VOL. 64, 1855:1864, APRIL, 2018

I.S.S.N 0070-9484



Fixed Prosthodontics, Dental materials, Conservative Dentistry and Endodontics

www.eda-egypt.org • Codex : 247/1804

INFLUENCE OF ORAL RINSE SOLUTIONS AND TOOTH BRUSHING ON STAIN ABILITY OF THERMOPLASTIC TOOTH COLORED PROSTHETIC MATERIALS

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ABSTRACT

EGYPTIAN

DENTAL JOURNAL

Objectives: The present study aimed to comparatively evaluate the influence of oral rinse solutions and tooth brushing on stainability of thermoplastic tooth colored prosthetic materials, using computerized spectrophotometry before and after immersion.

Materials and Methods: Fifty-six samples (Twenty-eight samples of each material); Acetal resin and polyether ether keton(PEEK) were constructed in the form of discs (10 mm in diameter and 2 mm in thickness). Samples were randomly divided into 4 subgroups (n=7) according to the oral rise solutions (chlorhexidine, benzydamine HCl, alcohol-free mouthwash) and artificial saliva as control. Simulated tooth brushing of samples for 4 min with rotary instruments was applied before immersion in mouth rinses. The mean of color values (L^*,a^*,b^*) of each specimen were measured before and one week after exposure with a Reflective spectrophotometer.

Results: regardless to staining solutions totally it was shown that Acetal resin material group recorded higher color change mean value ($4.75\pm0.52 \Delta E$) than PEEK material group mean value ($4.64\pm0.66 \Delta E$). The difference between both materials groups means values was statistically non-significant as indicated by two-way ANOVA (F=0.31, P=0.5748>0.05). On the other hand Listerine zero recorded the highest color change mean value ($5.05\pm0.5 \Delta E$) followed by Tantum V solution mean value ($4.91\pm0.37\Delta E$) then CHX solution mean value ($4.52\pm0.7 \Delta E$) while A. saliva solution recorded the lowest color change mean value ($4.29\pm0.52 \Delta E$).

Conclusions:1- There was a highly significant difference between alcohol free, benzydamine HCL & CHX mouth rinses. The listerine zero showed the highest value in staining potential while CHX was the lowest regarding acetal 2- Among the two thermoplastic restorative materials and although statistically non significant, PEEK was found to be the higher color stable material and the higher stain was taken up by acetal resin. 3- There were no significant differences between the discoloration effects of different mouth washes used in this study on PEEK material.

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INTRODUCTION

Oral rehabilitation is critical regarding functional and esthetic outcomes. At first glance, the esthetic appearance of any restoration is of enormous subjective concern for both patient and oral care provider, in addition biocompatibility and function that considered as major aspects.¹ Therefore, an adequate material choice and processing can guarantee longevity and patient satisfaction.^{2,3}

On the basis of superior esthetics, navigation in polymer science has provided us with tooth colored substitute called "Acetal resin". It is a thermoplastic monomer-free crystalline structure.⁴ The homopolymer, Polyoxymethylene (POM) is a chain of alternating methyl groups linked by an oxygen molecule. This material has been believed to have good biocompatibility rationalizing its use in total hip replacement and as artificial valve occluders.⁴ In dental field, it has been used as provisional restorations, splints and to form a stress absorbing element in a dental implant system.⁵ Its use as denture base materials was first advocated by **Smith**⁶ and subsequently marketed as alternative denture base and clasp material since 1986.

PEEK is relatively recent material in dentistry compared with composite, ceramics or zirconia. It is white, radiolucent, rigid material with reduced plaque affinity⁷⁻⁹and flexural modulus 140-170 MPa. Several applications of PEEK in prosthodontics as implant abutments, permanent fixed crowns and bridges, removable dentures and components were reported by Najeeb et al⁷.

