

Effect of accelerated aging on the microhardness and color stability of flexible resins for dentures

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Abstract: Acrylic resins have been widely used due to their acceptable esthetics and desirable characteristics such as easy handling, good thermal conductivity, low permeability to oral fluids and color stability. Flexible resins were introduced on the market as an alternative to the use of conventional acrylic resins in the construction of complete and partial removable dentures. Although these resins present advantages in terms of esthetics and comfort, studies assessing chromatic and microhardness alterations of these materials are still scarce in the related literature. The aim of this study was to evaluate the chromatic and microhardness alterations of two commercial brands of flexible resins in comparison to the conventional resin Triplex when submitted to accelerated aging. The resins were manipulated according to manufacturers' instructions and inserted into a silicone matrix to obtain 21 specimens divided into 3 groups: Triplex, Ppflex and Valplast. Triplex presented the highest microhardness value ($p < 0.05$) for all the aging periods, which was significantly different from that of the other resins, followed by the values of Valplast and Ppflex. Comparison between the flexible resins (Ppflex and Valplast) revealed a statistically significant difference ($p < 0.05$) as regards color. The flexible resin Ppflex and the conventional resin Triplex presented no statistically significant difference ($p < 0.05$) as regards aging. The accelerated aging significantly increased the microhardness values of the resins, with the highest values being observed for Triplex. Valplast presented the greatest chromatic alteration after accelerated aging.

Descriptors: Hardness; Color; Acrylic resins.

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Introduction

Acrylic resins were introduced in 1936 as an alternative to vulcanized rubber and have been used to construct the bases of complete and partial removable dentures. Among their characteristics are easy handling, good thermal conductivity, low permeability to oral fluids and color stability.¹

However, polymerization shrinkage is the greatest disadvantage¹ of this material. Dimensional alteration is a critical factor for the retention and stability of prostheses,² although some factors may compensate this effect, including water absorption by the acrylic resin,³ resilience of the gingival mucosa and the action of saliva.⁴

An increased awareness of esthetics in dentistry has led to the need for removable partial dentures (RPDs) that reveal little or none of the

Received for publication on May 28, 2009
 Accepted for publication on Nov 25, 2009

metal supporting structures or retentive elements. Krol and Finzen's⁵ review concerning the rotational path for RPDs insertion pointed to the development of RPD designs that avoid anterior direct retainers.⁶

Unfortunately, many clinical situations are not suitable for using these concepts, and conventional retainers in the anterior region are often necessary. Direct retainers fabricated in a tooth-colored material, such as acetyl resin (thermoplastic technopolymer) may be more esthetic.⁶

The resin denture base materials are composed by a monomer, (methylmethacrylate) and a polymer (polymethylmethacrylate, PMMA). The cure reaction of PMMA occurs in a water bath under controlled temperature during some hours or under microwave energy during some minutes.⁷

Acrylic prostheses present excellent resistance to the oral environment, solvents and UV radiation. However, there is a risk of toxicity and hypersensitivity to the material due to products of oxidation and other components of the system.⁷

Mucosal irritation caused by released methylmethacrylate have been reported.⁸ Some potential alternative materials to PMMA used in these cases are polycarbonate and nylon.⁹

Flexible resins were developed for the construction of provisional prostheses such as immediate RPDs,¹⁰ and are indicated for the construction of RPDs, mainly for anterior retention with esthetic requirements, due to the advantages of translucency and a natural appearance without laboratorial characterization. Furthermore, the flexibility of these materials prevents prosthesis fractures and allows lighter and more comfortable prostheses. Flexible resins require no tooth preparation as do conventional RPDs, and they reduce the chair time required to construct the prosthesis.^{11,12}

Although the related literature presents studies assessing the properties of these materials in terms of deformation and prosthesis retention, there is a lack of information about microhardness and color alterations associated to prosthesis aging.

The aim of this study was thus to evaluate the possible chromatic and microhardness alterations of the flexible resins Ppflex and Valplast in comparison to the conventional acrylic resin Triplex when sub-

mitted to accelerated aging.

Material and Method

Seven specimens were obtained for each of the three experimental resins: one heat-polymerized acrylic resin – Triplex (Ivoclar, Berlin, Germany) – and two thermo-injected flexible resins – Ppflex (Ideiaslab, Rio de Janeiro, RJ, Brazil) and Valplast (Valplast®; Albany, NY, USA).

Disks of autopolymerizing acrylic resin JET (Produtos Odontológicos Clássico, São Paulo, SP, Brazil) were obtained with a metallic matrix with 15 mm in diameter and 2 mm in thickness. These disks were included in metallic flasks with dental stone type III (Gesso Rio, São Paulo, SP, Brazil) and laboratorial silicone (Zetalabor, Zhermack, Badia Polesine, Rovigo, Italy) to obtain molds for resin pressing.

