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ATOMIC FORCE MICROSCOPY STUDIES OF TWO COMPOSITES BASED ON SURFACE ACTIVE GLASSES AND DIFFERENT COPOLYMERS AND THEIR STABILITY IN BIOLOGIC FLUID

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ABSTRACT. The surface morphology of two composites (glass ionomer cements), and of their constituent inorganic and organic phases was investigated by atomic force microscopy (AFM), in tapping mode. The inorganic phase consists of a blend of inorganic powders, which was realized from surface active glasses. The organic phase contains either B1 copolymer or T1 copolymer, in the same weight percentage in water, with 3% tartaric acid. The two composites, noted B1 and T1, were made of the same inorganic powder blend, and the organic phase, containing either B1 or T1 copolymer. AFM imaging, namely height and phase-detection imaging with high resolution and contrast, was improved by monitoring the force of tapping of AFM probe on the sample surface. Morphological and structural analysis of investigated surfaces shows micro- and nanoparticles of inorganic powders embedded within the nano- and microdomains of copolymers. For B1 composite, it is observed a surface enrichment in B1 copolymer, against T1 composite. The surface of B1 and T1 composites was investigated both in native state and after polishing and glossing. The composites were measured in air and after 24 h or 7 days in artificial saliva. No essential topographical changes occurred to their surfaces, exposed about 24 h in saliva, independent of the used advanced processing methods for composite surfaces. The glossing leads to a stable surface of composites, both in air and after 24 h or even after 7 days exposed in saliva. However, after 7 days in saliva, the surface roughness is substantially increased for the T1 composite compared to B1 composite. Thus, B1 copolymer appears to be more stable in saliva than T1 copolymer. These data demonstrate that morphological and surface roughness analysis of both native surfaces and of enriched surfaces with polymers is important in determining the surface organization and the stability of composites in different environmental conditions.

Keywords: glass ionomer composites; AFM; biologic fluid; stability

Introduction

Composites include at least two categories of constituent materials: matrix and reinforcement (filling materials). The matrix material surrounds and supports the reinforcement materials by maintaining their relative

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positions. The reinforcements impart their special mechanical and physical properties to enhance the matrix properties. A synergism produces material properties unavailable from the individual constituent materials [1, 2].

Polyacrylic acid-based glass-ionomer cements appeared in the 1960s. They include a basic component, a glass-like calcium aluminosilicate containing some fluoride, and an acidic polyelectrolyte, which is a homopolymer or a copolymer of unsaturated carboxylic acids. The glass-ionomer cement sets as a result of a reaction between an acid and a base. The product of the reaction, a hydrogel salt, acts as a binding matrix surrounding the silicate particles.

Among the key properties of the glass-ionomer cements are specific adhesion to enamel and dentine, aesthetic qualities and fluoride release, which inhibits secondary caries over a prolonged period. In the 1980s, resin modified systems have become available commercially. These materials involve the formation of an interpenetrating polymer network combining the acid-base cross-linking reaction of the metal ion-polyacid with the cross-linking polymerization of the monomer system or additive action of the polymers [3-5]. Methods were proposed both for the preparation of the glass component [6] and for the organic macromolecular component [7]. However, because of the mixing problems, these methods are generally accompanied by a number of disadvantages, such as the formation of aggregations of inorganic particles, irregularly coated by polymers, and the low efficiency of controlling the coating thickness of the composite surface.

In this study, we explore the importance of components organization at the surface of composite materials, in controlling both the surface chemistry and the morphology. In this respect, we developed new characterization methods for glass ionomer composites, owing to their potential applications in medicine, such as bone substitutes and dental biomaterials. These composites are made of inorganic phase, e.g. surface active glasses, and different copolymers, such as poly(alkenoic acids). Caution was taken to maintain a good homogenization so that no phase separation was observed.

Further, the structure control of the composite surface can be achieved, both by the preparation methods of the material and by surface engineering methods applied to the composite surface. Such methods comprise direct enrichment of the surface with one of the composite components or the application of thin films made of organic mixture, such as a gloss, with good adhesion on the composite surface.

On the other hand, the success of these methods, to form the composite or for the controlled enrichment of its surface with a polymer or a gloss depends on the accurate analysis of the final organization at the composite surface.

Physical chemistry of surfaces of composite materials offers diverse research methods, such as X-ray photoelectron spectroscopy (XPS), contact angle analysis (CA) and secondary ion mass spectrometry (SIMS), which had proved their utility in chemical characterization of surfaces. XPS and SIMS can be used also for the visualization of surfaces, but the resolution offered by these techniques is not sufficient to make possible the determination of morphology of the composites at nanoscale.

Anyway, the characterization of surface organization can be achieved by scanning electron microscopy (SEM) [8]. Generally, SEM visualizes the morphology of the composite surface and to evidence the role of surface enrichment of the composite with polymer, only in the case where the enrichment generates significant topographical modifications between constituent domains. This limitation can be overcome by using the atomic force microscopy (AFM), in tapping mode. Moreover, the AFM technique offers the possibility to determine the surface roughness, an important parameter which can bring information on the changes in surface organization by advanced processing techniques as well as on the degradation of the composite surface, exposed to different environments. However, to the best of our knowledge, no report has been devoted to the AFM investigations on these type of glass ionomer composites.

In this work, for the first time, we explore AFM observations to describe the surface morphology and the surface roughness of the two composite materials and of their constituents, in native state as well as after their surface processing, and in different environmental conditions and at the chosen regular time.

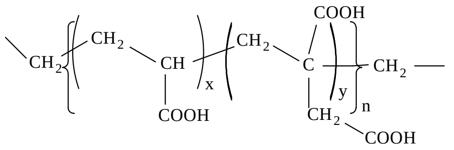
Thus, in the following we determine the bidimensional (2D-) and three-dimensional (3D-) topographical AFM images and the phase images for the surface of inorganic phase, i.e. inorganic powder (IP), of the organic phase (B1 or T1 copolymer), and of the composite materials, labeled as B1 or T1 composite, polished or glossed, with the aim to decipher the surface structure of these materials. Then, the surface morphology and the surface organization, as well as the surface roughness for 17 samples were investigated.

EXPERIMENTAL PART

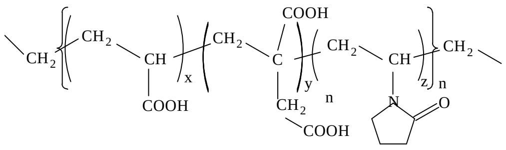
Preparation of films made from inorganic powders or organic matter

The *inorganic powder* (IP) was a blend of surface active glasses (glass ionomer products), viz. S1 and M glasses in the 7:1 mass ratio. The bulk composition of S1 glass is: SiO_2 (49%), Al_2O_3 (22%) and CaF_2 (29%): it is therefore a fluoro-aluminosilicate glass. The M glass has the following bulk composition: ZnO (16.72%), CaO (23.8%), Na_2O (9.33%) and SiO_2 (50.15%). These glasses were obtained from the corresponding oxides as described elsewhere [9-11]. After the raw materials were fused together, the melts were shock cooled in water. The glass fragments were ground and sifted to fine powders. Thin *films of this inorganic powder* were assembled on adhesive tapes, by rotating the tape on the surface of the IP powder, lying on optically polished glass. This film was subsequently used for AFM investigations.

