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Color Stability of Conventional PMMA, Modified MMA and Polyamide Denture Base Materials in Different Beverages

Geleneksel PMMA, Modifiye MMA ve Poliamid Protez Kaide Materyallerinin Farklı İçeceklere Karşı Renk Stabilitesi

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Abstract

Objective: This study aimed to determine how commonly consumed beverages affected the color stability of denture base materials over time.

Materials and Methods: Twenty disks (10.0-mm diameter, 2.0-mm thick) of conventional polymethylmethacrylate (PMMA) (Meliodent), modified methyl methacrylate monomer (MMA) (Bre-Crystal and Acryfee), and polyamide (Bre-Flex, Flexinylon, and T Crystal) acrylic resins with smooth and rough surfaces were prepared. The color of the specimens was measured using a colorimeter at that time (T0). Each specimen was immersed in coffee, coke, tea, and distilled water. The color of the specimens was measured again after 1-day (T1), 12-day (T2), and 36-day (T3) immersion periods. The CIE L*a*b* system was used to calculate the mean color changes for each material, which were then statistically compared using repeated measures ANOVA and Bonferroni intervals at 0.95.

Results: Regardless of time or beverage, there was no significant difference between smooth and rough surfaces ($p>0.05$). Across all time intervals, the modified MMA (Bre-cystal) demonstrated a statistically significantly lower color difference ($p<0.05$). Regardless of time, modified MMA (Acryfree) and conventional PMMA (Meliodent) specimens exposed to coke demonstrated significantly lower color stability than all others ($p<0.05$).

Conclusion: Beverages did not cause a statistically significant color change compared with distilled water after T1 and T3 periods. According to the NBS system, the color changes after the T3 period were between "slight" and "much". Modified MMA resin (Bre-Crystal) can be used as a denture base material in patients with PMMA allergy because of its high color stability in long-term use.

Keywords: Color stability, denture base, acrylic resin, PMMA, modified MMA, polyamide, polymers

Öz

Amaç: Bu çalışmanın amacı, yaygın olarak tüketilen içeceklerin farklı zaman aralıklarında protez kaide materyallerinin renk stabilitesi üzerindeki etkisini değerlendirmektir.

Gereç ve Yöntemler: Konvansiyonel polimetilmetakrilat (PMMA) (Meliodent), modifiye metilmetakrilat (MMA) (Bre-Crystal ve Acryfee) ve poliamid (Bre-Flex, Flexinylon ve T Crystal) akrilik rezinlerden oluşan 20 disk şeklinde (10 mm çap, 2 mm kalınlık) örnek pürüzsüz ve pürüzlü yüzeylerde hazırlandı. Tüm örneklerin başlangıç rengi kolorimetre ile ölçüldü (T0). Her örnek kahve, kola, çay ve distile suya daldırıldı. Örneklerin rengi 1 günlük (T1), 12 günlük (T2) ve 36 günlük (T3) daldırma sürelerinden sonra tekrar ölçüldü. Her örnek için ortalama renk değişikliklerini (ΔE) hesaplamak için CIE L*a*b* sistemi kullanıldı. Elde edilen veriler 0,95 güven aralığında ANOVA ve Bonferroni testleri kullanılarak istatistiksel olarak karşılaştırıldı.

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Bulgular: Pürüzsüz ve pürüzlü yüzeyler arasında renk değişimi açısından zaman veya içecekten bağımsız olarak anlamlı fark yoktu (p>0,05). Tüm zaman aralıklarında, modifiye MMA (Bre-cystal) daha yüksek renk stabilitesi gösterdi (p<0,05). Zamandan bağımsız olarak, kolaya daldırılan modifiye MMA (Acryfree) ve konvansiyonel PMMA (Meliodent) örnekleri, istatistiksel olarak anlamlı derecede daha düşük renk stabilitesi sergiledi (p<0,05).

