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Color Stability of Resins and Nylon as Denture Base Material in Beverages

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Keywords
Color stability; denture base acrylic resin.

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Accepted March 10, 2011

doi: 10.1111/j.1532-849X.2011.00791.x

Abstract

Purpose: Staining of prosthodontic materials may result in patient dissatisfaction and additional expense for replacement. This study aimed to determine the color stability of two heat-cured denture base acrylic (Lucitone 550, Vipi Cril) and one nylon denture base resin (Transflex) after immersion in beverages.
Materials and Methods: Forty disks of each resin (20.0-mm diameter, 3.0-mm thick) were prepared and stored in distilled water for 24 hours at 37°C. During that time (T_0), the color of all specimens was spectrophotometrically measured. Each specimen was immersed in coffee, cola, red wine, and distilled water as a means of control. After 15-day (T_1) and 30-day (T_2) periods of immersion, the color of the specimens was measured again. The CIE (Commission Internationale de L' Eclairage) $L^*a^*b^*$ system was used to determine mean ΔE (color changes) values for each material and compared statistically with two-way ANOVA and Bonferroni intervals at 0.95.
Results: In ΔET_0T_1 and ΔET_0T_2 the most severe staining was apparent with red wine ($p < 0.001$), followed by coffee ($p < 0.01$), when compared to the specimens stored in distilled water. Transflex also showed significant color change after immersion in cola ($p < 0.01$). In ΔET_1T_2 only red wine promoted significant staining of all resins ($p < 0.0001$).
Conclusion: Chromatic changes were exhibited by specimens immersed in red wine, followed by coffee. For Transflex, cola also promoted color changes. The values of color changes converted to National Bureau of Standard units showed them to be perceivable to the human eye.

Many resins have been used for denture base construction. These materials include heat-activated (polymerized using a water bath or microwave oven), chemically activated (cold-polymerized resins), and light-activated denture base acrylic resins. Polymethyl methacrylate (PMMA) polymers were introduced as denture base materials in 1937. Most PMMA resin systems include powder and liquid components. A cross-linking agent may also be added to the monomer component to improve solvent resistance of the cured polymer and so, reduce its susceptibility to solvent crazing.[1,2] Acrylic resins used for the manufacture of denture bases have displayed various degrees of in vitro cytotoxicity and in vivo allergic responses, probably caused by nonreacting components remaining after the polymerization process.[3] Some potential alternative materials to PMMA used in these cases include polycarbonate and nylon. Nylon is a generic name for certain types of thermoplastic polymers belonging to the class known as polyamides. These polyamides are produced by the condensation reactions between a diamine NH_2-$(CH_2)_6$-NH_2 and a dibasic acid CO_2H-$(CH_2)_4$-COOH.[4-6] The use of nylon as a denture base material has been described in the literature since the 1950s.[7] Nylon is a crystalline polymer, whereas PMMA is amorphous. This crystalline effect accounts for nylon's lack of solubility in solvents, high heat resistance, and high strength coupled with ductility.[7]

Some of the disadvantages reported in the early forms of nylon included a tendency to color deterioration, staining, high water sorption, and the development of a rough surface after a short period of time.[5,8] Color change of the denture base polymers may be caused by the oxidation of the amine accelerator

or by the penetration of colored solutions. Most materials used for prosthetic treatment are subject to sorption, a process of absorption and adsorption of liquids dependent on environmental conditions.[9] Color change may be associated with porosity caused by overheating or insufficient pressure during polymerization[10] or to excessive residual monomer,[10-12] surface characteristics,[13,14] and microporosity in the specimens.[10]

Staining of acrylic resins can lead to poor esthetics. A denture base polymer should have a smooth and glassy surface and be capable of matching the natural appearance of soft tissues. The material should be translucent for the best esthetic effect. Color and translucency should be maintained during processing, and acrylic resins should be not become stained and not change color in clinical use.[9] Color change of prosthodontic materials may result in patient dissatisfaction and additional expense for replacement.[15]

Determination of color by visual means is considered highly subjective.[16] Methods used to assess changes in shade include digital analysis,[17] projection of photographic slides, visual group ranking, and shade guide matching. Each method has its own limitations, advantages, and disadvantages.[18] Subjective human evaluation of resin shade has proved to be a poor method of analysis. The spectrophotometer, an advancement in color evaluation technology, operates on similar principles as the colorimeter; however, the spectrophotometer measures the reflected emission of spectral colors more precisely than the colorimeter. The spectrophotometer evaluates visible light through the color spectrum (400–700 nm) and expresses the analysis as a numerical value.[19]

Although there have been some studies on the color stability of acrylic resin denture bases,[20] the comparison of these resins with polyamides after immersion in beverages such as red wine remains unknown. The purpose of this study was to determine color stability of two heat-cured denture base acrylic resins and one nylon denture base material by subjecting them to three beverages (coffee, cola, red wine) and distilled water as a means of control. The null hypothesis was that denture base acrylic and nylon resins would not stain after immersion in beverages.

