Original Article

Evaluation of the Color Stability of Methyl Methacrylate and Nylon Base Polymer

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KEY WORDS
Color stability;
Spectrophotometer;
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ABSTRACT

Statement of the Problem: Evaluation of the color stability of materials used for the fabrication of the base of complete and partial removable dentures provides important information in relation to their clinical service. The color stability of nylon-based polymers as denture bases, compared to that of acrylic resins, has not been extensively evaluated since to date.

Purpose: The aim of the present *in vitro* study was to evaluate the color stability of conventional polymethyl methacrylate and nylon-based polymer materials used for the fabrication of the base of complete and partial removable dentures.

Materials and Method: Twenty samples were evaluated in the present *in vitro* study. One nylon-based polymer and one heat-cured acrylic resin were seleted for the purpose of the study. Ten disk samples, measuring 10 mm in diameter and 2 mm in thickness, were prepared from each material according to the manufacturers' instructions. The samples were evaluted with the CIELAB sysem using spectrophtometery at baseline and after irradiation with UV light for 100 and 200 hours and thermocycling. One-way ANOVA and post hoc paired t-test were used to compare the color stability of the two groups. Statistical significance was set at $p< 0.05$.

Results: After 100 hours of irradiation with UV light and thermocycling, color changes were tangible in both materials. After 200 hours of irradiation with UV light and thermocycling, both materials exhibited a decrease in glaze. In general, chromatic changes in the acrylic resin were more noticeable.

Conclusion: Accelerated aging affected the color stability of the acrylic resin and nylon-based polymer, $p< 0.05$ for $\Delta a200$ and $\Delta b200$ and $\Delta L100$; however, at the end of the study both materials exhibited clinically acceptable color stability ($\Delta E<3.7$).

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Introduction

The main disadvantage of materials used for the fabrication of complete or partial removable dentures is the fact that their esthetic appearance and physical and mechanical properties undergo rapid changes with time in the oral cavity. In relation to the esthetic appearance, color or chromatic stability is a criterion requiring more attention since staining affects the glassy surface and the shine of the denture, which are concerning factors for both patient and dentist. [1]

The most commonly used material for the fabrication of the denture base is polymethyl methacrylate (acrylic resin) which has the disadvantage of color change despite favorable functional, physical and me-

chanical properties, proper esthetic appearance and inexpensive equipment needed for its fabrication processes. [2] Polymethyl methacrylate slowly absorbs water with time, which is a property attributable to the polar nature of the resin molecules. Color changes of materials might be mediated by the amine-accelerated oxidation or by penetration of colored solutions. A large number of studies have reported color changes in resin-based restorative dental materials. [3-5] Color changes of the acrylic resin denture base have been reported after exposure to oral fluids and denture cleaning agents. [6-7]

The therapeutic uses of thermoplastic materials have significantly increased in the recent decade. They are new materials and prosthetic appliances are fabricated by injecting them after they are softened with heat, without any chemical changes. These materials have opened new horizons in the fabrication of dentures. [8-9]

One of the different types of thermoplastic materials are nylon-based polymers which have attracted a lot of attention in recent years as materials for denture bases due to their advantages, including proper esthetic appearance, lack of toxicity in patients allergic to metals and resin monomers, [10-11] higher elasticity compared to conventional heat-cured acrylic resins, adequate strength for use as denture bases, use of a thermal mold instead of chemical polymerization, absence of deformity during polymerization process , and absence of residual unpolymerized monomers. [12]

It appears that there is a need for the use of a color system in order to determine and adjust colors to solve esthetic problems. A color system uses principles based on which large arrays of color samples are definitely categorized in relation to each other. [13] Of all the different color systems available, CIELAB system, which depends on the theory of additional mixing of colors, has more applications in the dental field. [14] The aim of the present study was to compare the color stability of a nylon-based polymer with that of a polymethyl methacrylate resin as materials used for fabrication of the base of prosthetic appliances.

Materials and Method

Based on similar studies, 20 samples were prepared for the purpose the present *in vitro* study. A nylon-based polymer (Bredent Flex; GmbH&Co KG,Senden, Germany) and a heat-cured acrylic resin (Triplex; Ivoclar Vivadent AG Schaan/ Lichtenstein) were used in the present study. A total of 10 disk-shaped samples were prepared from each material according to the manufactures' instructions, which meaured 10 mm in diameter and 2 mm in thickness. [8]

Preparation of acrylic resin samples

The samples were prepared using the conventional technique with the use of a pressurized mold. The polymerization was carried out by heat in water at 70°C for 7 hours and at 100°C for 1 hour. A plastic disk was used as a mold. [15]

