Evaluation of roughness and micromorphology of epoxy paint on cobalt-chromium alloy before and after thermal cycling

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Abstract: It has been suggested that the epoxy paint used to coat metal substrates in industrial electrostatic painting applications could also be used to mask metal clasps in removable dental prostheses (RDP). The purpose of this study was to evaluate both the influence of thermal cycling and the *in vitro* roughness of a surface after application of epoxy paint, as well as to assess the micromorphology of a cobalt-chromium (CoCr) based metal structure. Sixty test specimens were fabricated from a CoCr alloy. The specimens were separated into three groups (n = 20) according to surface treatment: Group 1 (Pol) - polished with abrasive stone and rubbers; Group 2 (Pol+Epo) - polished and coated with epoxy paint; Group 3 (Epo) - air-abraded with aluminum oxide particles and coated with epoxy paint. The surface roughness was evaluated before and after 1000 thermal cycles (5°C and 50°C). The surface micromorphology was verified by scanning electron microscopy (SEM). The two-way repeated measures ANOVA showed significant differences among surface treatments ($p < 0.0001$), but no difference was found before and after thermal cycling ($p = 0.6638$). The CoCr-based metal alloy surfaces treated with epoxy paint (Groups 2 and 3) were rougher than the surfaces that were only polished (Group 1). Thermal cycling did not influence surface roughness, or lead to chipping or detachment of the epoxy paint.

Descriptors: Dental Clasps; Paint; Denture, Partial; Microscopy, Electron, Scanning.

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Introduction

Despite the advanced techniques now available to restore edentulous areas with dental implants, there are still some patients who are not good candidates for implant therapy. The reasons may be that these particular patients lack financial resources, have poor systemic health, fear dental surgery, or have either psychological or anatomical limitations.[1] Because of the emphasis placed on esthetic dentistry by the media, and the advances made in this field in the past 15 years, patients have come to demand prostheses that are not only comfortable, but also less noticeable, or look more natural.[2] As an outcome of the greater esthetic demands made by our patients, modern removable dental prostheses (RDP) are no longer acceptable if they require visible buccal and facial clasp retention arms.[3]

The development of dental materials and techniques has led dental professionals to recommend a planning approach involving the use of removable partial dentures made of esthetic materials. Nylon was introduced for use in bar-connections, dental seats, abutments and clasps.[4] Acetate resin was also introduced,[5,6] in addition to overdentures instead of using clasps on anterior teeth, but the disadvantage of overdentures is their high cost. All these alternatives may fail early on, before metal clasps do, due to chipping and fracture caused by flexibility differences and the elasticity modulus, lower retentive forces and the thermal expansion coefficient between the material and the RDP metal used.[2,7–12]

Epoxy paint is used in industrial applications for coating metal substrates in electrostatic painting. This study suggests that it could also be used in RDP to mask metal clasps, because it bonds to metal surfaces by means of an electrochemical process, and has good flexural ability.[13] Electrostatic painting is a form of application based on the principle that the paint particles and the surface to be painted have different electric charges.[13]

Epoxy paint is composed of a resin from the polyamide family, and has exclusive physical and esthetic properties. In a previous study developed at our laboratory, epoxy paint showed compatibility with human fibroblast cultures in cytotoxicity tests.

Surface roughness is an important characteristic of the materials being evaluated, because it interferes directly in the esthetic properties of the restorative material, such as brightness and surface smoothness, color alteration, staining and dental biofilm accumulation, bearing in mind that the presence of any heterogeneities, such as gaps, geometrical discontinuities and surface irregularities may lead to lower mechanical resistance of the material.[14–17] However, factors such as the surface roughness property of the paint applied to a metal alloy for use in RDPs and the possibility of chipping due to temperature changes, are not yet known. Thus, the purpose of this study was to evaluate the influence of thermal cycling and the application of epoxy paint on the surface roughness and the surface micromorphology of a CoCr-based metal.

