JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 3, March 2008, p. 597 - 601

Surface organization and stability of some composites exposed to biologic medium. Atomic force microscopy observations

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Two composites for dental use (glass ionomer cements), exposed to air and artificial saliva, were analyzed by atomic force microscopy (AFM). The composites differ only by their organic constituent, a copolymer based on modified alkenoic acids, while the inorganic component was the same glass powder blend. The surface of the composites was investigated in native state, and after glossing with a composite resin, in air and after 24 h or 7 days in artificial saliva. The different stability of the two composites after a long time contact with the biological medium is discussed on the basis of AFM images.

(Received November 29, 2007; accepted March 12, 2008)

Keywords: Surface active glass, Poly(alkenoic acids), Composites, AFM

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1. Introduction

Polymers and polymer based composites have important orthopedic and dental applications [1, 2]. Glass ionomer cements contain generally a glass-like calcium aluminosilicate containing some fluoride and an acidic poly-electrolyte, homopolymer or copolymer of unsaturated carboxylic acids. Resin modified systems are now commercially available. 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 [3-7].

In order to achieve the structure control of the composite surface, we can act upon the preparation methods of the material and by surface engineering methods, such as directed enrichment of the surface with one of the composite components or the application of a thin adherent finishing film, such as a gloss made of an organic mixture, applied on the composite surface.

An accurate analysis of final organization at the composite surface is necessary for the surface characterization and for the evaluation of its stability in various environments. For this purpose, atomic force microscope, AFM, is an adequate technique, by its capacity to visualize the morphology of the composite surface and to evidence the role of surface enrichment of the composite with polymer, by the generated topographical modifications. In a previous investigation [8] the potential of the AFM method, operating in tapping mode, with a simultaneous observation of topography and phase AFM images, in the characterization of composite materials was demonstrated. Particularly the possibility to determine the surface roughness, an important parameter which can bring about information on the changes in surface organization as well as on the degradation of the surface, exposed to different environments, is an important feature.

In the present work we use the two dimensional (2D-) and three-dimensional (3D-) topographical AFM images for the surface of the composite specimens, in their native state or glossed, with the aim to study their behavior in air or in a complex environment, such as the artificial saliva, and to find potential differences in the stability of the composites.

2. Experimental

The investigated composites were prepared from an inorganic powder and an organic phase. The inorganic phase was a blend of surface active glasses, like S1 and M glasses in the 7:1 mass ratio. The bulk composition for S1 glass was: SiO_2 (49%), Al_2O_3 (22%), CaF_2 (29%) and for M glass was ZnO (16.72%), CaO (23.8%), Na_2O (9.33%), SiO_2 (50.15%) [8-11]. The organic phase is an aqueous solution containing 48.5% copolymer (B1 or T1) and 3% tartaric acid. The B1 and T1 copolymers are both modified poly(alkenoic acids) (Fig.1).

The composite specimens, termed as B1 or T1 composite, depending on whether the B1 copolymer or T1 copolymer was used in its composition, were made from these two phases in the ratio of inorganic phase to organic phase 2.2:1 [8]. The inorganic phase constitutes the active filling (reinforcement material) of the composite, while the copolymers constitute the matrix material. The specimens had the form of disks of 6 mm diameter and 1 mm height [8, 9].

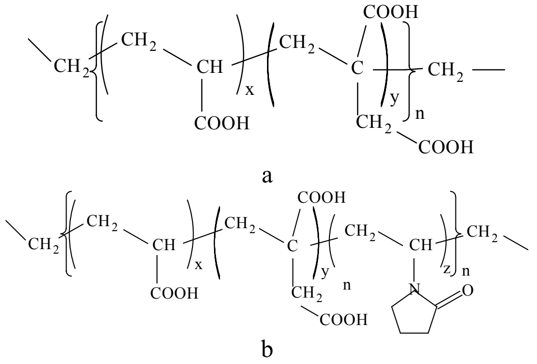


Fig.1. Formula of B1 (a) and T1 (b) copolymer

The finishing gloss applied on the surface of the disks, Vitremer^{TM}, manufactured by 3M-ESPE, is a unfilled resin, based on bisGMA (Bisphenol-A-glycidyl-dimethacrylate) and TEGDMA (triethylene glycol dimethacrylate). It was applied as a thin layer at the material surface and then cured by photo-polymerization for 20 s using the curing light L.E.Demetrom II from SDS Kerr.

The composition of the artificial saliva used as a simulation of the biological medium is 50 mmol/l KCl, 1.5 mmol/l Ca^{2+}, 0.9 mmol/l PO_4^{3-}, and 20 mmol/l tri-hydroxymethylaminomethane, buffer at pH 7.0 [12].

