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NANOMECHANICAL INVESTIGATION OF DENTAL RESTORATIVE MATERIALS USING ATOMIC FORCE MICROSCOPY

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Abstract: *The dental enamel is the hardest surface of teeth. The lifetime of teeth depends by mechanical and tribological properties of enamel. These properties are influenced by the mastication conditions including humidity, temperature and abrasion effects. The scope of this paper is to analyze the mechanical properties of restorative dental materials using advance techniques more exactly an atomic force microscope with a nanoindentation module. Nanoindentation and nano scratching provides information about hardness, elastic modulus, scratch resistance, also about storage/loss modulus; creep; fracture toughness and compliance, thus assuring you of the most complete surface mechanical testing solution without compromise. These relatively nondestructive mechanical characterization techniques may assist in better understanding the mechanical behavior of the dental materials and thus facilitate their preparation with excellent mechanical and tribological properties.*
Key words: *Dental materials, nanoindentation, nanoscratches, hardness, atomic force microscope.*

1. INTRODUCTION

The American Dental Association (ADA) Council on Scientific Affairs had prepared charts comparing the important features of many of the popular direct and indirect restorative materials (ADA, 2003). The service life of dental restoratives depends on a number of patient, material and procedure-related factors. Material's related factors include strength, hardness toughness, wear resistance, tolerance to water, dimensional stability, translucency, and colour stability [22].

The human teeth are the hard, resistant structures occurring on the jaws and in around the mouth area of vertebrates. The teeth are used, in principals, for masticating food, and for other specialized purposes. A tooth consists of a crown and one or more roots. The crown is the functional part that is visible above the gum. The root is the part that cannot see and supports and fastens the tooth in the jawbone. The shape of the crown and root vary among different teeth in the human mouth.

Hardness is the mean pressure that a material bears under load. This parameter is experimentally affected by several geometrical uncertainties, such as penetration depth, size and shape of the indenter.

All teeth have the same general structure and consist of three layers [14] as shown in Fig.1. The hardest tissue in the body is an outer layer of enamel, which is wholly inorganic.

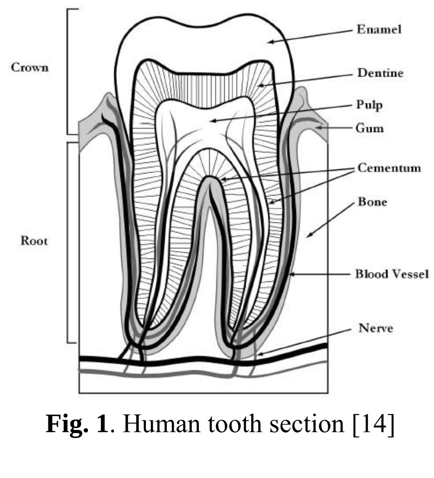

Fig. 1. Human tooth section [14]

The enamel covers part or the entire crown of the tooth. The typical value for enamel hardness range reported in literature is from 1 GPa to 8 GPa. Regarding enamel elastic modulus, we can say that the values range from 19.9 GPa to 91 GPa when the measurements are perpendicular to crystal orientation, and from 93 GPa to 113 GPa when the measurements are parallel to crystal orientation [18].

Anatomically speaking, the crowns of teeth are covered by dental enamel, which consists of 92% − 96% inorganic matter, 1% − 2% organic material and 3% − 4% water by its weight [8]. Enamel hardness is attributed to its high mineral content [2] and on the other hand the brittle property is due to its high elastic modulus and low tensile strength [15].

Despite enamel being a very strong substrate, clinically, enamel cracks and fractures can occur. Studies have shown that enamel is anisotropic material and its mechanical properties may be dependent on the type and direction of the stress applied, as well as the prismatic orientation [19; 17; 10; 20].

The main reasons for placing a dental restoration are: primary caries or noncarious defect such as abrasion/erosion, traumatic tooth fracture, developmental defect, cosmetic reasons, and restoration of an endodontically treated tooth or other unspecified defects or reasons [6]. The destruction of healthy tissue has always been a big concern, and still today, the caries represent the most widespread human disease [13].

Therefore restorative materials are expected to replace and perform as natural tooth materials. The demand of achievement is so great that most of the times restorative filling materials replace enamel and dentin, which have very different mechanical properties, namely hardness and elastic modulus. Thus, the goal of research when developing these restorative materials is to develop the ideal restorative material which would be identical to natural tooth structure, in strength adherence and appearance.