The *organic phase* contains either B1 copolymer (or T1 copolymer. The copolymers are both modified poly(alkenoic acids). Each copolymer was used as a 50% (weight/weight) aqueous solution. Finally tartaric acid was added to aqueous solution, resulting in a final composition of 48.5% copolymer (B1 or T1, respectively), 48.5% water and 3% tartaric acid.



Formula of B1 copolymer



Formula of T1 copolymer

Films for use as AFM samples were prepared from each of these copolymer solutions by casting 1 ml aliquot of solution onto mica (muscovite) substrates (1 cm x 1 cm squares) atomically plane and freshly cleaved. The films were dried at room temperature, in air environment, but protected against dust.

In all experiments, for the preparation of the organic phase deionized water, with resistivity of 18 MΩ·cm, was used. It was obtained from an Elgastat water purification system.

The glassware used in this research was washed and rinsed with ultra pure water before using. The B1 and T1 copolymer films, after drying, were observed by AFM.

Preparation of composite materials, B1 and T1 composite disks

The two kinds of composite specimens (glass ionomer cements), B1 and T1 composite, were made of the same inorganic powder blend (IP) described above in mixture with the organic phase, containing either B1 copolymer or T1 copolymer. The specimens were given the same labels as the copolymer, namely B1 or T1 composite. The inorganic phase constitutes the active filling (reinforcement material) of the composite, while the copolymers constitute the matrix material. In the preparation of both kinds of specimens, the same charging ratio was used: inorganic phase to organic phase 2.2:1 mass ratio.

The specimens were prepared, at 23^{0}C from the aqueous solutions of the synthesized copolymers (polyalkenoic acids) and the superficially active glasses, by mechanical homogenization of the powders and liquids. The specimens, having the form of disks of 6 mm diameter and 1 mm height, were obtained by hardening of fresh mixed pastes in Teflon molds which were hermetically closed and stored in water at 37^{0}C. After about 30 minutes, the specimens were taken out of the matrix and were immediately immersed in water at 37^{0}C, for 24 hours [9].

AFM investigations

The AFM visualization of the surface of the investigated materials was executed using the scanning microscope, the AFM JEOL 4210 equipment, operating in the intermittent contact, known as tapping mode. The cantilever used was a triangular one, with a very pointed tip made from silicon nitride. The probe (tip) was on the cantilever, oscillating with a resonant frequency in the range of 200-300 kHz and with a spring constant of 17.5 N/m. Both a low scanning rate, 1Hz, and a higher rate, in the range 2-6 Hz were used, in order to detect possible scanning artifacts or those resulting from the sample preparation. The scanning angle was also modified on different directions, in order to distinguish between real images and those corresponding to artifacts. The AFM images consist of multiple scans displaced laterally from each other in y direction with 512 x 512 pixels. An adequate low pass filtering was performed to remove the statistical noise without loss in the structural features of the material. All AFM experiments were carried out under ambient laboratory temperature conditions (about 20^{o}C) as previously reported [12-14]. AFM observations were repeated on different areas on the scanned surface (i.e. for different magnifications), resulting in scanned areas from 10 x 10 µm^2 to 1 x 1 µm^2 or scaled down even more (0.5 x 0.5 µm^2) for the same sample. The AFM images were obtained from at least five macroscopic zones separately identified on each sample. All the images were processed according to standard AFM proceeding.

For the beginning, the surface structure was investigated by AFM imaging separately for the films made from the inorganic phase, IP, i. e. a mixture of S1 and M glasses powder, or from the organic phase containing either B1 copolymer or T1 copolymer. In the following, the surface of the composite materials, B1 and T1 composite disks, was analyzed

- in their native, original state
- after mechanical polishing with a dental drill
- after application of a gloss on the composite disk surface.

The *polishing* was preceded by an initial smoothing of the surface with an extradure fraise with turbine E0130 (maillefer). The polishing was made with abrasive disks OptiDisc from KerrHawe and followed by a washing with water jet and drying.

The *finishing gloss* Vitremer^{TM} , manufactured by 3M-ESPE, is a resin without filling mass, based on bisGMA (Bisphenol-A-glycidyldimethacrylate) and TEGDMA (triethylene glycol dimethacrylate). It was applied as a thin layer at the composite material surface and then cured by photopolymerization for 20 s using the curing light L.E.Demetrom II from SDS Kerr.

The AFM measurements were executed both in the air and in contact with artificial saliva as a simulation of the biological medium, versus time, after one day, and after 7 days, in order to evidence and control the releasing process of B1 or T1 copolymer from the composite material. The composition of the *artificial saliva* was: 50 mmol/l KCl, 1.5 mmol/l Ca^{2+}, 0.9 mmol/l PO_4^{3-}, 20 mmol/l trihydroxymethylaminomethane, buffer at pH 7.0 [15].

RESULTS AND DISCUSSION

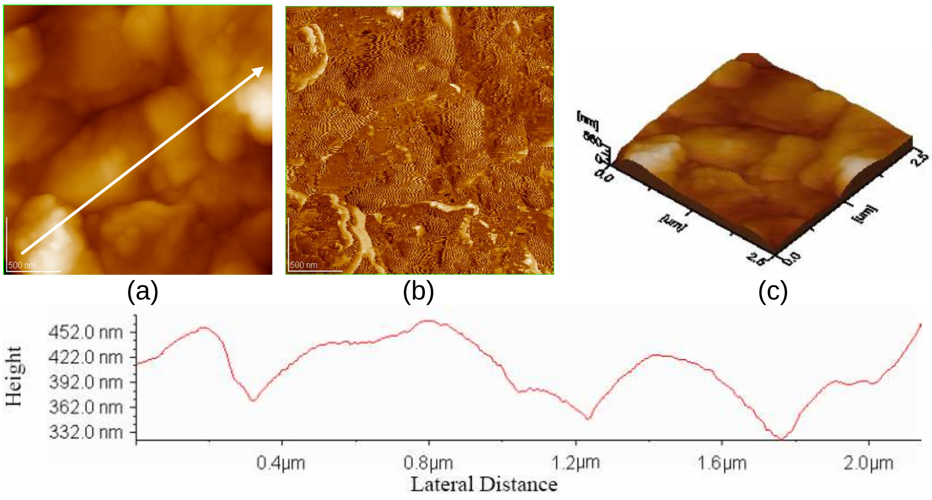
Generally, the degradation or the releasing rate of the copolymer from the composite surface is mainly controlled by the polymer erosion in contact with saliva. From these studies, with B1 and T1 composite disks in their native state, the hydrolytic liability of the copolymers can be estimated and the polymer which suffers a faster degradation (dissolution) in contact with saliva can be established. A modality to control the degradation/modification of surface structure in B1 and T1 composites is to gloss the disk surface with a blend of components that generally increases the stability of the composite surface against the environment (saliva).

We used the topographical and phase AFM images for evidencing the surface characteristics of B1 and T1 composite disks, for the identification of surface components, for revealing the existence of inorganic micro- and nanoparticles associated with the copolymer matrix. Moreover, the AFM offers the possibility to determine the surface roughness, described by the rms value (root mean square) and calculated directly from the 2D topographical AFM images [12-14].