Materials and methods

Denture base acrylic resin specimen construction

Two heat-cured denture base acrylic resins (Lucitone 550, Dentsply Ind. e Com. Ltda, Petrópolis, Brazil and Vipi Cril, Dental VIPI Ltda., Pirassununga, Brazil) were examined. Each type of acrylic resin specimen was processed in gypsum molds made by investing silicon disks in denture flasks (20.0-mm diameter, 3.0 ± 0.1 mm thick).[21] The specimens used in this study were smaller in diameter and greater in thickness than American Dental Association specification no. 12.[22] This modification in diameter was to permit the fitting of the specimens on the diffraction grating of the spectrophotometer, and the modification in thickness was to permit a better representative specimen of each denture base material color.[23] The heat-polymerized materials were mixed according to the powder/liquid ratio (21 g/10 ml for Lucitone 550 and 14 g/6.5 ml for Vipi Cril) recommended by manufacturers. They were then molded in flasks filled with gypsum, and the stone surfaces coated with a separator before they were processed and allowed to dry.

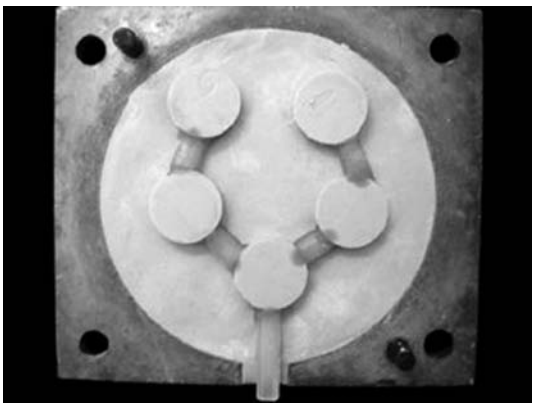

Figure 1 Silicon discs and waxed sprues for injection of thermoplastic material Transflex.

Lucitone 550 was polymerized in a water bath for 90 minutes at 73°C and then boiling water for 30 minutes. Vipi Cril was polymerized for 30 minutes at 70°C and then boiling water for 90 minutes. After deflasking, the specimens were abraded on both sides with 150- and 600-grit silicon-carbide papers. A slurry of water and pumice was applied to the surface of the specimen with a brush wheel, followed by a slurry of tin oxide with a cloth wheel.

Denture base nylon resin specimen construction

The thermoplastic nylon resin Transflex (Transflex, Curitiba, Brazil) specimens were fabricated according to the manufacturer's recommendations. The material was flasked using specially designed equipment for injection. A cartridge, which was designed to be inserted into the injection device, was heated up to 240°C and maintained at this temperature for 12 minutes before being injected into a stainless steel flask. A pressure injection of nitrogen gas was used (5 Kgf) to direct the melted polymer to the areas of the mold to be filled. Nitrogen pressure was maintained for 25 seconds before deflasking. Gypsum molds in the flasks were obtained by investing silicon disks with the same diameter of the acrylic specimens. The silicon discs were connected with each other and with the outside of the flask by waxed sprues (Fig 1). The specimens were deflasked and finished with tungsten-carbide trimmers and 120- and 220-grit sandpaper and polished with pumice on a black brush, followed by a slurry of tin oxide.

Testing conditions

Forty specimens were made for each material for a total of 120 specimens. All specimens were then stored in distilled water at 37°C[24] for 24 hours.[21,25] Before initial color measurement, visual observation of polished surfaces of all specimens was made, and the presence of any obvious porosity was noted.

Table 1 Results of 2-way ANOVA of ΔE T_0T_1 test for denture base resins

Source	*df*	SS	MS	F	*p* value
Beverages (A)	3.0	3.93.5	131.2	300.21	<0.0001
Denture base resins (B)	2.0	14.46	7.229	16.55	<0.0001
A × B	6.0	8.377	1.396	3.20	0.0063
Error	108	47.18	0.4369		
Total	119.0	463.5			

df, Degrees of freedom; SS, sum of squares; MS, mean square.