Mechanical and tribological properties of direct restorative filling materials are crucial not only to serve and allow similarity with human enamel and dentine but also to compare composites between them and determine objective criteria for their selection.

The principal goal of the present article is to outline a mechanistic framework for interpreting measurements from nano indentation and nano scratches test on dental restorative materials with Berkovich (pyramidal) indenter. Because the tips are very sharp, measurements was made in the plastic domain. Also, to investigate the hardness of the same commercial restorative materials were used the nanoindentation and the AFM techniques.

2. EXPERIMENTAL MEASUREMENTS

2.1 Restorative materials. Preparation of the samples

Microfill composites use particles very small in size (about 0.04 microns in diameter, 35–50% by weight). This type is usually used in front teeth because it is polishable quite well. However, having that many small particles might make the composite stiffer to work with [22]. In order to overcome the limitations of the micro and macrofilled composites, it is better to use a layer of microfilled composite over a bulk of macrofill in order to spatially increase the strength of the structure and provide a more polishable restoration and a translucent enamel-like appearance. Another approach utilises ‘Hybrid’ composites that are cross between microfilled and macrofilled composites. Hybrid composites contain particles between 0.6–1 microns in diameter and 70–75% by weight. Hybrid composites are formulated to be layered. Often, hybrid composites are formulated with more resin than fillers (flowable composites), to form a loose mix that can be delivered to cavities using a syringe. Flowable composites are used to seal the dentine of a tooth prior to placing the filling material. Due to the low level of fillers, they are more prone to shrinkage, so they are not recommended by themselves to fill large cavities.

Four commercial dental composite resins were investigated in this work. All tested composites are one-paste systems (Fig. 2). Information regarding their classification, indication, monomer composition, type and size of reinforcing filler particles, selected shade and the manufacturer are summarized in the table 1. Data were provided by the samples manufacturer. (http://www.kerrdental.com/kerrdental-msds-us-english).

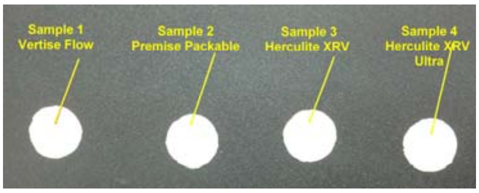

Fig. 2. Samples for experimental tests

2.2 Experimental Tests.

2.2.1 Nanoindentation tests

Knowledge of the mechanical properties of the dental materials is crucial for understanding how masticators strains are distributed throughout a tooth, and for predicting how stresses and strains are altered by dental restorative procedures, age and disease [12]. It is expected that under mastication loadings, a restoration with sufficient and identical mechanical properties to that of the adjacent tooth structure will have a longer lifetime [1].

In the past, in order to measure the mechanical properties, (hardness and elastic modulus) of a dental material, conventional mechanical tests such as compressive, tensile, and three–points bending tests were performed on different sections of the tooth such as enamel, dentine, and cementum [22].

Recently, indentation tests are becoming most commonly applied means of testing the mechanical properties. An AFM XE 70 (manufactured by the Park System Company) with a nanoindentation module enable the measurement of hardness on the surface of dental materials is used in experiment.

All experiments were performed in a clean room with control of humidity, temperature and air pressure.

Indentation tests are the most used way of testing the hardness of materials. This technique has its origins in the Mohs scale of mineral hardness and has been extended in order to evaluate material hardness over a continuous range. Hence, the adoption of the Meyer, Knoop, Brinell, Rockwell and Vickers hardness tests were performed. The nanoidentation technique has been established as the primary tool for hardness investigations of micro/nano scale. The test is usually performed with a pyramidal or a conical indenter.

Indentation data were obtained of investigated dental materials using an indentation force of 250µN. The tests were repeated five times. A Berkovich diamond tip (three-sided pyramidal) was used for all indentations. Temperature of investigated material was 20^{0}C and humidity 46 - 48%.

The analysis method used in the experimental determination of hardness is the Oliver and Pharr method. This is a standard procedure for determining the hardness and elastic modulus from the indentation load-displacement curves at micro and nano - scale. Hardness for each material was determined from the load-displacement curves during unloading. The Oliver-Pharr method was proven to be an efficient tool for mechanical characterization of soft or hard materials [16; 1; 4].