The degree of color change can be affected by a number of factors including: incomplete polymerization, water sorption, chemical reactivity, diet, oral hygiene, surface smoothness of material, cleaning measures and rinses.^{10,11} Discoloration of dental prostheses is measured as value developed over a specific period of time by a spectrophotometric technologies (e.g., CieLab-System) which are widely used in dental color studies.¹² The present study was designed using this technology to assess the effect of three different oral rinses (chlorhexidine, benzydamine HCl, alcohol-free mouthwash), and artificial saliva on the color change property of Acetal resin compared to PEEK. The following two null hypotheses were formulated:

- There is no difference in color change behavior of both acetal and PEEK materials among three oral rinses and artificial saliva used in this study
- 2- There is no difference in color change effect of three oral rinses and artificial saliva used in this study on both acetal and PEEK materials.

MATERIALS AND METHODS

Two thermoplastic materials (Acetal resin and PEEK), three staining solutions (chlorhexidine, benzydamine HCl, alcohol-free mouthwash) and artificial saliva as control were used in this study. Fifty-six samples (Twenty-eight samples of each material); Acetal resin and PEEK were constructed in the form of discs (10 mm in diameter and 2 mm in thickness) this sample configuration was selected because it fits the experimental system by allowing the medium to completely cover the samples. Also, it could be present in prosthetic appliances. Samples were randomly divided into 4 subgroups according to the oral rise solutions (n=7). Materials and staining solutions are listed in Table 1

Acetal samples construction:

The acetal resin (Thermoflex Acetal Resin Densply UK) samples were prepared in accordance with manufacturer's instructions. The pattern of the disc was made in wax (28 discs; 10 mm in diameter with thickness of 2 mm) and flasked using special Aluminum flask (Thermopress flask, bredent GmbH, Senden/ Witzighausen, Germany) mouldwith Class IV type plaster (Marble Stone, Pressing Dental San Marino, Italy). Heated softened acetal resin was injected into the mold then curing

Brand	Material type	Manufacturer	Lot #
Thermoflex Acetal Resin	Polyoxymethylene	Densply UK	1065
PEEK-BioHPP	Polyetheretherketone	Bredent-Senden-Germany	540XS016901
Hexitol	Chlorhexidine HCL 125mg100/ ml	Arab drug company, Cairo, Egypt	530330
Tantum Verde	Benzydamine HCL 0.15 g	EIPICO, under license of ACR Angelini, Italy	1510794
T	0.064% thymol, 0.092% eucalyptol, 0.064%		(170(0

TABLE (1) Materials names, types and manufacturers used in the study

methyl salicylate, 0.042% menthol

was done at 215C⁰ for 25 minutes and injection pressure of 4 bar. After curing the samples were deflasked, finished and polished using thermal resin finishing burs (Abraso-Star K 50, bredent GmbH, Senden/Witzighausen. Germany) and pumice at low speed then finally buffed with swans down mop for fine luster.

For all samples one surface was polished and the other one was only finished without polishing to resemble both the fitting and polished surface.

PEEK samples construction:

Listerine zero

Wax patterns of 28 discs (10 mm in diameter with thickness of 2 mm) were constructed and sprues were attached. The assembly was attached to the investment ring then invested using special investment material Brevest for 2 press (Bredent-Senden-Germany), after material setting the mould was then heated to 630°C then temperature was gradually increased by rate of 8°C/min until it reached 850°C in a preheated oven (IBEX-dental oven-USA) for wax burnout for 60 minutes before starting the melting process. Granular PEEK-BioHPP thermoplastic (BioHPP (granulate) 20g-Bredent-Senden-Germany) material was placed in the melting channel. Then the ring was placed back into the preheated oven for 20 minutes at temperature 400°C to get a creamy molten material

with uniform appearance indicating that the material was ready for pressing and injection pressure of 7 bar. By the end of the process the mould was allowed to cool for 35 minutes. The mould was then placed in water bath for 10 minutes then devesting was done first with scissors to remove the mould then using pneumatic devesting chisel. The fine blasting device was used to get the discs.

Johnson and Johnson, Italy

Tooth brush simulation

All the samples were stored in artificial saliva at 37°C±1°C for 24 hours. The rehydration simulated the first day of service for restorations in the oral environment. Simulated tooth brushing for 4 min with rotary instruments (ROBOTA chewing simulator operated on servo-motor (Model ACH-09075DC-T, AD-Tech Technology Co., Ltd., Germany) was performed using toothbrush heads with soft nylon bristles (Oral B Indicator; Procter & Gamble Nanning, Kwangsi, China) under 300-gr load.