AFM investigations on the films made from inorganic material and from organic material

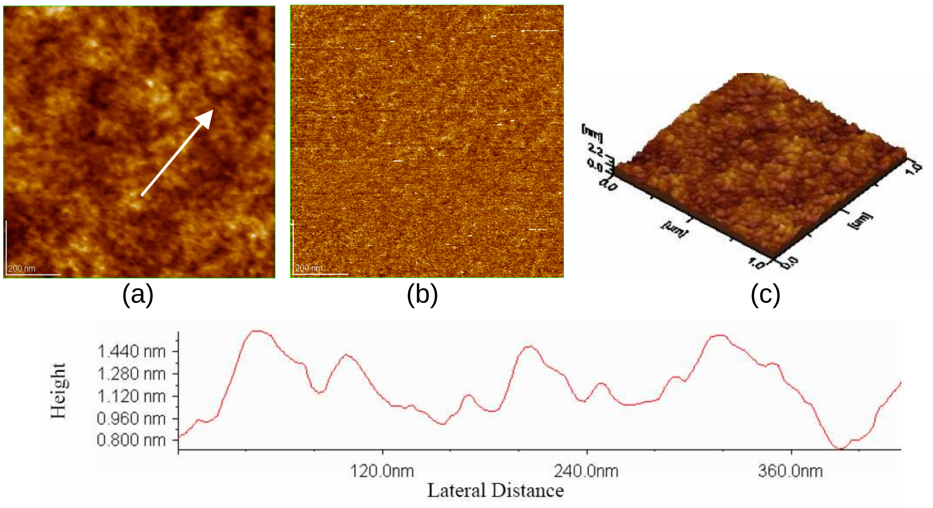
For the films made from the inorganic phase, the AFM images are shown in Figure 1, and for those of the organic phase in Figures 2 and 3: namely, in Figure 2 for the films containing B1 copolymer and in Figure 3 for films of T1 copolymer.

Figure 1 shows the morphology of the inorganic film surface. From the bidimensional (2D-) topographic AFM image (Fig. 1a), and from the three-dimensional (3D-) topographic image (Fig. 1c), as well as from the AFM phase image (Fig. 1b), the structuration of the inorganic powder into micro-agglomerates is seen (see, the arrow in panel a). From the cross section profile (Fig. 1d) we observe the microstructure of the inorganic film with particle sizes generally between 200 and 400 nm. In Fig. 1a it can be seen that the micro - agglomerates are formed from inorganic nano - powder



(d)

Fig. 1. AFM images of the film made from inorganic powder, deposited on adhesive tape. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 1a.

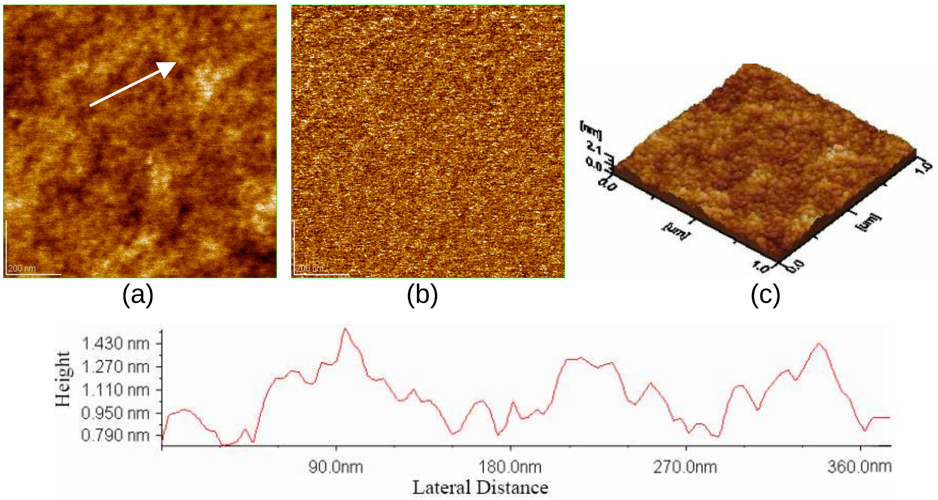


(d)

Fig. 2. AFM images of the organic film, containing B1 copolymer, deposited on mica support. Scanned area: 1 x 1 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 2a

by association. The inorganic film is rough; the rms value showing the surface roughness is given in Table 1.

In Figure 2, we present the surface morphology of B1 copolymer films, containing tartaric acid, deposited on a mica substrate. From the



(a) (b) (c)

(d)

Fig. 3. AFM images of the organic film, containing T1 copolymer, deposited on mica support. Scanned area: 1 x 1 μm^2. a) 2D topographic image; b) phase image; c) 3D topographic image; d) cross section along the arrow in Fig. 3a

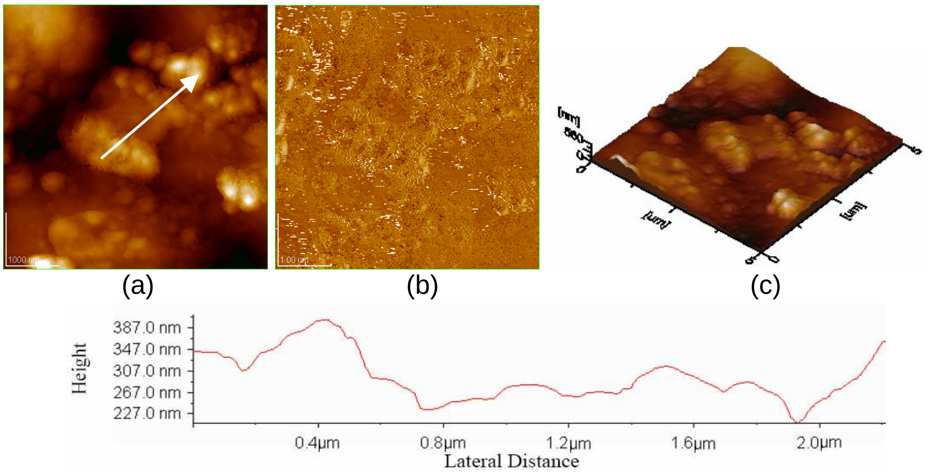
topographic AFM images (Figs. 2a, 2c) it is evident that the B1 copolymer forms nano domains, identified by their topographic characteristics. From the profile of the cross section (Fig. 2d), obtained along the direction given by the arrow in Fig. 2a, the dimensions of the nano domains are observed to be between 40 and 60 nm. The phase image (Fig. 2b) indicates the presence of a uniform film in every scanned area. The B1 copolymer film is smooth and the very low roughness of the B1 film is given in Table 1.

Figure 3 presents AFM images for the T1 copolymer film, deposited and oriented on the mica surface. The surface morphology (Figs. 3a, 3c) of the T1 copolymer film is similar to that characteristic to the B1 copolymer film (Fig. 2). The structuration of the T1 copolymer at the film surface results in nano domains situated in the range from 30 to 50 nm (Fig. 3d). The phase image (Fig. 3b) also indicates a T1 film smooth, with low roughness (Table 1).

From a comparison of Figures 2 and 3, a certain morphologic similarity is ascertained in the surface of B1 and T1 copolymers, which reflects a strong interaction between copolymer macromolecules, resulting in plane copolymer films. From this study it seems that both copolymers, B1 and T1, should be of interest in the realization of composite materials by individual mixing of their organic phases with the inorganic powder. As stated above, these composites (charging 2.2:1 ratio) were tableted, yielding B1 and T1 composite disk.

