which it can be calculated that:

$$\%filler_{exposed} = 100\% - \%matrix_{exposed} = 100\% - [\{O_{matrix}/C_{matrix}\}_{experimental} / \{O_{matrix}/C_{matrix}\}_{theoretical}] \text{ x } 100\% \qquad (5)$$

in which $\%Si_{measured}$, $\%O_{measured}$, $\%C_{measured}$ are directly measured using XPS, $\%O_{filler}$ is the percentage oxygen due to silica filler particles calculated, $\{O_{matrix}/C_{matrix}\}_{theoretical}$ is the O/C ratio that can be calculated theoretically from the molecular composition of methacrylates and urethanes in the composites (taken here as 0.35).

Statistical Analysis

A parametric Student's *t* test was used to evaluate the differences between the color parameters (ΔE, ΔL, Δa, Δb), elemental surface compositions and $\%filler_{exposed}$ during intra-oral wear in absence and presence of brushing, and as compared to prior to intra-oral wear. Tukey's test following one-way ANOVA was used to evaluate differences between BT, FL, ES and the respective other composites during intra-oral wear in a given brushing regime. The assumption of the equality of variances (Levene's test) and normal distribution of errors (Shapiro-Wilks test) was checked. Transforming data (square root or log transformation) was needed if the assumption was violated. The confidence level was set at 95%. The statistician was blinded with respect to the brushing regime used by the volunteer. All statistical analyses were performed in IBM SPSS Statistics, Version 22 (IBM Corp).

RESULTS AND DISCUSSIONS

The mean wearing time in the group of 15 volunteers ranged between 17-23 h per day. The mean color changes ΔE for all combinations of different brushing regimes, and resin composites are presented in Table 1.

TABLE 1. Mean change (ΔE, ΔL, Δa, Δb ± standard deviations) in color upon 30 days wear in absence and presence of toothpaste brushing *versus* freshly prepared samples for different resin composites (n = 15 volunteers for each material and brushing regime). BT is Beautifil II, FL is Filtek Z350 XT, and ES stands for Estenia C&B.

Brushing regime	BT	FL	ES
	ΔE		
No brushing	2.7 ± 0.8	3.3 ± 1.0[c]	2.0 ± 0.8[c]
Brushing with toothpaste	2.6 ± 1.4	3.0 ± 1.0	2.6 ± 1.2
	ΔL		
No brushing	-0.5 ± 1.0	-0.7 ± 0.9	-0.8 ± 0.7[a]
Brushing with toothpaste	-0.1 ± 1.3[b]	-0.9 ± 1.0	-1.7 ± 0.9[b]
	Δa		
No brushing	0.7 ± 0.4[b]	1.3 ± 0.4[b]	1.0 ± 0.4
Brushing with toothpaste	0.5 ± 0.4[b,d]	1.2 ± 0.4[b]	1.0 ± 0.6[d]
	Δb		
No brushing	2.1 ± 1.4	2.5 ± 1.4[c]	1.0 ± 1.1[c]
Brushing with toothpaste	1.3 ± 2.2	2.3 ± 0.8	0.4 ± 1.7

[a] indicates a statistically significant difference between the color parameters in the absence and in the presence of brushing during intra-oral wear ($p < 0.05$, Parametric Student's *t* test).
[b, c, d] indicate statistically significant differences ($p < 0.05$, Tukey's test following one-way ANOVA) between BT, FL, ES and the respective other composites during intra-oral wear in a given brushing regime.