The AFM visualization of the surface of the investigated materials was executed using the JEOL scanning microscope, the AFM-JEOL 4210 equipment operating in the intermittent contact, tapping mode. The cantilever used in this AFM equipment 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, 1 Hz, 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 [13-15]. 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.

The surface structure was investigated by AFM imaging separately for the two composite materials, B1 and T1 specimens, in the form of disks

- in their native state and after the application of a gloss on the disk surface (samples B1g, T1g), in air;
- in the above states but in contact with artificial saliva after 24 h and after 7 days.

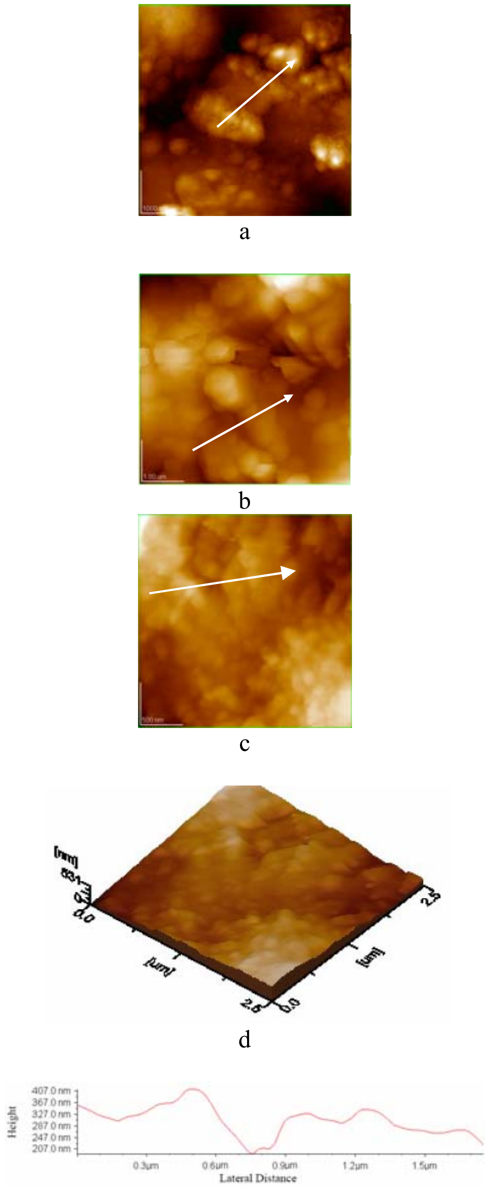
3. Results and discussion

Topographical and phase AFM images are used for evidencing the surface characteristics of the samples, for the identification of surface components, for revealing the existence of inorganic micro- and nanoparticles associated with the copolymer matrix. The values of surface roughness, described by the rms value (root mean square), and calculated directly from the AFM observation by the processing of topographical AFM images [13-15] are given in Table 1 for the investigated samples.

Table 1. Surface roughness of studied materials for different kinds of advanced surface processing, on the profiles along the arrows in 2D-topographic images.

Sample		Surface roughness, nm				
Scanned area in μm^2		5x5	2.5x 2.5	2x2	1x1	0.5x 0.5
B1	B1 composite	89.0	38.5	37.6	24.8	6.12
B1	24 h in saliva	92.0	40.0	38.0	25.0	7.00
B1	7 days in saliva	162	82.0	75.0		
B1g	glossed surface of B1 composite	6.10	5.80	5.50	5.10	5.00
B1g	24 h in saliva	4.80	3.90	3.40		
B1g	7 days in saliva	5.70	4.00			
T1	T1 composite	111	70.0	66.7	46.1	12.0
T1	24 h in saliva	92.5	50.2	21.3	21.0	8.10
T1	7 days in saliva	208	206	191		
T1g	glossed surface of T1 composite	6.17	2.45	2.27	2.10	2.05
T1g	24 h in saliva	6.45	6.10	5.22		
T1g	7 days in saliva	52.6	37.3			

Fig. 2 visualizes the surface morphology of *B1 composite disk* (native surface), in air (a) and in artificial saliva medium after 24 h (b), and after 7 days (Fig. 2c-e). Agglomerates of inorganic powder and clusters, are observed as higher light-colored formations, in the 2D- (Fig. 2a-c) and 3D- (Fig. 2d) topographical images, surrounded by the copolymer matrix (lower, dark-colored zones). The aggregates of inorganic powder have the size in the range from 100 to 300 nm (Fig. 2a, in substantial agreement with cross-section profiles (Fig. 2e) in the AFM images), and are embedded in the copolymer matrix [8].