Surface morphology and characterization of B1 and T1 composites

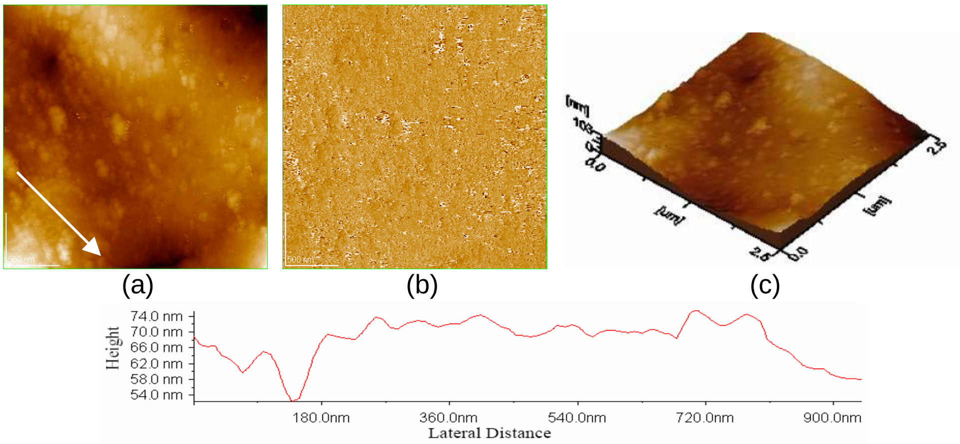
In the following the bidimensional (2D-) and three-dimensional (3D-) topographical AFM images, as well as the phase images are presented, for the surface of the two composite materials, B1 and T1 composite disks, with the aim to decipher the surface morphology of the composites and the surface organization of their components, the inorganic and the organic phase.



(a) (b) (c)

(d)

Fig. 4. AFM images of B1 composite disk surface. Scanned area: 5 x 5 µm^2. a) 2D topographic image; b) phase image; c) 3D topographic image; d) cross section along the arrow in panel 4a.



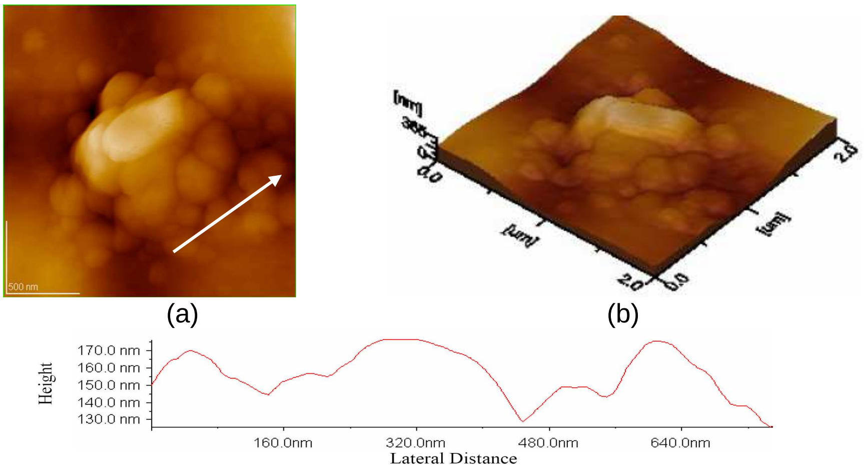
(a) (b) (c)

(d)

Fig. 5. AFM images of B1 composite disk surface. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image; c) 3D topographic image; d) cross section along the arrow in panel 5a.

The measurements for the *B1* and *T1* composite disks, respectively, were carried out on native surfaces (Figs. 4-6) and after their advanced processing by mechanical polishing (Figs. 7, 8) and glossing (Figs. 9, 10), in air (Figs. 4 -10) and in saliva environment (Figs. 11-19), after 24 hours (Figs. 11-13, 16, 18) or 7 days (Figs. 14, 15, 17, 19).

From AFM images (Figs. 4, 5) one can observe the morphological and chemical organization of the *native B1* composite disk surface. Agglomerates of inorganic powder, also called clusters, are observed as high formations, light-colored in the 2D- (Figs. 4a, 5a) and 3D- topographical images (Figs. 4c, 5c), surrounded by the matrix of B1 copolymer (the lower, dark-colored zones). The associates of inorganic powder have the size in the range from 100 to 300 nm (Figs. 4d, 5d), comparable with their size visualized in the film made only from inorganic powder (Fig. 1). However, the undulation in the cross section profiles (Figs. 4d, 5d) indicate the existence of inorganic nano-powders associated as micro aggregates embedded in the B1 copolymer matrix. We also state the existence of both, heterogeneous (Fig. 4) and more homogeneous zones (Fig. 5), what should indicate that the B1 copolymer does strongly interact with the inorganic powder, which is embedded in its polymeric matrix (Figs. 4b, 5b). From cross section profiles (Figs. 4d, 5d), as compared with the profile of the inorganic powder film (Fig. 1d), it is evident that the inorganic particles are smaller in the B1 copolymer matrix, and are protected against the segregation existent in the n ative film of inorganic powder. The values for the surface roughness of B1 disk are given in Table 1 and reflect the significant diminution of the roughness in presence of B1 copolymer.



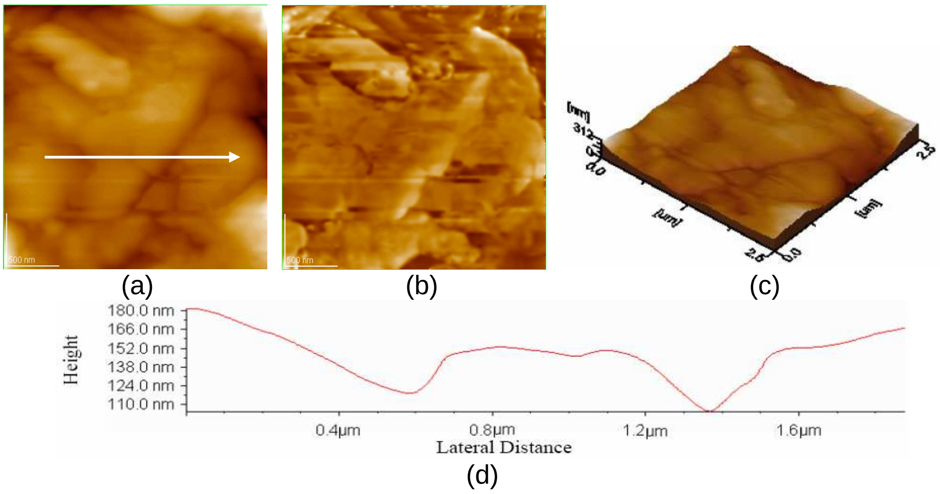
(a) (b)

(c)

Fig. 6. AFM images of T1 composite disk surface. Scanned area: 2 x 2 µm^2. a) 2D topographic image; b) 3D topographic image; c) cross section along the arrow in panel 6a.

The AFM images for the surface (only one example is given in Fig. 6) of the original T1 composite disk are quite similar to those for B1 composite (Figs. 4 and 5). The size of the IP agglomerates is situated in the range from 150 to 300 nm. However, the surface roughness of the T1 composite disk (Table 1) is higher than that of the B1 composite disk. A possible explanation is the lower enrichment of the surface of the T1 composite in T1 copolymer, leaving the IP aggregates higher than in the matrix of B1 copolymer. This situation would also explain the lower stability of the T1 composite surface, particularly after 7 days exposure to saliva, against the better stability of the B1 composite in the same conditions.

