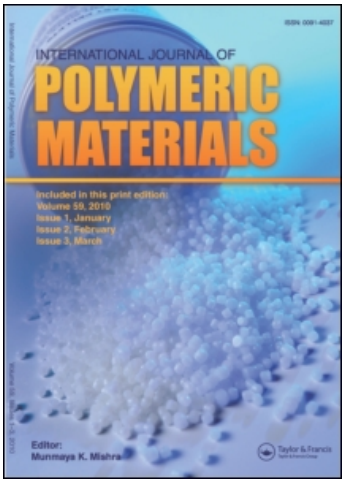

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A Novel Approach for Coating Acrylic Surfaces with Zirconia at Low Temperature

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A Novel Approach for Coating Acrylic Surfaces with Zirconia at Low Temperature

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A novel method for coating acrylic surfaces with thin ceramic layers is reported. A flat piece of polymethyl metacrylate was coated with a thin layer of zirconia at room temperature. This coating procedure is not the usual where a sol, produced by the sol–gel method, is used to dip the sample into it; in this case no zirconia sol is formed in order to avoid the production of high porosity films. The surface of the polymer substrate was previously functionalized to chemically attach the inorganic layer. In this way it was possible to obtain a thin coating with low porosity, high transparency and high wear resistance.

Keywords: Zirconia; Zirconium propoxide; Polymethyl metacrylate; Thin film coating; Sol–gel method; Optical transparency

1. INTRODUCTION

Many engineering and technological applications require materials with very specific and demanding properties. However, in some cases, even when the bulk properties of a material indeed fulfill those requirements, its surface presents poor properties resulting in a whole material with unacceptable properties for that specific application.

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One concrete and very important example of such as situation can be found in the acrylic materials field.

Indeed, acrylic materials are among the most important scientific and technological polymers nowadays, since it is possible to use them to produce paints and coatings of excellent quality. This is mainly due to their high UV resistance, which makes this kind of materials extremely important for outdoors applications. In addition to this, acrylic-based materials are hardly hydrolyzed, have excellent optical transparency and good compatibility with a number of additives and plasticizers. These are some of the reasons why acrylic polymers are widely used for indoor and outdoor paints, adhesives, paper applications, fabrics, waxes, elastomers, automotive parts, *etc*. [1–3].

Nevertheless, one of the main disadvantages of acrylic polymers is their poor resistance to wear which makes these materials very susceptible to scratching, thus affecting seriously the corresponding optical transparency. Indeed, even a simple soft cloth wipe, results in a noticeable reduction of the transparency due to the surface scratches; as wiping goes on, the acrylic material is no longer transparent and consequently not suitable for what it was originally designed for. This limitation is particularly important in the relatively new application of rubbermodified polymethyl metacrylate (PMMA) to be used for fabricating bulletproof windshields, where optical transparency is strongly required in addition to a high impact resistance.

Some optically transparent materials, such as silica, have already been covered with some type of ceramic thin film [4]. In fact, there are several techniques which are commonly used to coat different kinds of substrates with inorganic compounds, such as: CVD, sputtering, thermal oxidation, plasma-enhanced chemical vapor deposition (PECVD), flame hydrolysis, *etc*. [5–10]. However, in all the aforementioned methodologies, high temperature processing is a limiting factor, especially if a polymeric material is to be used as a substrate.

Some important effort has been devoted to protect polymeric materials with different kinds of ceramic coatings [11–23]. Recently, it has been reported the deposition of thin ceramic layers on the surface of polymers like polycarbonate and poly (ethylene therephtalate) by using the sol-gel method. However, the wear resistance of the resulting ceramic layer depends strongly upon the curing temperature: the higher the curing temperature, the higher the wear resistance. The

reason for this behavior is a reduction in the porosity of the thin layer obtained when the cure temperature is increased.

