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Original Article

Effect of Novel Cycloaliphatic Comonomer Incorporation on the Color Stability of Thermo-polymerized Denture Base Resin

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Abstract

Background: Denture during its *in vivo* service encounters myriad food pigments and numerous physico-mechanical dynamic changes. Denture discoloration is one of the unresolved problems that should be unraveled to satisfy the esthetic demands of the patients. **Aim:** This study aims to evaluate the color stability of a novel denture base copolymer with 10% and 20% (vol/vol) concentration of cycloaliphatic comonomer. **Materials and Methods:** Control group (G0) comprises specimens made without cycloaliphatic comonomer. The specimens of trial groups G10 and G20 were fabricated with 10% and 20% cycloaliphatic comonomer, respectively. For each group, thirty specimens (n = 30) were made. The specimens (n = 10) were immersed in three food colorant solutions (erythrosine, tartrazine, sunset yellow) for 56 days after artificial thermal aging. Ultraviolet-visible spectrophotometer was employed to measure the tristimulus values and calculate the color change (ΔE) of the specimens prior to and following rapid thermal aging or immersion of the specimens in the food colorants. **Results:** G0 showed the highest ΔE and G20 exhibited the least with each colorant. G10 had an intermediate imperceptible ΔE with each colorant. Also, significant differences (P = .000) existed between the food colorants within each group. The highest ΔE value was observed with sunset yellow and the lowest ΔE with tartrazine with each group. **Conclusion:** The addition of cycloaliphatic comonomer in denture base acrylic resins improved the color stability. The new copolymer with 20 Vol.% comonomer exhibited the highest color stability with all the food colorants.

Keywords: *Color stability, comonomer, cross-link, denture base, discoloration*

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Introduction

Polymeric dental formulations are prone for discoloration over time.[1] As it is important to replicate the esthetic perspectives of oral mucosa, color stability of denture base acrylic resins (DBR) is of prime concern. Thus, during denture fabrication, pigments incorporated in the denture base resins should be anchored firmly in the polymer matrix. In addition, these pigments or colorants should also be immune to unpropitious conditions during *in vivo* denture service.[2]

Several factors can cause discoloration of DBR. Intrinsic variables may affect color stability, such as the monomer to polymer conversion and the remnant unreacted monomer. Another potential source of color aberration

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is the occurrence of porosity during processing due to overheating or inadequate packing pressure. Pigments may also encounter chemical alterations or migrate from the polymer matrix.[3] Other variables concerning discoloration of the polymeric materials are roughness, water sorption, and chemical reactivity.[4]

Eating habits are directly associated with the color stability of DBR. Certain beverages, such as tea, coffee, and wine, have been documented to cause color change in acrylic resins.[5] The DBR is employed in the fabrication of intraoral prostheses which are to function in a dynamic oral environment encountering temperature fluctuations and change in salivary pH. In addition, the denture comes in close contact with diverse solid and liquid food materials, which are consumed at extreme temperatures that may induce thermal stress on the material. The DBR tends to absorb myriad contaminants during its *in vivo* service that change its physical structure and appearance. Furthermore, acrylic resin is an organic substance, and its translucency and color are likely to deteriorate.[6-8] The color deterioration poses an aesthetic threat and is objectively regarded from the patients' perspective on the point of acceptance to question prosthodontic workability and abilities. Salivary proteins and food are typically the initial strata to deposit on denture surfaces. Subsequent biofilm and calculus accumulation eventually lead to staining of the denture surface that may be hard to efface.[9] The effect of denture cleansers,[10] tobacco, salivary composition, and denture hygiene habits are other extrinsic variables that can be correlated with color stability.[9]

The DBR prepolymeric powder is pure, transparent prepolymer versatile to a broad range of pigments. Sulfides of mercury and cadmium, cadmium selenide, and ferric oxide are the pigments commonly used to obtain the shades of different tissues. These pigments may be either chemically attached to or mechanically mixed with the polymer beads. The later approach is frequently used and a mottled appearance of the denture is evident by the irregular distribution of the pigments. Both dyes and pigments used are dissatisfying since they leach out of the denture by the oral fluid which eventually lightens the denture's shade.[11]