Table 2 Results of 2-way ANOVA of ΔE T_0T_2 test for denture base resins

Source	*df*	SS	MS	F	*p* value
Beverages (A)	3.0	2288	762.8	1155.96	<0.0001
Denture base resins (B)	2.0	31.28	15.64	23.70	<0.0001
A × B	6.0	14.99	2.498	3.79	0.0018
Error	108	71.27	0.6599		
Total	119.0	2406			

df, Degrees of freedom; SS, sum of squares; MS, mean square.

At that time (T_0) the color of all specimens was measured with an ultraviolet-visible spectrophotometer (Varian Cary 100, São Paulo, Brazil). Reflectance values versus wavelengths were obtained for each specimen at 1-nm intervals between 360 and 830 nm. After the initial color measurements, the specimens were divided into four groups. They were immersed in solutions of coffee (Nescafé Tradição, Nestlé Brazil Ltda, Araras, Brazil), cola (The Coca-Cola Company, Curitiba, Brazil), red wine (Vinho Tinto Seco Campo Largo, Vinícula Campo Largo, Campo Largo, Brazil), or distilled water, which served as control. Each specimen was suspended with dental floss so it was not in contact with the container or other specimens. The coffee solution was prepared from 300 ml of distilled water with 3.6 g of coffee, according to the manufacturers' suggested concentration.[15] The specimens were kept in individual vials containing 20 ml of each beverage at 37°C and stored for 30 days. After a 15-day (T_1) and a 30-day (T_2) immersion, color measurements of all specimens were repeated. These times were selected based on the work of Hersek et al[9] where the staining of denture base acrylic resin with food colorants occurred. Before each measurement session, the colorimeter was calibrated according to the manufacturer's recommendations by using the supplied white calibration standard.

Colorimetric measurements

Measuring characteristics of the spectrophotometer were standard illuminant D65,[21] diffuse specimen illumination, and standard observer at 10°.[21] The CIE L*a*b* measurements make it possible to evaluate the amount of perceptible color change in each specimen. CIE L*a*b* is an approximately uniform color space with coordinates for lightness; that is, white-black (L*), redness-greenness (a*), and yellowness-blueness (b*). The color systems with rectangular coordinates are quantitative systems, and they have a meaningful relation to human visual perception of color differences. Total color differences were expressed by the formula ΔE^* ab $= [(\Delta\ L^*)^2 + (\Delta a^*)^2 + (\Delta\ b^*)^2]^{\frac{1}{2}}$, where Δ L*, Δ a*, and Δ b* were differences in the respective L*, a*, and b* values.[26]

Statistical analysis

Statistical analysis was performed within each immersion period with 2-way ANOVA to compare results from each denture base resin brand and beverage (Tables 1–3). Bonferroni adjustments for pairwise differences between denture base resins within beverages and between beverages within resins were performed ($\alpha = 0.05$).

To relate the color differences (ΔE) to a clinical environment, ΔE data were computed to National Bureau of Standards (NBS) units through the formula NBS units $= \Delta E \times 0.92$.[9,10,21,25,27-29] The critical remarks of color differences as expressed by NBS units are presented in Table 4.

Results

Figure 2 depicts the mean ΔE values of the tested combinations for each immersion time (T_0T_1, T_0T_2, and T_1T_2). According to two-way ANOVA and Bonferroni pairwise differences, in ΔET_0T_1 and ΔET_0T_2 the most severe staining was apparent with red wine ($p < 0.001$), followed by coffee ($p < 0.01$) when compared to the specimens stored in distilled water. Transflex also showed significant color change after immersion in cola ($p < 0.01$). In ΔET_1T_2, only red wine promoted significant staining of all resins ($p < 0.0001$). Figure 3 shows staining patterns from representative specimens of acrylic and nylon resins after immersion in beverages. The color changes for all

Table 3 Results of 2-way ANOVA of ΔE T_1T_2 test for denture base resins

Source	*df*	SS	MS	F	*p* value
Beverages (A)	3.0	770.6	256.9	825.84	<0.0001
Denture base resins (B)	2.0	2.030	1.015	3.26	0.0421
A × B	6.0	7.562	1.260	4.05	0.0011
Error	108	33.59	0.3110		
Total	119.0	813.8			

df, Degrees of freedom; SS, sum of squares; MS, mean square.

