

# In vitro evaluation of biological liquids adsorption on dental materials

D. SPRIDON<sup>a</sup>, M. VASILIU<sup>b</sup>, N. DUMITRASCU<sup>a</sup>

<sup>a</sup>Department of Physics, Faculty of Physics, Al. I. Cuza University, Iasi, Romania

<sup>b</sup>Faculty of Dentistry, "Petre Andrei" University, Iasi, Romania

Dental materials are subjected to various conditions such as pH and temperature of biological fluids, mechanical stress etc. having effects on both oral health and restoration success. In particular, surface energy of dental materials and their morphology are very important to control the processes at interface with biological liquids. Our study is focused on *in vitro* evaluation of certain dental materials from point of view of biological liquids adsorption based on known method undertaken from physics. Main parameters which characterize the adhesion properties of dental materials were evaluated using general formulas and contact angle measurements. The morphology of the chosen materials was performed by atomic force microscopy (AFM) working in tapping mode. Also, using AFM phase images were compared the chemical composition uniformity of analyzed surfaces. The samples investigated were certain commercial composites (*Adoro*, *ArtGlass*, *Gradia* and *Ceramage*) and ceramics (*InLine*, *Duceram* and *Heraceram*) and the studied biological liquids were water and artificial saliva. Results showed significant differences concerning the interface established between oral liquids and analyzed dental materials. Due to surface properties, the adhesion work of studied liquids onto the composites surface is lower comparing with one of the ceramic materials.

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## 1. Introduction

The interaction between the surface of dental materials and the biological liquids influences the success of the prosthetic and restorative dentistry, the oral cavity health and, on a long term, the health of human organism [1, 2]. The processes at the interface tooth-biological liquids induce various local and systemic diseases, from the common gingivitis and the inflammation of the tissues and bones, to the systemic diseases such as edema, ulcers, erythema, allergy, herpes and autoimmune diseases [3, 4, 5, 6]. Conversely, the attack of the oral fluids may cause the degradation of tooth surface layers and finally the degradation and dissolution of the dental material [7].

It is recognized the significant role of saliva in maintenance and protection of the dentition and soft tissues of the oral environment, assuring a wet friction between aliments and dentition [8]. Due to its complex chemical composition including the calcium, potassium, phosphate etc. and the antimicrobial factors (salivary lysozyme, lactoferrin, peroxidase, mucins) the natural saliva assures the equilibrium between mineralization and demineralization of enamel and the protection against bacteria [9]. Nevertheless, the dental materials interactions with saliva and bacterial flora may cause the fail of restorations by the adhesion of bacteria to teeth, as a first step in the pathogenesis of dental plaque or caries [10]. Attachment of bacteria from oral fluids onto dental material is mostly promoted by the adsorption of specific

salivary proteins followed by the formation of a microbial biofilm onto the dental surface [11, 12]. In addition, the adsorption/absorption of oral fluids and saliva compounds may have effect on the mechanical properties of the dental materials such as strength, hardness, elastic modulus and dimensional stability [7]. Moreover, the adsorbed layers onto the dental materials can distress the color and translucency of the teeth [13, 14, 15]. Practically it is indicated to use hydrophilic materials as sealants, for tooth restoration with less prone to marginal microleakage, for attaching fixed prostheses and for bonding orthodontic appliances. On the other side, there are indicated to use more hydrophobic materials to develop plaque resistant coatings for teeth and restorative materials.

Taking into account these effects, it is indicated to develop and apply dental materials which control the adsorption of oral liquids onto the surface.

The aim of this study was to investigate *in vitro* interaction between the surface of certain commercial dental materials (composites and ceramics) and the oral fluids by means of the major important parameters concerned in the adhesion of a fluid onto the solid surface, that are the energetic parameters of two phases and the surface roughness.

The evaluation of surface energetic parameters and the surface roughness by *in vitro* methods allowed a comparison of certain commercial composites and ceramics mentioning their ability to adsorb biological liquids.

## 2. Materials and methods

### 2.1 Materials

In connection with their ability to adsorb the biological liquids, the following commercial ceramic and composite materials were analyzed.