Abrasive medium

Slurry was prepared by mixing a 2:1 ratio of deionized water and a sodium fluoride 0.22% w/w (1000 ppm F) particle dentifrice (Colgate maxfresh; Colgate-Palmolive, Bangna-Trad, Amphur Muang, Chonburi, Thailand) immediately before brushing.

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After brushing, the samples were cleaned with running water followed by an ultrasonic bath for 10 min.

Preparation of the staining solutions

Artificial saliva was prepared, and it consisted of the following ingredients: 1g sodium carboxymethylcellulose, 4.3g xylitol, 0.1g potassium chloride, 5mg calcium chloride, 40mg potassium phosphate, 1mg potassium thiocyanate and 100g deionized water.¹³ Each oral rinse (chlorhexidine, benzydamine HCl, alcohol-free mouthwash) and the artificial saliva were maintained in a dark environment at $37^{\circ}C \pm 1^{\circ}C$ to stimulate the conditions in oral cavity. The staining solutions were changed twice a day throughout whole experimental time (one week).

Evaluation of color change

The color values (L*,a*,b*) of each samples were measured before exposure with a Reflective spectrophotometer (X-Rite, model RM200QC, Neu-Isenburg, Germany). The aperture size was set to 4 mm and the samples were exactly aligned with the device. A white background was selected, and measurements were made according to the CIE L*a*b* color space relative to the CIE standard illuminant D65. The CIE L*a*b* system is an approximately uniform color space with coordinates for lightness, namely white-black (L*), redness-green (a*), and yellowness-blueness (b*). The measurements were repeated 3 times for each samples, and the mean values of L*, a*, b* were calculated. After the baseline color measurements were obtained, the samples were immersed into the staining solutions. After one week of immersion, the samples were rinsed with distilled water for 5 minutes and gently brushed with a soft toothbrush for 15 seconds. At this point, color measurements were recorded with the same spectrophotometer, and these measurements were performed under the same conditions and in the same manner described

for the baseline measurements. The calculation of the color variation ΔE^* between two color positions (one week of storage and baseline) in 3-dimensional L*a*b* color space is as follows:

$$\Delta \mathbf{E}_{\text{CIFLAB}} = (\Delta \mathbf{L}^{*2} + \Delta \mathbf{a}^{*2} + \Delta \mathbf{b}^{*2})^{\frac{1}{2}}$$

Where: L =* lightness (0-100), a=*change the color of the axis (red/green) and b=* color variation axis (yellow/blue).

Statistical analysis

The results were analyzed using Graph Pad Instat (Graph Pad, Inc.) software for windows. A value of $P \le 0.05$ was considered statistically significant. Continuous variables were expressed as the mean and standard deviation. After homogeneity of variance and normal distribution of errors had been confirmed, two-way ANOVA was done to detect effect of each variable (materials groups and oral rinse staining solutions subgroups). One-way ANOVA followed by pair-wise Tukey's post-hoc tests were performed to detect significance between subgroups and main group. Student t-test was done for compared pairs. Sample size (n=7) was large enough to detect large effect sizes for main effects and pair-wise comparisons, with the satisfactory level of power set at 80% and a 95% confidence level.

RESULTS

Color change (ΔE) results (Mean±SD) for both groups as function of oral rinse staining solutions are summarized in table (2) and figure (1).

Effect of material; regardless to staining solutions totally it was shown that Acetal Resin material group recorded higher color change mean value ($4.75\pm0.52 \Delta E$) than PEEK material group mean value ($4.64\pm0.66 \Delta E$). The difference between both materials groups means values was statistically non-significant as indicated by two-way ANOVA (F=0.31, P=0.5748>0.05).

Effect of oral rinse staining solution; the difference between A. saliva and staining solutions means values was statistically significant as indicated by two-way ANOVA (F=3.4, P=0.0244 <0.05). Pair-wise Tukey's post-hoc test showed non-significant (p>0.05) difference between A. saliva and CHX solution.

