Effect of nanoscale particles incorporation on microhardness of polymers for oral prosthesis

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Abstract

Objectives: This study aimed to evaluate the influence of the incorporation of pigments on surface hardness of four acrylic resins subjected to thermocycling and analyze their elemental composition using energy dispersive X-ray spectroscopy (EDS). **Materials and Methods:** Twenty-one discs of each resin were fabricated, whereas seven had no additive, seven had 3% of nanoscale pigments and last seven had 10% of them. The percentage was obtained by measuring the total weight of each resin disc. Besides, seven discs composed by only nanoscale pigments were also fabricated, totalizing 91 discs. The pigment was weighed by using an analytical balance (BEL Analytical Equipment, SP, Brazil). The surface hardness was measured through a hardness tester machine before and after thermocycling (5–55°C, for 2000 cycles). Data were analyzed by ANOVA and Tukey's test ($P < 0.05$). The chemical composition of the discs composed only by nanoscale pigments was analyzed with EDS test. **Results:** Hardness of all resins decreased after thermocycling. The lowest values were observed on the discs with 3% of nanoscale pigments and discs fabricated only with them. EDS showed the presence of titanium dioxide. **Conclusion:** Discs with 7% of pigments (after thermocycling) showed higher hardness values.

Keywords: Acrylic resins, denture bases, geriatrics

Introduction

Oral prosthesis fabricated with acrylic resin may reproduce the shape, size, and color of supporting soft tissues to provide satisfactory esthetic outcomes.[1] Specific pigments for acrylic resins can be used to avoid the monochromatic appearance of the denture base. Several nanoscale pigments as dark carbon (C), zinc oxides (ZnO), titanium (Ti), and iron (Fe) have been incorporated into acrylic resins for improving the esthetic of the denture base.[2,3]

Staining resulted from thermal injury, absorption, and adsorption of substances may change the physical properties of polymers used to fabricate oral prosthesis.[4,5] Some authors suggested that the incorporation of nanoscale particles pigments increases the survival of resins and preserves their esthetic and color stability overtime.[6] However, there are few studies that evaluate the effect of nanoscale particles pigments incorporation on other physical properties of polymers, such as hardness.[7,8]

Surface hardness is an important property for prosthesis longevity since the higher the hardness is, the higher the resistance to abrasion.[9,10] The abrasion of acrylic resin surfaces increases the material roughness and promotes bacterial retention. As a consequence, the inflammation on the underlying tissue associated to the patient's discomfort may result in treatment failure.[9,11]

Therefore, the aim of this study was to evaluate the influence of the incorporation of pigments on surface hardness of four acrylic resins subjected to thermocycling and analyze their elemental composition using energy dispersive X-ray spectroscopy (EDS). The hypothesis assumed is that the nanoscale particles would not affect the hardness of tested acrylic resins, associated or not to the tested pigment, regardless of the artificial aging.

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Materials and Methods

Four acrylic resins and a nanoscale particles pigment were evaluated [Table 1].

Twenty-one discs of each resin were fabricated, whereas seven had no additive, seven had 3% of nanoscale pigment, and lasting seven had 10% of them. The percentage was obtained by measuring the total weight of each resin disc. Besides, seven discs composed by only nanoscale pigments were also fabricated, totalizing 91 discs. The pigment was weighed by using an analytical balance (BEL Analytical Equipment, SP, Brazil). The sample size ($n = 7$) was determined by preliminary tests. An adequate power (large effect size according to Cohen's effect size statistics) at an alpha level of 0.05 and power of 0.878 was obtained for detecting statistically significant differences.

Silicone rubber discs (Zetalabor, Zhermack SpA, Badia Polesine, Italy) with 30 mm in diameter and 3 mm in thickness were fabricated by using a metallic matrix.[10] Then, the discs were embedded into two-part flasks (Classico Dental Products, Sao Paulo, Sao Paulo, Brazil) with dental stone type III (Soli-Rock, Herodent, Vigodent, Rio de Janeiro, Rio de Janeiro, Brazil) to create the molds. The flasks were maintained in a hydraulic press (Midas Dental Products Ltd., Sao Paulo, Brazil) for 2 min. After dental stone crystallization, the flasks were opened and the silicone disks were removed.

The acrylic resins were manipulated according to the manufacturer's instructions [Table 1] and packed into the mold of each flask. The flasks were closed and maintained in a hydraulic press (Midas Dental Products Ltd., Sao Paulo, Brazil) during 2 min. Each acrylic resin was polymerized according to the manufacturers' instructions [Table 1]. The pigment incorporation followed the manufacturer's instructions and the quantity of pigment used were either 3% or 7% of the total weight of the acrylic resin. The pigments were weighed using a precision digital scale (BEL Equipamentos Analtico, Sao Paulo, Sao Paulo, Brazil).[11] The negative control samples were fabricated with only pigment (Poli-Cor).

