



Effect of Different Bleaching Materials On Color of Stained Resin Composite By Photocatalytic Treatment

Ameer AL-Ameedee^{1,2}, Hala Ragab¹, Essam Osman¹, Ziad Salameh³,
Roland Habchi⁴ and Ayad F. Alkaim^{5*}

1. Faculty of Dentistry, Beirut Arab University, Beirut, **LEBANON**

2. Faculty of Dentistry, Babylon University, Hila, **IRAQ**

3. School of Dentistry, Lebanon University, Beirut, **LEBANON**

4. Nano sciences and Nanotechnologies, Lebanon University, Beirut, **LEBANON**

5. College of Science for women, Babylon University, Hila, **IRAQ**

Email: ayad_alkaim@yahoo.com

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ABSTRACT

In this work, ZnO, and TiO₂ (Hombikat UV 100) and TiO₂ doped with 0.5 % of Pt, and Pd metals, that prepared by photo deposition method. The bare TiO₂ and prepared samples were characterized by powder X-ray diffraction (XRD), UV-vis diffuse reflectance spectra (UV-vis DRS), nitrogen adsorption BET, and atomic force microscopy (AFM) were evaluate the effect of photochemical activation by kinds of semiconductors (ZnO, TiO₂, Pt/TiO₂, and Pd/TiO₂) in bleaching gels with UV-light type A, with the purpose of accelerating the process of pigmented component oxidation on Filtek Z350XT resin composite (3M ESPE). The bare catalysts and metal doped prepared where testing by taken twenty-five disc-shaped of the Filtek Z350XT resin composite specimens (3M ESPE) were used in this study, then immersion in tea staining solutions, after that they were randomly divided into five groups specimens (each group n = 10) according to the type of whitening chemical materials treatment applied (ZnO, Pt/TiO₂, TiO₂, Pd/TiO₂ and TiO₂/UV 100). The color measurements were taken: at baseline, after immersion and after chemical treatment procedures by using a stereomicroscope (vita easy shade device). The results recorded, tabulated and statwastically analyses. The results showed the highest mean color difference ΔE values were: group two Pt/TiO₂, group three TiO₂, group five TiO₂ / UV 100, Pd/TiO₂ and group one ZnO respectively. However, there was no statistically significant difference in-group three TiO₂. In addition, a whitening effect was demonstrated with group two Pt/TiO₂ and group five TiO₂ / UV 100 showed statistically significant lowest in a color space compared to others groups. In addition, results show immersion tea staining solutions had a positive influence on the color changes of resin composite.*

Keywords: ZnO, Pt/TiO₂, TiO₂, Pd/TiO₂, bleaching.

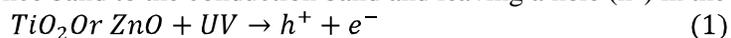
INTRODUCTION

Resin composites made for the field of dentistry in the 1940s, as aesthetic rather than a functional problem. Resin composites are widely used because of their good property as aesthetics, adequate strength, moderate cost compared to the ceramics, and their ability to bond to the tooth structure. Color matching

of resin composite restorations with the tooth color was good because of wide range of available color shades. In addition, the appearance of microfilled and Nano filled types of resin composites give restorations with a nice surface finish and a smooth texture to make a more natural appearance.[1, 2]

