INFLUENCE OF INCORPORATION OF FLUOROALKYL METHACRYLATES ON ROUGHNESS AND FLEXURAL STRENGTH OF A DENTURE BASE ACRYLIC RESIN

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ABSTRACT

Fluorinated denture base acrylic resins can present more stable physical properties when compared with conventional polymers. This study evaluated the incorporation of a fluoroalkyl methacrylate (FMA) mixture in a denture base material and its effect on roughness and flexural strength. A swelling behavior assessment of acrylic resin specimens (n=3, per substance) after 12 h of FMA or methyl methacrylate (MMA) immersion was conducted to determine the solvent properties. Rectangular specimens (n=30) were allocated to three groups, according to the concentration of FMA substituted into the monomer component of a heat-polymerized acrylic resin (Lucitone 550), as follows: 0% (control), 10% and 20% (v/v). Acrylic resin mixed with concentrations of 25% or more did not reach the dough stage and was not viable. The surface roughness and flexural strength of the specimens were tested. Variables were analyzed by ANOVA and Tukey’s test (α=0.05). Immersion in FMA produced negligible swelling, and MMA produced obvious swelling and dissolution of the specimens. Surface roughness at concentrations of 0%, 10% and 20% were: 0.25 ± 0.04, 0.24 ± 0.04, 0.22 ± 0.03 μm (F=1.78; p=0.189, not significant). Significant differences were found for flexural strength (F=15.92; p<0.001) and modulus of elasticity (F=7.67; p=0.002), with the following results: 96 ± 6, 82 ± 5, 84 ± 6 MPa, and 2,717 ± 79, 2,558 ± 128, 2574 ± 87 MPa, respectively. The solvent properties of FMA against acrylic resin are weak, which would explain why concentrations over 20% were not viable. Surface changes were not detected after the incorporation of FMA in the denture base acrylic resin tested. The addition of FMA into denture base resin may lower the flexural strength and modulus of elasticity, regardless of the tested concentration.

Key words: Acrylic resins. Denture bases. Fluorocarbon polymers. Fluorine. Mechanical stress. Surface properties.

INTRODUCTION

Polymethyl methacrylate (PMMA) resins have been used for the fabrication of denture bases for over 50 years. Despite the advantages of PMMA, most notably the ease of fabrication with very simple equipment, some limitations have been documented in previous studies. Denture bases consisting of PMMA resins are subject to water sorption, which can alter their mechanical properties4. High water sorption and solubility of denture base acrylic resins can have a serious impact by reducing their flexural strength and fatigue limit10. Moreover, water sorption and chemical reactivity of acrylic resins are associated with discoloration and consequently with the esthetic acceptability of dental prostheses11. Another important limitation of PMMA resins is their potential to support the formation of biofilm in that the surface roughness and free energy of conventional denture base materials may promote microbial adherence17. The use of fluorinated polymers can overcome some of these limitations of conventional denture base resins more especially as they have an extremely low surface energy and display excellent hydrophobicity and resistance to softening by solvents19. Earlier attempts were made to improved denture base acrylic resins by the introduction of fluorine into the pendant ester groups of methacrylic monomers, and these fluorinated denture base resins have shown decreased water sorption13. In addition these fluoroalkyl-based denture lining materials have produced good results for resistance to stain, water sorption and solubility when compared with other lining materials12. It is in this way that fluorinated resins present more stable mechanical properties when compared with conventional...
polymers. Other interesting properties which have expanded their use have been their potential resistance to microbial adherence19.

A possible approach to the manufacture of fluorinated denture base materials would be through the incorporation of fluoroalkyl methacrylates (FMA) in a proprietary material. FMA-acrylate copolymers were previously prepared for engineering-related applications and it was noticed that the wetting-resistance, water-resistance and thermal stability of these materials were markedly improved after the introduction of fluoride into polymer chains6. It was also found that the hydrophobicity of methyl methacrylate (MMA) - FMA copolymer is largely dependant on its fluoroine concentration22.

Virtually all denture base materials use the conventional polymer/monomer dough molding process14. The polymer beads contain the initiator, benzoyl peroxide; thus, the incorporation of FMA into the monomer component should be able to dissolve the polymer. A simple assay technique using swelling behavior assessment15 has the potential to show gross differences between FMA and MMA as solvents. In other words, this assay might clarify any possible association between the incorporation of FMA into the monomer and any problems that may occur with the packing or polymerization of the denture base resin. The mechanical behavior of the resin presents additional challenges and although less water sorption can result in desirable effects8,10, some experimental fluorinated denture base polymers presented lower diametral tensile and flexural strength than PMMA13.