The presence of hydrophilic monomers in the polymer resin matrix would pave a way for water sorption which directly leads to adsorption and absorption of various other exogenous pigments from food and beverages. This is because water sorption is a prequel of color instability. Cross-linkers containing ethoxy ($-CH_2-CH_2-O-$) moieties are hydrophilic and tend to absorb water.[12] One common example for cross-linkers in denture base resins containing ethoxy moiety is ethylene glycol dimethacrylate (EGDMA). Higher cross-linkers such as di-EGDMA or tri-EGDMA contain corresponding ethoxy groups and have increased water sorption. The methyl methacrylate (MMA) monomer's modifications with other characteristic comonomers are not uncommon.[13] A recently identified cycloaliphatic crosslinking comonomer, tricyclodecane dimethanol diacrylate (TCDDMDA), has been copolymerized with P(MMA).[14,15] This novel copolymer P(MMA-*Co*-TCDDMDA) exhibited better mechanical properties and biocompatibility than the conventional P(MMA).[16-19] However, there are no literature concerning the color stability of this copolymer. Hence, the present study aims to evaluate the color stability of P(MMA-*Co*-TCDDMDA) copolymer at 10% and 20% (vol/vol) concentration of TCDDMDA comonomer in MMA monomer. The null hypothesis is that the color stability of the denture base resin would not be affected by the addition of TCDDMDA comonomer.

Materials and Methods

Thermo-polymerizable DBR (DPI; Dental Products of India, Mumbai, India) and TCDDMDA comonomer (Sigma-Aldrich, St. Louis, MO, USA) were used. The addition of TCDDMDA in MMA and fabrication of control (G0 group; P[MMA]) and trial copolymeric specimens (G10 and G20 groups; P[MMA-*Co*-TCDDMDA]) were fabricated, finished, and polished by the method described elsewhere.[16] Thirty (n = 30) disc-shaped specimens (15 mm diameter; 3 mm thick) were fabricated per group (total n = 90). The specimens were made by single investigator. Color change (ΔE) was measured using a ultraviolet (UV)-visible spectrophotometer (CM 3600d; Konica Minolta Sensing Americas, Inc, NJ, USA). From the data collected prior to and following rapid thermal aging or immersion of the specimens in the food colorants, this instrument was used to measure the tristimulus values and calculate the ΔE. Initial color measurements were taken on each group's acrylic specimens in randomly selected three regions roughly in the middle of the specimen. The average of the three readings of a specimen was noted and the mean of each group was computed.[20]

The specimens of both control and trial groups were now placed in a weathering chamber (Envirotronics– C1500/-70; Weiss-Voetsch environmental testing instruments (Taicang) Co., Ltd, Jiangsu, China) and exposed to the UV-B light at an irradiance level of 80 W/m^2 for artificial thermal aging. Specimens were aged by switching irradiation for 4 h at 5°C and 4 h at 55°C in 100% humidity.

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The specimens were treated with distilled water for 18 min every 102 min (American Society for Testing and Materials; ASTM test D2565).[20] Three grams of permitted food colorants (erythrosine [E], Tartrazine [T], and sunset yellow [Y]) were dispensed in an individual conical glass flask to which 100 mL of distilled water was incorporated. The oral environment was simulated by the addition of 50 mL artificial saliva to each flask. Three sets of solutions were concocted for each food colorant, as there were 3 groups to be tested. Ten specimens (n = 10) of each group were soaked in each colorant solution and coded accordingly. The specimens in the colorant solutions were placed distantly to avoid contact between specimens. The color stability of the specimens was measured after 56 days. It is claimed that acrylic specimens shall be exposed to various beverages for a minimum of 56 days to perceive a clinically discernible discoloration.[21]

After 56 days, the specimens were retrieved from the colorant solution, thoroughly washed with distilled water, and blotted. Each of the acrylic specimens was then analyzed for final color values in the same spectrophotometer. The color change for each specimen was calculated using the formula: $\Delta E = ([\Delta L^*]^2 + [\Delta a^*]^2 + [\Delta b^*]^2)^{½}$, where L * stands for value, a* for red-green axis, and b* for yellow-blue axis. Values of ΔE >3.3 are visually perceptible and clinically unacceptable. The experiment was executed following a triple-blind procedure.

Statistical analysis

For statistical analysis, Statistical Package for the Social Sciences software (SPSS Inc., Chicago, IL, USA, version 21.0) was employed. Kolmogorov–Smirnov test indicated the data were normally distributed ($P > 0.05$) and the mean and standard deviation (SD) were computed. The level of significance was tested with one-way analysis of variance (ANOVA) followed by the Tukey honest significant *post hoc* test (α =0.05). P <.05 was considered for statistical significance.

Results

The mean ΔE and SD of the groups were tabulated in Table 1. A statistically significant difference existed among the groups and the food colorants (P = 0.000). *Post hoc* multiple comparisons showed significant differences (P = 0.000) between the groups (G0 vs. G10; G0 vs. G20; G10 vs. G20) within each food colorant. G0 showed the highest and visually perceptible discoloration and G20 showed the least insignificant color changes with each colorant. G10 had an intermediate imperceptible color change with each colorant. Also, significant differences (P = 0.000) existed between the food colorants (E vs. T; E vs. Y; T vs. Y) within each group. The highest ΔE value was observed with sunset yellow and the lowest ΔE with tartrazine with each group. Hence, P(MMA-*Co*-TCDDMDA) copolymer had better color stability than conventional P(MMA).