Table 4 NBS system of expressing color difference

Critical remarks of color differences	NBS units
Trace	0.0–0.5
Slight	0.5–1.5
Noticeable	1.5–3.0
Appreciable	3.0–6.0
Much	6.0–12.0
Very much	12.0–+

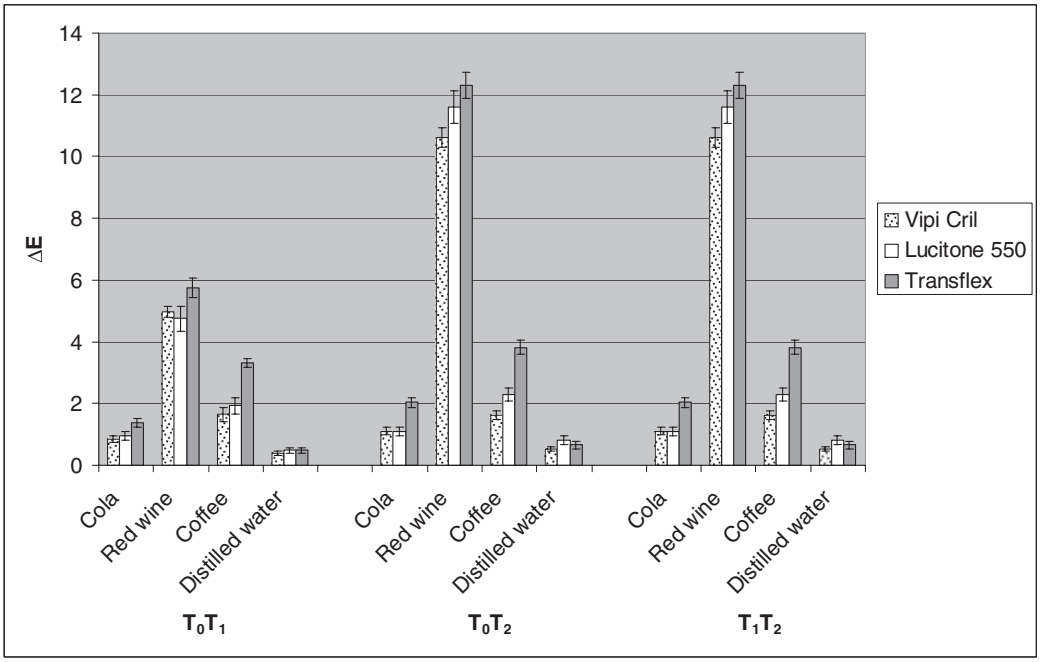

Figure 2 Mean color differences (ΔE) and standard errors (vertical lines) of Vipi Cril, Lucitone, and Transflex in T_0T_1, T_0T_2, and T_1T_2 immersion periods in the beverages.