#### a. Composites

- *Adoro* (Ivoclar Vivadent AG, Schaan, Liechtenstein), a microfilled composite having simplified processing technique, stability of surface quality in the oral cavity, high wear resistance, used in invisible dental reconstructions and polymer based crown and bridge material.

- *ArtGlass* (Heraeus Kulzer GmbH, Wehrheim, Germany), a new type of material highly cross-linked structures, hardness similar to enamel, can be easily adjusted and repaired intra-orally; used for metal-free crowns, veneers, inlays, onlays or metal supported crowns, bridges, and implant supra-structures.

- *Gradia* (GC America, Illinois, USA), an innovative hybrid MFR formulation, natural opalescence, smooth surface, wear resistance; used in lightcured indirect restoration, crown and bridge, inlays, onlays and veneers.

- *Ceramage* (Shofu Dental Corporation, Kyoto, Japan), filled with micro-fine ceramic, having properties similar to the ceramics; used for metal-free anterior and posterior restorations.

#### b. Ceramics

- *InLine* (Ivoclar Vivadent AG, Schaan, Liechtenstein), a leucite-based ceramic restorative material, indicated in metal-ceramic restorations.

- *Duceram* (Dentsply Ceramco, Burlington, USA), a porcelain fused to metal, ease to handle, perfect reproduction of natural opalescence in incisals and precise control of the materials placement; it is used for the manufacture of crowns, anterior and posterior bridges, inlays and onlays, veneers.

- *HeraCeram* (Heraeus Kulzer GmbH, Wehrheim, Germany), a synthetic quartz glass with low shrinkage, indicated in manufacturing of dental prosthesis.

The samples were prepared by known mechanical and thermal procedures, as intended for clinical purpose. It used samples with surfaces of about 2 cm<sup>2</sup> areas, flat, smooth, chemical homogeneous, without morphological irregularities and defects.

The *artificial saliva* (AFNOR S90-701) was prepared using reagents of analytical grade without previous purification. The pH of artificial saliva was kept constant at 8.01 (pH-meter 5/6 OAKTON), also its temperature at 37°C.

### 2.2 Methods

When a liquid drop is deposited on the surface, the contact angle  $\theta$  shaped at interface is a measure of the surface wetting characteristics. In our experiments the value of  $\theta$  is given by the interaction forces established between the two phases, the saliva and the dental surface.

The main energetic surface parameters that characterize the adhesion properties of materials are the surface energy and its dispersive and polar components as well the adhesion work, a measure of the interface forces at the contact liquid - surface. Usually, these surface parameters can be calculated from basic formula [16], using contact angle measurements. The surface energetic parameters are calculated by means of the following equation system [16,17]:

$$- W_A = \gamma_{LV} (1 + \cos \theta) \quad (1)$$

$$- W_A = 2\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + 2\sqrt{\gamma_{SV}^p \gamma_{LV}^p} \quad (2)$$

$$- \gamma = \gamma^p + \gamma^d \quad (3)$$

where  $\theta$  is the measured contact angle,  $\gamma_{LV}$  is the liquid-vapor surface tension,  $\gamma_{SV}$  surface energy (Gibbs free energy),  $\gamma_{SV}^p$  and  $\gamma_{LV}^p$  respectively the polar component of the solid surface and liquid surface energy and  $\gamma_{SV}^d$  and  $\gamma_{LV}^d$  are the dispersive energy component of solid surface and liquid.

The energetic characteristics of the solid materials are determined solving the equation system (1), (2) and measuring the contact angle of two liquids with known surface tension components onto solid surface.

The same procedure was used to calculate the artificial saliva surface tension. There were measured the contact angles of artificial saliva on two polymers with known surface energy components, polypropylene and polyethylene terephthalate [18]. The surface tension components of water and formamide are presented in **Table 1**. Also are presented the calculated surface tension components of artificial saliva.

Table 1. Surface vapor tension ( $\gamma_{LV}$ ) and the polar ( $\gamma_{LV}^p$ ) and dispersive components ( $\gamma_{LV}^d$ ) of water and formamide [18], also the calculated values for saliva.