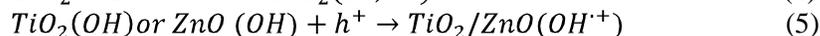
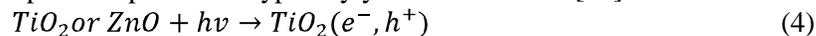
The dental resin composite restorations success mainly depend on their color stability and surface properties. However, discoloration after prolonged exposure to the oral environment filed was still a major challenges, leading to an miss color match of the restoration, patient dissatisfaction and replacement[3]. The amount of color change may be affected by a many of factors, the structure of resin composite including, the filler particles characteristics, the degree of conversion and water sorption. Colored food materials and drinks, smoking habits and oral hygiene are also important causes affecting the color of resin composites. Finishing and polishing procedures may also influence resin composite surface quality. Finally, roughening of the surface caused by wear may be affect the gloss and, consequently, increase extrinsic staining[4]. Different methods to remove superficial stains from resin composite restorations. For example, tooth- brushing, polishing techniques or bleaching procedures using the commercially available bleaching [5]. The tooth brushing was a slower process in removal of stains. Therefore, it was preferred to use more rapid methods, either polishing or bleaching techniques[6]. However, polishing procedures might could not restore resin composite restorations to their original color. This may be because of the deep penetration of stains into the surface. Polishing act by removal layers from the surface of the resin composite material restoration and increase the surface roughness of the restoration. While dental bleaching appears to be a non-destructive method in the removal of stains [6] and became more popular for whitening stained teeth[7]. As dental bleaching might safer for dental tissues, they might not be entirely harmless for the resin composite material which has a high erosive or degenerative characteristics, [8] and effects by the decomposition of their peroxide content into free radicals, these free radicals undergo oxidation or reduction reactions which could affect the teeth and the resin composite restorative materials[7].

Recently, studies revealed the effectiveness of TiO_2 as a bleaching agent because of its oxidizing capacity on the components responsible for tooth discoloration. These studies said that it was a fast, effective and harmless method in teeth whitening. Therefore, it was important to clarify the effect of the bleaching with TiO_2 and other materials as ZnO on the color change of stained resin composite surface. Titanium dioxide (TiO_2) was a white pigment of inorganic constitution, chemically inert and thermally stable, and has high power of reflectance and opacity. When present in the composition of the bleaching agent it seems to have the same function as the colorants because when it was irradiated with blue light, its electrical charge undergoes alteration resulting in destabilization of hydrogen peroxide[9]. Another property that TiO_2 seems to present was its greater absorption of light by the gel. This phenomenon consists of the capacity of the pigment to scatter light in the adjacent areas due to refraction and diffraction. However, nothing has yet been proved. Moreover, ZnO , and TiO_2 was a photocatalysts under ultraviolet rays[9]. This interaction between UV light and TiO_2 has been extensively studied for the treatment of polluted water. The mechanism of the UV/ TiO_2 or UV/ ZnO process has been discussed extensively in the literature. When TiO_2 or ZnO was irradiated with light energy equal to or higher than its band-gap, an electron (e^-) can be promote from the valence band to the conduction band and leaving a hole (h^+) in the valence band



In aqueous phase, the photo-induced h^+ was apparently capable to oxidize surface hydroxyl groups or surface-bond water-molecules to produce nonselective and highly reactive hydroxyl radicals (OH^\cdot) step (2). The OH^\cdot radicals are considered to be the dominant oxidizing species contributing to the photocatalytic degradation of organic substrates [10]. Nevertheless, the e^- can recombine with the h^+ step (3), causing a decrease in the availability of the photoinduced h^+ [11]. Therefore significant enhancements in photo catalytic activity have been reported in TiO_2 materials modified by the surface deposition of

metals [12]. The presence of a metal at the surface of TiO₂ results in the formation of a Schottky barrier at the metal-semiconductor interface, which facilitates the interfacial electron transfer and subsequently encourages the charge carrier separation and can trap the photo-generated electrons efficiently[13]. This process of metal doping was described by the series of reactions (4)–(6). Depending on the preparation conditions, this photo-deposition procedure typically yields small metal[14].



Where Mⁿ⁺ was metal ion doped.

The aim of the present study was to evaluate the effect of photochemical activation by kinds of semiconductors (ZnO, TiO₂, Pt/TiO₂, and Pd/TiO₂) in bleaching gels with UV-light type A, with the purpose of accelerating the process of pigmented component oxidation.