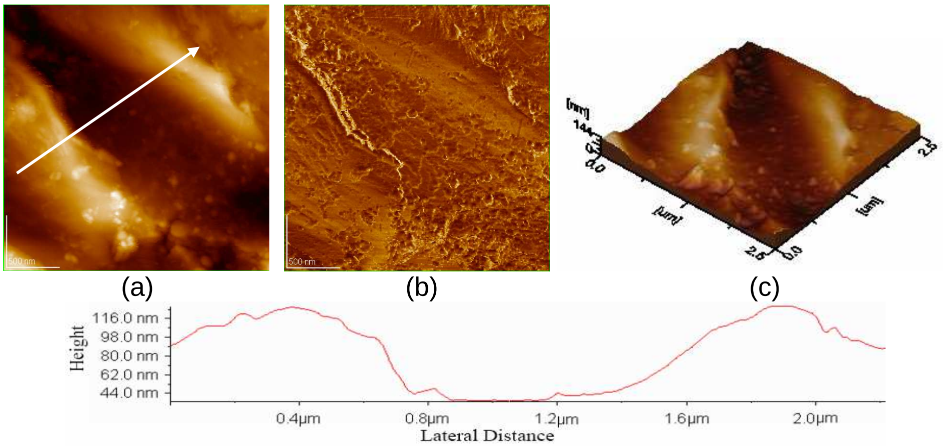
Figure 7 shows AFM images for the surface of B1 composite disk, mechanically polished. In the same way with the morphology of the original B1 composite disk surface, here, also the existence of agglomerates of inorganic powder in the B1 copolymer matrix is observed. Thus, by the surface polishing of the B1 composite disk another plane from the bulk of the disk is evidenced and the AFM observations indicate a resemblance in the disposition of inorganic powder clusters both in the bulk and at the surface of B1 composite. Nevertheless, by a more thoroughly study of the cross section profiles, the existence of some larger agglomerates is ascertained in the polished surface (Fig. 7d) as compared to the original surface of B1 composite (Fig. 5d). This observation should indicate a trend to the surface enrichment in B1 copolymer during the fabrication process of B1 composite disk, having as the consequence a rather good protection of the IP particles against the tendency to segregation in the disk surface. The surface roughness (Table 1) is a little decreased by polishing, suggesting good mechanical properties for the B1 disk.



(a) (b) (c)

(d)

Fig. 7. AFM images of the polished B1 composite disk surface (B1p). Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image; c) 3D topographic image; d) cross section along the arrow in panel 7a.



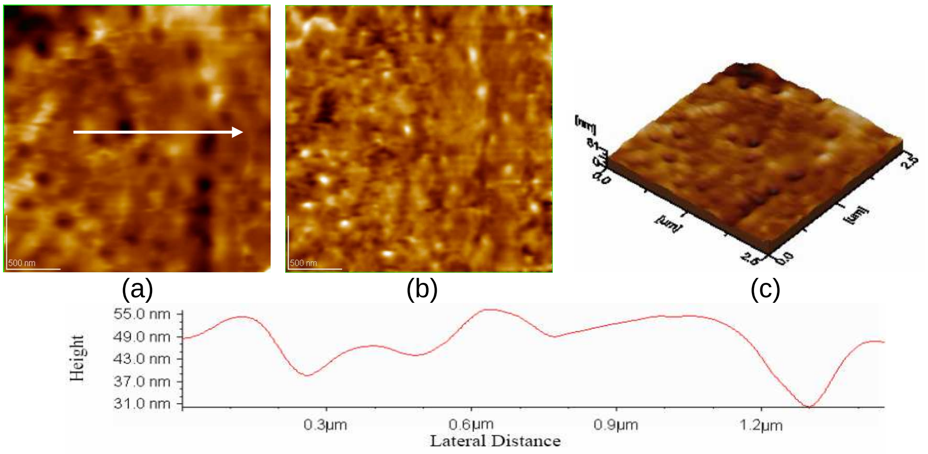
(a) (b) (c)

(d)

Fig. 8. AFM images of the polished T1 composite disk (T1p) surface Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 8a

At the surface of the T1 composite disk, mechanically polished (Fig. 8), the existence of IP agglomerates embedded in the copolymer matrix can be observed. A thorough analysis of topographic images (Figs. 8a, 8c) and particularly of the phase image (Fig. 8b) reveals the lamellar aspect of T1 copolymer. An arrangement in rows of the IP micro particles in the T1 copolymer matrix is observable (Figs. 8a, 8d). Therefore, we could infer that unlike B1 copolymer, the T1 copolymer does not homogenize (in bulk) sufficiently well the IP phase in the fabrication process of the disk. However, the surface roughness of the T1 disk, after polishing (Table 1), is lower than that of the native T1 disk, and comparable with that of the polished B1 composite disk, suggesting quite good (bulk) mechanical properties for the T1 composite.

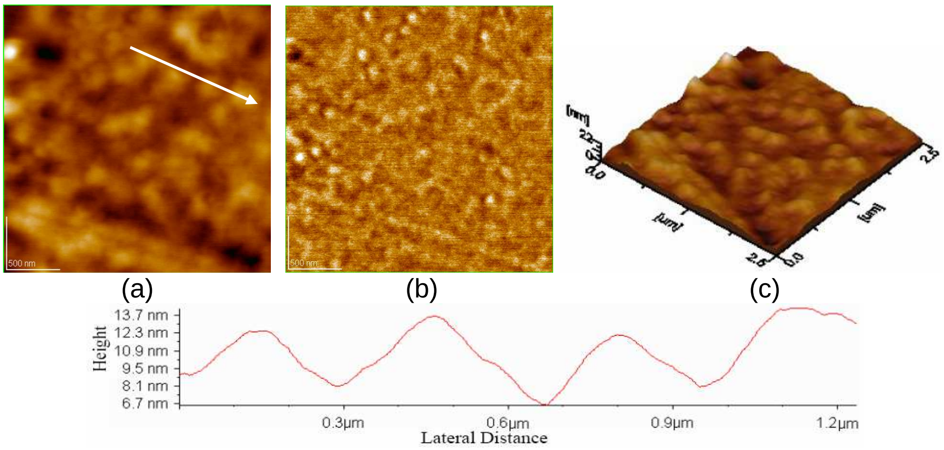
The surface processing of B1 composite disk by glossing leads to a surface enrichment with a film made of an organic gloss, of polymeric nature. The gloss film gave AFM images shown in Fig. 9. From these images it can be seen that the gloss film follows the surface of the B1 disk, and the IP associates are still visualized both in the topographic images (Figs. 9a, 9c) and in the phase image (Fig. 9b). From the cross section profile (Fig. 9d) IP clusters are identified with a size of about 100 – 300 nm. The glossed surface of the B1 composite disk presents a much lower roughness versus the original disk (Table 1). This means that the gloss film fills the zones between the IP particles existent on the disk surface. Since the IP particles can still be visualized in the glossed surface, we can estimate that the gloss film is thin and presents a good adherence to the B1 composite disk.



