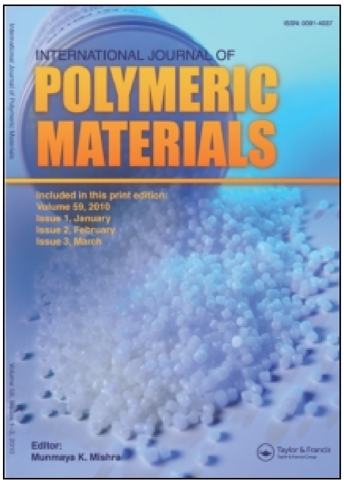

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SYNTHESIS AND CHARACTERIZATION OF A WEAR-RESISTANT HYBRID POLYMER-CERAMIC COATING FOR DENTAL APPLICATIONS

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A novel hybrid ceramic-polymer coating was developed to protect teeth enamel against both the acidic attack of the metabolic products of microbes and the stains produced by external agents. This material must also have a good abrasion resistance if it is to be used effectively as a dental coating. Accordingly, intensive abrasion experiments on teeth coated with this composite were performed, and the thickness reduction of the coating layer was determined by Raman spectroscopy; this revealed a high wear resistance of the composite developed, which is also biocompatible, inexpensive, easy to apply, highly transparent, and glossy; all important characteristics for dental applications.

Keywords: poly(methyl methacrylate-acrylic acid), silica, composite, hybrid, polymer-ceramic, dental, wear-resistant, coating, hydroxyapatite, dental enamel

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INTRODUCTION

Hydroxyapatite (HAp) is the main inorganic constituent of tooth and bone tissue. In fact, bone is a natural hybrid material where the constituents (HAp and collagen, the organic part) work synergistically to produce tough materials with a huge capacity to absorb mechanical impact. In case of teeth, enamel is the toughest and most abrasion resistant material in the human body, constituted almost exclusively by hydroxyapatite crystals (about 95%) and kept together by an organic matrix that binds tightly the mineral crystals that cover the crown surface of the tooth [1–4]. The chewing process produces strong and continuous compression and shear stresses, producing fatigue in this tissue; this results in the appearance of small crevices, cracks, or fissures on the surface of the teeth, ideal places to nest bacteria colonies. Under appropriate conditions (pH, food, certain diseases), an overpopulation of these colonies appears, moving the biochemistry of the mouth out of equilibrium. The main effect of these overpopulated bacteria colonies is the local production of organic acids that react with the mineral phase of the enamel, producing demineralization and destruction of the calcified tissue. In other words: caries. This process is carried out in two stages: first, and attack on the inorganic part of teeth (HAp) by the organic acids and then the degradation of the organic tissue by enzymatic or mechanical means, once the inorganic component is no longer present to reinforce the structure [5–7].

Caries is, perhaps, the main challenge in public health worldwide, because it affects nearly 95% of the total human population at some stage of their lives. This represents an enormous loss of working hours and millions of dollars dedicated to medical care; additionally in many cases one or more teeth are lost [8–9]. One of the important strategies to prevent caries for some years now, is to coat the pits and fissures on teeth surface with a physical barriers that prevents the bacteria colonies from populating the surface [10]. However, filtration, poor adherence, and degradation of the coating made these attempts futile. Commercial pit and fissure sealant, made of BIS-GMA resin reinforced with inorganic fillers, has been the preferred material to seal the teeth fissures, acting as a preventing agent for tooth decay. Nevertheless, this technique is exclusively used for the occlusal faces of bicuspid and molar teeth. Up to now, dentistry practice lacks an effective, modern, simple, long-lasting, and low cost material to be utilized widely as a preventive coating to fight tooth decay before it appears.

On the other hand, nano-technology provides interesting opportunities to develop novel materials with tailored properties: recent reports using hybrid inorganic–organic coating material have proven to be extremely effective as tribological enhancers and corrosion-resistant agents. Accordingly, the aim of the present work is to report the use of a novel hybrid ceramic-polymer coating with high wear resistance as an alternative for protecting teeth against attack by external agents know to promote caries or staining. The wear resistance of the coating was determined with the aid of micro-Raman spectroscopy.