Liquid	$\gamma_{LV}^p$ (mN/m)	$\gamma_{LV}^d$ (mN/m)	$\gamma_{LV}$ (mN/m)
Water	51	21.8	72.8
Formamide	18.7	39.5	58.2
Saliva	41.0	19.6	60.6

The contact angles of water, formamide and saliva were measured using an optical technique equipped with a photo camera enabling automatic contact angle measurements and its time evolution. The thermodynamic equilibrium was attaining 10 seconds after the drop placed onto the surface. The measurements were made with drops of 1  $\mu$ l volume, at the room temperature and atmospheric pressure. Images were digitized and analyzed with the ImageJ program. Minimum 30 measurements of  $\theta$  were

made for each interface liquid-surface and the results were expressed as an average on measured values with an error of  $\pm 2^\circ$ .

The samples morphologies were visualized and compared by atomic force microscope (Solver Pro NT-MDT), working in tapping mode, with commercial standard silicon-nitride cantilever NSC01 and tips radius  $\leq 10\text{nm}$ . The different areas (5 of each sample) with dimensions from  $30\mu\text{m} \times 30\mu\text{m}$  and  $10\mu\text{m} \times 10\mu\text{m}$  to  $1\mu\text{m} \times 1\mu\text{m}$  were scanned, with the aim of studying the surface morphological details from micro to nano scale. The AFM  $z(x, y)$  maps were used to estimate statistical parameters of dental material surfaces morphology.

The root-mean-square roughness ( $R_{\text{rms}}$ ), an indicator of the surface roughness or smoothness, was calculated for each surface by the following formula:

$$R_{\text{rms}} = \sqrt{\frac{1}{x_{\text{max}}} \int_0^{x_{\text{max}}} z^2(x) dx} \quad (4)$$

where  $z(x, y)$  is the height of the surface element at the point of coordinates  $(x, y)$  and  $x_{\text{max}}$  is the maximum value of the lateral displacement  $x$  during the measurements, at a given value of the coordinate  $y$ .

Simultaneously with morphology it was recorded the phase shift on different areas of the investigated surfaces allowing a qualitative remark in relation to the chemical composition uniformity of samples.

### 3. Results

One of the most important characteristics of the saliva in the oral environment is its ability to freely wet the surface of the teeth and mucous. Practically, the wettability of the dental material was revealed entire by the values of contact angle established between the drop of biological liquid and the surface. In Fig1 are presented the images of the artificial saliva drop onto two materials with extreme wettabilities, respectively the samples of Adoro (a) and Duceram (b), screening hydrophobic and respectively hydrophilic properties.

Since the measure of the surface wettability is expressed by the adhesion work ( $W_A$ ) of a liquid onto the surface, it was calculated  $W_A$  of artificial saliva onto the surface of studied dental materials by means of the formula (1) and the results are shown in the Table 2. In the formula (1) it used the value of the saliva surface tension ( $\gamma_{LV}$ ) calculated by us and shown in the Table 1.

With the purpose of explaining the above findings we calculated the surface energy of the dental samples and their polar and dispersive components based on system of equations (1) and (2) and using contact angles measured for water and formamide. The results are shown in the Table 3.

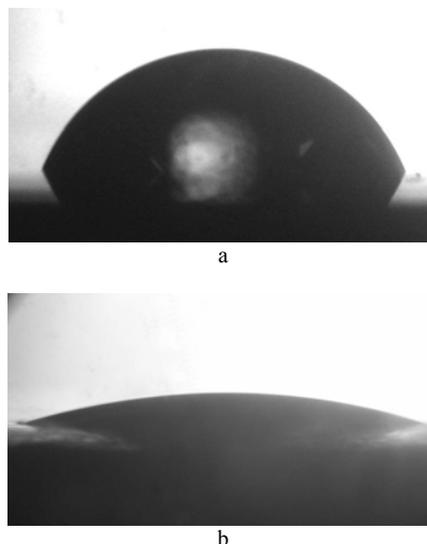


Fig. 1. Artificial saliva drop with volume of  $1 \mu\text{l}$  onto the dental material surface: a) Adoro sample; b) Duceram sample (magnification 20x).