Afterward, the discs were divested, finished with polishing points (Maxicut; Edenta AG, Hauptstrasse, Switzerland), and polished with 360-, 600-, and 1200-grit abrasive paper under water irrigation at 300 rpm using an automated polishing machine (APL-4; Arotec, Cotia, Sao Paulo, Brazil). The dimensions of each disc were measured using a precision digital caliper (Mitutoyo, Tokyo, Japan). All discs were stored in distilled water at 37 ± 2°C during 24 ± 2 h (CIENLAB, Campinas, Sao Paulo, Brazil) for hydration and residual monomer release before the initial microhardness measurement.[12]

The hardness test was performed before and after thermocycling by using a microhardner (HMV-2T; Shimadzu Corp., Kyoto, Japan) under 25 g load during 10 s. Five indentations were made for each disc, and a mean was obtained for each sample according to ASTM C1327.[3] After baseline hardness measurement, discs were thermocycled in a thermocycling simulation machine (MSCT-3, Convel, Aracatuba, Sao Paulo, Brazil).

Discs were submitted to 2000 cycles of thermocycling in distilled water with alternated 30 s bathes from 5 ± 1 to 55 ± 1°C.[13]

The chemical composition of discs fabricated only with pigments was analyzed through EDS. Data were obtained using a scanning electron microscope (SEM; JSM5600 LV; JEOL, Tokyo, Japan). The primary electron energy was 15 keV. The other testing parameters were set to WD: 20 mm, process time: 10 s, live time: 100 s, and dead time:

Table 1: Material, manufacturer, chemical composition, and polymerization procedure of the denture base acrylic resins

Material	Manufacturer	Chemical composition	Polymerization procedure
Classico	Classico Dental Products, Sao Paulo, Brazil	Liquid: MMA monomer, topanol Powder: MMA polymer, DBP, pigments	Immersion of flask in water. Hot water bath ½ h heated; ½ unheated, 1 h in boiling
Onda Cryl	Classico Dental Products, Sao Paulo, Brazil	Liquid: MMA monomer, ethylene glycol dimethacrylate Powder: Copolymer of MMA, DBP	Microwave polymerization: 3 min at 30% power; 4 min at 0% power and 3 min at 60% power
QC-20	Dentsply Ltda., Rio de Janeiro, Brazil	Liquid: MMA, ethylene glycol dimethacrylate, hydroquinone, terpinoleno and N, N-dimethyl-p-toluidine Powder: Copolymer (methyl-n-butyl) methacrylate, benzoyl peroxide and minerals colorants	Immersion of flask in water at 100°C for 20 min
Lucitone	Dentsply Ltda., Rio de Janeiro, Brazil	Liquid: MMA, ethylene glycol dimethacrylate and hydroquinone Powder: Copolymer (methyl-n-butyl) methacrylate, benzoyl peroxide, and minerals colorants	Immersion of flask in water at 73°C for 90 min and at 100°C for 30 min
Pigment	Classico Dental Products, Sao Paulo, Brazil	Organic and inorganic pigments	Immersion of flask in water Hot water bath ½ h heated; ½ unheated, 1 h in boiling

DBP: Dibutyl phthalate; MMA: Methyl methacrylate

30–40%. Two different areas were selected for each sample. Magnification ranging between ×50 and ×100.

Statistical analysis

The effect of resin material, pigment, and aging was analyzed by three-way analysis of variance (ANOVA). The resin material is hierarchical to the pigmentation factor because there is no intercorrelation between factors. The resin material factor was considered within the pigmentation to differs the resins between the pigment concentrations. The means were compared by the Tukey's HSD test ($\alpha = 0.05$). Differences with $P < 0.05$ were considered statistically significant.

Results

The hardness of all groups decreased after thermocycling [Table 2 and Figure 1]. The acrylic resin QC-20 [Table 1] with 3% of pigment showed the lowest mean of superficial hardness [Table 2]. The independent analysis of resin material, pigment concentration, and aging revealed that each factor was statistically significant; however, there was no significant difference for interaction between factors [Table 3].

When the hardness was compared to different pigment concentrations regardless the resin material and aging, the Tukey's HSD test ($\alpha = 0.05$) showed a significant reduction in the hardness mean for some groups in comparison to the others [Table 4]. It was observed that the nonpigmented samples and 7% pigment showed higher surface hardness than the others, regardless of the type of resin and aging [Table 4].

In addition, the Tukey-Kramer test revealed a significant difference between the hardness of the resin QC-20 with 3% of pigment concentration, 7% of pigment concentration, and no pigmentation when hardness was compared to each resin at different pigment concentrations regardless the period [Figure 2].