MATERIALS AND METHODS

Materials: Zinc Oxide, Titanium dioxide UV100 was commercially available and can be obtained from (Sachtleben Chemie, Germany), palladium (II) chloride (99.9% Aldrich), and hexachloroplatinic acid hexahydrate (Alfa Aesar), have been used without further purifications.

Preparation of Metal Loaded TiO₂: M/loaded TiO₂ was prepared by suspending 1.0 g of TiO₂ powder in 100 mL of (1% methanol/deionized water) by sonication for three minutes, followed by the addition of the desired amount of as-prepared colloidal metal under continuous magnetic stirring. The reaction vessel was then irradiated with the light intensity of 1 mW.cm⁻² (Philips 4 lamps) under inert environment by purging with argon gas overnight [15]. After irradiation, the obtained powder was washed with deionized water several times and then dried overnight in an oven at 60 °C.

Samples preparation: Twenty-five disc-shaped resin composite specimens Filtek Z350XT (Color shade A3, 3M ESPE) were used in this study. The specimens were prepared in a split teflon ring. The resin composite was bulk packed inside the hole of the split teflon ring that supported by the copper ring using the manufacturer's plastic spatula. Two transparent polyester strips (Myler; Henry Schien, Melville, NY, USA) covered with two glass microscope slides were placed at the top and bottom of the ring.

To adapt the resin composite inside the ring and achieve a smooth surface finish, the two glass slides were gently compressed together from both ends of the slides with the thumb and index fingers of one hand to expel the excess material. The specimens were allowed to polymerize while compressed between the two glass slides for 40 seconds exposure time to the top and bottom surfaces respectively, using a light polymerizing unit (Light cur unit halogen light, GNATUS, Fotopolimerizador optilight plus, Brasil.)

With mean light intensity of 460 mW/cm². For the purpose of standardization for the distance between the light source and the specimens, the tip of the light source placed in contact with the cover glass which was 2 mm thick during light polymerization. All specimens kept dry at room temperature until all fabricated. The specimens after stored in distilled water for one week at 37 °C to insure complete resin polymerization we taken the first color measurements then all fabricated discs immersion in the tea staining solutions: tea (Yellow Label tea, Lipton, Rize, Turkey) with distal water (Glandosane, Cell Pharm GmbH, Medical Park, Hannover, Germany) for one week at 37 °C. The specimens then removed from the immersion solutions and gently rinsed with distilled water for one minute and air dried before taken the second color measurements. the temperature control by using water path unit (PORTEX LTD. Hythe Kent England ID; 75302).

Chemical bleaching materials: The photocatalytic experiments of bleaching materials were conducted under ambient atmospheric conditions and at natural pH using Philips mercury lamp UV (A) 365 nm,

contains four lamps of 15 W for each one (Germany) as the light source, The incident photon flux (2 mW.cm^{-2}) was determined by UV-meter (Dr.Honle). For each run, 0.03 g of materials powders was dispersed in 20 mL aqueous solution containing of second color measurements. Prior to the beginning of irradiation, the mixture was allowed to equilibrate in the dark with stirring for 5 minutes, then dried and measured the optical properties.

Color measurements: The color of all specimens was measured before immersion in tea stain solution (baseline), after immersion and also after chemical materials treatment procedures by use a stereomicroscope: vita easy shade device (VITA Zahnfabrik H.Rauter GmbH & Co. KG, Bad Säckingen, Germany) using the Commission Internationale de l'Eclairage (CIE Lab) color space system which provides information about the location of an objects color in a uniform three-dimensional color space. It quantifies the color in terms of three coordinates values L^* , a^* and b^* where L^* represents brightness or lightness (value), which means the position of the object on the white/black axis while a^* and b^* correlates both for hue and chroma; a^* represents the position of an object in the red/green axis and b^* represents the position on the yellow/blue axis. The total color difference (ΔE) calculated according to the following equation:

$$\Delta E^* = [(L_O^* - L_I^*)^2 + (a_O^* - a_I^*)^2 + (b_O^* - b_I^*)^2]^{1/2}$$

Where ΔE^* = color change, L^* = luminance reflectance, a^* = red-green color coordinates, b^* = yellow-blue coordinate, O = baseline, I = treatment interval.