Table 2. Adhesion work ( $W_A$ ) of artificial saliva onto dental materials surface

Type of material	Dental material	$W_A$ (mJ/m <sup>2</sup> )
Composites	Adoro	83.6
	ArtGlass	87.7
	Ceramage	89.9
	Gradia	91.7
Ceramics	Duceram	118.8
	InLine	100.7
	HeraCeram	109.9

Table 3. Dental materials surface energy ( $\gamma_{SV}$ ) and its components ( $\gamma_{SV}^p, \gamma_{SV}^d$ ).

Type of material	Dental materials	$\gamma_{SV}^p$ (mN/m)	$\gamma_{SV}^d$ (mN/m)	$\gamma_{SV}$ (mN/m)
Composite	Adoro	11.2	34.1	44.1
	ArtGlass	28.4	19.9	47.9
	Ceramage	19.7	25.3	43.0
	Gradia	37.8	11.2	48.7
Ceramic	Duceram	44.3	11.8	56.1
	InLine	12.4	33.6	46.0
	Hera Ceram	11.1	37.6	48.7

The surface morphology and its chemical composition influence the surface wetting and adhesion properties. These characteristics of the dental materials were visualized and compared by AFM images and phase imaging Fig. 2 and Fig. 3.

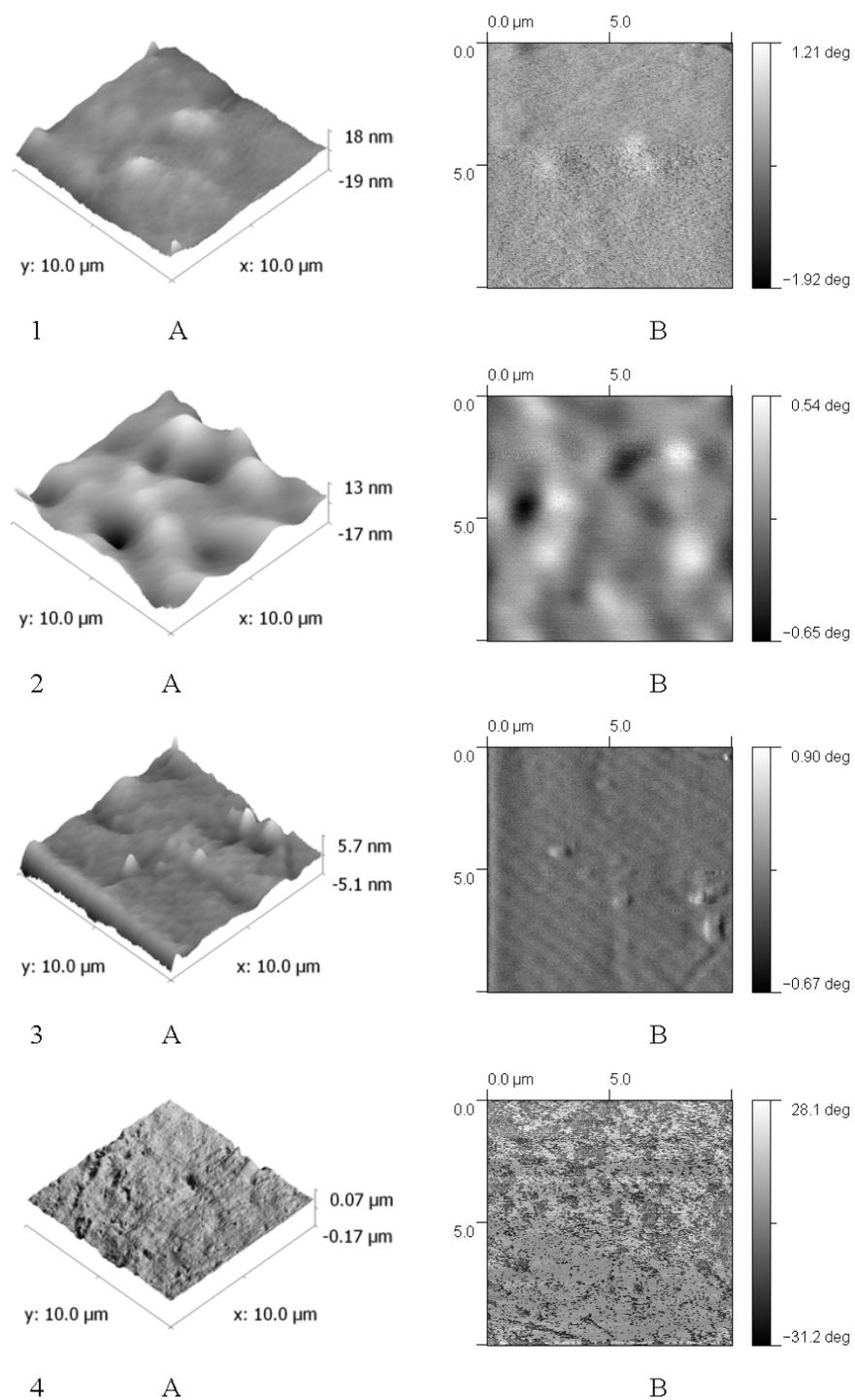


Fig. 2. AFM images: 1. Adoro, 2. Artglass, 3. Ceramage, 4. Gradia; A.3D morphology (10μm X 10μm); B. phase image