This reduction in porosity has several contributions: a) water and alcohol are rapidly removed through evaporation, b) all the unreacted alkoxide molecules react when the temperature is increased, filling the pores, reducing the porosity and densifying the layer, c) a possible phase transition temperature can be reached in the ceramic layer during the curing process, increasing the mechanical stability and d) some sintering can be obtained at higher temperatures, also increasing the mechanical stability. However, in all cases, the curing temperature can not be higher than the glass transition temperature of the corresponding polymer, since the rigidity of the substrate would be lost and some degradation of the material could be induced.

The aim of this work is to modify the surface of a commercial sample of rubber-modified PMMA, making it resistant to mechanical wear. This would allow the use of this kind of material as a polymeric windshield with good optical transparency and high impact resistance. In our particular case, the coating is a zirconia thin layer deposited on the PMMA surface, aimed to protect the polymeric surface while preserving the optical transparency.

2. EXPERIMENTAL

2.1. Reactives

Zirconia propoxide (70 wt% in 1 -propanol) (Aldrich Chem. Co.), propyl alcohol (99 wt%) (J. T. Baker), nitric acid (65 wt%) (J. T. Baker), sulfuric acid (99.7 wt%) (J. T. Baker) and distilled water were used.

PMMA commercial plates modified with styrene-butadiene rubber (SBR) were kindly supplied by Industrias Resistol S. A. de C. V. (Mexico).

2.2. Substrate Preparation

Prior to the actual functionalization procedure, the PMMA surface was cleaned to remove grease, dust, *etc*. out from the surface; then the

PMMA surface was functionalized by binding on it OH groups, as indicated by the reaction scheme shown in Eq. (1). The functionalization was carried out through a hydrolysis reaction of the methoxy groups of the PMMA under acidic conditions. This chemical reaction was carried out at room temperature and pressure conditions, and for different reaction times. Then, the polymeric surface was washed several times with distilled water in order to remove any acid residues.

$$\mathrm{PMMA{-}CO{-}O{-}CH_3 + H_2O \xrightarrow{H^+} PMMA{-}CO{-}OH + CH_3OH} \tag{1}$$

2.3. Coating Deposition

A wear resistant zirconia-based thin film was incorporated on the PMMA surface, previously functionalized with OH groups, through a condensation reaction with the zirconium propoxide as shown in Eq. (2): the hydroxyl groups anchored on the PMMA surface react with the propoxy groups of the alkoxide; here R stands for the propyl group.

$$\mathrm{PMMA{-}OH + R{-}O{-}Zr{-}(OR)_3 \rightarrow PMMA{-}O{-}Zr{-}(OR)_3 + ROH} \tag{2}$$

This coating was achieved by dipping the PMMA surface into a mixture of the alkoxide with 1-propanol 1:14 mol; the zirconium propoxide was mixed with 1-propanol in order to improve the wetability of the PMMA surface. The PMMA substrate was immersed into this solution at constant rate (15 mm/min), remaining into the solution for 5 min to allow the chemical reaction to take place; then it was removed out of the solution at the same constant speed. During this procedure there is no sol formation. Figure 1 shows a schematic diagram of the immersion apparatus designed in our laboratory.

After this first immersion, the PMMA surface was rinsed with distilled water to fully hydrolyze the unreacted propoxy groups of the alkoxide; in this way it was possible to obtain zirconium oxides and hydroxides, covering the whole PMMA surface. This surface was then dried at 80°C using a N_2 atmosphere. This chemical reaction is shown