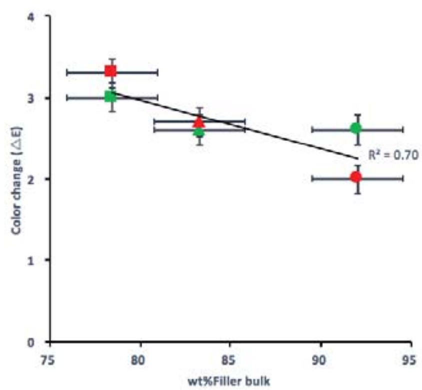
All composites showed various degrees of color change ΔE, that were significantly different from zero. FL had the highest color change (3.2, averaged over both brushing regimes), whereas ES had the lowest averaged color change (2.3). The brushing regime did not have a significant effect on the color change ΔE of any given composite types. All composite resins showed negative ΔL values, implying that they all became slightly (but not statistically significant) darker after 30 days of intra-oral wear, regardless of the brushing regime in two out of the three composite types. The Δa and Δb showed positive values in all composites that were significantly different from zero. It indicated color shifts towards red and yellow, respectively, with no influence of the brushing regime.

TABLE 2 The most occurring elemental surface compositions of the three composites prior to and after intra-oral wear under different brushing regimes and the decomposition of the C_{1s} and O_{1s} photoelectron binding energy peaks. n equals three samples for data prior to intra-oral wear yielding an average SD over all elements of 2%, and n equals 15 samples after intra-oral wear in different volunteers yielding an average SD over all elements of 0.5%. BT is Beautifil II, FL is Filtek Z350 XT, and ES stands for Estenia C&B.

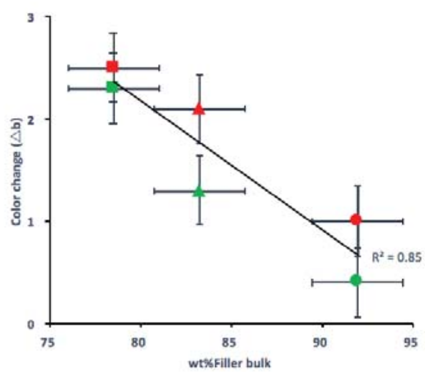
Composite	Prior to intra-oral wear									
	%C	%O	%Si	%N	%C1	%C2	%C3	%C4	%O1	%O2
BT	59.0	24.4	4.0	2.3	42.4	11.0	5.6	0.2	15.8	8.6
FL	56.4	28.2	9.2	3.7	41.2	9.8	4.9	0.6	9.7	18.5
ES	59.0	25.0	6.2	3.0	46.2	7.4	5.2	0.3	17.4	7.7
Composite	**After intra-oral wear, no brushing**									
BT	64.9[b]	21.9	3.2	6.6[a]	38.5	17.4[a]	7.6	1.5[a]	10.5[a,b]	11.5
FL	62.1	23.6[a]	4.5[a]	7.4[a]	35.4	17.4[a]	7.8[a]	1.5[a]	11.1	12.6[a]
ES	60.5	23.3[b]	5.4	7.1[a]	36.4[a]	15.2[a]	7.4[a]	1.5[a]	11.8[a]	11.5
Composite	**After intra-oral wear, toothpaste brushing**									
BT	60.9	23.9	4.4	6.8[a]	34.8[a]	17.0[a]	7.4	1.6[a]	12.0[a]	11.9[a]
FL	61.5	24.1	5.4[a]	7.0[a]	35.9	16.8[a]	7.3[a]	1.6[a]	10.8	13.3[a]
ES	57.4	25.3	6.7	6.9[a]	32.6[a]	16.6[a]	7.3[a]	1.4[a]	12.2[a]	13.1[a]

[a] indicates a statistically significant difference between the elemental compositions in the absence and presence of brushing during intra-oral wear ($p < 0.05$, Parametric Student's *t*-test) as compared to the elemental composition prior to intra-oral wear.
[b] indicates a statistically significant difference between the elemental compositions in the absence and presence of brushing during intra-oral wear ($p < 0.05$, Parametric Student's *t*-test).