The aims of this study were: (1) to compare a FMA mixture as a solvent for denture base acrylic resin compared with MMA, and (2) to investigate the influence of incorporation of FMA on roughness and flexural strength of a heat-polymerized denture base material.

**MATERIAL AND METHODS**

**Sample and Fabrication of Specimens**

The sample comprised 6 circular acrylic resin specimens to be used for swelling behavior assessment. Thirty rectangular specimens were employed for flexural strength and roughness testing. Rectangular specimens were further divided into three groups, according to the presence of FMA (Zonyl TM Fluoromonomer; DuPont Chemical Solutions Enterprise, Wilmington, DE, USA). Concentrations of 0% (Control), 10% and 20% (v/v) were substituted into the monomer component of a heat-polymerized acrylic resin (Lucitone 550; Dentsply International Inc., York, PA, USA). Concentrations were defined during a pilot study, when different concentrations of FMA were mixed. Dough stage was not reached for 25% or more after 24 h following manipulation at room temperature. For the 20% concentration, packing was possible after approximately 30 min.

Metal master patterns were individually invested in high-viscosity silicone (Zetalabor; Zhermack S.p.A, Badia Polesine, Rovigo, Italy), and supported by type III dental stone (Herodent; Vigodent SA Ind. Com., Rio de Janeiro, RJ, Brazil) within flasks. Each flask contained six circular (14.0 x 4.0 mm) or two rectangular patterns (65.0 x 10.0 x 3.3 mm). After the dental stone had set, the flasks were separated, and the master patterns were removed from the silicone mold. Denture base resin was mixed according to the manufacturer’s recommendations. A portion of monomer (10 mL) and polymer (21 g) was mixed for each flask, thus a dough stage was reached and then placed into the molds. A pneumatic press (PM-2000; Techno Máquinas Ltda., Vinhedo, SP, Brazil) was used for packing the denture base resin initially at 500 kgf and, finally, at 1250 kgf maintained for 60 min. The resin was polymerized in an automatic polymerization water tank (Dental School of Ribeirão Preto, Ribeirão Preto, SP, Brazil). Temperature and time were 73ºC for 90 min, followed by 30 min at 100ºC. Next, the specimens were bench cooled overnight before deflasking. The excess resin was trimmed with a bur (Maxi-Cut; Maillefer SA, Ballaigues, Switzerland). Each specimen was then finished using 200-, 400-, 600- and 1,200 -grit wet/dry sandpaper (Norton; Saint-Gobain Abrasivos Ltd, Guarulhos, SP, Brazil) in a polishing machine (DPU-10; Panambra Ind. e Téc. S.A., São Paulo, SP, Brazil) at 250 rpm for 60 s. Specimen dimensions were confirmed with a digital caliper (Model CD-6” CSX-B; Mitutoyo Sul Americana Ltda., Suzano, SP, Brazil).

**Swelling Behavior**

A swelling behavior assessment was carried out according to the procedures described by Loyaga-Rendon15. Six circular (14 x 4mm) acrylic resin specimens (Lucitone 550; Dentsply International Inc.) were immersed in MMA or in FMA. Three specimens were submerged in 20 mL of MMA monomer (Sigma-Aldrich Brazil, São Paulo, SP, Brazil) at 37ºC for 24 h, and the swelling behavior of the acrylic resin was evaluated based on the presence or absence of an obvious swelling characterized by a change in shape observed by naked eye observation and softening of the resin by means of spatula scratching. The same procedure was conducted simultaneously with immersion in FMA. The monomer that caused a negligible swelling behavior was arbitrarily considered a weak solvent, while the one showing a clear and obvious swelling, a strong solvent.

**Surface Roughness**

The surface roughness tester SJ-201P (Mitutoyo Corp, Kawasaki, Japan) was used to measure the specimens’ surface roughness after 30 days of immersion. The profiler was set to move a diamond stylus across the specimen surface under a constant load. The scanning duration for each line was 10 s with a constant force of 4 mN (0.4 gf) on the diamond stylus (5 µm radius). The surface morphology was measured with a linear variable differential transformer. The surface roughness was derived from computing the numerical values of the surface profile. The $R_a$ value ($\mu$m) describes the overall roughness of a surface and is defined as the mean value of all absolute distances of the roughness.
profiles from the mean line within the measuring distance. Five measurements with a length of 4.8 mm and incremental distance of 1 mm between each scanning line were carried out for each specimen. Vertical resolution was .01 µm, which also represents the accuracy of Ra. The mean Ra was calculated from 5 lines as the mean roughness of the specimen.

**RESULTS**

Specimens immersed in MMA showed obvious swelling and underwent a certain degree of dissolution. However, the acrylic resin did not suffer any significant change after immersion in FMA for 24 h.