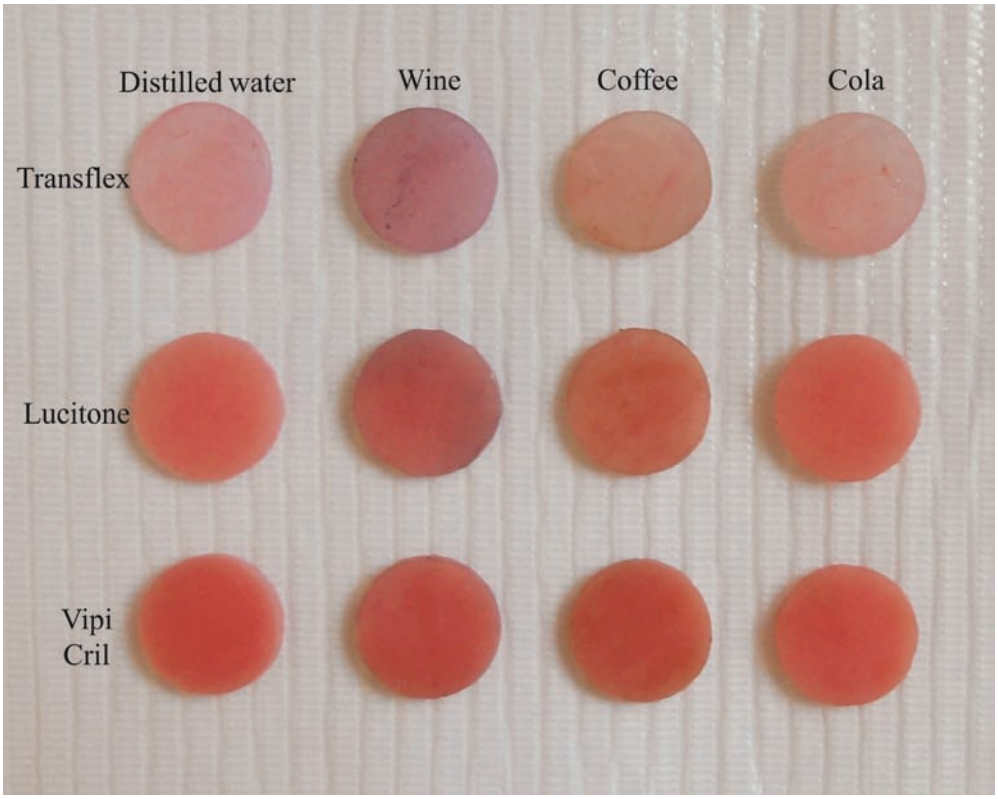

Figure 3 Staining patterns from representative specimens of acrylic and nylon resins after immersion in beverages.

materials after 30 days were in the categories of "trace" or "much," based upon the NBS system (Table 4) for expressing color difference.

Discussion

In this study, the conventional heat-polymerized denture base acrylic resins Lucitone 550 and Vipi Cril and the nylon denture base material Transflex were used to compare the color changes caused by three beverages (coffee, cola, red wine) thought of as stainers with distilled water as control. The most severe staining was apparent with red wine when compared to the specimens stored in distilled water. Coffee was the second-most staining beverage, affecting both acrylic and nylon denture base materials. Transflex also showed significant color change after immersion in cola. Color difference, as converted to NBS units, showed visually perceptible color changes caused by red wine and coffee (Fig 3).

The two denture base acrylic resins used in this study had the same base chemical structure, that is, PMMA. Each of them probably contains small quantities of different cross-linking agents, pigments, and plasticizers. The hydrophilic nature of a polymer is, in large part, a function of the chemistry of its monomers and its polymerization linkages.[26] Monomers commonly used as cross-linking agents and their resultant polymers are not considered extremely hydrophilic but may absorb water to a potentially damaging extent. It has been stated that there is a relationship between staining of resin-based materials and water sorption as well as hydrophobicity/hydrophilicity of these materials. Hydrophobic materials are stained by hydrophobic solutions in oil, and hydrophilic materials with high water absorption are stained by hydrophilic colorants in aqueous solutions.[27] The solvent diffuses into the polymer network and separates the chains, creating an expansion; however, the polymer network contains porosity and free volume between chains, especially in the region near cross-links, which permits the water sorption to occur without any polymer expansion.[26] If the denture base acrylic resin can absorb water, then it is also able to absorb other fluids, which results in its color change.[30-34]

The nylon denture base material is hygroscopic, its moisture content varying slowly with the surrounding conditions. Hargreaves[5] found that the frequency of amide groups along the chain affects the water sorption and the chemical properties of each type of nylon. Thus, as 610 nylon has the most widely spaced amide groups, it absorbs the least water and has the best chemical resistance. The same author observed that nylons 11 and 12 both contain very long methylene chains and have relatively low melting points and water absorption levels.[5]

Kurtulmus et al[17] showed no significant difference in mean values of liquid sorption among polymerization methods of some heat-polymerized and nylon resins; however, they found that the denture base material containing cross-linking agents absorbed fewer solutions than the materials without cross-linking agents. The results of this study showed that Transflex (nylon 12) produced slightly larger color changes, which may be attributed to the differences in composition, processing, finishing, and polishing of this material. Well-polished surfaces are generally considered less susceptible to staining than are rough surfaces. Although this study did not measure surface roughness, Transflex, the material that had a different finishing, exhibited the greatest color change. Therefore, not only storage solutions, but also finishing treatments may have significantly affected the surface staining of denture base acrylic resins. Two comments can be made concerning the experimental acrylic and nylon resin specimens: first, the acrylic specimens were, for reasons of reproducibility of the clinical situation, smoothed with abrasive paper (150- and 600-grit) and then subjected to pumice and tin oxide polishing; on the other hand, the finishing of nylon specimens was carried out according to the manufacturers' instructions, using different abrasive paper grain. Causative factors that may contribute to the color change of denture base acrylic resins include stain accumulation, dehydration, water sorption, leakage, poor bonding, surface roughness, wear, or chemical degradation.[17,20,35,36]