Characterization of materials prepared: X-ray diffraction (XRD) data for the Rietveld phase analysis of TiO_2 had been recorded on a Phillips PW1800 diffract meter using reflection geometry with variable divergence slits, $\text{Cu-K}\alpha 1$, and a secondary monochromator. The phase analysis by the Rietveld method was carried out by using the TOPAS 2.0 (Bruker AXS) software. The average crystallite sizes of samples were quantitatively calculated using Scherrer formula after correcting the instrumental broadening. All samples were degassed at 110°C prior to nitrogen adsorption measurements. The Brunauer–Emmett–Teller (BET) surface area (SBET) of the powders was analyzed by nitrogen adsorption using a Micrometrics ASAP 2020 nitrogen adsorption apparatus (USA). Micrometrics flow sorb. II 2300 GR nitrogen adsorption apparatus (USA). All measurements for the surface area were repeated three times and the average for these measurements was calculated. UV–vis diffused reflectance spectra of the samples were obtained for the dry-pressed film samples using a UV–vis spectrophotometer (Varian Cary 100). Lab sphere USRS-99–010 BaSO_4 was used as a reflectance standard in a UV–vis diffuse reflectance experiment. The surface morphologies of the films were investigated by a (NTMDT) Solver (P47-PRO) scanning probe microscope operating in the contact atomic force microscopy (AFM) mode with a scan speed of 1 Hz.

Statistic analysis: A randomly selected sample from each treatment group was used to examine color changes. This assessment was performed using a vita easy shade. The data for color and measurements were collected, tabulated and statistically analyzed. Data were presented as mean, standard deviation (SD) which was a measure of variation between values, which was a measure values. LDE and Bonferroni post hoc test was used for pairwise comparison between the means when the ANOVA test was significant. The significance level was set at $p = 0.05$. Statistical analysis were performed with SPSS 20.0 (Statistical Package for Scientific Studies Inc., Chicago, IL, USA) for Windows.

RESULTS AND DISCUSSION

Characterization of materials: Characterizations of materials prepared have been done in our previous work[16]. X-ray diffraction (XRD) was considered one of most important properties affecting photo catalytic efficiency of TiO_2 . [17] For TiO_2 (anatase type), the major peaks were observed at 2θ values of 25.3° , 48.2° , 55.0° and 62.6° which are assigned to (101), (200), (220), (211) and (204) reflections of

anatase [18]. Figure 1 showed the XRD patterns of undoped TiO₂ and each M/TiO₂ sample, the results indicate that the doping of metals (Pt, and Pd) had no deleterious effect on the crystal phase of TiO₂[19]. Might be there were two factors could cause this result, one was that the deposited metals " Pt, Pd" were highly dispersed in the support matrix, the other was the percentage of metals were too low[20]. The diffraction peak corresponding to 101-crystal plane of each sample was selected for calculating the crystal size by using the Scherrer equation step (8). for the peak (101) reflection at 2θ (25.40) by using the full width at half maximum (fwhm) [21], the results are illustrated in table 1.

$$P = \frac{k\lambda}{\beta \cos\theta} \quad (8)$$

Crystal size (P) can be estimated based on the peak width (B) giving a shape factor (k) of 0.9, λ (the wavelength of the CuKα 1 x-ray source) of 0.1541 nm, β (full peak width at half maximum corrected for instrumental broadening).

Specific surface areas BET: Specific surface areas of the undoped TiO₂ and the M/TiO₂ samples with different doping elements were measured and the results are shown in Table 1. As shown in Table 1, the surface area strongly depends on the kind of metals doping. The surface area of the doping metals decreased as follow Pt/TiO₂, Pd/TiO₂, this was decreasing depend on the density of metals doping. The decrease in the crystallite size of doped samples leads to an increase in the surface area of the catalyst as compared to the undoped sample[22].