In Table 2, the elemental surface compositions of the different composites prior to and after intra-oral wear are presented. The elemental composition after intra-oral wear became relatively similar for all composites. In general, the %Si decreased significantly after intra-oral wear and was not impacted by the brushing regime for all composites. Similarly, the %N increased significantly by a factor 2 to 3 for all composites after intra-oral wear, again with no statistically significant impact of the brushing regime. Also, the functionalities in which the carbon was involved changed after intra-oral wear, and the $\%C_2$ (C-N/C-O at 286.3 eV) and $\%C_3$ (C=O/O-C-O at 288.1 eV) increased significantly, regardless of the brushing regime.

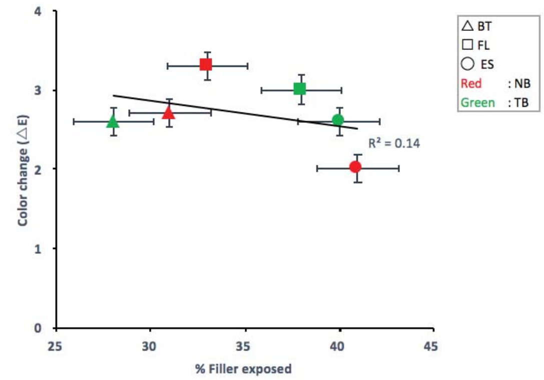


Axis	Mean	SD	SE	95% confident interval	
				upper bond	lower bond
X	84.70	6.12	2.50	89.60	79.60
Y	2.70	0.44	0.18	3.06	2.34

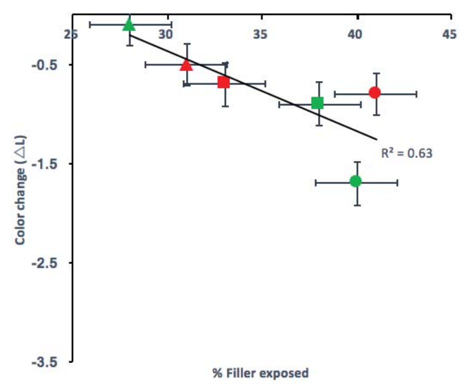


Axis	Mean	SD	SE	95% confident interval	
				upper bond	lower bond
X	84.70	6.12	2.50	89.60	79.60
Y	1.60	0.83	0.34	2.28	0.92

(a)



Axis	Mean	SD	SE	95% confident interval	
				upper bond	lower bond
X	35.17	5.27	2.15	39.47	30.86
Y	2.70	0.44	0.18	3.06	2.34



Axis	Mean	SD	SE	95% confident interval	
				upper bond	lower bond
X	35.17	5.27	2.15	39.47	30.86
Y	-0.78	0.53	0.22	-0.35	-1.22

(b)

FIGURE 2. wt%Filler$_{bulk}$ as given by the manufacturer as a function of the color changes (ΔE and Δb) prior to and after intra-oral wear, under different brushing regimes (NB: no brushing, TB: brushing with toothpaste) **(a)**. %Filler$_{exposed}$ derived from XPS data after intra-oral as a function of the color changes (ΔE and ΔL) prior to and after intra-oral wear, under different brushing regimes (NB: no brushing, TB: brushing with toothpaste) **(b)**.

In Fig. 2, the optical color changes ΔE and Δb have been related to the wt%filler$_{bulk}$ given by the manufacturer and assumed to correspond with the wt%filler in the bulk composite. Δb decreases significantly with wt%filler$_{bulk}$ from over +2 to almost zero for ES, indicating less yellowish discoloration when the wt%filler$_{bulk}$ increased. Moreover, the difference between Δb in the absence and in the presence of brushing increased with increasing wt%filler$_{bulk}$. For ΔL and Δa no relations were observed with the wt%filler$_{bulk}$, which explains why the color change ΔE shows only a decreasing trend with the wt%filler$_{bulk}$ with a lower correlation coefficient than observed for Δb.