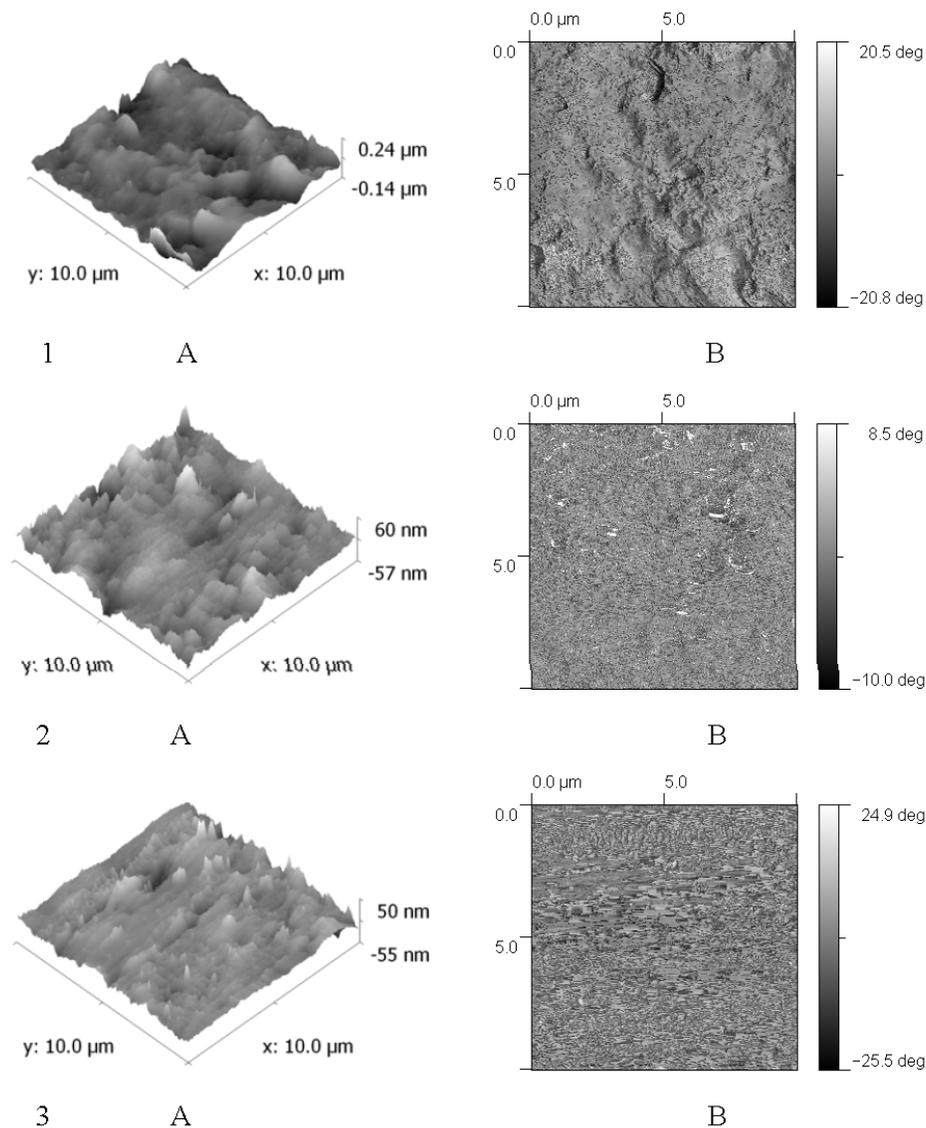


Fig. 3. AFM images: 1. Duceram, 2. InLine, 3. HeraCeram, A.3D morphology (10 $\mu\text{m}$  X 10 $\mu\text{m}$ ); B. phase image.

#### 4. Discussion

Our results proved various degrees of the dental materials wetting by artificial saliva. This is an expected result taking into account the different chemical structure of the samples and the variety of processes running at the interface saliva-dental material. All the composites shown the lowest values of  $W_A$ , meaning that composites are more hydrophobic as compared with the ceramics. Since  $W_A$  is a measure of interatomic and intermolecular forces across the interface saliva-dental material, it may conclude that lower bond strengths are established in the case of composites.

Morphology and surface roughness influence the adhesion work by the particular microstructure, surface

irregularities and porosity, the molecular contact between the two phases being important as a first step in the physical and chemical adhesion. Due to the surface defects and porosity, a larger area may be exposed to the saliva adsorption. From the AFM images (Fig2A and Fig3A) and roughness values presented in the Table 4, obvious differences between the analyzed materials were recorded. The surface roughness expressed by a statistic measure named the root-mean-square roughness ( $R_{\text{rms}}$ ) can explain a higher adhesion work, a larger area being available to the physical adsorption of liquid molecules. Thus, it observes that all composites are almost the same microstructure and roughness, the composite materials being smoother than the ceramic one.

Table 4. Root-mean-square roughness ( $R_{\text{rms}}$ ) of dental material surfaces ( $10\mu\text{m} \times 10\mu\text{m}$ )

Type of material	Dental material	$R_{\text{rms}}$ (nm)