After deflasking of the autopolymerizing acrylic resin disks, the evaluated resins were manipulated according to the manufacturers' instructions to fill the molds. The flask filled with the resin Triplex was pressed under 80 bar pressure immersed in cold water and, after boiling, the resin was kept at 100°C for 45 minutes. The flask was cooled at room temperature during 30 minutes. For the resins Ppflex and Valplast, the molds in the flasks were filled at 270°C. After polymerization, the flasks were opened and the specimens were polished (Politriz APL-4 - Arotec, Cotia, SP, Brazil) with 600, 800 and 1,200 grit sandpaper.

The specimens were then submitted to initial Knoop microhardness evaluation by the digital microhardness tester HMV-2T, calibrated with a load of 50 g for 10 seconds, immediately after polishing.

All specimens were submitted to initial color evaluation by a spectrophotometer of visible ultraviolet reflection (UV-2450 - Shimadzu, Kyoto, Honshu, Japan), as established by literature^{13,14,15}, and color alteration was calculated according to the CIE L*a*b* system established by the *Comission Internationale de l'Eclairage* – CIE¹⁶ through the formula $\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$.

After the initial evaluations, the specimens were submitted to accelerated aging for non-metallic specimens – Ultraviolet B/condensation. The specimens

were positioned into a chamber of accelerated aging (Equilam, Diadema, SP, Brazil) for alternating periods of ultraviolet light and condensation of distilled water. Each accelerated aging period was conducted for 12 hours. During the first eight hours, ultraviolet light focused at $60 \pm 3^\circ\text{C}$. A period of condensation with no light at $45 \pm 3^\circ\text{C}$ occurred during the remaining four hours. The evaluations were performed initially and after each period of 504 and 1,008 hours of aging for microhardness and 252, 504 and 1,008 hours for color alteration, for a total of 3 measurements for each test. The data were evaluated by 2-way repeated-measures ANOVA and the Tukey HSD test ($\alpha = .05$).

Results

The results are presented in tables 1 to 4.

The factors material and aging presented a statistically significant influence ($p < 0.05$) on the Knoop microhardness values of the resins, as can be observed in table 1.

The variation of microhardness values according to aging for the three experimental resins is presented in table 2. The results show that the resin Triplex presented the highest value of microhardness ($p < 0.05$) after all the aging periods, which was significantly different than that of the other resins. There was a statistically significant increase in mi-

crohardness values ($p < 0.05$) for all materials after the different aging periods (initial, 504 and 1,008 hours).

The sources material and aging presented a statistically significant influence ($p < 0.05$) on the chromatic stability of the resins, as can be seen in table 3.

The results of the chromatic stability test are presented in table 4. The flexible resin Valplast was statistically different ($P < 0.05$) from the other resins, and the conventional resin Triplex was statistically similar ($P < 0.05$) to the flexible resin Ppflex only after the period of 504 h.

Discussion

Today's esthetic requirements call for constructing RPDs without metallic structures or retention systems in the anterior region.⁶

The indication of more esthetic materials without metallic support such as flexible resins is limited due to the lack of information provided by manufacturers or literature regarding alterations in microhardness and chromatic stability.

According to the manufacturers, the flexible resin Ppflex presents the surgical polypropylene as active principle and other components such as bactericides, anti-organic and anti-fungal substances.¹¹ The flexible resin Valplast is composed by thermo-

Table 1 - Analysis of variance results for the Knoop microhardness values.

Source	DF	Type III SS	Mean Square	F Value	p Value
Resin	2	3405.0775161	1702.5387581	17949.3101	0.00001
Aging	2	96.0447623	48.0223811	506.2843	0.00001
Resin x Aging	4	40.7536911	10.1884228	107.4132	0.00001
Residue	54	5.1220405	0.0948526		
Total	62	139.6601423			

$p < 0.05$ statistically significant difference.

Table 2 - Knoop microhardness means and standard deviations (in parentheses) for the aging periods of the resins tested.

	Initial	504h	1,008h
TRIPLEX	23.669 (0.073) A, α	26.094 (0.094) A,b	24.286 (0.285) A, c
PPFLEX	7.047 (0.047) B, α	8.903 (0.062) B,b	10.844 (0.100) B, c
VALPLAST	7.047 (0.047) B, α	9.377 (0.047) B,b	11.320 (0.073) B, c

Means followed by the same capital letter in the column and lowercase letter in the line do not differ statistically at the 5% level of significance ($p < 0.05$) by Tukey's test.

Table 3 - Analysis of variance results for the chromatic stability values.

Source	DF	Type III SS	Mean Square	F Value	p Value
Resin	2	90.2771498	45.1385749	93.7518	0.00001
Aging	2	14.9811519	7.4905759	15.578	0.00004
Resin x Aging	4	8.4025331	2.1006333	4.363	0.00425
Residue	54	25.9993076	0.4814687		
Total	62	139.6601423			

p < 0.05 statistically significant difference.

Table 4 - Chromatic alteration means and standard deviations (in parenthesis) for the aging periods of the resins tested.