Preparation of nylon-based polymer samples

The nylon material was placed in a cartridge and heated in a furnace (Furnace 110-220 V; 60 Hz, Thermoplastic Comfort System Inc., USA) up to 280°C for 15 minutes to liquefy it. The stone mold was homogeneously exposed to 232°C heat for 10 minutes under hot light bulbs. Both halves of the flask, along with the cartridge containing liquified nylon, were placed on each other within the cylinder (Thermoplastic Comfort System Inc., USA). Then they were placed inside a piece of injection equipment (Injector Press; Thermoplastic Comfort System Inc., USA). The injection was carried out in 3 minutes under a pressure of 6 bars. The flask was cooled for 30 minutes before opening and then opened. The sprue was separated using a disk and the acrylic resin and nylon polymer samples were polished with 800-, 1000- and 1200-grit abrasive paper to achieve a smooth, shiny and homogeneous surface. [15]

All the samples were stored in distilled water at 37°C for 24 hours after preparation to make sure of completion of the polymerization process. This stage was carried out by the use of a heater. The nylon-based polymer samples were coded from A to J and the acrylic resin samples were coded from 1 to 10. Then the samples were irradiated with the UV light. The light source was a 1700-W xenon borosilicate lamp in a piece of Sun Test equipment (Atlas Sun EST XXL/ XXL Chicago Lionoic, USA) with an irradiation surface area of 400 W/m^2. [16]

The samples were exposed to the UV light for 100 hours. Then the samples underwent a thermocycling procedure at 5–55°C, consisting of 1800 rounds (SD MechatronikGmbH, Germany). Then the UV light irra-

diation procedure was repeated for another 100 hours, followed by another thermocycling procedure in the same manner. The sequences used in the present study were the same as those used in the Weather-Ometer test equipment, which carries out accelerated aging, during which first irradiation is carried out, followed by storage in water. [8, 17]

Colorimetric evaluation

The CIELAB coordinates of each sample were determined with the use of a reflexive spectrophotometer at a wavelength of 360–750 nm under the D65 light source (Xrite SP64 Spectrophotometer; Michigan, USA) at three stages (before irradiation and after 100 and 200 hours of irradiation plus thermocycling procedure). All the measurements were made by one operator. Then color changes of the samples were determined using the formula below:

$\Delta E\ (l,a,b) = [(\Delta L)2 + (\Delta a)2 + (\Delta b)2]1/2$

$\Delta L = L_B - L_I$

$\Delta a = a_B - a_I$

$\Delta b = b_B - b_I$

I=Interval of UV exposure (100 or 200 hour)

B= base line

One-way ANOVA and paired t-test were used to evaluate the color stability in the two groups at a significance level of $p< 0.05$. [16]

Table 1: The results of paired t-test to compare the variables between the two groups

Dependent variable	Material	Mean	SD	t-value	P-value
ΔE100	Nylon	1.22	.52	-.450	.658
	Acrylic	1.33	.56		
ΔE200	Nylon	3.22	.98	-.289	.776
	Acrylic	3.32	.54		
Δa100	Nylon	-.64	.44	-1.057	.305
	Acrylic	-.86	.51		
Δa200	Nylon	.01	.87	5.593	.000
	Acrylic	1.95	.66		
Δb100	Nylon	-.59	.43	1.887	.075
	Acrylic	-.27	.33		
Δb200	Nylon	-.04	.43	4.743	.000
	Acrylic	.84	.41		
ΔL100	Nylon	.24	.80	2.417	.033
	Acrylic	.90	.32		
ΔL200	Nylon	3.08	1.09	-1.645	.117
	Acrylic	2.43	.63		

Results

After collection of data and statistical analysis of the variables under study between the nylon-based polymer and the acrylic resin, the following results were obtained. In all comparisons, the absolute values of the changes have been considered. Table 1 presents the results of t-tests to compare the variable between the nylon-based polymer and acrylic resin samples. The values 1,100 and 200 next to the variables signify the results at baseline and after 100 and 20 hours of UV light irradiation and thermocycling.

Discussion

Changes in the color of prostheses might be an indication of damage to and aging of dentures, sending signs to the patient that they should replace or repair the prosthetic appliances. [18] Color changes in materials take place through various mechanisms; reduction products of pigments, changes in surface structures due to abrasion and extrinsic staining are some factors involved in color changes. [8] The aim of the present study was to evaluate color stability of a nylon-based polymer and an acrylic resin during an accelerated aging procedure.