EXPERIMENTAL

PMMA-PAAc (polymethymetacrylate-polyacrylic acid) copolymer of high molecular weight and with large content of PMMA, was chemically linked to commercial silica nano-particles of 18 nm in diameter (Degussa), to produce a hybrid composite that can be bonded, also chemically, to the tooth surface, and that possess high wear resistance and high transparency and gloss. The copolymer was synthesized by free radical polymerization using freshly distilled methylmetacrylate, industrial grade, and acrylic acid (Industrias Resistol, Mexico) monomers. The reaction medium was a mixture, in equal parts, of isopropanol and ethanol (Baker, Co.); the MMA:AAc ratio was 90:10 wt, the initiator was 2,2′-azobisisobutryonitrile (AIBN) at a concentration to obtain a molecular weight of 500,000 g/mol. The polymerization was carried out at 80°C under strong agitation and nitrogen atmosphere for 2 h.

An esterification reaction was carried out between the hydroxyl groups of the silica nono-particles and the carboxyl group of the AAc of the copolymer, as shown schematically by the reaction scheme [11].

$$\text{(Silica Particle)} - \text{OH} + \text{HO} - \text{OC} - \text{(Copolymer)} \rightarrow$$
$$\text{(Silica Particle)} - \text{O} - \text{OC} - \text{(Copolymer)} + \text{H}_2\text{O}$$

100 ml of the copolymer solution were mixed with 30 ml of the silica particles. Then, small amounts of nitric acid were added to keep the pH equal to 3. Finally, the compound was kept under reflux for 4 h to complete the esterification reaction. The water, produced during the reaction, was removed to make the esterification reaction irreversible. Four different coating solutions were prepared with different silica: copolymer ratio: (1) 12:88; (2) 20:80; (3) 25:75 and (4) 30:70.

Clean non-erupted molar teeth were etched with phosphoric acid at 37% dental grade (Degufil) for 15 s and then washed with distilled water and dried; after that, a layer of coating was applied with a clean paintbrush, waiting 2 min for drying and then a second layer of

TABLE 1 Systems Used and Their Coating Thickness

Sample	Ceramic:Copolymer ratio	Thickness (μm)
1	12:88	25.0
2	20:80	23.0
3	25:75	28.0
4	30:70	22.5
Blank	–	–

coating was applied. The samples were divided into 5 groups, namely blank samples and samples protected with the four different silica:-copolymer ratios; additionally, films of three different hybrid coatings were also prepared. The thickness of the coating was determined using confocal microscopy. The results are reported in Table 1.

A special device to produce an intensive brushing on the coated tooth was built in the authors' laboratory using a continuous-variable speed motor, where a standard dental brush (Oral B-40) was adapted. In all cases, a commercial toothpaste and water was used. The speed of the motor was adjusted to emulate a normal tooth brushing procedure (120 rpm): under normal brushing conditions, one tooth is in contact with the brush around 2 s, meaning that in one day (brushing teeth 3 times a day) one tooth is in contact with the brush for 6 s; brushing a tooth normally during a trimester is equivalent to an intensive brushing for 9 min.

Micro-Raman spectroscopy (DILOR model Labram) was used to determine the way the coating was removed by brushing. Initially, the tooth is coated with an hybrid ceramic-polymer coating. The micro-Raman instrument makes a chemical analysis on the external surface, resulting in a spectrum where the organic compounds of the hybrid coating are shown. As the brushing procedure reduces the thickness of the coating, the inorganic nature of the tooth enamel is appearing; finally, when the coating is completely removed by brushing, the Raman instrument detects only the inorganic structure of the tooth enamel.

RESULTS AND DISCUSSION

Figure 1 shows a micro-Raman spectrum of the hybrid coating: a film of the hybrid coating was obtained by coating a teflon plate with the hybrid coating and, once dried, it was removed from the support. This film was placed on a brass plate and illuminated with the laser light of the Raman instrument. In this figure a broad band centered at 2945 cm^{-1} corresponding the C–H stretching vibration of the