Table 1: Mean ΔE and standard deviation of the groups immersed in food colorants

Food colorant	Group	Mean±SD (ΔE)
Erythrosine	G0*, a	5.82±0.06
	G10*, b	2.78±0.13
	G20*, c	1.92±0.17
Tartrazine	G0#, a	4.48±0.12
	G10#, b	2.05±0.07
	G20#, c	1.50±0.06
Sunset yellow	G0†, a	6.19±0.03
	G10†, b	3.19±0.05
	G20†, c	2.20±0.02

Same symbol: Statistically significant difference among the groups in each food colorants (P=0.000). Same letter: Statistically significant difference within the groups in all food colorants (P=0.000). SD: Standard deviation

Discussion

The chemical structure of the colorants employed in this experiment bear charged and ionizable groups. These colorants belong to the organic azodyes group that are miscible in water, heat-resistant, and stable with alkalies, and acids.[22] The study's findings indicate that tartrazine demonstrated the least color changes in denture base resin specimens, while sunset yellow exhibited the highest discoloration. The P(MMA) DBR being hydrophilic, attract water-soluble dyes to the surface and get discolored caused by electrostatic changes.[11]

The specimens of the 3 groups have identical basic composition except for additional cross-linking agent TCDDMDA in G10 and G20 groups which may explain the conspicuous variations in the color stability of the resins. Discoloration in acrylic resins is a resultant of interactions between the colorants and the denture specimens at molecular level. Extrinsic staining, formation of colored degradation products, and changes in surface structure due to wear can all result in color instability in resin materials. Increased lightness and decreased chroma of denture polymers are the resultant of surface deterioration. The etiologic factors causing discoloration of esthetic dental polymeric materials include water sorption, oxidation of the unreacted carbon-carbon double bonds (C = C) that produces colored peroxide compounds, surface roughness, stain accumulation, anhydration, wear or chemical degradation, of which the first three are of prime significance.[11]

The staining mechanism of denture base materials has been elucidated by water sorption, polymeric matrix expansion,

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and staining agent migration toward polymeric chains.[23] Cross-linkers as a composition in the monomer decreased water sorption and solubility.[24] Nevertheless, the chemical structure of the cross-linkers determines the rate of water sorption. The hydrophilic $(-CH_2-CH_2-O-)_n$ moiety present in the cross-linkers increases water sorption.[12] Also, while high molecular weight comonomers (di-/tri-/poly-EGDMA) enhance the double-bond conversion and reduce the polymerization shrinkage, they decrease the crosslinking density of the polymer, which may eventually lead to increased water sorption due to high loads of hydrophilic $(-CH_2-CH_2-O-)_n$ moiety and apparently accelerated discoloration.[25] From the above context, it may be inferred that degree of conversion and color stability are independent parameters *per se* Hence, in the present research, G0 group containing cross-linker with $(-CH_2-CH_2-O-)_n$ moiety possessed increased discoloration when compared to G10 and G20 where the $(-CH_2-CH_2-O-)_n$ moiety was reduced and substituted with TCDDMDA comonomer which does not possess ethoxy moiety. This explication shall be corroborated with the research conducted by Haselton *et al*.[26] in which, denture resin containing tri-EGDMA presented more discoloration than the less complex methacrylate resins. The high color stability of G10 and G20 can also be substantiated with a higher degree of conversion, less or negligible unreacted residual monomer, and smoother surfaces than the G0 group.[15,17]

Colorimetric measurements provide a repeatable method of determining color and exclude the subjectivity of visual color comparisons. When color changes occur below the level of visual perception, spectrophotometric color measurements provide repeatable and reliable results. The CIELAB (Commission Internationale de l'Eclairage) system is recommended by the international commission on illumination. This color system has the benefit of being arranged in a roughly uniform three-dimensional color space with elements that are evenly spaced based on visual color perception.[27] Mathematical transformations can be used to construct a color graph with independent variables in the form of L*, a*, and b* coordinates. The effect of denture cleansing agents, beverages, and mechanical load cycling on the color stability of the *P*(MMA-*Co*-TCDDMDA) copolymer has yet to be explored through explicable future researches.

Conclusion

Within the limitations of the present research, it can be concluded that the addition of TCDDMDA more common in DBR improved the color stability. P(MMA-*Co*-TCDDMDA) with 20 Vol.% TCDDMDA showed the highest color stability with all the food colorants.

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Conflicts of interest

There are no conflicts of interest.

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