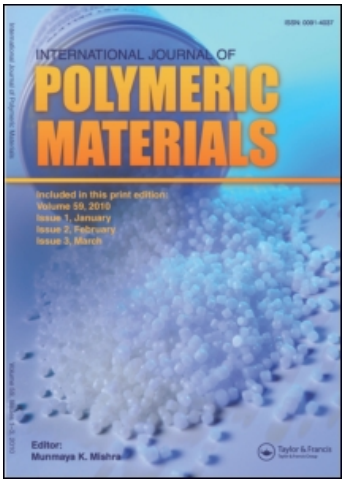

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

PREPARATION AND BEHAVIOR OF A STAIN-PROTECTING HYBRID COATING FOR TEETH

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Online publication date: 06 September 2010

To cite this Article delaIsla, Agustín , Estévez, Miriam , Vargas, Susana , Castaño, Víctor M. and Rodríguez, Rogelio(2004) 'PREPARATION AND BEHAVIOR OF A STAIN-PROTECTING HYBRID COATING FOR TEETH', International Journal of Polymeric Materials, 53: 8, 645 — 651
To link to this Article: DOI: 10.1080/00914030490472854
URL: http://dx.doi.org/10.1080/00914030490472854

International Journal of Polymeric Materials, 53:645–651, 2004

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490472854

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PREPARATION AND BEHAVIOR OF A STAIN-PROTECTING HYBRID COATING FOR TEETH

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A novel hybrid polymer-ceramic coating was synthesized by using PMMA-PAAc copolymer and nanosized silica particles. The coating was applied to actual human molar teeth and tested against staining by coke soda and solutions of coffee and tobacco. The changes in color, indicative of the degree of chemical attack on the surface of the teeth, were minimal when this hybrid coating was used, especially when compared with blank (not-coated) samples and with teeth protected with commercial protective coatings (standard PMMA-based solutions).

Keywords: hybrid coating, silica nanoparticles, stain protection, dental enamel, demineralization, dental coating

INTRODUCTION

Caries poses one of the main challenges to public health worldwide because it affects, according to the World Health Organization, nearly

Received 26 April 2002; in final form 16 May 2002.
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95% of the human population at some stage of their lives, representing enormous losses of working hours, millions of dollars dedicated to medical care, and the loss of one or more teeth for many people [1]. This widely spread disease is defined as a localized bacterial pathological process. In fact, as a part of the natural ecological equilibrium of the oral cavity, many bacteria are found normally in the mouth, but some agents, such as pH, food (particularly that rich in sugars), other diseases, and so on can induce an overpopulation of the colonies, which in turn brings the biochemistry of the mouth out of equilibrium.

The causes of caries can be summarized into four leading parameters [2,3], namely: micro-organisms, substrate, host, and time (i.e., period of exposure). It is important to realize that caries involves a true destruction of the calcified tissue, carried out in two stages: first, an attack on the inorganic part of teeth (basically hydroxyapatite) that is de-calcified by the acids resulting of the natural metabolism of the bacteria and then the degradation of the organic tissue by enzymatic or mechanical means, once the inorganic component is no longer present to protect the structure.

As for the role of the host in the development of caries, some factors have been identified as key for the disease [4]: composition of the dental enamel, composition of saliva and presence of crevices or cracks on the surface of the teeth, which enable the bacteria to colonize the piece. Thus, one of the leading strategies to prevent caries is to coat the surface of teeth with a physical barrier that prevents the colonies of bacteria from populating the surface. Indeed, the use of thermocured acrylic resins was popular for some time over 50 years ago, until the poor adherence and degradation of the material made it obsolete. In 1940 the self-curing acrylic resin was tested [5] with good aesthetic results: however, its attack toward the gum tissue made it unfit for this purpose. From the 1950s the BIS-GMA resin, reinforced with inorganic fillers [5] has become the preferred sealer for cracks of teeth as a preventing agent for caries. Nevertheless, this 50-year-old technology has important technical and practical shortcomings and it is exclusively used for the occlusal faces of molar teeth. In summary, the dentistry practice lacks an effective, modern, and simple material to be utilized as coating against caries.

On the other hand, today's materials science and technology offers interesting opportunities for developing novel materials with tailored properties. In the particular case of coatings, recent reports showed that hybrid inorganic-organic materials used as advanced coatings [6–9] have proven to be extremely effective tribological enhancers and corrosion-resistant agents.