Sonuç: Çalışmada kullanılan içecekler, T1 ve T3 periyodlarından sonra distile suya göre istatistiksel olarak anlamlı bir renk değişimine neden olmadı. NBS sistemine göre T3 periyodundan sonra renk değişimleri "hafif" ile "çok" arasındaydı. Modifiye MMA rezin (Bre-crystal), uzun süreli kullanımda yüksek renk stabilitesi nedeniyle PMMA alerjisi olan hastalarda protez kaide materyali olarak öne çıkabilir.

Anahtar Kelimeler: Renk stabilitesi, protez kaidesi, akrilik rezin, PMMA, modifiye MMA, poliamid, polimerler

Introduction

Denture base materials made of polymethylmethacrylate (PMMA) have dominated the market for more than 50 years (1). For denture-wearing patients with allergy susceptibility, hypoallergenic denture base materials provide an alternative to traditional PMMA, lowering the likelihood of adverse responses brought on by lingering methyl methacrylate monomer (MMA) (2,3). Modified methacrylate-based denture base resins had a much lower residual monomer concentration than heat-polymerized PMMA (4,5).

Polyamides are thermoplastic polymers formed through the condensation reaction of a diamine and a dibasic acid (6). PMMA is an amorphous polymer, whereas polyamide is crystalline. Some of the disadvantages of nylon are discoloration, staining, high water absorption and a rough surface after a short time (7,8).

All dental materials must maintain color stability because changes in color are signs of material deterioration or aging (9). Patients may become dissatisfied and incur additional costs for replacement as a result of changes in the color of prosthodontic materials (10).

The majority of prosthetic materials are prone to sorption, a liquid absorption and adsorption process that is influenced by environmental factors (1,11-13). The specimens' color may change due to surface features, microporosity, an excess of residual monomer, overheating or underpressurization during polymerization, or any combination of these factors (14,15).

Despite research on the color stability of acrylic resin denture bases (16,17), there is little data comparing these resins to monomer-free and polyamide resins when submerged in liquids. This *in vitro* study's goal was to determine how frequently ingested liquids including coffee, tea, and coke affected the color stability of PMMA and modified MMA acrylic as well as polyamide denture base materials over time. The first null hypothesis stated that denture base acrylic, conventional PMMA, modified MMA, and polyamide resins would not stain after being immersed in beverages. The second null hypothesis was that surfaces roughness of the tested materials would not effect on color stability.

Materials and Methods

For each material, twenty disk-shaped specimens with a diameter of 10 mm and a height of 2 mm were prepared.

Meliodent, a brand of conventional PMMA resin made by Heraeus Kulzer in Senden, Germany, was mixed using the manufacturer's suggested powder-to-liquid ratio of 35 g to 14 mL. Meliodent was polymerized in a water bath for 90 minutes at 70 °C, followed by 30 minutes at 100 °C.

Two different monomer-free modified MMA (Bre-Crystal, Bredent, Senden, Germany and Acryfree, Perflex, Netanya, Israel) resin specimens were flasked using injection-specific equipment. The polymerization took place in 2-3 minutes at 100 °C in a cartridge that was heated to 260 °C for use in an injection device.

Three different polyamide (Bre-Flex, Bredent, Senden Germany; Flexinylon, Bredent, Senden, Germany; and T Crystal, Perflex, Netanya, Israel) resin specimens were preheated at 222 °C for 15 minutes. The heated and softened resin was injected into the mold in 90 seconds. Each specimen had smooth and rough surfaces after deflasking.

Prior to the color measurements, all specimens were kept in distilled water at 37 °C for 48 hours. A colorimeter (CR 2000; Minolta Inc, Osaka, Japan) was used to measure the color of each specimen at that time (T0).