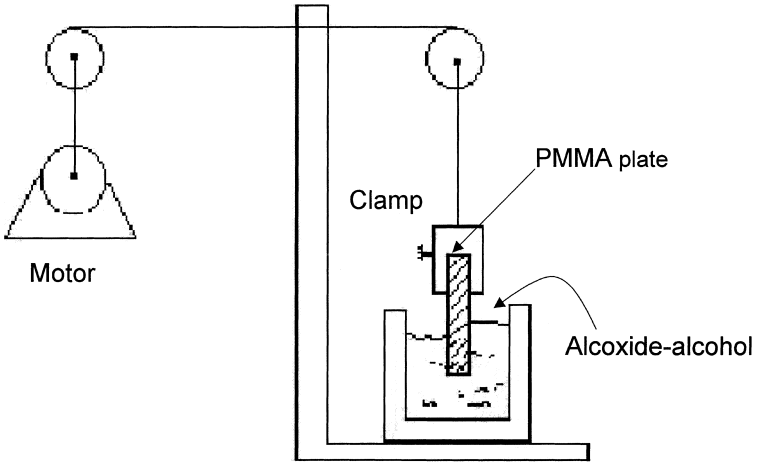

FIGURE 1 Schematic diagram of the immersion apparatus with controlled velocity.

in Eq. (3).

$$\text{PMMA—O—Zr—}(\text{OR})_3 + 3\text{H}_2\text{O} \rightarrow \text{PMMA—O—Zr—}(\text{OH})_3 + 3\text{ROH} \quad (3)$$

Through a second immersion into the mixture alkoxide-propanol, a condensation reaction takes place between the hydroxyl groups on the PMMA surface and the propoxy groups of the alkoxide, forming the zirconia film; this reaction is shown in Eq. (4).

$$\begin{aligned}&\text{PMMA—O—Zr—}(\text{OH})_3 + \text{RO—Zr—}(\text{OR})_3 \rightarrow \\ &\rightarrow \text{PMMA—O—Zr}(\text{OH})_2\text{—O—Zr—}(\text{OR})_3 + \text{ROH}\end{aligned} \quad (4)$$

It is important to point out that this is not the usual way to produce thin films by the sol–gel method, where the substrate is immersed into a sol; in this case there is no sol formation, *i.e.*, the PMMA was not immersed in a zirconia sol.

Because the polymeric surface was dried at 80°C, practically all free water was removed from the surface; thus, the other possible condensation reaction is between the hydroxyl groups on the PMMA surface and the partially hydrolyzed zirconium propoxide.

By repeating this procedure several times, it was possible to deposit, on the PMMA surface, a zirconia layer with controlled thickness. This

procedure allows to obtain a zirconia thin layer with less porosity with respect to films prepared by the usual sol–gel method. In fact, the minimum porosity in a sol–gel prepared film, is given by the interstitial spaces left by the particles of the sol. In this procedure, a sol formation does not exist therefore the porosity is exclusively controlled by the chemical reactivity of the alkoxide (which also affects the sol–gel prepared films); then the film's porosity is reduced with a concomitant increment in the wear resistance.

2.4. Atomic Force Microscopy Characterization

Atomic Force Microscopy (AFM) is an appropriate technique to characterize the texture of a specific surface, allowing to observe, for example, the quality and the thickness of coatings, fractures, inhomogeneities, interfaces, *etc*.

A Digital Instrument Dimension 3000 AFM was used for the AFM characterization at a scanning rate of 2–4 lines/sec; all measurements were performed at room temperature by using a silicon nitride tip, and the scanning area was of $100 \times 100\,\mu m$, with 500 readings.

2.5. Wear Resistance

The wear resistance was determined by measuring the weight loss on the flat surface of the zirconia-coated PMMA, while this surface was ground by using an abrasive wheel disk grade 1200. The instrument, shown in Figure 2, was operated at 76 rpm during 1000 spins, keeping

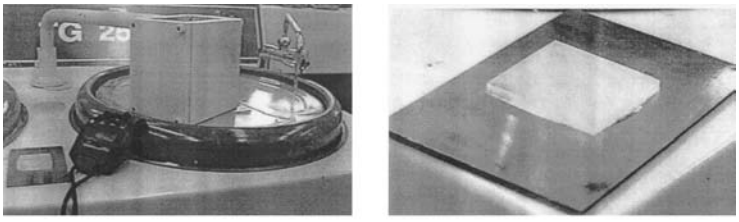

FIGURE 2 Schematic diagram of: (a) the abrasion apparatus and (b) the sample holder.