Mean Ra ± standard deviation were 0.25 ± 0.04 for Group 0%, 0.24 ± 0.04 for 10% and 0.22 ± 0.03 for 20%. No significant difference was found among the means (one-way ANOVA, F=1.78; p=0.189), which indicates that the incorporation of FMA did not alter surface topography of the finished resin.

The means and standard deviations for flexural strength and modulus of elasticity are displayed in Table 1. One-way ANOVA showed significant differences in flexural strength (F=15.92; p<0.001) and modulus of elasticity (F=7.67; p=0.002) among the three groups. Tukey HSD test showed that the 0% group had the highest flexural strength and modulus. The decrease in both variables is similar for 10% and 20% concentrations. However, values for the experimental concentrations comply with the minimum values (65 MPa and 2,000 MPa, respectively) set forth by ADA specification No.12.

### DISCUSSION

The resin matrix of specimens employed for the swelling behavior assessment showed negligible change after immersion in FMA, whereas visible degradation was found after immersion in MMA. This property is important because it explains why concentrations higher than 20% were not viable. During polymerization, the monomer diffuses in the polymer and partially dissolves it. This diffusion is dependent on time, temperature, type of monomer and the polymeric structure and glass transition temperature (Tg) of the polymer. If dissolution of the polymer beads does not occur, the dough stage might not be reached after mixing; in addition, benzoyl peroxide from the beads might not be available for initiating polymerization. The maximum concentration that enabled packing and curing was 20%, so this may be the projected limit for incorporation of FMA in the acrylic resin tested.

An important limitation of this study was that only a visual method was employed for swelling behavior assessment. It is expected that more sophisticated assays might detect diffusion of FMA in MMA. However, the present methodology fulfilled its purposes. In other words, it showed that there are gross differences between FMA and MMA regarding dissolution of conventional denture base acrylic resin. Due to the magnitude of difference, the significance of bias and of the dichotomy in the nature of the variable this may be considered as minimal.

Surface roughness is an important feature associated with biofilm formation. Ra values were near to 0.2 µm, which can be considered as minimally susceptible to microorganism colonization. Higher roughness after FMA incorporation would be a possible result, if it interfered in the polymerization. This would happen by the exposure of polymer beads, as stated by Braun, et al. The similarity in roughness indicates that surface porosity was similar in the three groups. It can be inferred that both materials have the same texture, without considering surface energy. Nevertheless, further research should investigate the interaction of incorporated FMA with the effects of other agents, such as diet, and the effects of brushing and cleaning of dentures, which are known to produce surface roughness.

Compared to methods used to change energy surface in

### TABLE 1- Mean results and standard deviation for the flexural strength assessment according to different FMA concentrations

| Groups | Flexural strength (MPa) | Modulus of elasticity (MPa) |
|--------|-------------------------|-----------------------------|
| 0% (control) | 96 ± 6^a | 2,717 ± 79^a |
| 10% | 82 ± 5^b | 2,558 ± 128^b |
| 20% | 84 ± 6^b | 2,574 ± 87^b |

Means followed by the same uppercase letters in columns are not significantly different (one-way ANOVA and Tukey HSD post hoc test; α=0.05).
denture base acrylic resin, such as the substitution of monomer with methacrylic acid or phosphate-containing monomer, percent decline in flexural strength seems to be more discrete than the former and similar to the later. A decrease in denture base acrylic resin flexural strength can result in greater fracture incidence by impact or occlusal forces. However, the difference found was close to that observed between microwave- and heat-polymerized acrylic resins. As long as the mean values were not smaller than those set forth by the ADA for flexural strength and modulus of elasticity for denture base acrylic resins, perhaps the differences have no clinical importance.

A possible explanation for lower mean flexural strength and modulus of elasticity resides in the intermolecular interaction. The presence of fluorine in methacrylic polymers results on different intermolecular distances. Fluorinated polymers usually have lower mechanical strength than conventional materials due to decreased cohesive energy that reduces the effect of polymer chain entanglement. However, part of this decline can be explained by the dilution of other components of the liquid, such as the crosslinking agent ethylene glycol dimethacrylate (EGDMA). There is association between increasing concentrations of crosslinking agent and increased flexural strength and modulus, as well as decreased water sorption and solubility. This way, corrections on EGDMA levels of the monomer component during incorporation of FMA might attenuate flexural strength difference among experimental groups.

Two other limitations should be stated. Firstly, the scarce literature on this subject, since no study was found describing the incorporation of FMA in proprietary materials, with only a small number assessing the use of fluorinated polymers for dental applications. Another concern that should be addressed is the potential conflict of interest, as long as the FMA mixture was supplied by its manufacturer. The present results point out that the incorporation of FMA is quite feasible but other physical, chemical and biological properties must be tested before these findings can be applied in clinical research. Distortions caused by a conflict of interest are probably minimal and should be avoided by granting an independent source of funding for future research. Furthermore, information about the source of the FMA was not acknowledged by the researcher responsible for obtaining the specimens and the dependent variable assessors were blinded to the experimental groups.