Following the initial color assessments, specimens were submerged in distilled water as a negative control and three staining solutions (coffee, tea, and coke) as test groups. Five teabags (Lipton Yellow Label Tea; Unilever, Istanbul, Turkey) were dipped into 1,000 mL of heated water to create the tea solution. Twenty g of coffee (Nescafe Classic; Nestle, İstanbul, Turkey) was dissolved in 1,000 mL of boiling distilled water to create the coffee solution (18). Every 30 minutes, both solutions were swirled for 10 seconds until they reached a temperature of 37 °C. Pour 1,000 mL of Coca-Cola (Coca-Cola Co, Çorlu, Turkey) at room temperature into a container to prepare it for coke solution. Distilled water was used as a control group. Every three days, staining solutions were changed. The color of the specimens was once more measured after 1-day (T1), 12-day (T2), and 36-day (T3) soaking periods. Between time intervals, samples were kept in distilled water in a water bath at 37 °C. One day's worth of storage was chosen as

the benchmark period. However, according to the coffee producer, it takes 15 minutes on average to finish one cup of a beverage, and daily coffee consumption among drinkers is 3.2 cups. As a result, one day of storage represented the beverage's consumption over a month (19).

Color changes were described using the Commission Internationale d'Eclairage (CIE) L*a*b* color space. The formula for total color differences is: $\Delta E^*=[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{½}$ where ΔL*, Δa*, and Δb* are differences in the corresponding L*, a*, and b* values, respectively (20). To measure the color values, a colorimeter (CR 2000; Minolta Inc, Osaka, Japan) was used. Prior to immersion, the initial color values were recorded. Values for color change were also calculated after T1, T2, and T3 periods. The colors of all specimens' smooth and rough surfaces were measured.

The data were transformed to National Bureau of Standards (NBS) units using the equation [NBS units = ΔE*0.92] in order to connect the amount of ΔE* to a clinical environment. Table 1 shows the critical remarks about color differences as expressed by NBS units.

Statistical Analysis

The software program (SPSS Inc; Chicago, IL, USA) was used to compute mean values and standard deviations for each group. The data were statistically evaluated using repeated measure analysis of variance and the Duncan test. Post-hoc tests and Bonferroni adjustments were used to determine whether there was a significant difference within and between subgroups.

Table 1. 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

NBS: National Bureau of Standards

Results

The results of repeated test all variables (time, denture base materials, surface features, and beverages) were statistically significant (p=0.038), according to ANOVA (Table 2).

Regardless of time or beverage, there was no statistically significant difference between smooth and rough samples (p=0.414). The results of between different variables (surface features, denture base materials and beverages) were not statistically significant (p=0.326) (Table 3).

Figure 1 shows the mean ΔE values of the tested combinations for each immersion time. At the end of T1, T2, and T3 period, Bre-crystal exhibited statistically significant lower color difference (p<0.05).

Figure 2 shows the mean ΔE values of the specimens in beverages for each immersion time (T1, T2 and T3). At the end of T2 period, tea caused statistically significant color change than distiled water (p<0.05). After T1 and T3 periods, beverages did not cause statistically significant color change than distilled water (p>0.05).

Regardless of time, modified MMA (Acryfree) and conventional PMMA (Meliodent) specimens exposed to coke demonstrated statistically significant lower color stability than all others (p<0.05) (Figure 2).

Based on the NBS system, the color changes for all materials after T3 period ranged between "slight" and "much". In the "trace" and "too much" categories, no color change was observed.

Table 2. Within subjects effects of ΔE for denture base resins

Source	df	SS	MS	F	p-value
Time (T)	2	6.934	3.467	2.385	0.093
T x surface (S)	2	4.450	2.225	1.530	0.218
T x material (M)	10	32.266	3.227	2.220	0.016*
T x beverage (B)	6	71.482	11.914	8.195	<0.0001*
T x S x M	10	70.906	7.091	4.878	<0.0001*
T x S x B	6	8.872	1.479	1.017	0.414
T x M x B	30	159.161	5.305	3.650	<0.0001*
T x S x M x B	30	66.977	2.233	1.536	0.038*
Error (time)	384	558.215	1.454		

df: Degrees of freedom, SS: Sum of squares, MS: Mean square
*Statistically significant (p<0.05)