constant the flow of the water of the cooling system; the weight load was set to 52.5 g. Coated PMMA surfaces were epoxy-glued to a sample holder as can be observed in the same figure. The weight loss by the sample was determined with an accuracy of $\pm 1 \times 10^{-5}$ g. The instrument used for the wear experiments was designed in our laboratory [24] and it is similar to one described elsewhere [25, 26]. An uncoated PMMA sample was used as a reference. After the wearing procedure, the sample was washed with distilled water and dried at 80°C in dry air for two hours.

3. RESULTS AND DISCUSSION

In Figures 3a and 3b the FT-IR spectra of pure and 3-days-functionalized PMMA (3f-PMMA), are shown, respectively. The bands at 3432, 3547 and 3636 cm^{-1}, shown in Figure 3b, correspond

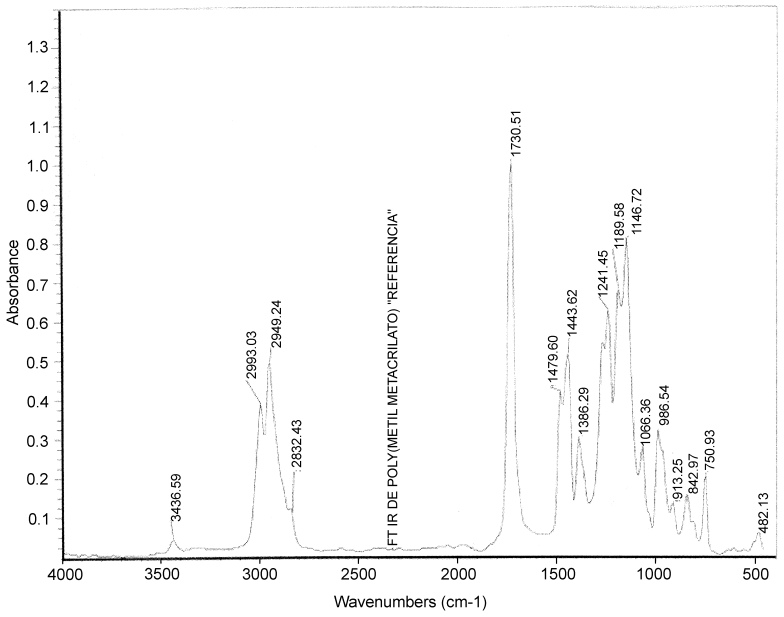

FIGURE 3a FT-IR of pure PMMA sample.

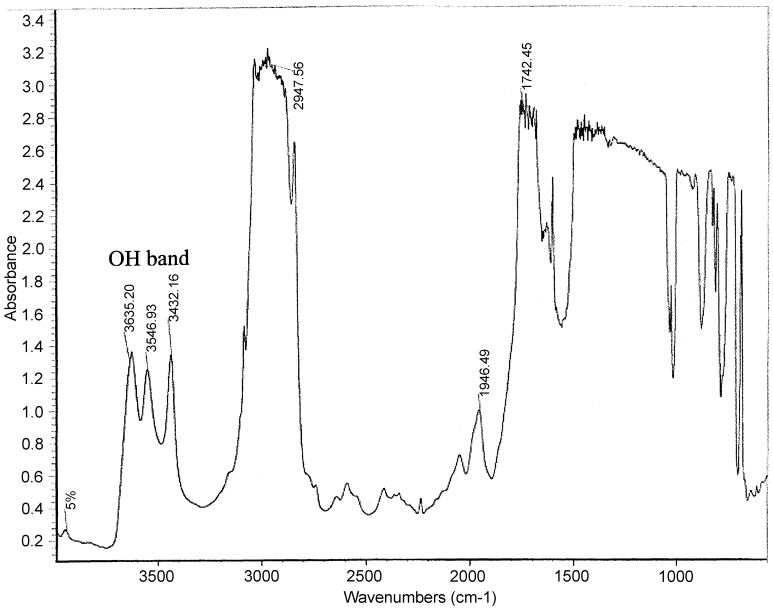

FIGURE 3b FT-IR of a PMMA sample functionalized during three days.