	252h	504h	1,008h
TRIPLEX	1.621 (0.145) B,a	1.834 (0.186) B,a	1.795 (0.175) B,a
PPFLEX	1.738 (0.213) B,a	2.225 (0.167) B,ab	2.830 (0.171) C,b
VALPLAST	3.442 (0.375) A,a	4.327 (0.381) A,a	5.752 (0.377) A,b

Means followed by the same capital letter in the column and lowercase letter in the line do not differ statistically at the 5% level of significance (p < 0.05) by Tukey's test.

plastic nylon and is available in three shades: clear pink, rose and ethnic.¹²

The highest values of microhardness presented by the resin Triplex in comparison to the other resins were expected since it is a conventional resin based on polymethylmethacrylate without flexible agents in its composition such as plasticizers.¹⁷

The significant increase in microhardness for the three materials after accelerated aging is probably a result of their complete polymerization and their submission to two different forms of energy. Several studies^{18,19,20} have stated that all elastomers present continuous polymerization shrinkage that begins during polymerization and continues after clinical set. A volatile byproduct (formaldehyde) is obtained during polymerization of this type of silicone.^{19,20,21} Another explanation is that all resins were submitted to two forms of energy after polymerization, UV and temperature. They could be the main factors to the increase in microhardness values during the experiment.

There was no statistically significant difference in the microhardness values of resins Ppflex and Valplast after accelerated aging since both resins present flexible substances in their composition.^{11,12} On the other hand, the conventional resin Triplex, which does not have these substances in its composition, presented significantly higher values of mi-

crohardness (P < 0.05) after accelerated aging.

All resins exhibited a high ΔE value of color alteration after accelerated aging. Valplast presented the highest values, which were significantly different from those of the other materials.

A ΔE color alteration above 3.3 is considered perceptible.²² Therefore, only the flexible resin Valplast presented significant color alterations (ΔE_{504} 4.327 and ΔE_{1008} 5.752).

Both conventional and flexible resins suffered color alteration following aging due to intrinsic and extrinsic factors.²³ The intrinsic factors include discoloration of the material, with alteration of the matrix.²⁴ In general, this intrinsic discoloration occurs with aging as a result of physical-chemical conditions such as thermal and humidity changes. Extrinsic factors such as absorption and adsorption of substances in conventional resins may also lead to discoloration.²⁵ Other factors are also responsible for color instability, such as staining, dehydration, water absorption, leakage, roughness, chemical and aging degradation, oxidation, and pigment formation due to product degradation²⁶ and amine oxidation²⁷ in conventional resins. Absorption and adsorption may lead to staining of the resins by pigments in the oral environment, and are more responsible for chromatic alterations than inherent color instability of the material.²⁷

These factors may also occur in flexible resins that present a composition similar to that of conventional resins.

The results showed no statistically significant chromatic alteration difference between the flexible resin Ppflex and the conventional resin Triplex (Table 4) only after the period of 504 h. These resins probably present a smaller amount of monomer in their composition than the flexible resin Valplast, or, rather, Valplast presents a greater amount of reagents such as benzoyl peroxide.²⁸ Some studies that compared the chromatic alterations of autopolymerizing and heat-polymerized acrylic resins²⁹ observed greater chromatic instability for the autopolymerizing resins since these present a great amount of additional reagents such as benzoyl peroxide. This reagent remains after polymerization and may alter the material's color.²⁷ In addition, oxidation of the aromatic dimethyl-p-toluidine in autopolymerizing resins^{27,29,30} may generate greater color degradation. It is important to highlight that autopolymerizing resins present low conversion rates during polymerization with a high amount of residual monomer as a final product, which could interact with pigments in the polymer and deteriorate color.^{27,28,29}

As can be seen in table 4, there is a statistically significant color alteration difference between the values

of the flexible resins tested (Triplex: $\Delta E_{504} = 1.834$, $\Delta E_{1008} = 1.795$; Ppflex: $\Delta E_{504} = 2.225$, $\Delta E_{1008} = 2.83$; Valplast: $\Delta E_{504} = 4.327$, $\Delta E_{1008} = 5.752$). This may result from the presence of anti-organic, anti-fungal and antioxidant substances considered color stabilizers^{11,27,29,30} in the resin Ppflex, while the manufacturer of the resin Valplast did not confirm the presence of these substances on its composition.

In order to derive clinical implications from the results of this study, one must consider the difference between the oral environment and the *in vitro* conditions of the study. Considering this limitation, it can be stated that the flexible resins did not present a microhardness increase that may clinically compromise their flexibility after accelerated aging. However, the resin Valplast presented a chromatic instability following accelerated aging that could be clinically significant.

Conclusions

Accelerated aging significantly increased the values of microhardness of the resins tested, with the highest values being observed for the resin Triplex.

The resin Valplast presented the greatest chromatic alteration value after accelerated aging, which was significantly different from those of the other resins tested.

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