Methodology

Experimental design

The experimental units were composed of 60 cobalt-chromium (CoCr) alloy discs (n = 20). The factors under study were *surface treatment* on three levels (a - polished cobalt-chromium alloy; b - polished cobalt-chromium alloy coated with epoxy paint; c - cobalt-chromium alloy air-abraded with aluminum oxide particles and coated with epoxy paint) and *time* on two levels (a - before thermal cycling; b - after thermal cycling). The response variable was evaluated by mean roughness (Ra), a continuous quantitative variable measured in µm.

Test specimen fabrication

Plastic buttons (Corozita®, Taubaté, Brazil) with internal holes (10 mm in diameter and 2 mm high) were used to make the patterns for casting the CoCr test specimens. The holes were filled with self-curing resin (Duralay®, Reliance Dental Mlg Co., Worth, USA). The buttons were ground with aluminum oxide abrasive papers (Norton®, São Paulo, Brazil) of different granulation (180, 400 and 600 grit), until a flat surface was attained. The buttons were prepared with a feed-canal forming pin provided in the lining, and were cast by electric induction heating. The CoCr metal alloy (Wironit Extra-Duro, Bego Bremer Goldschlagerei Wilh. Herbest Gmbh & Co., Bremen, Germany) was composed of 64% cobalt, 28.65% chromium, 5% molybdenum, 1% silicon, 1% manganese and 0.35% carbon by weight. The oven temperature was adjusted to 930°C, increasing 5°C per minute for 40 minutes, following the lining manufacturer's instructions. When the temperature of the electric induction machine reached 1300°C, the electric centrifugal was activated to promote the injection of the molten alloy into the cast under negative pressure, as recommend by the manufacturer. Specimens were cooled and then cleaned using 50-µm aluminum oxide particles at a pressure of 80 lb (Knebel®, Porto Alegre, Brazil).

Surface treatments

The test specimens were randomly divided into three groups (n = 20) according to different surface treatments:

a. Pol Group: polished (control group);
b. Pol+Epo Group: polished and coated with epoxy paint;
c. Epo Group: air-abraded with aluminum oxide particles, and not polished or coated with epoxy paint.

The procedure used for the Pol and Pol+Epo groups consisted of polishing with stone discs (mounted stone no. 2, 13 mm, Schelble Abrasivos Piranha®, Petropólis, Brazil) and abrasive tips (Cromox®, São Paulo, Brazil), following a standard recommendation for polishing metal alloy.[5,18] The procedure for the Epo Group was to use only air abrasion with 50-µm aluminum oxide particles under 80-lbs pressure (Knebel®, Porto Alegre, Brazil) without using conventional polishing.

After polishing, the Pol+Epo and Epo groups were cleaned with water to remove any residues from the surface. Epoxy paint in white powder form was then applied (Politherm Nobac C®, Weg Nobac, Jaraguá do Sul, Brazil) by means of electrostatic powder painting. Application was performed in a painting cabin, using a low-pressure compressed-air spray gun. In applying powdered paint, the piece to be painted receives a positive electric charge and the powdered paint is given a negative charge. There are two electrodes connected to a high voltage source (from 50 to 90 Kv) at the tip of the electrostatic gun. When the powder goes through it, it receives a negative charge, and, according to the principle of electromagnetic attraction, it is attracted to the metal piece attached to the ground.[13] The piece is then put into an oven at a temperature of about 200°C, for 10 minutes, in which the product is polymerized, following the manufacturer's instructions.

Roughness and thermal cycling tests

All the test specimens were cleaned with deionized water in an ultrasound bath for 10 minutes, dried on absorbent paper and tested with a roughness meter to measure surface roughness expressed in µm of digital roughness (SurfCorder® SE 1700, Kosakalab, Tokyo, Japan). The appliance was calibrated with a measurement filter in 0.25 mm (*cut-off*), with a readout speed of 0.1 mm/sec and with an evaluation length of 1.25 mm. Three readouts were taken with the profilometer needle passing through the geometrical center of the samples, in three randomized transversal readings. The parameter evaluated was Ra (roughness average), which is the arithmetical mean obtained by the deviations in roughness of the profile of the three values obtained. The values were then noted, tabulated and submitted to statistical analysis.