a

b

c

d

e

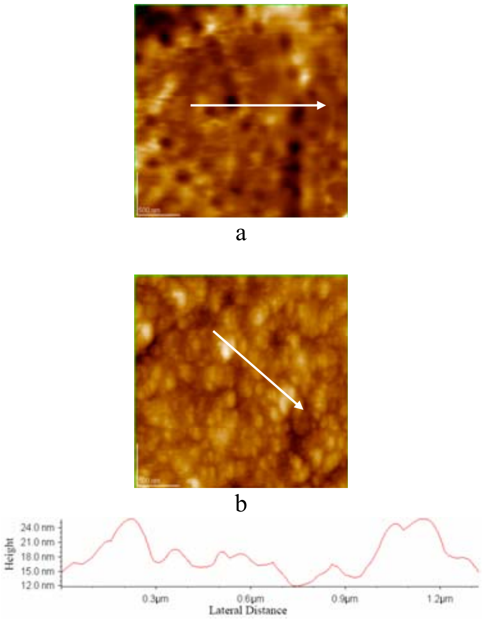
Fig. 2. 2D topography images of the B1 composite surface: (a) in air, (b) in saliva, after 24 h and (c) after 7 days in saliva; (d): 3D-image of (c). Scanned area: 5 x5 µm^2 (a, b), 2.5 x 2.5 µm^2 (c, d); (e) Cross section along the arrow in Fig 2c.

After *24 hours* in saliva, the morphology of B1 composite disk (Fig. 2b) is similar to that observed in air after preparation (Fig. 2a), thus showing the stability of the original B1 composite in saliva for 24 hours.

After 7 days in saliva, the surface morphology of B1 composite (Fig. 2c, d) is still similar to that of the original disk. However, a substantial increase of the surface roughness is to be seen (see Table 1 and cross section profile, Fig. 2e). This should indicate a certain erosion of the B1 copolymer in the surface of the B1 composite disk, leaving the inorganic powder at its surface, without the protection it had after the preparation or after 24 hours in saliva.

The *glossed surface* of the B1 composite disk, as seen in AFM images (e.g. Fig. 3a), has a much lower roughness than the original native surface (Table 1).

From the AFM images of the surface of the glossed B1 composite in air (Fig. 3a), and after 7 days in saliva (Fig. 3b), it results that the gloss layer does protect the B1 composite surface against the saliva fluid. Comparing the surface morphology of the glossed B1 composite measured in air (Fig. 3a), and after exposure to saliva (Fig. 3b), the stability of the gloss film is evidenced. Its surface roughness is practically constant after 7 days exposure to saliva (Fig. 3c, Table 1). Nevertheless, after 7 days of exposure to saliva, the morphologic texture of the B1g surface 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 this film was not constant, rigorously controlled during its deposition process on the B1 composite disk surface. The gloss film is fairly stable and its adhesion on the disk surface is quite good.



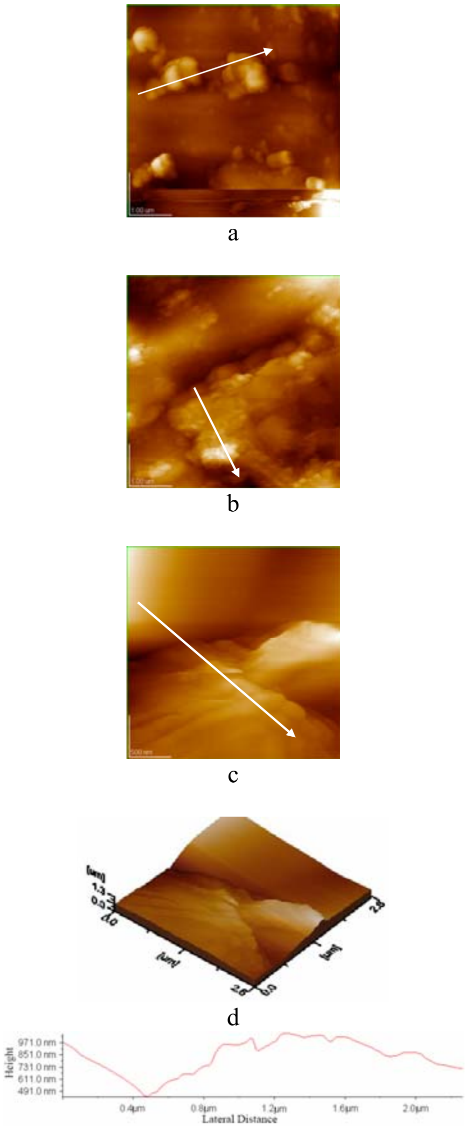
a

b

c

Fig. 3. 2D topography AFM images of the glossed surface of B1 composite disk in air (a) and after 7 days in saliva (b). Scanned area: 2.5 x2.5 µm^2; (c) cross section along the arrow in Fig 3b.