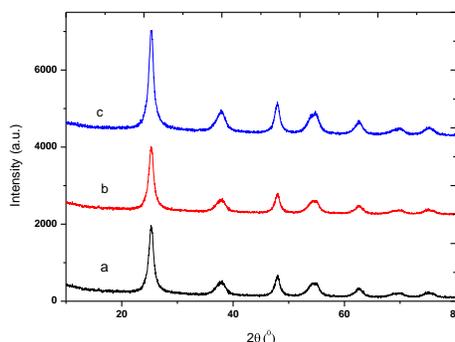


Figure 1: The XRD spectra of ((a) TiO₂; (b) Pt/TiO₂; (c) Pd/TiO₂).

Table 1: physicochemical properties of undoped and Pt, Pd, Rh, and Ru doped titanium catalyst

Sample	Crystalline size ^a (nm)	Surface area ^b (m ² .g ⁻¹)	Average diameter ^c (nm)	Band gap ^d (e.v.)
TiO ₂	8.13	250	82.44	3.17
Pt/TiO ₂	8.21	223	59.55	3.16
Pd/TiO ₂	8.29	225	65.38	3.16

a Average crystallite size determined by XRD using the Scherrer equation. b Specific surface area data calculated from the BET method. c Average diameter calculated from the AFM method. d Band gap calculated from uv-vvisible absorbance by depending on Kubelka–Munk equation.

Atomic Force Microscopy AFM: Figure 2 displays typical AFM images of TiO₂ and M/TiO₂ films. It can be seen that these films are quite uniform. In compared with TiO₂ thin films, the surfaces grain sizes and the average surface roughness of M/TiO₂ ones decrease. The particle-size distributions of TiO₂ and metals doping on TiO₂ films in AFM images were about 55–82 nm, much greater than the crystallite sizes calculated from the XRD results. The increase in the crystallite sizes of TiO₂ particles in AFM results was due to the aggregation of the primary crystallites [23]. The surface roughness and the average diameter were observed to slightly affecting on addition of metals deposition as shown in table 1.