(a) (b) (c)

(d)

Fig. 9. AFM images of the glossed B1 composite disk (B1g) surface. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 9a



(a) (b) (c)

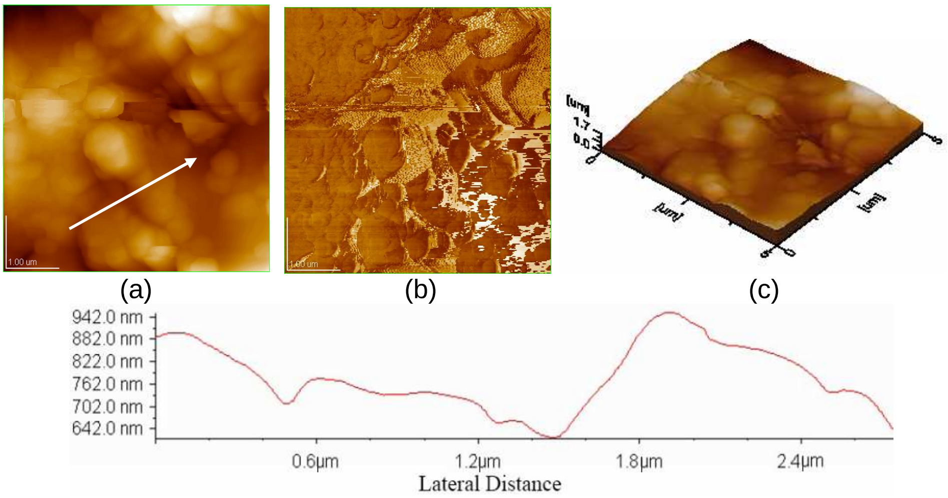
(d)

Fig. 10. AFM images of the glossed T1 composite disk (T1g) surface. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 10a

The morphology of the gloss layer, deposited on the surface of the native T1 composite disk, was also visualized by AFM (Fig. 10), in the environment (air). From the analysis of these images, it results that the gloss layer is adherent to the disk surface, and the IP phase associates are evidenced both in topographic images (Figs. 10a, 10c) and in the phase image (Fig. 10b). From the cross section profiles (Fig. 10d), clusters of inorganic phase are identified, with sizes about 150 – 300 nm. The gloss layer presents a very low roughness against the native T1 composite disk (see Table 1). This result is explained by the filling of the zones between the IP particles with gloss at the disk surface, similarly to the case of the glossed B1 disk (Fig. 9). Since the inorganic particles (ordered in rows) can still be visualized in the glossed surface of T1 composite disk, we can estimate that the gloss film is thin and adheres well to the disk.

In the following the behavior of B1 and T1 composite disks in saliva was investigated. After 24 hours in saliva, the morphologies of B1 composite disk (Figs. 11, 12) and of the T1 composite disk (Fig. 13) are similar to those observed in air after preparation (Figs. 4, 5, 6). The same heterogeneous zones (Fig. 11, with high rms values) or homogeneous (Fig. 12, with low rms values) are observed at the B1 composite surface. For the T1 disk, the rms values are slightly lower than for the native T1 disk in air (Table 1), but the values are comparable (within the limit of experimental errors) with those characteristic to the B1 disk surface, in similar conditions. We conclude that the original B1 and T1 disks present high stability in saliva for 24 hours.

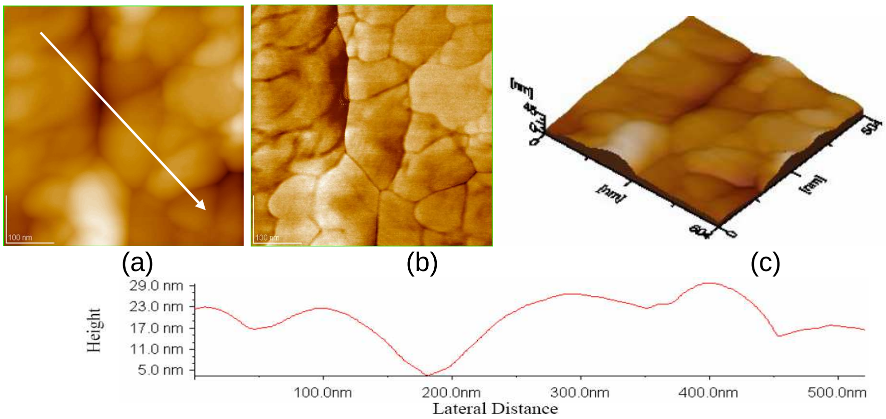
After 7 days in saliva, the surface morphology of B1 disk (Fig. 14), as well as that of the T1 disk (Fig. 15) is still similar to that of the original disks (Figs. 5, 6) or to that of the disk after 24 hours in saliva (Figs. 12, 13).



(a) (b) (c)

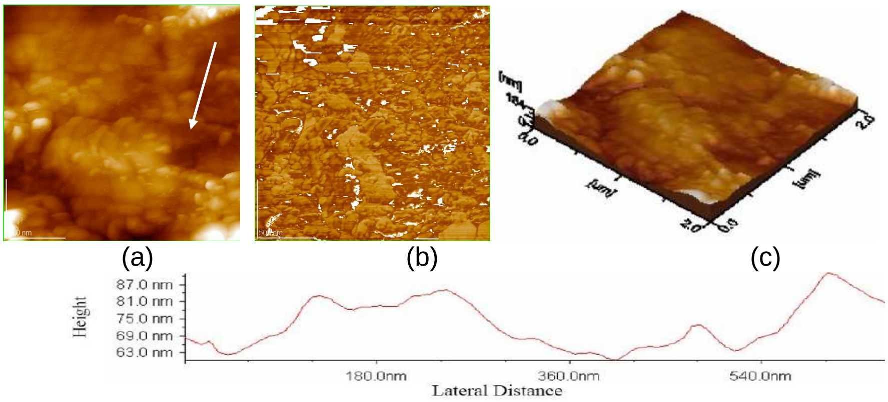
(d)

Fig. 11. AFM images of B1 composite disk surface after 24 h in saliva. Scanned area: 5 x 5 µm^2. a) 2D topographic image; b) phase image; c) 3D topographic image; d) cross section along the arrow in panel 11a.



(d)

Fig. 12. AFM images of the B1 composite disk surface, after 24 h in saliva. Scanned area: 0.5 x 0.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 12a

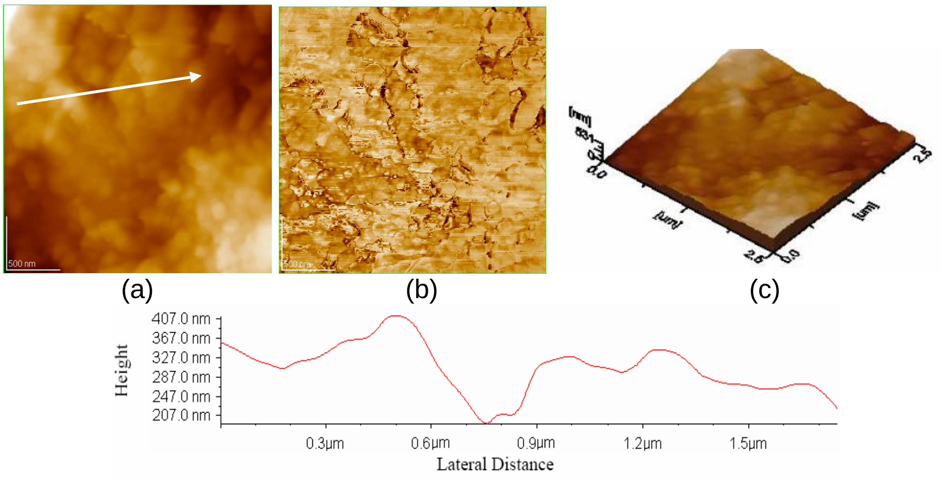


(d)

Fig. 13. AFM images of the T1 composite disk surface, after 24 h in saliva. Scanned area: 2 x 2 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 13a

However, a substantial increase of the surface roughness is to be seen, especially for the T1 composite (see Table 1). This should indicate a certain erosion of the T1 copolymer in the surface of the T1 disk, leaving the inorganic powder without coating layer as it had after the preparation or after 24 hours in saliva.