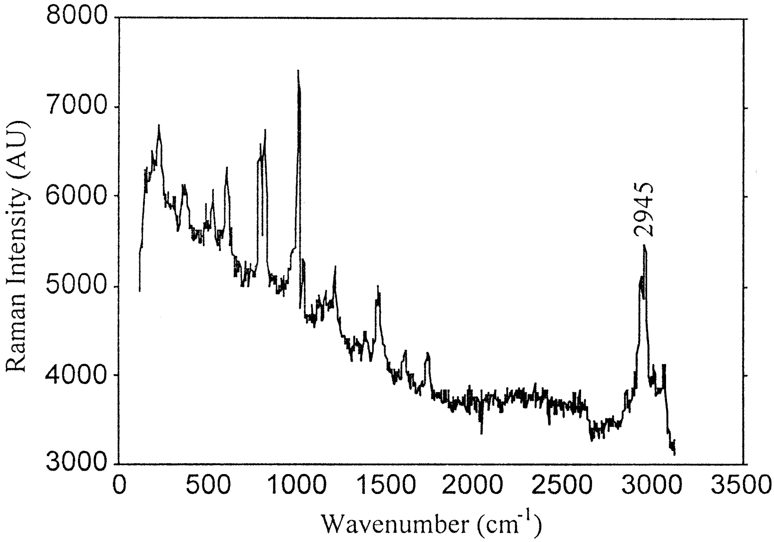

FIGURE 1 Raman spectrum of the hybrid coating.

aliphatic hydrocarbons of the organic part of the hybrid coating is clearly seen. This band has a medium-to-strong intensity and will be used as a diagnostic band.

As a reference, a Raman spectrum was obtained of a plain tooth without any coating, as shown in Figure 2. Strong fluorescence produced by the HAp and, on the top of this, a band at $956\,cm^{-1}$ corresponding to the P-O stretching vibration of the phosphate are shown. In Figure 2b a magnification of the spectrum from 500 to $1300\,cm^{-1}$ is shown.

A series of Raman spectra were obtained as a function of the brushing time. Figure 3 shows a sequence of Raman spectra for the tooth coated with the sample No. 3 (containing 25% ceramic). The spectrum in Figure 3a corresponds to 9 min brushing; both bands (956 and $2945\,cm^{-1}$ appear, the band at $2945\,cm^{-1}$ being significantly more intense than the other one. However, as the brushing time is increased, the band at $956\,cm^{-1}$ being to grow until finally, after 45 min brushing (Figure 3e), this band becomes much more intense than the band at $2945\,cm^{-1}$. In Figure 4 it is possible to see another series of Raman spectra when the tooth was coated with hybrid sample No. 2 (containing 20% ceramic); the behavior is similar but it is not so resistant to the brushing abrasion as the former one.

The ratio of the intensities I_{2945}/I_{956} is a measure of how resistant is the hybrid coating after the intensive brushing. For this reason this