TABLE 3. %Filler$_{exposed}$ derived from XPS data of the three composites prior to and after intra-oral wear, in the no brushing and toothpaste brushing regime (for XPS data, see Table 2). ± signs indicate SD values, with n equal to three samples for data prior to intra-oral wear equal 15 samples after intra-oral wear in different volunteers. BT is Beautifil II, FL is Filtek Z350 XT, and ES stands for Estenia C&B.

Composite	Prior to intra-oral wear (%)	After intra-oral wear (%)			
		no brushing		toothpaste brushing	
		Contact angle	XPS	Contact angle	XPS
BL	20 ± 13	48 ± 13	31 ± 17[a]	37 ± 13	28 ± 18[a]
FL	50 ± 7	35 ± 18	33 ± 14[a]	37 ± 17	38 ± 16[a]
ES	39 ± 2	39 ± 16	41 ± 14	40 ± 15	40 ± 18

[a] indicates a statistically significant difference between the %filler$_{exposed}$ in the absence and in the presence of brushing during intra-oral wear ($p < 0.05$, Parametric Student's *t* test) as compared to the %filler$_{exposed}$ prior to intra-oral wear. There is no statistically significant difference between the elemental compositions in the absence and in the presence of brushing during intra-oral wear.

Table 3 summarizes %filler$_{exposed}$ reflecting surface-exposed filler particles as derived from the XPS data using equation 3-5 prior to and after intra-oral wear. Filler exposure increased significantly after intra-oral wear in all composite types, without a statistically significant impact of absence or presence of brushing. There is little or no relation between %filler$_{exposed}$ and the optical color change ΔE (Fig. 3), as observed versus wt%filler$_{bulk}$ (compare Fig. 2 and Fig. 3). ΔL shows a minor decreasing trend with %filler$_{exposed}$ (Fig. 3), and for Δa and Δb no relations were observed with %filler$_{exposed}$.

Physical, mechanical, and chemical properties of dental composite resins vary between types and brands and change over time during intra-oral wear [4, 11, 16] through a multitude of factors underscoring the complexity of intra-oral degradation. The particulate resin composites focused on in the present study were chosen for their worldwide use in modern aesthetic dentistry today and specifically for their similarity in photoinitiator/co-initiator (CQ/amine) system difference in monomer formulation and filler amount.

Most composite discoloration studies are carried out *in vitro* by immersion of a resin composite in water or beverages such as tea, coffee, wine [17, 18, 19], mouthrinse [20], and simulated anthocyanin pigment [21]. However, this situation does not represent the clinical situation in which there are many other factors simultaneously at work, such as the temperature of the beverages [22], smoking, type of food [23], salivary contact, oral biofilm coverage, and tooth brushing. This makes the present study stand out from others.

From a clinical point of view, degradation relates mainly to mechanical and aesthetic aspects, such as fracture, marginal disintegration, and discoloration [13]. Here we demonstrate that discoloration ΔE of a dental composite, as a major factor in the aesthetic performance of composite restorations, after 30 days of intra-oral wear relates with its bulk filler particle content, but not with the filler particle exposure at the surface. In all three composites evaluated, discoloration was due to $\Delta L < 0$ (slightly darker), $\Delta a > 0$ (slightly more reddish) and $\Delta b > 0$ (slightly more yellowish). Yellow discoloration became less when the wt%filler$_{bulk}$ increased (Fig. 2) and was always accompanied by a doubling or tripling of the %N exposed at the surface of the composite. In general, the absence of brushing had no impact on discoloration.

Discoloration of restorative material is a change in color affecting the appearance of restoration and can be calculated as ΔE. In the oral environment, the color change is caused by a combination of intrinsic and extrinsic factors. Intrinsic factors are, for instance, the ratio camphorquinone/amine, the degree of C=C conversion, and the filler size, whereas food, colorants in beverages [24, 25], cigarette smoking [26], oral biofilm [27], and mechanical wear due to habitual oral hygiene are categorized as extrinsic factors.