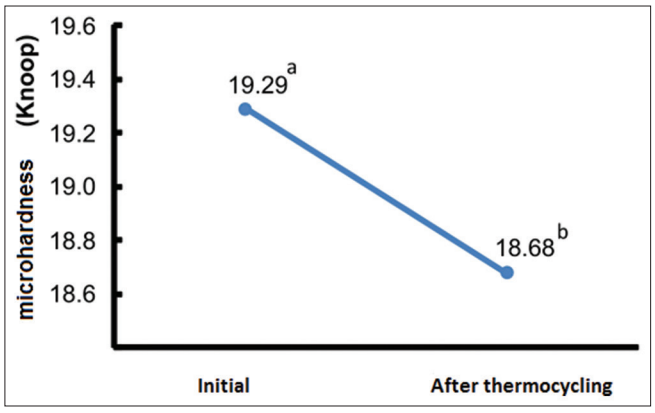

Figure 1: Average values of hardness for each period, regardless of pigment and resin used. *Lowercase letters between the different resins indicates statistically significant difference between periods ($P < 0.05$)

The pigment morphology was analyzed by using an SEM and EDS techniques. The EDS/MEV showed pigment was composed by C, oxygen (O), and Ti [Figure 3].

Table 2: Mean results (standard deviation) for hardness (Knoop)

Pigments	Resins	Period	Of time
		Baseline	After thermocycling
No pigments	Classico	20.18 (0.38)	18.92 (0.43)
	Onda Cryl	19.60 (0.81)	18.60 (0.52)
	Lucitone 550	19.91 (0.39)	18.80 (0.76)
	QC-20	19.28 (0.38)	18.99 (0.62)
3% of pigments	Classico	19.00 (0.83)	18.91 (0.82)
	Onda Cryl	18.85 (1.05)	18.43 (0.80)
	Lucitone 550	19.64 (0.47)	19.12 (0.87)
	QC-20	18.00 (0.80)	17.45 (1.07)
7% of pigments	Classico	19.56 (0.86)	19.23 (0.45)
	Onda Cryl	19.50 (0.28)	18.39 (0.56)
	Lucitone 550	19.30 (1.00)	18.91 (0.86)
	QC-20	19.14 (0.91)	18.92 (0.71)
Only pigments	Classico Poli-Côr	18.83 (0.85)	18.17 (0.28)

Table 3: Results of three-way analysis of variance for hardness (Knoop)

Source	df	SS	MS	*F*	*P*
Period	1	169.367	122.689	23.49	<0.01*
Pigmentation	3	147.057	49.019	9.38	<0.01*
Resin (pigmentation)	9	241.397	26.822	5.13	<0.01*
Period×pigmentation	3	20.391	0.6797	1.30	0.276
Period×resin (pigmentation)	9	41.103	0.4567	0.87	0.550
Error	156	814.902	0.5224		
Total	181	1.434.216			

**P*<0.05 indicates statistically significant difference. SS: Sum of square; MS: Mean square

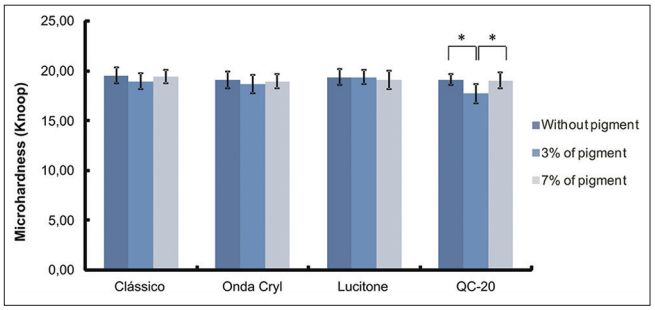

Figure 2: Mean results of Knoop microhardness for each resin at different pigment concentrations, regardless the period of evaluation. *Only the specimens with 3% of pigmentation concentration from the resin QC-20 showed statistically significant difference compared to the other specimens of the same resin brand

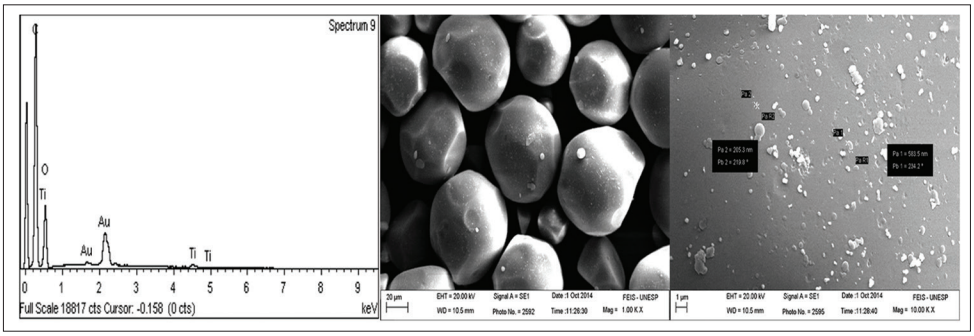

Figure 3: Energy dispersive X-ray spectroscopy/MEV image of the pigment powder

Table 4: Mean results of hardness (standard deviation) for pigmentation, regardless the resin and period of evaluation