to the presence of hydroxyl groups, meaning that the —$COOCH_3$ group on the PMMA surface has been transformed to —COOCH group, following the hydrolysis reaction shown in Eq. (1). These bands, which are intense with respect to the weak band at 3437 cm^{-1} shown in the spectrum of Figure 3a, mean that the functionallization of the PMMA surface was carried out successfully. The density of OH groups on the PMMA surface was not possible to evaluate, but the high relative intensity of the OH bands for the coated PMMA relative to pure PMMA, means that there has been a significant increment in the number of OH groups on the PMMA surface to attach zirconia molecules for the coating.

Typical AFM images of uncoated and coated PMMA samples are shown in Figures 4a and 4b, respectively. In Figure 4a, a flat PMMA surface with some small defects can be observed. This PMMA surface has optical quality, due to the type of application this material was originally designed for.

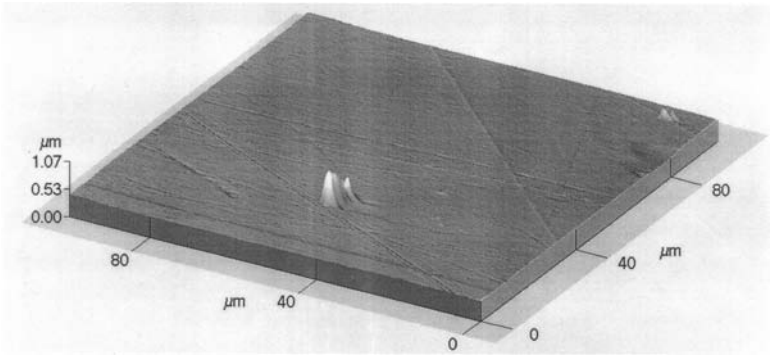

FIGURE 4a Atomic Force Microscopy image of uncoated PMMA.

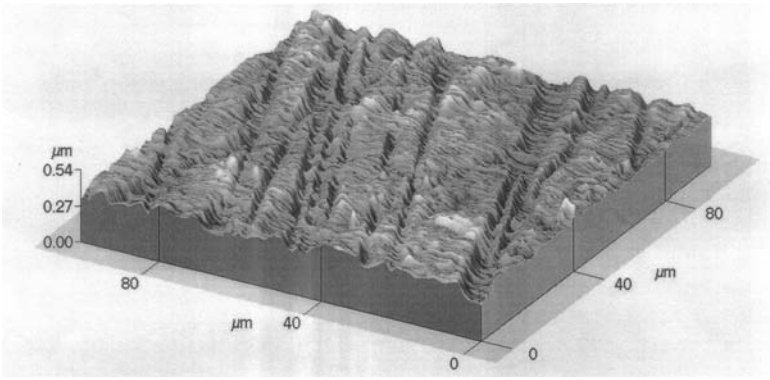

FIGURE 4b Atomic Force Microscopy image of PMMA surface coated with zirconia layer.

Figure 4b shows the PMMA covered with a zirconia layer. This image illustrates some small tracks left during the immersion process, which could not be avoided even when the immersion velocity was digitally-controlled to have a high stability. When the PMMA surface is introduced into the liquid (alkoxide), the meniscus between them changes with the position of the PMMA surface respect to the liquid when this is being immersed, reaching a critical value in the contact angle. Beyond this a jump is produced between the liquid and the PMMA. The wetting properties (surface tension) of the alkoxide relative to the PMMA (for the first immersion) or the zirconia (for multiple immersions), controls to large extent these tracks. The ripple

produced by this tracking has a rms value of 36 nanometers, as provided also by the AFM; this value is practically independent of the number of immersions, after the first immersion.