Interaction between variables

With A. saliva solution; it was shown that PEEK material group recorded statistically non-significant higher color change mean value ($4.43\pm0.69\Delta E$) than Acetal Resin material group mean value ($4.16\pm0.48\Delta E$) as demonstrated by t-test (t=0.74, P=0.4732>0.05).

With CHX solution; also, it was shown that Acetal Resin material group recorded statistically non-significant higher color change mean value $(4.64\pm0.75 \Delta E)$ than PEEK material group mean value $(4.40\pm0.82 \Delta E)$ as demonstrated by t-test (t=0.5, P=0.6287>0.05).

With Tantum V solution; it was shown that Acetal Resin material group recorded statistically non-significant higher color change mean value $(5.02\pm0.55 \Delta E)$ than PEEK material group mean value $(4.79\pm0.26 \Delta E)$ as demonstrated by t-test (t=0.9, P=0.3813>0.05). With Listerine zero solution; it was shown that Acetal Resin material group recorded statistically non-significant higher color change mean value (5.16±0.29 Δ E) than PEEK material group mean value (4.94±0.84 Δ E) as demonstrated by t-test (t=0.6, P=0.5788>0.05).

In Acetal resin materials group; it was shown that Listerine zero recorded the highest color change mean value ($5.16\pm0.29 \Delta E$) followed by Tantum V solution mean value ($5.02\pm0.55\Delta E$) then CHX solution mean value ($4.64\pm0.75 \Delta E$) while A. saliva solution recorded the lowest color change mean value ($4.16\pm0.48 \Delta E$). The difference between A. saliva and staining solutions means values was statistically significant as indicated by two-way ANOVA (F=3.9, P= 0.0243 <0.05). Pair-wise Tukey's posthoc test showed non-significant (p>0.05) difference between A. saliva and CHX solution

In PEEK materials group; it was shown that Listerine zero recorded the highest color change mean value ($4.94\pm0.84 \Delta E$) followed by Tantum V solution mean value ($4.79 \pm 0.26 \Delta E$) then A. saliva solution mean value ($4.43 \pm 0.69 \Delta E$) while CHX solution recorded the lowest color change mean value ($4.40 \pm 0.82 \Delta E$). The difference between solutions means values was statistically non-significant as indicated by two-way ANOVA (F=0.96, P= 0.4305 > 0.05).

Variables	Acetal Resin			PEEK				
	ΔL	Δa	Δb	ΔΕ	ΔL	Δa	Δb	ΔΕ
A. saliva	-3.97	-0.47	-1.07	4.16 ^A _b ±0.48	1.43	-2.37	-1.27	4.43 ^A _a ±0.69
СНХ	3.77	1.13	0.27	4.64 ^A _b ±0.75	1.70	-1.03	3.57	4.40 ^A _a ±0.82
Tantum V	-4.97	-0.03	0.63	5.02 ^A _a ±0.55	-0.90	-0.30	-2.83	4.79 ^A _a ±0.26
Listerine zero	3.33	1.00	3.80	5.16 ^A _a ±0.29	2.07	-0.63	-1.77	4.94 ^A _a ±0.84
Total	-0.46	0.41	0.91	4.75 ^A ±0.52	1.08	-1.08	-0.58	4.64 ^A ±0.66
P value	0.0243*			<0.0001*				

TABLE (2) Color change (ΔE) results (Mean±SD) for both groups as function of oral rinse staining solutions

Different superscript large letter in same row indicating significant between materials (Tukey's p<0.05) Different subscript small letter in same column indicating significant between solutions (Tukey's p<0.05) * : significant (p<0.05) ns: non significant (p>0.05)

* ; significant (p<0.05) ns; non-significant (p>0.05)

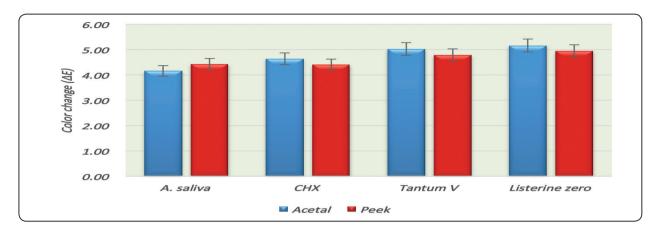


Fig. (1) Column chart of the mean values of color change for both groups as function of oral rinse staining solutions

DISCUSSION

Color of dental restorative material is one of the optical properties, and it is the visual perception of an object, or substance regarding the light reflected, or transmitted through.¹⁴ Tooth-colored fillings and natural dental prostheses are important expectations to achieve patients and dentists satisfaction.