For the T1 composite disk surface without gloss, some of the AFM images are given in Fig. 4. While the surface roughness of the T1 specimen in air (Fig. 4a) is somewhat higher than for the B1 composite disk, after 24 hours in saliva the surface morphology of the T1 disk (Fig. 4b) is similar to that observed in air after the disk preparation. This time the rms values are even 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. Therefore, the native T1 disk is stable in saliva, after 24 hours exposure.



a

b

c

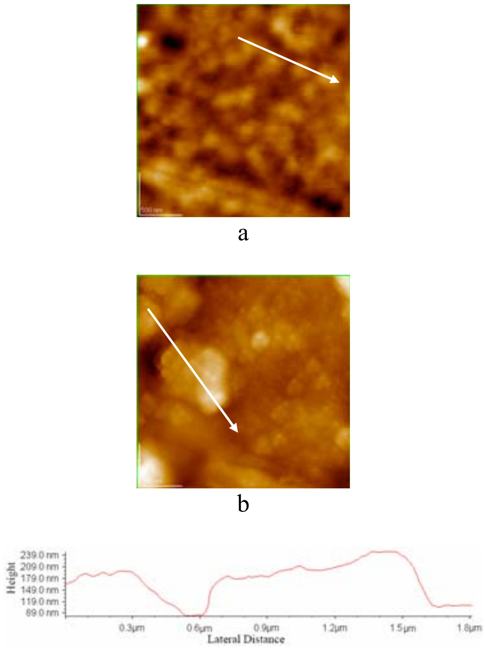
d

e

Fig. 4. 2D topography images of the T1 composite surface in air(a) and in saliva, after 24 h (b); scanned area: 5 x5 µm^2; after 7 days in saliva (c), scanned area: 2.5 x2.5 µm^2. 3D-image (d) of image c; (e) Profile along the arrow in Fig. 4c.

Although after 24 hours in saliva, the surface morphology of the T1 composite disk (Fig. 4b) is still apparently unchanged, after 7 days in saliva, a substantial increase of the surface roughness is observed (Fig. 4c, Table 1), much over the limit of experimental errors. This is a possible indication for an erosion of the T1 copolymer at the disk surface, so the inorganic powder is no more protected by embedding into the copolymer matrix.

For the *glossed T1 disks*, the AFM images are given in Fig. 5, in air (Fig. 5a), and after 7 days in artificial saliva (Fig. 5b, c). After 24 hours exposure to saliva, the surface morphology of the glossed T1 composite does not significantly change. The gloss film is stable on this surface too, the surface roughness being practically constant (Table 1) after a 24 hours exposure to saliva. However, after the *7* days in saliva, the morphologic texture of the glossed surface of T1 composite is evidently modified (Fig. 5b, c), and the surface roughness (Table 1) increases.



a

b

c

Fig.5. 2D topography images of the glossed surface of T1 composite disk in air (a) and after 7 days in saliva (b). Scanned area: 2.5 x2.5 µm^2; (c) cross section along the arrow in Fig. 5b.

It results that the gloss layer protects the surface of the T1 composite disk against saliva medium for 24 hours, but after 7 days the disk presents striking erosion. This could be explained by an erosion of the gloss layer deposited on the disk, assuming that the gloss film was uniformly deposited on the whole surface of the T1 disk. The stability of the gloss film deposited on the surface of the T1 composite seems, thus to be lower than on the B1 composite surface.

These investigations indicate that the B1composite 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 further suggests the probability of a better mixture of the inorganic powder with the B1 copolymer, and the existence of specific interactions between B1 copolymer and the polymer constituents of the gloss film.

4. Conclusions

The present study proves that AFM observations make possible the analysis of the surface structure for glass ionomer composites and the characterization of their stability in a biological fluid.

A statistical analysis of a great number of AFM images and of their cross section profiles, as well as the use of surface roughness, measured by rms values, and used as a descriptive parameter, have proved their major importance in the assessment of the surface structure and stability of these composite materials.

From the study of B1 and T1 composite disks, in their native state and in contact with saliva, we estimate that the T1 copolymer presents a more pronounced hydrolytic lability than B1 copolymer, being faster degraded (dissolved) in saliva.

Glossed B1 and T1 composites are more stable in artificial saliva, i.e. surface properties of the composite material can be improved and controlled by glossing its surface 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 accounted for a more pronounced degradation of the gloss on this T1 composite. The higher stability of the gloss on B1 composite could be due to its better adhesion on the surface, due to the stronger specific interactions.

Thus the B1 copolymer presents an advantage against the T1 copolymer in the realization of these composite materials. B1 copolymer seems to better homogenize the inorganic powder, improving the merging of organic and inorganic bulk phases, constituting the B1 composite.

Acknowledgement

This research was realized having financial support from CEEX project no.132/2006.

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