Table 3. Between subjects effects of ΔE for denture base resins					
Source	**df**	**SS**	**MS**	**F**	**p-value**
Surface (S)	1	30.331	30.331	6.811	0.010*
Material (M)	5	907.762	181.552	40.769	<0.0001*
Beverage (B)	3	42.386	14.129	3.173	0.025*
S x M	5	136.358	27.272	6.124	<0.0001*
S x B	3	18.519	6.173	1.386	0.248
M x B	15	210.144	14.010	3.146	<0.0001*
S x M x B	15	75.906	5.060	1.136	0.326
Error	192	855.015	4.453		

df: Degrees of freedom, SS: Sum of squares, MS: Mean square
*Statistically significant (p<0.05)

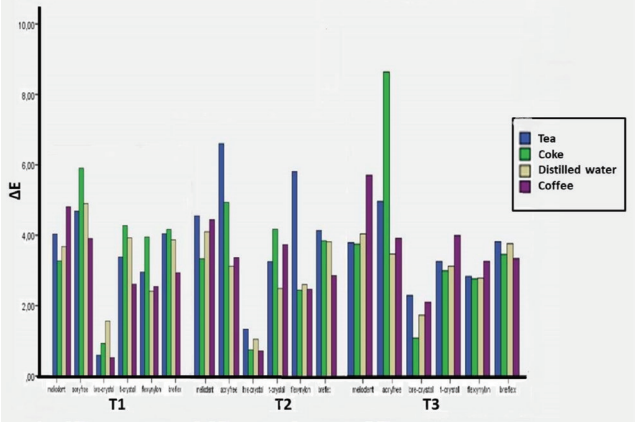

Figure 1. Mean color differences (ΔE) of denture base materials in T1, T2, and T3 immersion periods

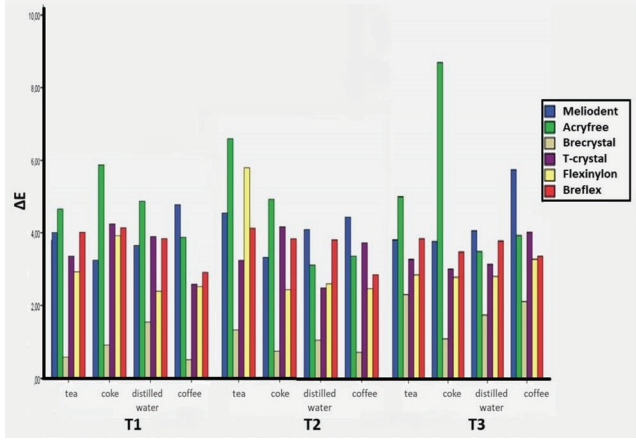

Figure 2. Mean color differences (ΔE) of denture base materials in beverages for T1, T2, and T3 immersion periods

Discussion

In tested denture base specimens at T1 and T3 time intervals, the beverages did not cause a significant difference in color change when compared to distilled water. Because tested denture base materials stained after immersion in tea at T2 time intervals, the first null hypothesis of this study was partially accepted.

There was no statistically significant difference between smooth and rough specimens, regardless of time or beverage. Thus, the second null hypothesis was accepted. The color stability of denture base material is critical for keeping the aesthetic appearance of the removable acrylic prosthesis (16). Although color stability of polished, smooth surfaces is vital for the aesthetic success of the removable dentures, this study considered color change values of both smooth and rough surfaces. The rough surfaces were produced against the plaster surface to replicate the tissue surface in clinical applications. The smooth surfaces were created utilizing the double-sided flask process, which involved polymerizing the materials against the glass surface in the flask. It is not possible to manufacture absolutely smooth surfaces *in vitro* because denture base resins can not be prepared against the glass surface in real clinical conditions. Although the technique of preparing the denture base materials against the glass surface does not fully reflect clinical conditions, it was chosen because it provides gloss surface standardization. Because polyamide-based resins are more difficult to polish than PMMA resins (7,21), the color changes of both smooth and rough surfaces were calculated. In a study examining the color stability, surface roughness, and surface porosity of acrylic resins, it was found that the attributes of surface roughness and color stability were not directly related to one another (15).