The specimens were submitted to thermal cycling in a machine set to 1000 thermal cycles. A thermocycler (MSCT-3®, São Carlos, Brazil) was used to perform the thermal cycling; its purpose is to simulate sample aging by alternating 30-second immersions of 5°C and of 50°C. The specimens were dried with absorbent paper and submitted to final surface roughness tests, using the same parameters for the initial roughness readouts.

Surface micromorphology evaluations

Five test specimens from each group were selected for qualitative analysis by means of scanning electron microscopy (SEM). The sample was cleaned with acetone to remove any contaminants, such as dust, grease or oil, from the surface. Samples were metalized by vacuum evaporation with a carbon film, using a thin film to prevent interference in the surface morphology. Images were obtained by scanning electron microscopy (LV-SEM, JOEL®, model JSM- 5900 LV, North Billerica, USA), using 25–30 spotsize, 10–25 kV, and 200× and 500× magnifications.

Statistical analysis

The Pol, Pol+Epo and Epo groups were treated as independent variables. Initially, the data were submitted to exploratory analysis, using the PROC LAB procedure of the SAS statistical program (SAS Institute Inc., Cary, USA, Release 8.2, 2001). The two-way repeated measures analysis of variance (ANOVA) was performed. The level of significance adopted was 5%.

Results

There was significant difference among the groups ($p < 0.0001$), but there was no difference before and after thermal cycling ($p = 0.6638$). The groups vs. cycling interaction was not significant ($p = 0.6275$). Table 1 shows that groups in which the metal alloy was coated with epoxy paint (Pol+Epo and Epo) presented higher surface roughness, as compared to the group in which the alloy was only polished (Pol). There were no significant differences among the groups before or after thermal cycling ($p > 0.05$).

Figures 1A to 1F show the SEM photomicrographs at 200× and 500× magnification of the surfaces for all groups after thermocycling. In the Pol group, the type of polish of the metal surface is attributed to the polishing method used (Figures 1A and 1B). In the Pol+Epo Group (Figures 1C and 1D), the metal alloy plus epoxy paint produced a polished surface (see white arrows) free of cracks and fissures, but with some agglomerates on the surface (see black arrows). In the Epo Group (Figures 1E and 1F), the metal surface presented some surface agglomerates (see black arrows) resulting from the application of epoxy paint, but no cracks or fissures.

Table 1 - Mean (in µm) and standard deviation of surface roughness for treatments before and after thermal cycling, and the results of the analysis of variance.

Group	Thermal cycling			
	Before		After	
	Mean	Standard deviation	Mean	Standard deviation
Pol	0.12 Ab	0.06	0.11 Ab	0.05
Pol+Epo	0.21 Aa	0.08	0.21 Aa	0.13
Epo	0.24 Aa	0.09	0.26 Aa	0.11

Means followed by different letters (capitals in the rows and lower case in the columns) are statistically different, according to ANOVA ($p < 0.05$).

Discussion

Ceramic, resin and thermoplastic nylon have all been used in an effort to disguise metal clasps, but their longevity is limited due to wear, deformation, high water sorption, softening, loss of surface finish, loss of retention, color instability, chipping, cracks and low resistance to fatigue and fracture.[7–9] Moreover, these esthetic materials have many other problems, such as warpage, surface roughness, bacterial contamination, and difficulty to polish.[19]

In the present study, epoxy paint was chosen to mask the clasps. This type of paint was selected because of its adherence, flexibility, high physical resistance, good chemical resistance to detergents and excellent anticorrosive protection.[13] This paint does not demand any type of preparation prior to painting, since it is supplied in the fluidization receptacle of the equipment used for electrostatic powder application. Although some monomers in epoxy paints may cause contact allergy in patients,[20] epoxy paint seems to be safe for dental use (as seen in a previous study developed at our laboratory, which showed compatibility with human fibroblast cultures in *in vitro* cytotoxicity tests), although future studies are required to evaluate its biocompatibility.