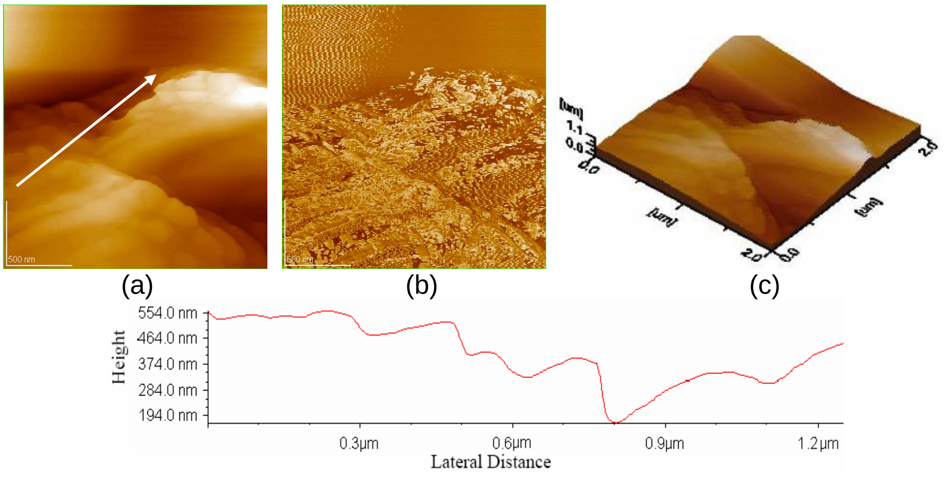
Further, the surface of the glossed B1 and T1 disks was visualized by AFM, also after 24 hours in saliva (Fig. 16, 18) and after 7 days in saliva (Figs. 17, 19). From the analysis of AFM images it results that the gloss layer does protect the B1 disk surface against the saliva fluid. Comparing



(a) (b) (c)

(d)

Fig. 14. AFM images of the B1 composite disk surface, after 7 days in saliva. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 14a

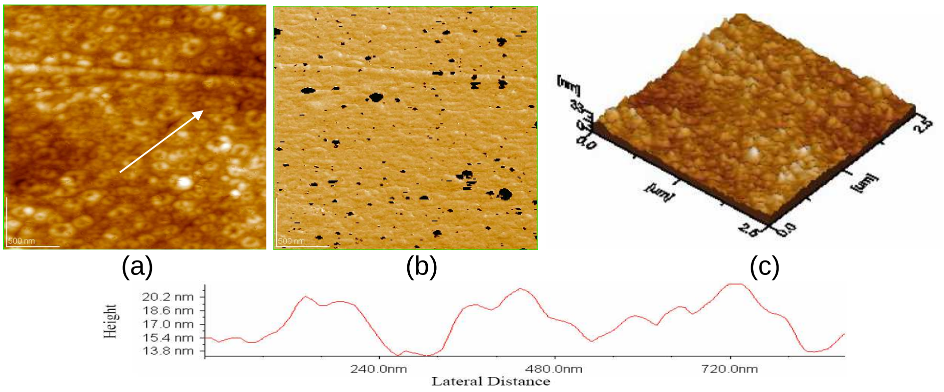


(a) (b) (c)

(d)

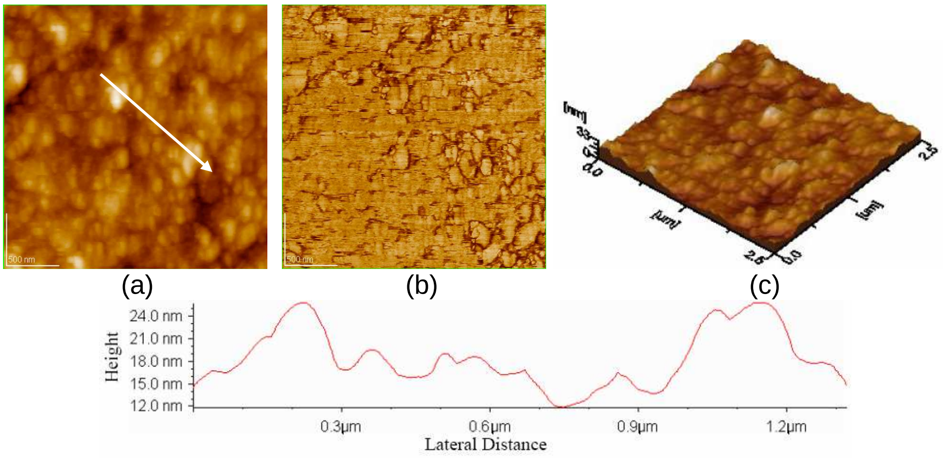
Fig. 15. AFM images of the T1 composite disk surface, after 7 days in saliva. Scanned area: 2 x 2 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 15a

the surface morphology of the glossed B1 disk measured in air (Fig. 9), and after exposure to saliva (Figs. 16, 17), the stability of the gloss film is evidenced, and its surface roughness remains practically constant. After 7 days of exposure to saliva, the morphologic texture of the disk surface



(d)

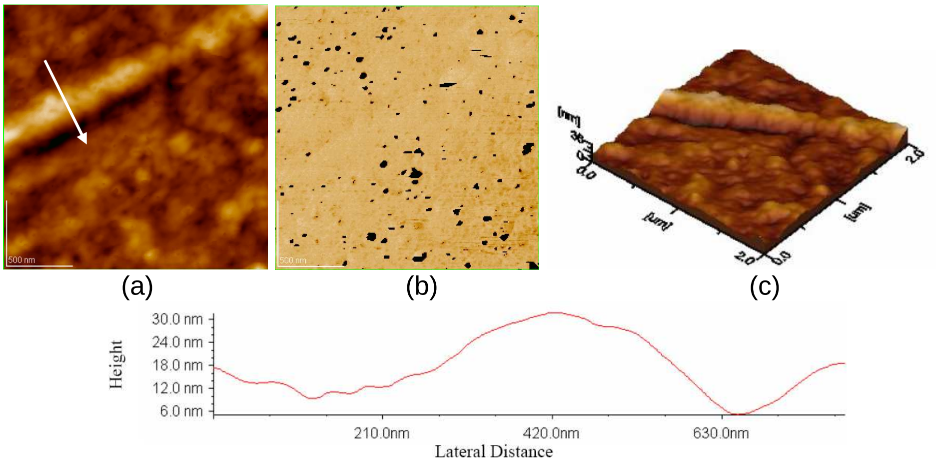
Fig. 16. AFM images of the glossed B1 composite disk (B1g) surface, after 24 h in saliva. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 16a



(d)

Fig. 17. AFM images of the glossed B1 composite disk (B1g) surface, after 7 days in saliva. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 17a

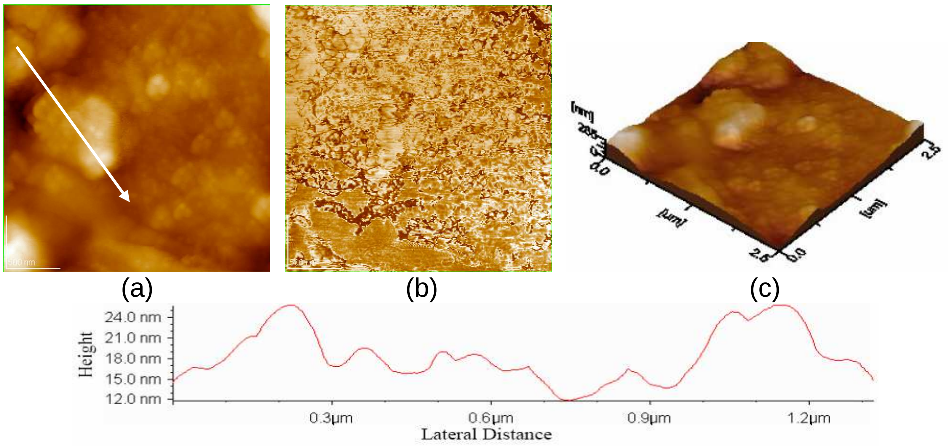
begins to be more evidently outlined than after 24 hours in saliva. This could be explained either by a slight erosion of the gloss film, or by the fact that the thickness of the gloss film was not constant, rigorously controlled during its deposition process on the disk surface. Generally, the gloss film is fairly stable and its adhesion on the disk surface is quite good. It increases the surface stability of the disk, and this is also evidenced by the reduced surface roughness of the film (see Table 1). In the future, the long term stability (a month ore more) of the glossed disk in saliva will be investigated.