The thickness of the zirconia film was measured by AFM on samples partially coated with the film, obtaining a value of (130 + 18) nanometers for 5 immersions. The transparency of the coating was determined by using a laser-based turbidimeter designed in our laboratory, obtaining a value of (99.9 ± 0.1)% transparency.

PMMA samples with different number of immersions (5, 9 and 12) were prepared. The thicknesses of the zirconia coatings were determined for these samples. In Figure 5 it is possible to see a plot of the film thickness as function off the number of immersions; as can be noticed, the relation between these variables is not liner. This can be explained thinking that the zirconium is tetravalent, then the number of OH groups attached to the PMMA surface growth following a power law with the number of immersions. Denoting by T the film thickness and by I the number of immersions, the experimental data follows the relationship:

$$T = 0.729\, I^{3.2} \tag{5}$$

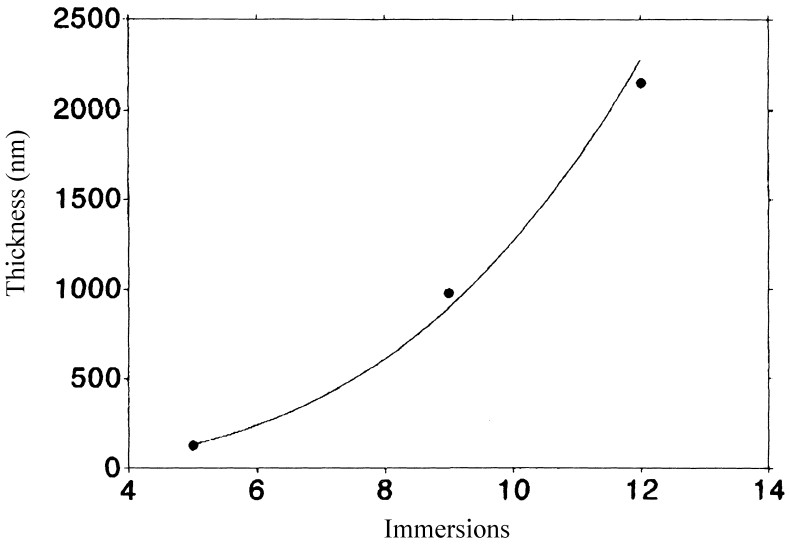

FIGURE 5 Dependence of the film thickness on the number of immersions.

Every time the sample is immersed into the alkoxide, each OH group becomes three OH groups.

The wear results are shown in Figures 6 and 7. Figure 6 shows how the samples lose weight as a function of the grinding time. As can be noticed, the uncoated surface loses weight faster as compared with the others samples, indicating a poor wear resistance. The sample with the smaller loss of weight corresponds to the one with 5 immersions, followed by the sample with 9 immersion and finally the one with 12 immersions, respectively. From this figure it is possible to observe that pure PMMA losses weight 58% faster than the sample coated with 5-immersions.

The wear resistance of the zirconia film progressively deteriorated as the number of immersions goes above some value (5 for this particular system). One possible explanation for this behavior is that, when the number of immersions is high, the zirconium propoxide is progressively hydrated forming a sol, which produces films with high porosity and poor mechanical properties. Then, for thicker films, a porosity gradient is produced which deteriorates the mechanical properties.