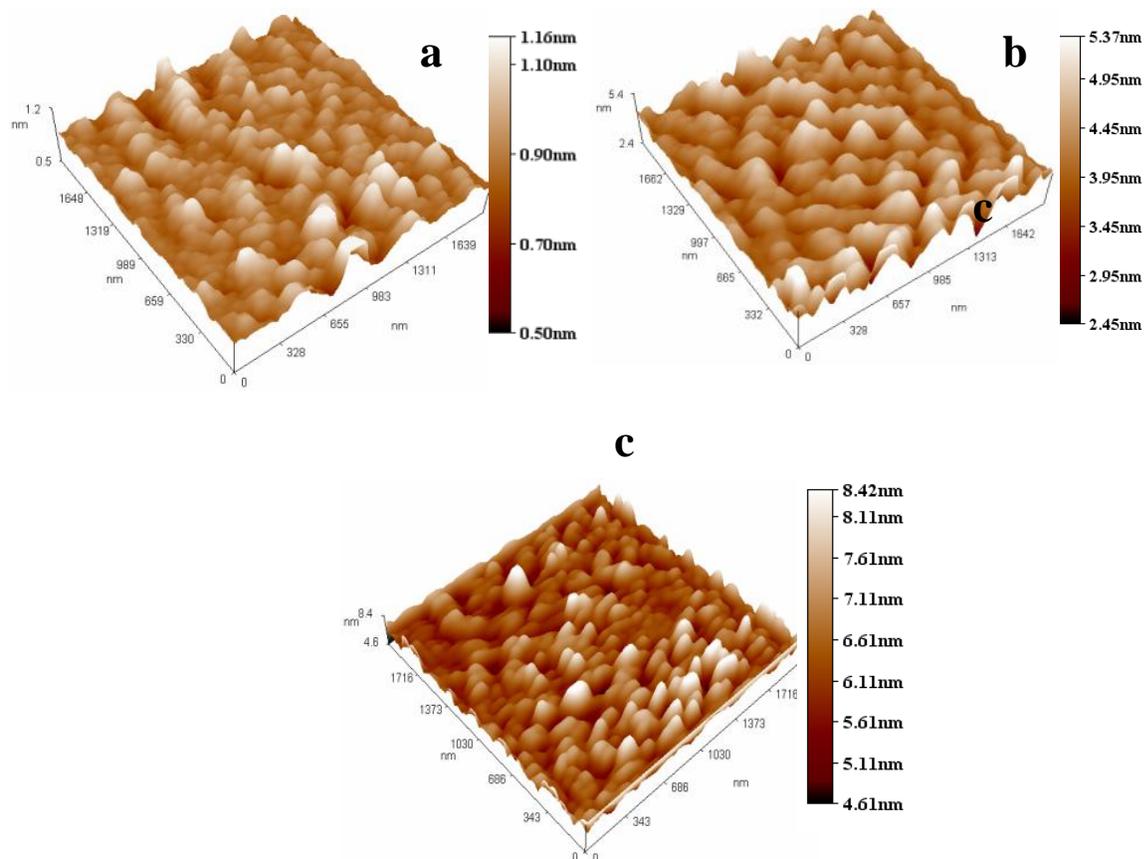


Figure 2: AFM images of ((a) TiO_2 ; (b) Pd/TiO_2 ; (c) Pt/TiO_2 thin film.

Color measurement: Discoloration of resin composite remains a major cause for the aesthetic failure of materials. Such discoloration might be caused by intrinsic and extrinsic factors. The intrinsic factors involve the discoloration of the resin material itself. Every component of resin composite material may take part in this phenomenon. The resin composite could absorb water, then it was also able to absorb other fluids which results in discoloration[8]. Susceptibility of the microfilled composite, used in the present study, for staining could be attributed primarily to their high resin content and the related water sorption values. Discoloration could be evaluated with various instruments. Instrumental colorimetric, used in the present investigation, can eliminate the subjective interpretation of visual color comparison.[24] In this study, color measurements were performed by VitaEasyShade tool using the CIE (Commission Internationale de l'Éclairage) $L^*a^*b^*$ color system. Color measurements were assessed utilizing (L^*) value. The major parameter causing the color change was found to be (L^*) rather than the chroma (a^* and b^*)[25].

Differences' in the CIE $L^* a^* b^*$ color space;

If ΔL^*+ : means specimen after was lighter than before during time intervals.

If ΔL^*- : means specimen after was darker than before during time follow up.

If Δa^*+ : means specimen after was redder than before during time follow up.

If Δa^*- : means specimen after was greener than before during time follow up.

If Δb^*+ : means specimen after was yellower than before during time follow up.

If Δb^*- : means specimen after was bluer than before during time follow up.

To ensure excellent aesthetics, it was necessary for tooth colored restorations to maintain intrinsic color stability and resistance to surface staining. Extrinsic factors for discolorations were known to cause staining of composite restorations. The tea had been reported[26]. In a study by Luce and