Thus, the aim of the present work is to report the use of a novel hybrid coating as a feasible alternative for protecting teeth against the attack of agents known to promote caries, which were simulated by using coke soda and tobacco and coffee solutions. The attack was evaluated by measuring the changes in color of the surface of the teeth.

EXPERIMENTAL

Commercial silica nanoparticles of 18 nm in diameter (Degussa) were utilized along with PMMA-PAAc (poly(methyl methacrylate)-poly (acrylic acid)) copolymer to produce the hybrid compound according to a previously reported methodology [9]. The copolymer was synthesized by free radical polymerization using fresh distilled methylmetacrylate, and industrial grade acrylic acid (Industrias Resistol, Mexico) monomers. As a reaction medium a 50–50 mixture of isopropanol-ethanol (Baker, Co.) was used. The initiator was 2,2′-AzobisIsoButyroNitrile (AIBN). The polymerization was carried out at 80°C under strong agitation and nitrogen atmosphere for 3 h, producing a polymer with molecular weight of 500,000 g/mol.

A esterification reaction was carried out between the silica nanoparticles, previously functionalized according to procedure described in detail elsewhere [9,10], and the PMMA-PAAc copolymer by slowly mixing 100 ml of the copolymer solution with 30 ml of the functionalized silica particles. Then, small amounts of nitric acid were added to keep the pH equal to 3. Finally, the mixture was kept under reflux for 4 h to complete the esterification.

Non-erupted molar teeth were extracted from several volunteers and cut into 4 pieces each with a diamond saw and were washed with distilled water and dried. The pieces were etched with phosphoric acid at 37% dental grade (Degufil) for 15 s and then washed with distilled water and dried. The samples were divided into 4 groups: blank samples, samples protected with a commercial bonding agent (Prime Bond from Caulk Dentsply), samples protected with a commercial protecting resin (Degufil H from Degussa), and, finally, samples protected with the hybrid ceramic-polymer compound.

The bonding agent was polymerized according to the procedure recommended by the supplier, that is, cured with a halogen lamp (Kulzer Translux EC) for 20 s. The commercial resin was polymerized also by following the standard curing procedure with the same halogen lamp for 40 s. All the samples were immersed for 15 days each in the three following staining agents: commercial coke soda (Coca Cola) at its normal pH (3.4), coffee infusion, and tobacco solution in ethanol, all in sealed vessels. The coffee infusion was prepared by percolation

using a commercial coffee (Nescafe, Mexico) and the tobacco solutions were prepared by dissolving 10 cigarettes in 100 ml ethanol. The attack on the teeth was detected through the changes in color of the teeth surfaces, by using a lvoclar-Vivadent Kerascope colorimeter, a standard instrument for detecting color changes in dentistry.

RESULTS AND DISCUSSION

Figure 1a shows a plot of the change in color according to the ADA (American Dental Association) standards of all the teeth samples subjected to coke soda attack. It is extremely impressive to realize

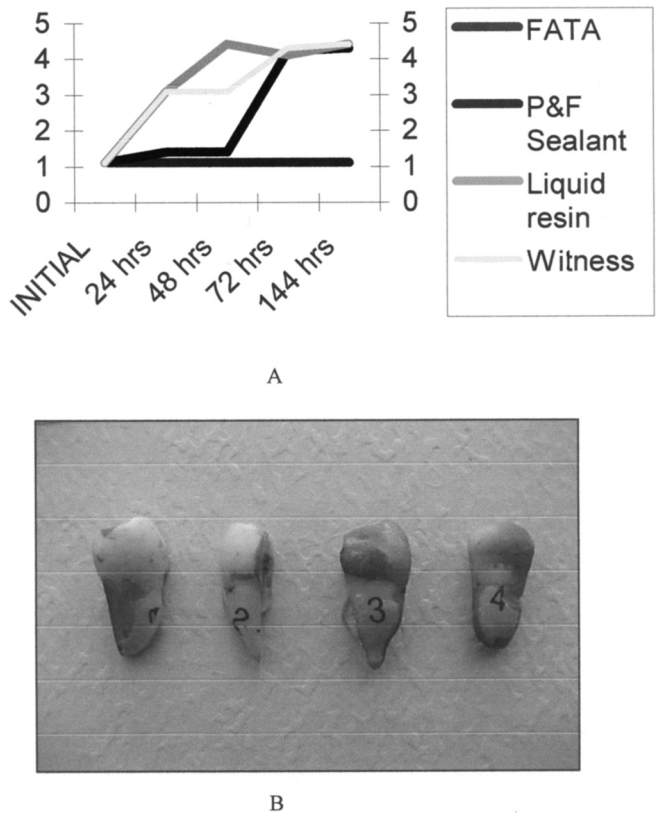
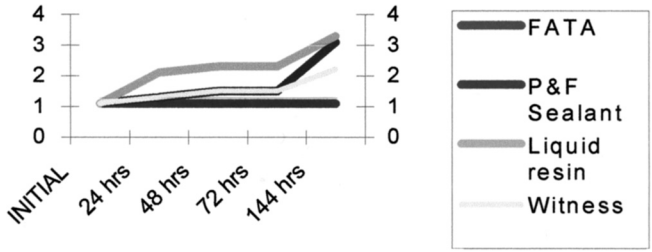