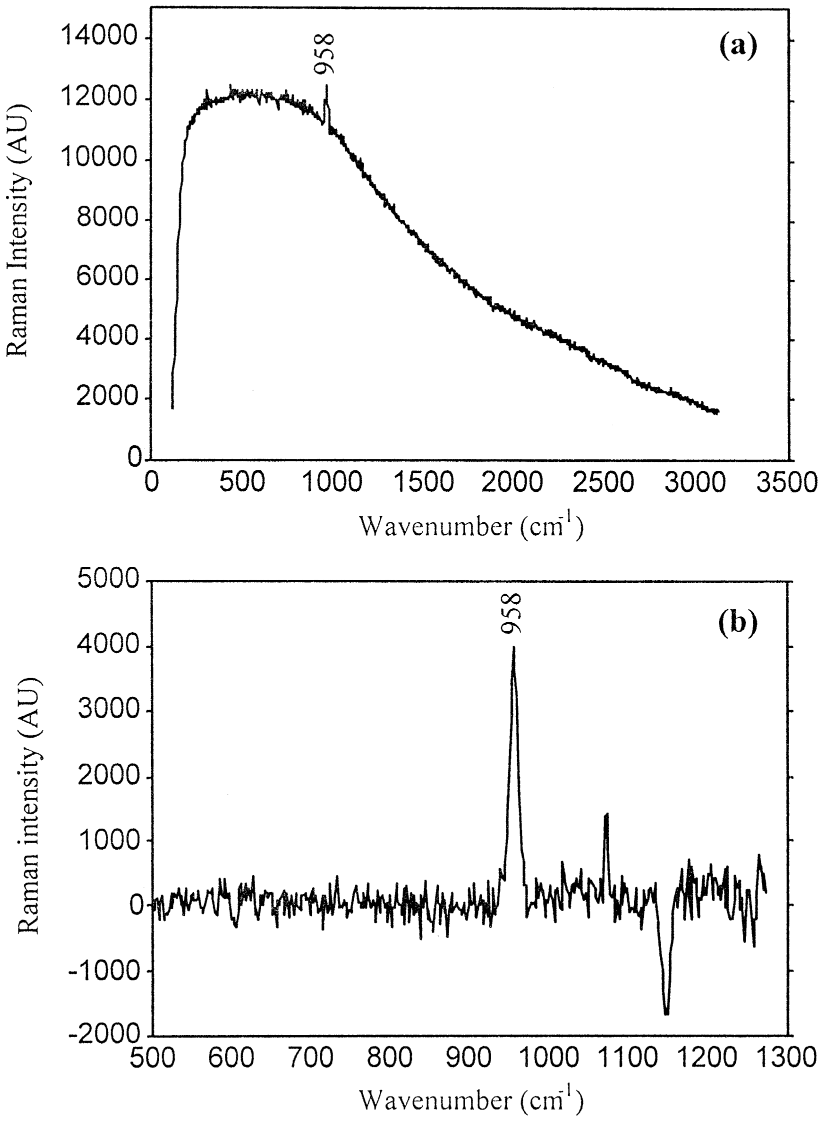

FIGURE 2 Raman spectrum of tooth enamel: (a) complete spectrum from 100 to 3000 cm^{-1} where a strong fluorescence is present; (b) a detail showing a magnification of the spectrum from 500 to 1300 cm^{-1}.

was used to determine the rate the coating was removed by abrasion. Figure 5 contains the plot of I_{2945}/I_{956} as a function of the brushing time; in this plot the initial thicknesses of the coatings are indicated.

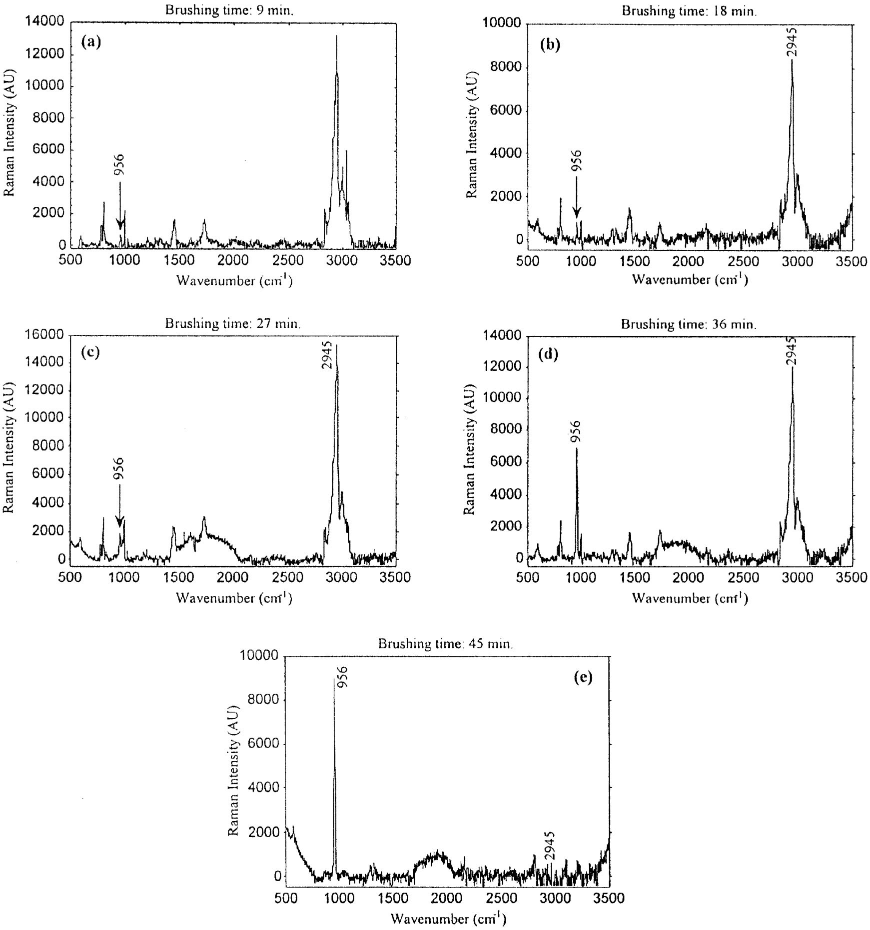

FIGURE 3 A series of Raman spectra taken at different brushing times for a tooth coated with coating No. 3 containing 25% of ceramic particles.