The results observed in the present study showed that there were significant differences among the groups ($p < 0.0001$), especially lower surface roughness for the Pol Group, compared to the other groups. Moreover, a higher mean surface roughness could be observed for the groups in which the metal alloy was coated with epoxy paint (Pol+Epo and Epo). A rougher surface due to the epoxy paint coating could be the result of the formation of some agglomerates caused by the deposition method of the paint on the surface (Figures 1C to 1F). Irregularities and the formation of particle aggregation on the surface could be attributed to using the electric paint method (different charges: negative for the metal and positive for the paint), and also to the application method (with a gun).[13]

The polishing of the Pol+Epo Group did not influence the surface roughness values. The same roughness was observed for the Epo Group as the Pol+Epo Group, showing that polishing was statistically indifferent as regards roughness.

The results shown in Table 1 showed that polishing produced the same surface smoothness on epoxy paint as on the CoCr alloy. However, it should be borne in mind that there are ways of enhancing epoxy paint application performance, namely that the surface needs to be rough to increase contact surface and adherence, and that air abrasion may be the most recommended technique, because it leaves the

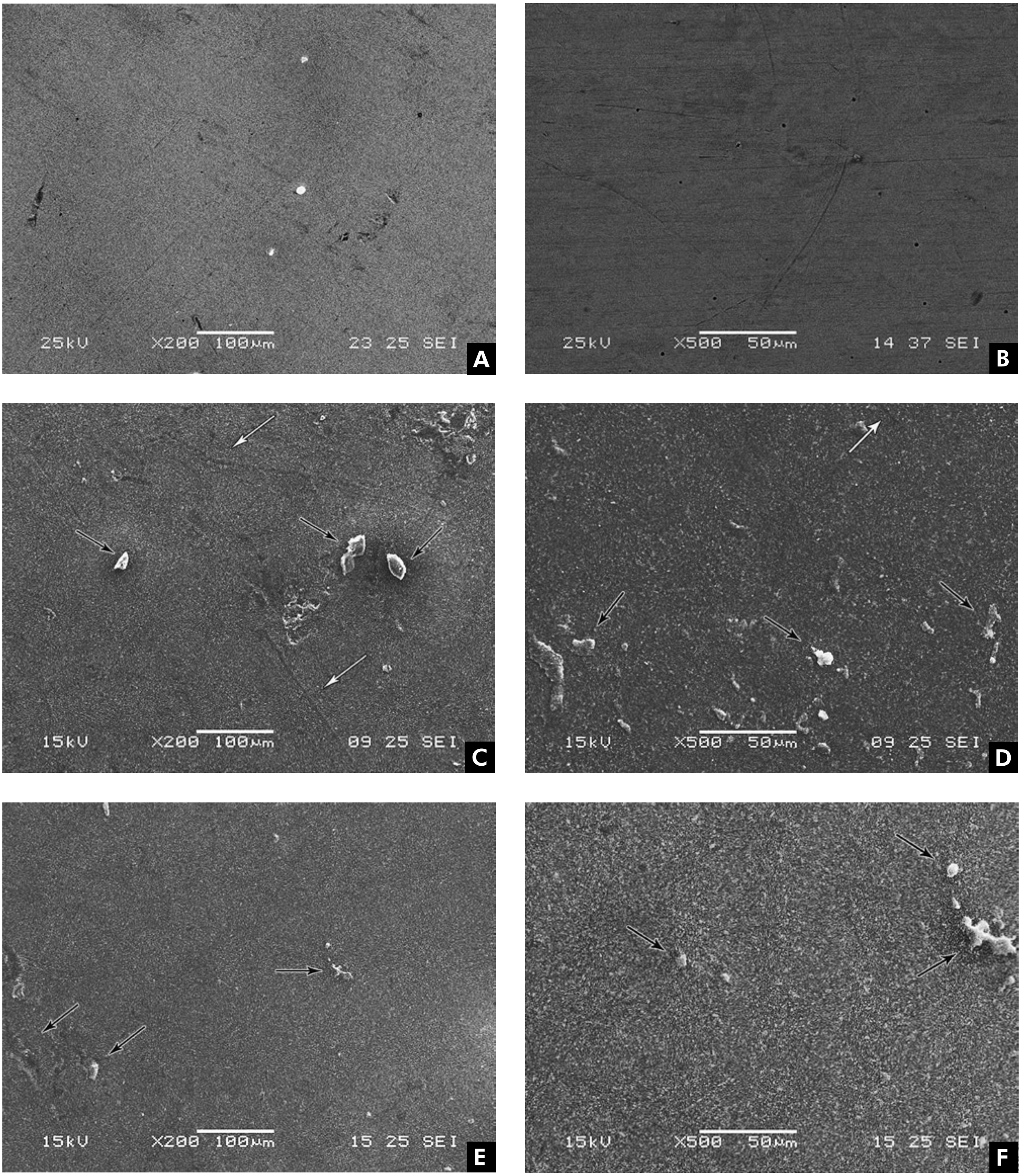

Figure 1 - Micromorphological images of the surface of Pol (**A** and **B**), Pol+Epo (**C** and **D**) and Epo (**E** and **F**) groups after thermal cycling at 200× and 500× magnification. White arrows show the presence of scratches and black arrows show the presence of agglomerates.

surface with ideal roughness for good anchorage of the paint coat.

Leitão and Hegdahl[14] reported that the surface is considered rough if it is characterized by peaks and valleys of high amplitude and reduced waviness. The surface roughness value (Ra) considered critical for the retention and adhesion of microorganisms is 0.2 μm.[14,15] According to the results of the present study, the mean surface roughness for the Pol Group, before and after thermal cycling, was between 0.11 μm and 0.12 μm, therefore, satisfactory values. However, the roughness values for the Pol+Epo and Epo groups ranged from 0.21 to 0.26 μm, both critical for the retention and adhesion of microorganisms. The probable explanation is that the agglomerates that formed as a result of the epoxy paint application could have some influence on roughness values.