Since polyamide denture base materials are hygroscopic, moisture content may fluctuate depending on environmental conditions. Each polyamide type's chemical composition and water absorption are influenced by the frequency of amide groups throughout the chain (8). It is suggested

that the concentration of amide groups in nylon 6 and 66 materials be lowered since the sorbed moisture rises with the concentration of amide groups. Strong hydrogen bonds are established between the amide groups as a results of this formation, the binding of water molecules to these places diminished (22). Kurtulmus et al. (12) found no significant differences in liquid sorption values between different heat-polymerized acrylic and polyamide resin polymerization techniques, however denture base materials with crosslinking agents absorbed less solution than materials without crosslinking agents. Lai et al. (13) investigated the color stability and water absorption of four denture base materials and discovered that PMMA materials had better color stability and lower water absorption, while copolyamide materials had the highest water absorption value and silicone materials had the lowest. On the other hand, when Pfeiffer and Rosenbauer (1) compared the water solubility and water absorption of hypoallergenic and standard PMMA resins, they found that the hypoallergenic denture base materials had water absorption that was at least as high as that of PMMA material.

According to the findings of the current study, modified MMA resin (Bre-Crystal) produced the lowest color difference values. The color stability of the polyamide resins used was slightly better than Meliodent. There were similar ΔE values for polyamide groups across all time intervals, but there was a significant difference between hypoallergenic, MMA-free resins. It can be attributed to differences in composition and processing of this materials.

Staining develops over time as a result of the use of various dyestuffs and beverages, as well as the aging of materials. Coffee, tea, and coke were used as staining materials in the current study, as in previous studies (9,19). After a one-day immersion period, tea, coffee, and coke did not produce a statistically significant color change when compared to distilled water. Similarly, Buyukyilmaz and Ruyter (17) reported that after 96 hours of immersion in coffee and tea solutions, the discoloration values of different denture base materials were the same.

Tea generated a statistically significant color change after 12 days when compared to distiled water. Since Turkey has the largest tea consumption per capita (3.16 kg), dentists and denture-wearing patients should take into this consideration (23).

NBS parameter, which just needs to assess ΔEab values rather than separate L*, a*, and b* values, is useful for color comparison and quality control applications (20,24). For all time intervals, the changes found between 0.36 and 7.16 could be classified as “trace” or “much” using the NBS system that expresses color difference. These results were in line with those of a study that examined the expresses of color difference and utilized two heat-cured denture base acrylics and one nylon denture base resin (11).

One of the limitations of this study was the lack of SEM images of the surface of the samples. In future studies, CIEDE2000, which is the most current formula should be used to evaluate the color stability. Other factors, such as thermal cycling or wear, influence the overall color change (24,25). The lack of such a test environment can be viewed as a limitation and an area for future research.

Conclusion

The following conclusions were reached within the scope of the study:

1. The staining solutions (tea, coffee, and coke) did not cause a significant color change in tested denture base specimens when compared to distilled water at T1 and T3 time intervals.

2. The color stability of the modified MMA resin (Bre-Crystal) was the best at all time intervals.

3. The smoothness or roughness of the surfaces of all tested denture base materials had no effect on color stability.

Ethics

Ethics Committee Approval: This study does not require ethics committee approval.

Informed Consent: This study does not require informed consent.

Peer-review: Externally and internally peer-reviewed.

Authorship Contributions

Concept: H.A., Design: H.A., A.G., Data Collection or Processing: H.A., P.O., Analysis or Interpretation: R.D., Literature Search: G.D.G., A.G., Writing: G.D.G., P.O.

Conflict of Interest: No conflict of interest was declared by the authors.

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