As can be noticed, in all cases, except one, the coating supports the brushing abrasion during 27 min, but for the coating containing 25% ceramic particles, the resistance reaches 45 min, being equivalent to 15 months daily brushing time.

In order to properly compare the performance of the three different coatings applied to the teeth, the intensities ratio was divided by the thickness of the coating; this normalized intensities ratio is shown in Figure 6. Finally, in Figure 7 a plot where all curves were scaled to start from one is reported.

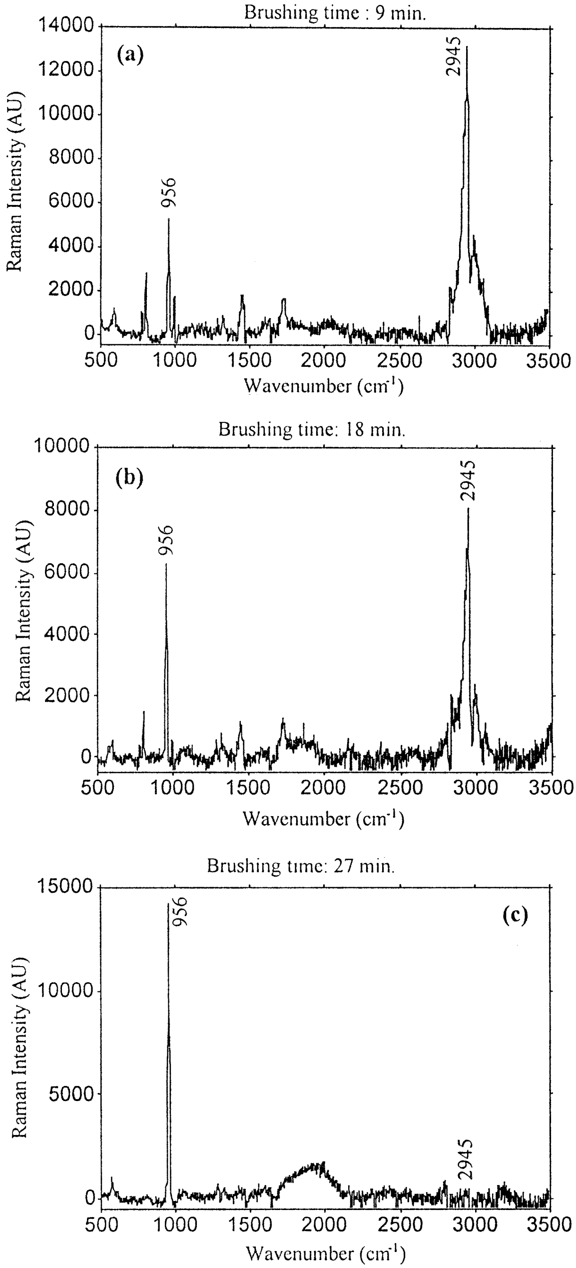

FIGURE 4 A series of Raman spectra taken at different brushing times for a tooth coated with coating No. 2 containing 20% of ceramic particles.

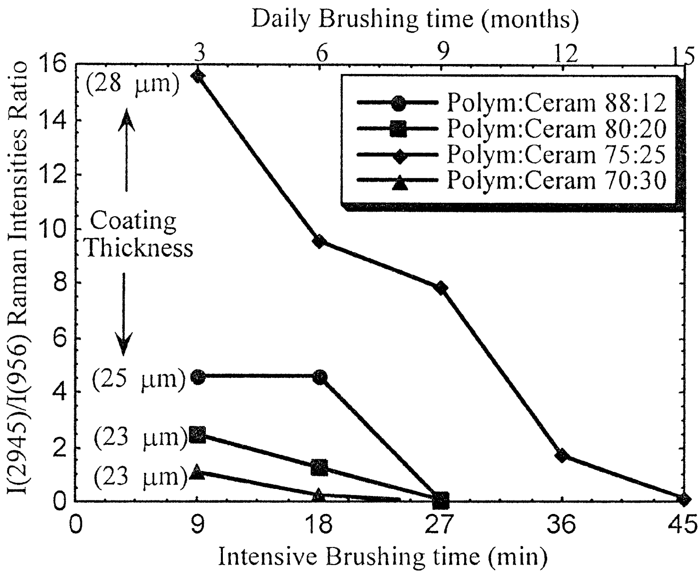

FIGURE 5 The intensities ratio I_{2945}/I_{956} is plotted as a function of the brushing time. The scale in the upper part of the figure indicates the daily brushing time in months.