Pigment	Hardness
No pigment	19.28 (0.74) A
3% of pigment	18.67 (1.03) B
7% of pigment	19.12 (0.78) A
Only pigment	18.50 (0.70) B

Different capital letters at the column indicate statistically significant difference (P<0.05, Tukey's test)

Discussion

The hypothesis that the incorporation of nanoscale pigments would not affect the surface hardness of tested acrylic resins was partially confirmed. Although there was no significant difference for the interaction between factors, differences in hardness were observed between pigment concentrations and tested resins. In the present study, the hardness values decreased after thermocycling [Tables 2 and Figure 1]. This factor may be explained by some authors that reported water absorption when the acrylic resin is immersed in the aqueous environment.[10,14,15]

In addition, considering that thermocycling simulates the clinical environment for dental materials, the water molecules may penetrate into the resin and breaks the polymeric chains through hydroxylation. This fact produces slight expansion of the resin and affects the crosslink of polymeric chains, creating a softener effect between the aqueous environment and the superficial layer of the acrylic resin.[5,13,16]

QC-20 resin with 3% pigment showed lower results [Table 2] as displayed in Figure 2. This fact can be associated to its fast polymerization cycle,[15] whereas the components evolved in the chemical activation can be responsible for the lowest results of superficial hardness (Knoop) since the chemically activated acrylic resins exhibit the lowest results when compared to the heat-activated.[17]

Furthermore, the QC-20 samples with 3% of pigment concentration were different from the samples with 7% of pigment concentration and those with no pigmentation, regardless the period of evaluation. Considering the different pigment concentration for this same resin brand, it was observed that only the samples with 3% of pigment concentration showed statistically significant difference from those at other concentrations but this result did not happen to the other acrylic resin brands. Intrinsic pigmentation with different concentrations is widely used to improve the esthetic features of denture base acrylic resins.[1,18] However, higher percentages of pigments are clinically used. Therefore, we conducted a study to standardize the appropriate concentration of pigment.[1] As a result, we found that the percentage values of 3% and 7% are those that are closest to clinical reality.[1] In pigments' composition, some organic and inorganic particles were observed (information offered by the company Classic Ltda., São Paulo, SP, Brazil).

The EDS showed the presence of TiO_2 [Figure 3] that is widely incorporated to others polymers to increase the lifetime of such materials.[6,19] The incorporation of TiO_2 into polymers may improve the mechanical and optical properties of the polymers due to the small size [Figure 3], large specific area of the nanoparticles, and quantum effect, as well as strong interfacial interaction between the organic polymer and inorganic nanoparticles.[20,21]

The literature has suggested that different concentrations of pigments and addition of fibers in acrylic resins promote slight alteration in their physical properties.[8,22] Some authors observed that this modification occurs as a result of higher concentration of organic weigh in the pigmented resins which helps to reduce the absorption of water particles in the aqueous environment. Moreover, the coloring particles promote straight links between the polymeric chains, which decreases the concentration of residual monomers.[19,22]

Table 4 shows that the 7% of pigment concentration is closer to the results of the acrylic resin without pigments indicating that this concentration provides satisfactory esthetic without being prejudicial to the physical and mechanical properties of the acrylic resins. In other words, 7% of pigment concentration allows characterization of the oral prosthesis and maintains its durability that can be associated with the presence of TiO_2.

Despite the reduced values of hardness in all groups, the means are within the specification n° 33 of the American National Standards Institute (ANSI)/American Dental Association, (2003),[23] which establishes that the hardness of acrylic resin teeth must not be lower than 15. Since there is no specification for the hardness of acrylic resins, in the present study, this parameter was used as a standard. Thus, the results of superficial hardness of the dentures base acrylic resins tested in this research before and after thermocycling and at all pigment concentrations are clinically accepted. Besides, the hardness of polymers tested in the present study is similar to the results of Farina *et al*.[24]

Conclusion

It can be concluded that QC-20 and Classico resins had higher hardness values and lower, respectively. The thermal cycling statistically decreased the hardness of the evaluated resins. The incorporation of nanoscale particles with 7% concentration improved hardness.

Acknowledgment

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Conflicts of interest

There are no conflicts of interest.

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