Accelerated aging procedure [8] is a process which shows the effect of environmental factors such as UV light and thermal and moisture changes. This technique was introduced in 1978 for the evaluation of color stability of dental resin materials. Several studies have shown the effect of accelerated aging on the color stability of denture liners and resin-based restorative materials; [18-19] however, its effect on denture base materials has not been evaluated properly and adequately. [18] Studies have shown that the maximum color changes during a period of 1440 hours of accelerated aging test occur during the first 300 hours [8] and since this test consists of intermittent irradiation with the UV light, comprising the two-thirds of the total duration of the test, in the present study 200 hours of irradiation with UV light was selected for the final evaluation of color changes in the materials. [2] This amount of irradiation is equal to the amount of irradiation a restoration is exposed to in one year in the oral cavity. [18]

Since color is a mental–physical phenomenon and it is different in different people and even in one individual at different times and since measurements with an accurate tool refutes the effect of subjective assessment errors and can be used as an evidence in different situations and locations, in the present study color was evaluated by a reflexive spectrophotometer (Xrite SP64 Spectrophotometer, Michigan, USA), which has a high

rate of accuracy, is portable and is easy to use. In addition, a commonly used color system (CIELAB system) was used for the evaluation of color changes of the samples because it is used in the dental field due to complete and continuous coverage of the color spectrum. [20]

The "L" index indicates lightness and darkness (from white to black). The cells in the human eye consist of rods and cones; rods are responsible for visualization of black and white, and cones are responsible for visualization of colors. The rods outnumber cones; therefore, the human eye perceives any loss of transparency and shine much faster, which is very important in color stability and clinical success. [21]

Based on the results of the present study and evaluation of the "L" index, at the end of 200 hours of irradiation and thermocycling, the acrylic resin and nylon-based polymer lost their shine and luster. The decrease in shine during the first 100 hours in the acrylic resin was more than that of the nylon-based polymer, i.e. the acrylic resin had become darker. However, after 200 hours, both materials exhibited a similar loss of shine. Both the acrylic resin and the nylon-based polymer had become more opaque after 200 hours compared to the 100-hour interval.

Powers *et al.* [22] carried out a study on composite resins and reported that after accelerated aging the matrix of the resins underwent abrasion and the fillers were exposed. As a result, the surface of the resin became chalky and the surface roughness increased. [22] In the present study, a decrease in the shine might also be attributed to the damage to the resin matrix.

Since the "a" index indicates green chroma (-) or red chroma (+), in case of the acrylic resin, the changes were toward red after 100 hours and toward the green after 200 hours. Changes in the "a" index in relation to the nylon-based polymer were not significant after 100 and 200 hours. There were no significant differences in changes of "a" toward red between the nylon-based polymer and acrylic resin after 100 hours; however, after 200 hours, changes in the "a" index toward green in the acrylic resin were significant compared to the nylon-based polymer.

The "b" index indicates yellow chroma (+) or blue chroma (-). In relation to the acrylic resin and the nylon-based polymer the changes were toward yellow after 100 hours; the changes were toward blue in the acrylic resin and toward yellow in the nylon-based polymer after 200 hours. Yellow changes in the nylon-based polymer were less than those in the acrylic resin after 200 hours compared to those after 100 hours: therefore, the maximum yellowing in the nylon-based polymer had occurred after 100 hours. Changes in the "b index toward yellow were not significantly different between the nylon-based polymer and the acrylic resin after 100 hours. However, changes in the "b" index toward blue in the acrylic resin were significant compared to those in the nylon-based polymer after 200 hours.

Based on a study by Liberman *et al.*, [19] changes in the "b" index can only be perceived by naked eye when its numeric value is higher than 1.5. In the present study, Δb for both materials was less than the value mentioned above after 100 and 200 hours; therefore, changes in the yellow-blue chroma could not be perceived by visual evaluation.

Acrylic resins undergo color changes in the oral cavity; however, the important consideration is the range of these color changes; they should be in a range not perceived by the eye. In the CIELAB color system, this range of color change is shown by ΔE, which is the algebraic difference between the two colors and almost all the studies have used this system after its introduction. [8]

ΔE>1 indicates a tangible difference between the two colors, which can be perceived visually by at least 50% of the observers. The yielded value (ΔE>2.7) means a difference in color which is unacceptable from clinical point of view. However, some researchers consider ΔE>3.3–3.7 as unacceptable from clinical point of view. [19] In the present study, color changes in the two materials (Figure 1) after 100 hours was >1, which was perceptible. ΔE was less than 3.7 after 200 hours, which is acceptable from clinical viewpoint.

There are many factors which might have affected the color changes in the materials under study described as follows.