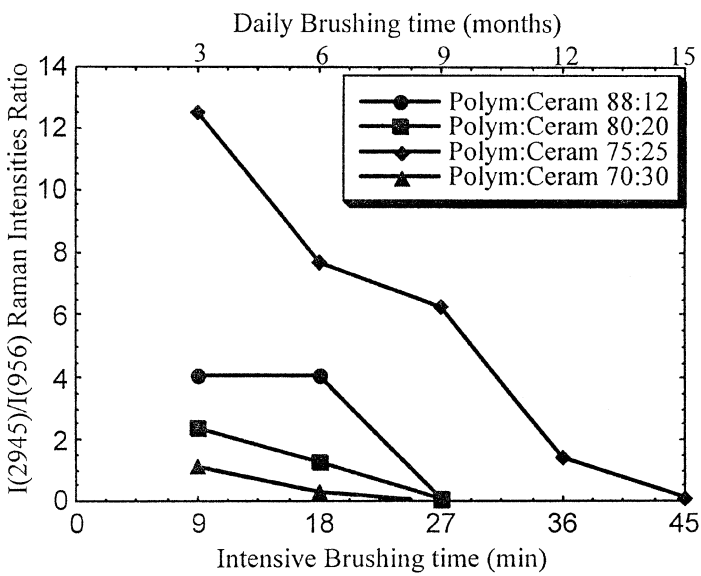

FIGURE 6 Same as in Figure 5, but normalized by the thickness of the coating.

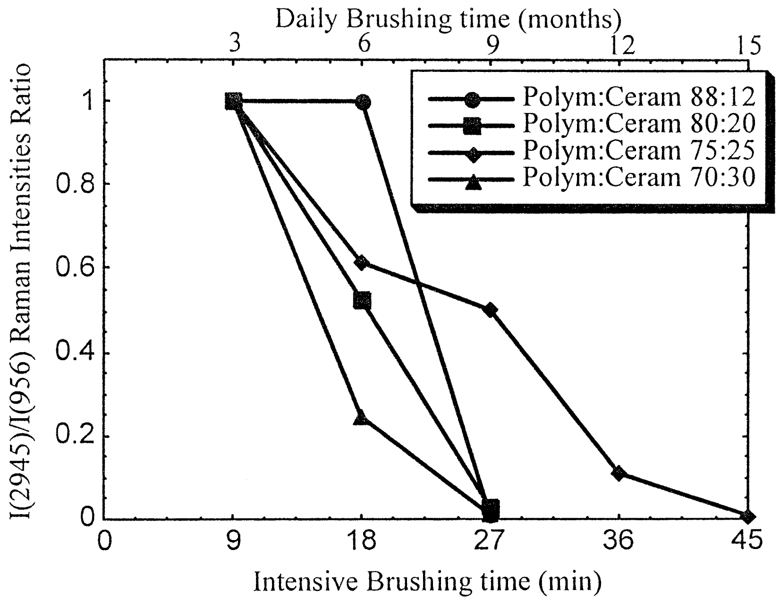

FIGURE 7 Same as in Figure 6 but all curves were scaled to start from one.

The sample containing the largest amount of ceramic was sample No. 4; however, this was not the sample with the highest wear resistance. One possible reason for this behavior is that, at this large amount of ceramic particles (30%), some aggregation of the particles is possible; if the particles aggregate, the abrasion properties are significantly reduced.

CONCLUSIONS

Novel hybrid ceramic-polymer coatings, used to protect the surface of the dental enamel again staining and caries, were demonstrated to have high wear resistance against brushing. This was determined using mirco-Raman spectroscopy: once the hybrid coating is removed by brushing, the Raman instrument detects only the HAp of the enamel. The results show that a hybrid coating containing 25% of ceramic particles had the highest wear resistance, corresponding of 15 months of daily brushing three times a day.

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