The degree of color stability can be affected by many factors such as: incomplete polymerization, chemical reactivity, water sorption, and surface roughness of material.^{10,11} Polishing ability and material structure not the only parameters providing color stability for a longer period of time but also patient's dietary habits and cleaning measures are key factors.^{15,16}

Acetal resin or POM has been introduced in the dental market as an esthetic, thermoplastic material possess good short-term mechanical properties, but as a co-polymer has better long term stability,¹⁷ owing to its crystalline structure which improves the material strength and wear resistance. Curing process through injection molding technique allows better internal adaptation if compared with conventional heat cured and microwave polymerized resins.^{18,19}

Available 20 different color shades of acetal;17 of which are comparable with Vita-pan shade guide scale and 3 pink, enables its use as a successful denture base material and tooth- colored clasps especially in larger retentive undercuts than recommended for Cobalt- Chromium alloys due to its low modulus of elasticity (2.9 to 3.5kN/mm2).^{4,5} This may be advantageous in clinical situations where esthetics and/or periodontal health are extremely important.²⁰Additionally, its usage as stress absorbing action elements, provisional restorations and splints,^{17,19,21-24} proving to be the "Gen- X material in esthetic restorative dentistry".

Polyetheretherketone (PEEK) is another semicrystalline thermoplastic polymer and is considered as a promising alternative in fixed and removable prosthetic dentistry with observed mechanical properties,²⁵ and adequate mechanical stability to fulfill the basic requirements in the restorative field as showed by recent studies. ^{26,27} For advanced PEEK based materials Behr²⁸ reported great fracture resistance of fixed dental prosthesis exceeding that required to withstand forces assumed for anterior(300 N) and posterior region(500-600 N).

Additionaly, biocompatibility and low elastic modulus (3.6 GPa)²⁹ of PEEK that could be modified by reinforcing it with carbon fibers, for example in order to simulate that of cortical bone(18 GPa),³⁰ made it possible to be offered commercially as a titanium substitute for dental endosseous implants. Regarding esthetics, biocompatibility and light

weight, another important application of PEEK in prosthodontics was also reported by Zoidis⁹ as an alternative framework material for removable partial dentures.

Discoloration of dental prostheses and restorations is attributed to either^{31,32}: intrinsic factors related to heredity, age, and processing modes of these restorations, ³³ or extrinsic factors derived mainly from colorants of food products such as caffeinecontaining beverages or mouth rinses,³⁴ which in turn adhere on restoration surfaces by³⁵: physical and chemical electrostatic forces (van der Waals) and hydrophobic interdigitation.

Such color changes can be evaluated by visual perception or preferably by instrumental techniques like spectrophotometer since it eliminate the subjective interpretation,³⁶ and the risk of manual errors^{37,39} as it stores and transforms data into a spreadsheet for statistical analysis by special software.

Hence spectrophotometer was used in this study to measure the total color change (ΔE) of the three axes: L*, a*, and b* for two thermoplastic materials (acetal and PEEK) at base line and one week after immersion in three different oral rinses compared to artificial saliva. In order to accurately reflect clinical conditions of personal cleaning procedures, the specimens were subjected to simulated tooth brushing for 4 min with rotary instruments before immersion in oral rinses.