Other factors that may also alter the behavior of the epoxy paint on metal have been analyzed in other studies. Morley and Stockwell[21] emphasized that the real conditions of the oral cavity should be simulated when evaluating the behavior of restorative materials, particularly changes in temperature. Asmussen[22] asserted that the duration of heating and cooling periods in the mouth is normally short; however, the cycles are repeated with greater frequency. The events of temperature alteration in the oral cavity were simulated for approximately one year, and corresponded to 1000 thermal cycles.[9,23] This value represents the number of times the metal structure of an RDP would be subjected to temperature variations in the oral cavity.

In the present experiment, an endeavor was made to simulate the possible deterioration or chipping of the epoxy paint applied. According to the results, it was observed that thermal cycling did not influence the surface roughness values, demonstrating that the material (epoxy paint) was capable of withstanding the thermal variations with no structural alterations. Although there were differences between the coefficient of linear thermal expansion of CoCr (5.4 to 6.9×10^{-6}/F)[24] and epoxy paint (31.0×10^{-6}/F),[25] the number of cycles and the temperature used during thermocycling were most probably not enough to cause physical and structural changes in the CoCr alloy and epoxy paint interface. According to SEM image analysis, the epoxy paint surface was shown to be free of cracks and fissures, suggesting that the thermal cycling did not lead to degradation of the surface morphology.

Therefore, it could be suggested that, in the future, epoxy paint may be considered an alternative for camouflaging RDP clasps, in addition to being economically feasible for restoring the patient's masticatory function and esthetics. Nevertheless, further *in vitro* and *in vivo* studies are needed to evaluate such factors as biocompatibility, patient acceptance, mechanical properties and different paint colors.

Conclusion

The surface roughness of a CoCr alloy treated with epoxy paint was greater than the roughness of the alloy that was only polished. Thermal cycling did not influence the surface roughness of a CoCr alloy with or without epoxy paint application. Thermal cycling did not cause chipping or debonding of epoxy paint, and the surface proved free of cracks and fissures, with an aspect similar to that of the control group.

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