Theoretically, a material is classified as color stable if $\Delta E = 0$ in time. The present study demonstrated that all resin composites showed measurable discoloration, regardless of the absence or presence of tooth brushing. The color change ΔE observed after 30 days of intra-oral wear) varied between 2.0 – 3.3 (Table 1), comparable to what was found *in vitro* after two months of immersion of resin composites in water. This magnitude of change has clinical relevance, although there is no consensus regarding perceptibility thresholds and acceptability thresholds for color differences. Many reports defined perceptibility thresholds at $\Delta E = 1$, and acceptability thresholds at $\Delta E = 3.7$ [28]. Hence the color differences observed after this relatively short observation period of 30 days can be classified as perceptible but still acceptable.

Concurrent with the color changes ΔE observed across all composite types after intra-oral wear, was a general two to three-fold increase in %N and %filler$_{exposed}$. The changes were generally not impacted by the absence or presence of tooth brushing, indicating that they reflect intrinsic changes in the composite/at the composite surface. Therefore, brushing with toothpaste should not be categorized as a factor causing discoloration but as a control measure to prevent extrinsic staining. i.e., diffusion of discolorants from beverages or saliva into the composite.

Optical color stability ΔE has been attributed in the past to a high %filler particle [29]. The present study fully confirms this (compare the wt%filler in the bulk as given by the manufacturer with the ΔE values in Table 1). However, no confirmation can be obtained from the %filler exposed at the surface, which attests to the fact that color is as much, if not more, a bulk property, i.e., controlled by bulk properties, rather than a surface-associated one. Higher color stability with the number of filler particles in bulk can be simply explained by the fact that filler particles are not prone to any chemical degradation of absorption process like the composite matrix, while furthermore filler particles in the bulk of a composite are known to hamper diffusion of discolorants through the matrix. Most current composite matrixes are based on methacrylate chemistry and are more prone to chemical degradation by acids and esterase [30].

In the bulk composite, excess of amines as the co-initiator in the two-component photoinitiator/co-initiator system may attract discolorants [31, 32]. Major increases in %N were observed after intra-oral wear using XPS. Yield the conclusion that amines diffuse from the bulk to the composite surface to attract discolorants to yield a predominantly yellow discoloration (see Δb values in Table 1). In the absence of a significant and systematic effect of the absence or presence of brushing, the causative discoloration is presumably the photoinitiator camphorquinone, known to produce a yellowish hue [32]. This suggests that the color stability of dental resin composites might be improved by finding a proper replacement of the traditional two-component photoinitiator/co-initiator.

Future perspective for another alternative of improvement could be by replacing the current methacrylate-based matrix. Recently, the new degradation-resistance matrix system compared to the current methacrylate chemistry-based matrix has been developed, derived from Oxirane/Acrylate interpenetrating polymer network restorative resin System (OASys) [33].

Since more than five years ago, an effort to find better alternatives photoinitiator/co-initiator system has already been initiated. The photoinitiator systems derived from phosphine oxides formulated with the methacrylate monomers matrix have been evaluated, finding diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide to be satisfactory with a $\Delta E < 3.3$ after 1-month immersion of composites in water [34]. Although the discoloration observed with this photoinitiator system was called "satisfactory," it is indeed within the acceptability threshold [28]. A $\Delta E < 3.3$ is above the perceptibility threshold and still comparable to what we found after 30 days of intra-oral wear of composites with the traditional camphorquinone/amine two-component system. This demonstrates that the quest for a better photoinitiator/co-initiator system is not over yet, and the results from the present study stress the need for better alternatives.

CONCLUSION

In the absence of significant and systematic effects of brushing or not brushing, the causative discoloration is presumably the photoinitiator camphorquinone, known to produce a yellowish hue. This suggests that the color stability of dental resin composites might be improved by changing the two-component photoinitiator/co-initiator system, and various alternatives of improvement would be a toward a direction for future research.

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