According to the results of the present study regarding the restoration materials tested, the null hypothesis was accepted. Although acetal recorded higher color change, there was satistically no significant difference in color change mean value of acetal ($4.75\pm0.52 \Delta E$) and that of PEEK material group ($4.64\pm0.66 \Delta E$). Since color stability significantly depends on surface roughness and surface free energy,⁴⁰ also several studies showed that there is a positive correlation between high surface roughness and discoloration of restorative materials,^{41,42} the present results could be attributed to approximated surface roughness and grain size of acetal 110-150 gm and that of PEEK 80grn which is considered slightly more fine and smoother.⁴³

In addition relatively close manufacturing techniques that permit accurate adaptation of the material in its mould would probably affect the final density, porosity and hence roughness of the restoration.⁴⁴ Also standardization of finishing and polishing procedures and instruments would seem to produce a smooth surface, and play crucial role in reducing pigmentations.⁴⁵On the other hand , being semi-crystalline , both acetal and PEEK could have similar degrees of pigmentation since degree of crystallinity, is one of the important factors affecting the ability of the materials for water or staining solution sorption.^{46,47}

Relative color change results of both acetal and PEEK in this study were inclusively supported in researches by almost good color stability of each material. **Heimer** ⁴⁸ concluded that PEEK showed the significantly lowest discoloration after a 1-week storage over all coloring media; red wine, curry, and chlorhexidine as compared to PMMA and COMP. **Tannous**⁴⁹ **and hallmann**⁵⁰ confirmed that PEEK as an attractive prosthodontic material have a reduced degree of discoloration. Also acetal resin, results of **Ozcan et al**⁵¹ reseach showed clinically acceptable color changes of acetal after 300 hours of thermocycling.

In the present study, according to the results regarding oral rinses and artificial saliva, the null hypothesis was partially rejected. Although there was non significant difference in color change potential of oral rinses and artificial salive on PEEK, statistically significant difference of their staining potential was recorded with acetal resin; Listerine zero recorded the highest color change mean value $(5.16\pm0.29\Delta E)$ followed by Tantum V solution mean value $(5.02\pm0.55\Delta E)$ then CHX solution mean value $(4.64\pm0.75\Delta E)$ while A. saliva solution recorded the lowest mean value $(4.16\pm0.48\Delta E)$ of color change.

This could be justified by the susceptibility of the acetal resin to water sorption, with subsequent hydrolysis that might alter the original color of the tested material. ^{47,52} This water sorption is important sign since if the resinous material is capable of absorbing water, it can also absorb other fluids.⁵³

Therefore, regarding listerine zero **Gürgan et al**⁵⁴showed that irrespective of alcohol concentration, both alcohol-containing and alcohol-free mouth rinses could affect the hardness of resin-restorative materials. also composite resin discoloration has been reported following the use of Listerine® mouth rinse.⁵⁵

Composition and coloring material incorporated in the mouth rinses may be another possible reasons for the increased color differences (ΔE^*) values caused by such solutions, so the color change of Benzydamine hydrochloride used in this study may be attributed to the type of colorant; quinoline yellow used in the mouth rinse. Thus, according to polarity variations of coloring constituents, the staining potential for each solution could be determined. This was supported by **Ruyter et al.**⁵⁶ who have reported that constituents of tea that have high polarity are released first and adsorbed onto the material surface followed by those with lower polarity in coffee.

With regard to staining effect of CHX in the present study, it was in accordance to research which has been reported discoloration of restorative materials following their immersion in CHX mouth rinse.^{57,58}More over CHX has been found to induce brown stains on enamel, composite restorations, oral mucosa, and tongue.⁵⁹⁻⁶¹Three mechanisms have been suggested to explain this discoloration: ^{62,63} A. non-enzymatic browning reactions (Maillard reactions), B. formation of pigmented (Fe, Sn)-sulphides, and C. reaction of dietary chromogens with CHX.

CONCLUSIONS

- 1- There was a highly significant difference between alcohol free, benzydamine HCL & CHX mouth rinses. The listerine zero showed the highest value in staining potential while CHX was the lowest regarding acetal
- 2- Among the two thermoplastic restorative materials and although statisticaly non significant, PEEK was found to be the higher color stable material and the higher stain was taken up by acetal resin.
- 3- There were no significant differences between the discoloration effects of different mouth washes used in this study on PEEK material.

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