(a) (b) (c)

(d)

Fig. 18. AFM images of the glossed T1 composite disk (T1g) surface, after 24 h in saliva. Scanned area: 2 x 2 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 18a



(a) (b) (c)

(d)

Fig. 19. AFM images of the glossed T1 composite disk surface (T1g), after 7 days in saliva. Scanned area: 2.5 x 2.5 µm^2. a) 2D topographic image; b) phase image c) 3D topographic image; d) cross section along the arrow in Fig. 19a

For the same tests in saliva with glossed T1 composite disks, the AFM images are given in Figure 18 (after 24 hours) and in Figure 19 (after 7 days in artificial saliva). From the comparison of surface morphology of the glossed T1 composite disk in air (Fig. 10), and after exposure to saliva, it results that here the gloss film is also stable, the surface roughness being practically constant (Table 1) after a 24 hours exposure to saliva.

After the 7 days exposure to saliva, the morphologic texture (Fig. 19) of the glossed T1 composite disk surface becomes more evidently outlined than after 24 hours. Its surface roughness (Table 1) increases much over its value in air, or in saliva for 24 hours.

Therefore, from the analysis of AFM images, it results that the gloss layer protects the surface of the T1 composite disk against saliva medium after a 24 hours exposure, but after 7 days in saliva the T1 copolymer presents striking erosion, reflected also by the increase of surface roughness. This could be explained by a pronounced erosion of the gloss layer, deposited on the T1 composite disk, after immersion for 7 days in saliva, assuming that the gloss film was uniformly deposited on the whole surface of the disk. It seems that the stability of the gloss film deposited on the surface of the composite from the T1 composite disk is lower than for its deposition on the B1 composite surface.

Table 1.

Surface roughness, determined by AFM, of the tested materials: inorganic powder (IP), B1 copolymer, T1 copolymer, composite materials: B1 and T1 composite specimen, for different kinds of processing, exposed to air or in saliva.

Sample		Surface roughness, nm				
Scanned areas (μm^2)		5 x 5	2.5x2.5	2 x 2	1 x 1	0.5x0.5
Sam-ple	Type of processing					
IP	Inorganic film	191	67.3			
B1	Organic film: B1 copolymer	0.28	0.26		0.23	
T1	Organic film: T1 copolymer	0.36	0.35		0.24	
B1	B1 composite disk	89.0	38.5	37.6	24.8	6.12
B1p	Polished B1 composite disk	70.0	35.0	32.8		
B1g	Glossed B1 composite disk	6.10	5.80	5.50	5.10	5.00
B1	B1 disk, 24 h in saliva	92.0	40.0	38.0	25.0	7.00
B1	B1 disk, 7 days in saliva	162	82.0	75.0		
B1g	Glossed B1 disk, 24 h in saliva	4.80	3.90	3.40		
B1g	Glossed B1 disk, 7 days in saliva	5.70	4.00			
T1	T1 composite disk	111	70.0	66.7	46.1	12.0
T1p	Polished T1 composite disk	95.0	31.4	30.5		
T1g	Glossed T1 composite disk	6.17	2.45	2.27	2.10	2.05
T1	T1 disk, 24 h in saliva	92.5	50.2	21.3	21.0	8.10
T1	T1 disk, 7 days in saliva	208	206	191		
T1g	Glossed T1 disk, 24 h in saliva	6.45	6.10	5.22		
T1g	Glossed T1 disk, 7 days in saliva	52.6	37.3			

The above mentioned investigations indicate that the composite material B1, presents some advantage over the T1 composite, as regards the homogeneity of the surface structure and the adhesion of the gloss film on the disk. This situation suggests the probability of a better mixture of the inorganic powder (IP) with the B1 copolymer (in bulk) and at the same time indicates the existence of specific interactions between B1 copolymer and the polymers within the gloss film. Since the distinction between the two composites consists only in the used copolymer, we could conclude that the B1 copolymer presents more adequate characteristics than T1 copolymer for the realization of dental composites.

CONCLUSIONS

AFM observations make possible a profound analysis of the surface structure for the dental composites, as well as for the films made from the constituents of the composites: the inorganic phase (a mixture of surface active glasses) and the organic phase, differing only by the used copolymer (B1 or T1). The analysis of the surface structure for the films, made of the inorganic phase, and separately for the films made of the organic phase, indicates a micro and a nano structuration in the inorganic powder films and an advanced nano structuration of the B1 or T1 copolymer films.

B1 and T1 composite disks were prepared from the composite materials, formed from the inorganic phase and the organic phase (containing B1, respectively T1 copolymer) in the mass ratio of about 2.2:1. The surface morphology of the B1 and T1 composite disks, native, polished or glossed, was visualized by AFM, both in air environment and after 24 hours or after 7 days in saliva.

From the study of B1 and T1 composite disks, in their native state, in contact with saliva for 7 days, we estimate that the T1 copolymer presents a more pronounced hydrolytic lability than B1 copolymer, in fact T1 copolymer is degraded (dissolved) faster in saliva. Surface morphology and roughness of B1 and T1 composite disks are also comparatively discussed for different surface processing types, namely for the original, native disks and those mechanically polished. No significant topographic (morphologic) modifications of the surface for the two composites were observed for the samples polished in contact with air against the native disks evidencing quite good mechanical properties.

The morphologic organization differences in the surface of B1 and T1 composite disks, particularly after 7 days in saliva, lead to the following findings, the B1 copolymer seems to resist better than T1 copolymer to the erosion process in saliva, particularly for extended exposures (viz. 7 days). B1 copolymer seems to better homogenize the inorganic powder, insuring a better integration of organic and inorganic bulk phases, constituting the B1 composite.

Glossed B1 and T1 composite disks did not present a significant degradation of surface structure after 24 hours, or after 7 days of exposure to saliva. This means that the surface properties of the both composite materials can be improved and controlled by glossing the surface of the composites with a blend of polymeric components.

However, for the glossed T1 composite, after 7 days in saliva, an important increase of surface roughness is observed, which could be explained by a more pronounced degradation of the gloss on T1 composite, against that on the B1 composite. The higher stability of the gloss film applied on the B1 composite surface could be due to the better adhesion of the gloss on the B1 composite surface, due to the stronger specific interactions between the gloss components and the B1 copolymer.

On the basis of comparisons of B1 composite stability versus T1 composite, we can suggest that B1 composite is a better potential candidate for medical use.

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