The monomer remaining in the acrylic resin after polymerization might react with the pigments within the polymer, resulting in color changes (reduction products of pigments). [23] The UV light might affect other polymers, cutting the different polymer chains to produce elements capable of effecting color changes. [17] Ben-

zoyl peroxide in the powder of the acrylic resin acts as an initiator at temperatures over 60°C and the residual unreacted free radicals might be factors for color changes. [17] In relation to color changes of the nylon-based polymer, attention might be paid to the presence of amine group in its structure, the oxidation of which might result in color changes. [23]

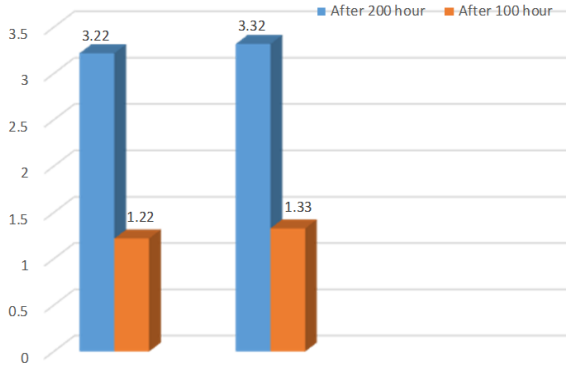

Figure 1: Color changes of the materials after 100 and 200 hours of UV light irradiation plus thermocycling

In the present study, the acrylic resin exhibited more chromatic changes compared to the nylon-based polymer, which might predominantly be attributed to the monomers remaining in the acrylic resin because thermoplastic materials have a very small amount of monomer. The results of the present study are consistent with those of a study by Pinto, [24] in which only the effect of thermocycling was evaluated and the nylon-based material (Flexiplast) exhibited acceptable color stability from a clinical point of view at the end of the study. Such consistency between the results of the two studies might be attributed to the similar study design of these studies. However, the results of the present study do not coincide with those of a study by Goiato, [23] in which the Valplast nylon-based polymer did not exhibit acceptable color stability after accelerated aging, which might be attributed to different nylon materials used in these two studies. Materials such as antioxidants might be added to the composition of some polyamides, which might be effective in preventing oxidation and color changes. [31]

The results of the present study are different from the study of Lai *et al.*, [25] in which the Flexite Supreme nylon exhibited favorable ΔE in colored solutions such as tea but ΔE was not favorable in coffee; and the study of Takabayashi, [26] in which the mechanical and physical properties of some thermoplastic materials and conventional acrylic resins were compared, with polyamides exhibiting definite and unacceptable staining in coffee; and also a study published by Kurtulmus *et al.*, [27] in which the effects of saliva and nasal secretions were evaluated on resin materials, with DeFlex nylon exhibiting unacceptable discoloration from a clinical point of view. The differences in the results of these studies might be attributed to differences in study designs.

Concerning the above studies, the nylon-based polymer was placed in a colored solution and favorable color stability was not shown, which might be attributed to the hydrophilic nature of nylon, the color nature of the yellow stain in the colored solutions, [25] and the presence of tannic acid in tea and coffee, which lead to the sorption of pigments to the base materials of denture. [28] In relation to saliva, the surface roughness of nylon might have played a role, by considering the fact that studies have shown a direct relationship between surface roughness on one hand and accumulation of plaque and adhesion of candida species on the other. [29]

The results of the present study in relation to the acrylic resin are similar to those of a study of Ergun and Nagas [17] in which the heat-cured Triplex acrylic resin exhibited favorable ΔE at the end of the study, which might be attributed to the similarity of the materials and study designs. The results of the present study in relation to the acrylic resin are consistent with those of a study by Liberman *et al.* [19] in which the heat-cured Minacryl exhibited favorable ΔE after 24 hours of irradiation These similar results might be attributed to less surface roughness and less water sorption by the acrylic resin compared to nylon, which results in less pigment adhesion. [19]

Koran *et al.* [31] showed that color changes brought about by stains and disinfecting agents are more severe than those by accelerated aging in the resins used for the fabrication of maxillofacial prostheses. It can be concluded from all the studies carried out to date that extrinsic agents involved in color change have a very great role in discoloration of acrylic resins. In the present study, only the intrinsic factors were evaluated. Therefore, a final verdict about the color stability of materials can be reached when both extrinsic and intrin-

sic factors involved in color changes are evaluated simultaneously. The results of the present study can be used in future studies on the color stability of acrylic resins used in prostheses, especially the thermoplastic resins.

Conclusion

Accelerated aging affected the color stability of acrylic resin and nylon-based polymer. The color stability of both materials was clinically acceptable, with none being superior to the other ($\Delta E<3.7$). Both the acrylic resin and the nylon-based polymer exhibited a decrease in shine at the end of the study and both materials became more opaque. The nylon-based polymer and the acrylic resin exhibited the maximum color changes (a, b) after 100 and 200 hours, respectively.

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Conflict of Interest

The authors of this manuscript certify that they have no conflict of interest.

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