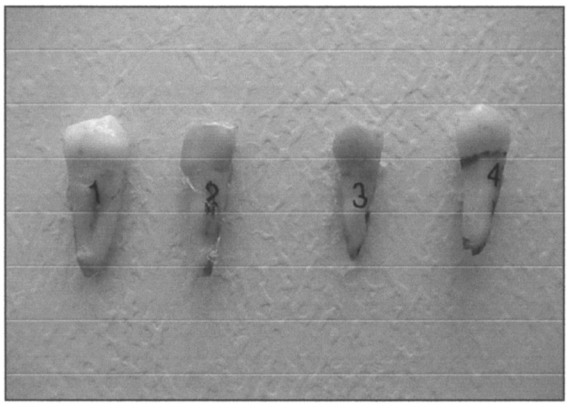
FIGURE 1 (A) Graphic of changes made by acid attack with Cola soft drink (B) Photographs of the samples after the test. FATA-Hybrid Ceramic Polymer. P&F Sealant, prime bond from Dentsply. Liquid Resin-Degussa Resin. Witness-Blank, untreated tooth.

how effective the hybrid coating is in protecting the teeth, because no changes in color were detected during the experiment. The blank samples were obviously severely attacked from the very beginning of the experiment. The commercial resin, even with the bonding agent, is far from performing as the hybrid coating does. These results can also be visually appreciated in the series of photographs shown in Figure 1b, which correspond to the coatings shown in Figure 1a.

Figure 2a summarizes the results of attack with the coffee solution. Again, the only effective way of preventing the staining of the teeth is by using the hybrid coating, as can be appreciated from the photographs of Figure 2b. Finally, the effect of tobacco is illustrated in



A

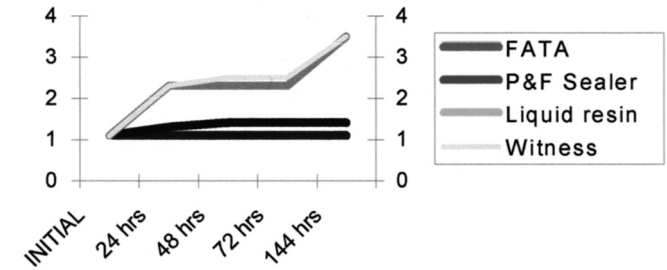


B

FIGURE 2 (A) Graphic of color changes by tincture attack with coffee. (B) Photographs of the samples after the test. The teeth covered with pit and fissure sealer and liquid resin were more penetrated than the blank tooth. Explanations as in Figure 1.

Figure 3a, where no change in color could be detected whatsoever on the surface of the hybrid compound-protected teeth, as opposed to the other groups of samples, in which the coating was attacked by the stain molecules of the tobacco. A visual inspection of the samples (in Figure 3b) shows clearly the effectiveness of our coating and the poor performance of the other coatings.

The nature of all the chemicals employed in the preparation of the hybrid coating ensures a non-toxic character, a key parameter if one is to think about actual medical applications. Nevertheless, detailed clinical studies on animals are being carried out to test the long-term toxicity, along with some other side effects that could result from this technology. Additionally, the tribological behavior of the hybrid coating, when applied to teeth, will be separately reported.



A

B

FIGURE 3 (A) Graphic of color changes made by tincture with tobacco. (B) Photographs of the samples after the test. The teeth covered with liquid resin were penetrated similar to the blank tooth. Explanations as in Figure 1.

CONCLUSIONS

The results demonstrate not only the effectiveness of the hybrid compound as a stain-resistant coating for teeth, for the case of coke, tobacco, and coffee, recognized as some of the most severe enemies of the teeth surface, but also as a protection again the acid attack produced by coke, which produces a demineralization of the dental enamel. In all cases no change in color could be observed when the teeth surface was protected with the hybrid coating. The results also show the feasibility of employing nanotechnology for producing advanced novel polymer-based materials.

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