Campbell,[27] tea, coffee and snuff were used as chromogenic agents and coffee was found to stain more than tea and snuff. In a previous study, red wine, tea, coffee, mouth rinse and ultraviolet irradiation were used as staining agents[28], it was showed that red wine caused the most severe discolorations. Results are shown in figures (3-6), the results collected in the present investigation were showed an increase in mean ΔE values following immersion in tea stain solution for all groups and showed a decrease in mean ΔE values following chemical bleaching treatment. The highest mean color difference ΔE values were: group two Pt/TiO₂, group three TiO₂, group five TiO₂ / UV 100, Pd/TiO₂ and group one ZnO respectively. as compared to baseline values: these were supported by other studies [24, 29, 30]. Creansor et al. They reported that soft drinks might contain several different types of acids that contribute to the low pH value. Carbonated beverages contain carbonic acid formed by carbon dioxide in solution. Even when the carbon dioxide had been blown off and drinks have become 'flat', the pH remains low. Such acidic pH and that of tea are thought to be responsible for the surface roughness of the tested resin composite [33]. The results were showed as comparing each group among all time follow up (before immersion in tea stain solution, after immersion in tea stain solution, after chemical treatment or bleaching) they were significance differences except were showed no significant differences in: ΔE - TiO₂ group3 p=0.406, b2 p=1.558, b3 p=1.750. And the results were showed as comparing each group between before immersion in tea stain solution and after immersion in tea stain solution time follow up among all were showed no significance differences except were showed significant differences (p=0.001) in: L1,b1, L2, L3, L4, b4, L5, b5. finally the results were showed as comparing each group between before immersion in tea stain solution and after immersion in tea stain solution time follow up among all were showed significance differences except were showed no significant differences in: ΔE - TiO₂ group3 p=0.066, b2 p=0.135, b3 p=0.137. Group two Pt/TiO₂ and group five TiO₂/UV 100 showed statistical significant differences lowest in a* color space compared to others groups.

The results obtained indicate that the resin composite tested reversed nearly to baseline color, whereas among all groups except samples subjected to group three which treated with TiO₂ was showed some whitening that was statistical not significant differences p=0.406 compared to before immersion in tea stain solution (baseline). Furthermore, the whitening effect of all materials could be improved and such a contradiction might be due to the short period of immersion in tea staining solutions in the study compared to more longer immersion time (longer than one month). A limited period of tea staining may lead to less surface staining, rather than deeper penetration that was easily removed with plashing procedures. The use of these different chemical bleaching materials on restorative materials had different effects on surface roughness depending on the composition of the material, bleaching agent and regimen treatment employed [31]. However, Lu et al. [3] They reported that there was correlation between surface roughness and stain resistant of the resin composite. The smoothest surfaces were not necessarily the most stain resistant. The staining susceptibility of resin composite was not related to extrinsic factors, such as surface roughness alone, but to intrinsic factors such as monomer, silane coating and filler composition. Furthermore, it has been reported that various resin composites have different levels of water sorption, depending on the types of monomer. Therefore, the staining susceptibility of composite material was generally related to the degree of water sorption[32]. In this vitro, study had several limitations. One was the lack of thermo cycling that could influence the degree of total color change. Specimens in the present investigation were not thermally cycled. Thermal cycling was an important factor that affected the surface texture of resin composite restorations. Thermo cycling was an in vitro process through which the tested materials were subjected to large temperature extremes compatible with the oral cavity. The difference in thermal expansion coefficient or thermal conductivity coefficient between filler particles and resin matrix may result in a difference in thermal volumetric changes between resin matrix and filler particles. Furthermore, it must be mentioned that hydrolytic degradation of bonding between resin matrix and filler particles also occurred during thermal cycling as result of water absorption. It was also reported that water absorption would be accompanied by hygroscopic expansion in the resin matrix and filler phase, thereby enhancing the weakening

filler–matrix interface. All these factors led to the dislodgement of filler particles and therefore should be considered in future research.

Another limitation of the study was the short period of immersion (one week) in the staining solutions. In addition, the type of resin matrix had been shown to play an important role in stain susceptibility of resin composite material. Therefore, several types of resin composite materials should be tested in further research.