CONCLUSIONS

The solvent properties of FMA against acrylic resin are weak when compared to MMA, which might help explaining why concentrations over 20% were not viable. Topographical changes were not detected after the incorporation of FMA in the heat-polymerized denture base acrylic resin tested. The addition of FMA may lower the flexural strength and modulus of elasticity, regardless of the tested concentration. However, this decrease may be clinically acceptable.

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REFERENCES

1. Arima T, Hamada T, McCabe JF. The effects of crosslinking agents on some properties of HEMA-based resins. J Dent Res. 1995;74:1597-601.
2. Barbosa DB, Souza RF, Pero AC, Marra J, Compagnoni MA. Flexural strength of acrylic resins polymerized by different cycles. J Appl Oral Sci. 2007;15:424-8.
3. Bollen CM, Lambrechts P, Quirynen M. Comparison of surface roughness of oral hard materials to the threshold surface roughness for bacterial plaque retention: a review of the literature. Dent Mater. 1997;13:258-69.
4. Braden M. Some aspects of the chemistry and physics of dental resins. Adv Dent Res. 1988;2:93-7.
5. Braun KO, Mello JAN, Rached RN, Del Bel Cury AA. Surface texture and some properties of acrylic resins submitted to chemical polishing. J Oral Rehabil. 2003;30:91-8.
6. Chen Y, Zhang C, Chen X. Emulsifier-free latex of fluorinated acrylate copolymer. Eur Polym J. 2006;42:694-701.
7. Dhir G, Berzins DW, Dhuru VB, Periathambly AR, Dentino A. Physical properties of denture base resins potentially resistant to Candida adhesion. J Prosthodont. 2007;16:465-72.
8. Dixon DL, Ekstrand KG, Breeding LC. The transverse strengths of three denture base resins. J Prosthet Dent. 1991;66:510-3.
9. Ellis B, Faraj SA. The structure and surface topography of acrylic denture base materials. J Dent. 1980;8(2):102-8.
10. Fujii K. Fatigue properties of acrylic denture base resins. Dent Mater J. 1989;8:243-59.
11. Guler AU, Yilmaz F, Kulunk T, Guler E, Kurt S. Effects of different drinks on stainability of resin composite provisional restorative materials. J Prosthodont. 2005;94:118-24.
12. Hayakawa I, Akiha N, Keh E, Kasuga Y. Physical properties of a new denture lining material containing a fluoroalkyl methacrylate polymer. J Prosthet Dent. 2006;96:53-8.
13. Kurata S, Yamazaki N. Mechanical properties of poly(alkyl alpha-fluoroacrylate) as denture-base materials. J Dent Res. 1989;68:481-3.
14. Lai CP, Tsai MH, Chen M, Chang HS, Tay HH. Morphology and properties of denture acrylic resins cured by microwave energy and conventional water bath. Dent Mater. 2004;20:133-41.
15. Loyaga-Rendon PG, Takahashi H, Hayakawa I, Iwasaki N. Compositional characteristics and hardness of acrylic and composite resin artificial teeth. J Prosthet Dent. 2007;98:141-9.
16. Oliveira LV, Mesquita MF, Henriques GE, Consani RL. The effect of brushing on surface roughness of denture lining materials. J Prosthodont. 2007;16:179-84.
17- Radford DR, Sweet SP, Challacombe SJ, Walter JD. Adherence of *Candida albicans* to denture-base materials with different surface finishes. J Dent. 1998;26:577-83.

18- Sato S, Cavalcante MR, Orsi IA, Paranhos HFO, Zaniquelli O. Assessment of flexural strength and color alteration of heat-polymerized acrylic resins after simulated use of denture cleansers. Braz Dent J. 2005;6:124-8.

19- Stansbury JW, Antonucci JM. Dimethacrylate monomers with varied fluorine contents and distributions. Dent Mater. 1999;15:166-73.

20- Vallittu PK, Ruyter IE, Nat R. The swelling phenomenon of acrylic resin polymer teeth at the interface with denture base polymers. J Prosthet Dent. 1997;78:194-9.

21- Yannikakis S, Zissis A, Polyzois G, Andreopoulos A. Evaluation of porosity in microwave-processed acrylic resin using a photographic method. J Prosthet Dent. 2002;87:613-9.

22- Yoshida N, Abe Y, Shigeta H, Nakajima A, Ohsaki H, Hashimoto K, et al. Sliding behavior of water droplets on flat polymer surface. J Am Chem Soc. 2006;128:743-7.