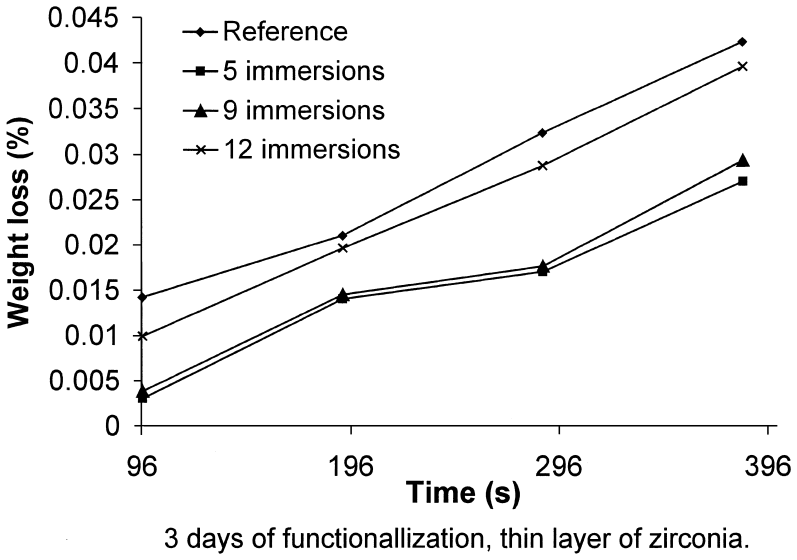

FIGURE 6 Wear resistance as a function of the grinding time for coatings of different thickness.

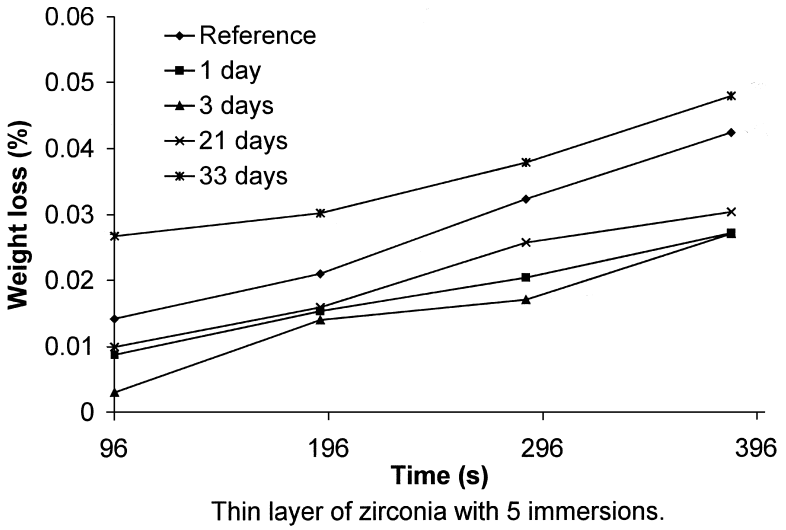

FIGURE 7 Wear resistance as a function of the grinding time for coatings with different functionalization periods.

Additionally, the film thickness grows fast with the number of immersions. When the number of immersions is around 5, the zirconia coating provides a good resistance to abrasion, reducing the weight loss. It is important to recall that this scratching protection is achieved by a film of only 130 nm in thickness.

Figure 7 shows the effect of the functionalization time on the weight loss as a function of the wearing time. For all these experiments, the samples were immersed 5 times. As in the former figure, the reference corresponds to the uncoated sample. The best wear resistance was obtained when the PMMA sample was functionalized for 3 days in the acidic solution; in this case the uncoated sample losses weight 55% faster than the sample functionalized for 3 days.

The worst case was when the functionalization time was as long as 33 days. This means that the PMMA was chemically-degraded by the nitric acid; this degradation is noticeable when the functionalization time is long enough (typically longer than 15 days), because the PMMA plates show a yellowish color, indicating that some kind of degradation is indeed taking place. The optimum time for this process is around 3 days.

4. CONCLUSIONS

A novel approach to coating polymeric surfaces was developed. The results clearly indicate that a wear-resistant surface can be obtained when a zirconia thin film is deposited on the surface of PMMA. A thin zirconia film of only 130 nm improves the abrasion resistance by an almost twofold factor. The optimum results were obtained when the number of immersions is around five, while the maximum functionalization time that provides the best performance is around 3 days. These results demonstrate the technological feasibility to produce an optical-quality transparent ceramic coating able to protect the polymeric surface from scratching.

Acknowledgments

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