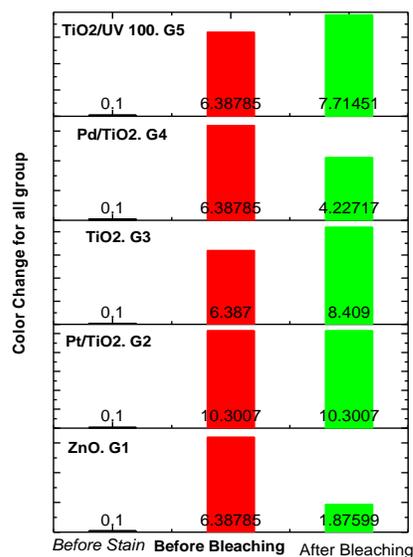


Figure 3: Effect of catalyst type on color change for all group

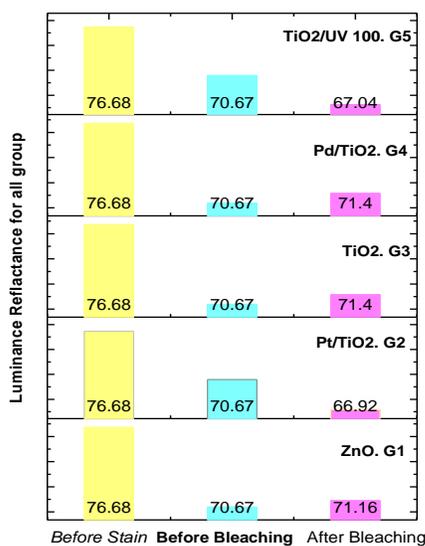


Figure 4: Effect of catalyst type on Luminance reflection for all group

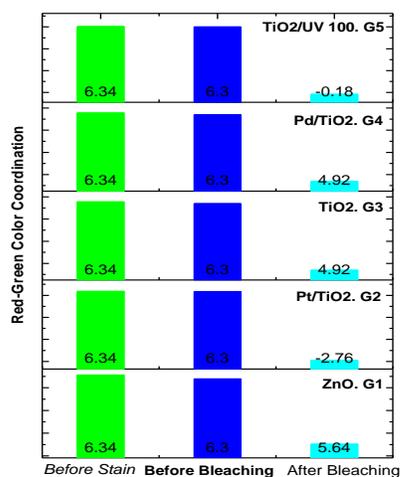


Figure 5: Effect of catalyst type on Red-green color coordination

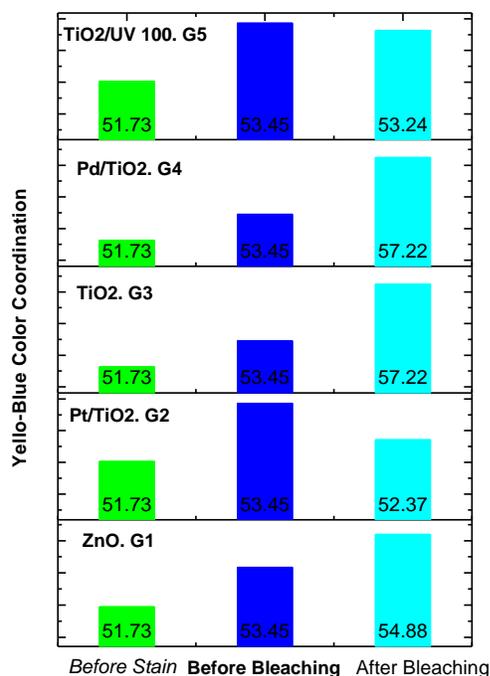


Figure 6: Effect of catalyst type on yellow-blue color coordination

APPLICATIONS

The results show immersion tea staining solutions had a positive influence on the color changes of resin composite. A whitening effect was demonstrated with group two Pt/TiO₂ and group five TiO₂/UV 100 showed statistical significant differences lowest in a* color space compared to others groups.

CONCLUSIONS

Based on the results obtained from the investigation, the following conclusions could be derived:

1. Immersion tea staining solutions had a deleterious effect on color of resin composite.
2. Whitening had adverse effects were obtained with different chemical treatment materials.
3. There were correlation between ΔE color significant increase and L^* color space changes of resin composite.
4. The ΔE color change values of group two Pt/TiO₂ the highest statistical significant mean color difference compared to others groups However, there was no statistical significant differences in group three TiO₂. In addition, a whitening effect was demonstrated with group two Pt/TiO₂ and group five TiO₂/UV 100 showed statistical significant differences lowest in a^* color space compared to others groups.

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