In the first and second immersion periods, the most severe staining of specimens was apparent with red wine. This is in agreement with the studies of Guler et al[37] and Rutkunas et al,[38] in which the highest color difference for all restorative materials was observed in the red wine groups. Omata et al,[32] examining the surface staining mechanism of a photopolymerized composite, observed that wine caused the most severe staining, followed by tea and coffee. Apparently, the quantity of alcohol in the wine played a significant role in the staining of the surface of the specimens.[33] The denture base acrylic resins have been reported to be critical in color stability, which is affected by different alcohol concentrations and pH solutions.[33] Several studies have reported that alcohol facilitates staining by softening the resin matrix. Therefore, it could be possible that the alcohol component in wine (10% alcohol by volume) roughened the denture base resin surfaces, thereby resulting in increased staining.[33] Since the pH of red wine is about 3.7, it is possible that the acidic pH may have had an effect on the structure of the materials.[34] In our investigation, the differences determined in color were large after 15–30 days in red wine compared with the first immersion period. It seems that time influenced color change, probably by the cumulative effect of surface degradation promoted by alcohol and pH and the subsequent adsorption of natural and artificial red wine colorants.

This study contemplates the staining effects of coffee. In a previous work,[33] the staining effect of coffee was significantly lower than that of red wine, which is in accordance with our results. Lai et al[20] found clinically unacceptable color changes of silicone and copolyamide materials stored in coffee solution for 180 days. Buyüyilkmaz and Ruyter[39] demonstrated that after 1000 hours of immersion of three heat-polymerized and three autopolymerized denture base polymers in coffee and tea solutions, coffee produced a higher staining value than tea. The stainability of polymers by coffee has been attributed to the presence of yellow colorants with different polarities. Tannic acid has been proved especially responsible for the staining of this beverage.[37] Other influential factors of coffee staining are the addition of sugar and the processing method, such as filtering.[37] It has been suggested that staining by coffee was due both to adsorption and absorption of colorants, probably due to compatibility of the polymer phase with the yellow colorants of coffee. Moreover, as an aqueous solution, it might be expected that polymers had absorbed water molecules of this beverage.

Transflex displayed staining after immersion in cola. Cola gains its color through the addition of caramel, which exhibits colors ranging from the palest yellow to the deepest brown and is made by heating sugar or glucose in the presence of alkali or mineral acid.[33] Although cola had the lowest pH and might damage the surface integrity of the materials, it did not produce as much staining as red wine and coffee.

The sensitivity of water absorption and the solubility behavior of materials seem to be closely related to the hydrophilicity of the resin matrix. The specimens immersed in distilled water exhibited the least color change. In accordance with the NBS system of expressing color difference, the specimens immersed in distilled water could be categorized into the two groups of "slight." Similarly, Lai et al[20] demonstrated that all flange materials tested demonstrated color stability in air and water.

Color determination in dentistry can be divided into two categories: visual and instrumental. Instrumental spectrophotometry can potentially eliminate subjective errors in color assessment.[34] In this study, the color of each specimen was measured using the spectrophotometer Varian Cary 100. CIE L*a*b* measurements make it possible to evaluate the amount of perceptible color change in each specimen.[27] The NBS parameter is important for color comparison and quality control functions, because only the allowable ΔE^*ab values need to be specified instead of the individual L*, a*, and b* values.[9,10,15,25,28-30] Based on the NBS rating system of expressing color difference, the alterations found in this study could be categorized into 0.30 and 11.32 of "trace" and "much." Nevertheless, in daily clinical practice, we realize there are far too many complaints about staining of dental materials.

Specimens in this study were not thermocycled or brushed.[31] We found combined influences (i.e., interactions) between the finishing treatment and staining medium for both the Lucitone 550, Vipi Cril, and Transflex specimens. These factors may be considered for future research.

Conclusions

Within the limits of the study, the following conclusions were drawn:

1. The greatest chromatic changes were found in red wine immersion, followed by coffee and cola.
2. The staining effect of red wine and coffee on the three commercially available resins used as denture base material was found to be at clinically acceptable levels.
3. The specimens immersed in distilled water exhibited the least gloss change.
4. Transflex displayed staining after immersion in cola.
5. Vipi Cril demonstrated the least color change after Lucitone and Transflex.

Acknowledgments

The authors thank Transflex Laboratory, (Ponta Grossa, PR, Brazil), for donating the specimens of nylon denture base material used in this study and Dr. Fábio André dos Santos for providing statistical advice and assistance.

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