Composites	Adoro	2.47
	ArtGlass	3.74
	Ceramage	0.795
	Gradia	2.32
Ceramics	Duceram	40.4
	InLine	12.6
	HeraCeram	8.1

As a conclusion, the interaction of the saliva with the dental materials may be controlled by their surface energy, chemical composition, also by surface roughness. The ceramics roughness varies in a much larger range of values, probably, due to the mechanical procedures of preparation.

By means of AFM phase images the uniformity of chemical composition was analyzed and all the materials provided chemically homogeneity, as it is seen in the Fig2B and Fig3B.

Future studies will be made including supplementary environment conditions, such as the influence of the pH and temperature of saliva upon the energetic parameters of dental materials.

## 5. Conclusions

The energetic parameters of the dental materials surface, its morphology and roughness, also the chemical composition have an important influence over the initial phases of the biological liquid adsorption, minerals deposition and biofilm formation, and later to the chronic phases of the interface saliva-surface. A comparison of the energetic characteristics of the two phases, artificial saliva and solid surface may provide information about the processes at interface.

The *in vitro* methods, preloaded from physics allowed comparing two kinds of commercial dental materials (ceramics and composites) by calculating the surface energetic parameters and the surface roughness from point of view of their availability of adsorption and subsequent immobilization of oral fluids onto the surface of specimens. The contact angle measurements provided an easy, rapid and cheap method in choosing the adequate materials to have the best restoration.

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\*Corresponding author: dspridon@plasma.uaic.ro