Before and after indentation process, the AFM contact mode was used to scan the surface. The topography of the samples surface was then obtained by AFM scanning. Figure 3 shows the trace of nanoindentation place on the Vertise Flow material at 20^{0}C with an indentation force of 250 µN, for instance.

The optical microscope of the AFM test system was used to accurately locate the regions of interest.

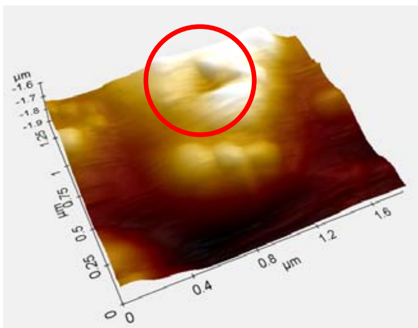

Fig. 3 Nanoindentation of Vertise Flow dental material at 20^{0}C with a force of 250µN

Table 1* Classification of resin composites regarding filler size and size distribution (clinical application)

Type of composite resins/ commercial name	Samples dimensions (disc)	Particles size. characteristics	Clinical use
XRV Herculite Ultra Nanohibride resin	Diameter - 15mm Width – 1mm Hand made Curing time: 40 seconds.	Enamel type, color A1, reinforcement particles which range from ~ 0:5 µm to 3 µm.	Moderate stress areas requiring optimal polishability
XRV Herculite Enamel Microhibride resin	Diameter - 15mm Width – 1mm Hand made Curing time: 40 seconds.	Enamel type, color A2, large filler particles, with an average size of 15 µm – 20 µm and also a small percentage in weight of colloidal silica, which has a particle size ranging from 0:01 µm m to 0:05 µm m.	High-stress areas requiring improvement polishability
Premise Packable Trimodal hybride resin,	Diameter - 15mm Width – 1mm Hand made Curing time: 40 seconds.	Dentine type, color A3, Universal Trimodal, Nanocomposite featuring a unique 3-filler blend (0.02 µm; 0.4 µm and Pre-polymerised filler) and 84% filler loading, Midifiller/minifiller hybrid, but with lower filler fraction	Situation in which improved condensability is needed
Vertise Flow Uncured methacrylate ester monomers	Diameter - 15mm Width – 1mm Hand made Curing time: 40 seconds.	Midifller hybrid, but with fine particle size distribution Non-hazardous inert mineral fillers, non-hazardous activators and stabilizers	Situation in which improved flow is needed and/or where access is dificult

* ***Observation:*** All samples were prepared in the Laboratory of Faculty of Dental Medicine, from Cluj-Napoca, Romania

Indentations were spaced sufficiently far apart so that the indentation behavior was not affected by the presence of adjacent indentations. The instrument's software corrected all data for thermal drift and instrument compliance.

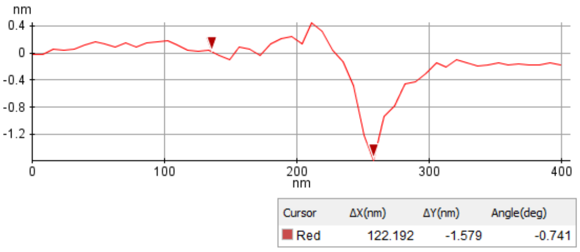

Fig. 4 Indentation depths of Vertise Flow material at 20°C with a force of 250µN

Using the XEI Software the cross-section of the indentation places is obtained in order to measure the indentation depth.

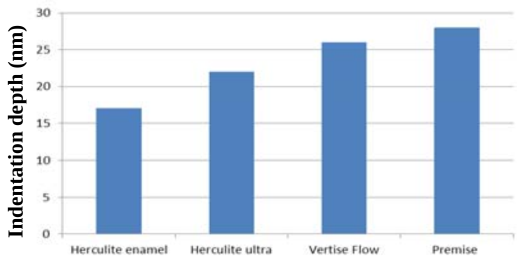

Fig. 5 Indentation depths for restorative dental materials material at 20°C with a force of 250µN

The hardness was estimated by using XEI Software based on the Oliver-Pharr approach, analyzing the load-unload curves performed during experimental campaign. Hardness is directly provided by software. Figure 6 presents the hardness of Vertise Flow material at 20°C, which is equal by 1.55GPa for a contact depth of 21.4nm.

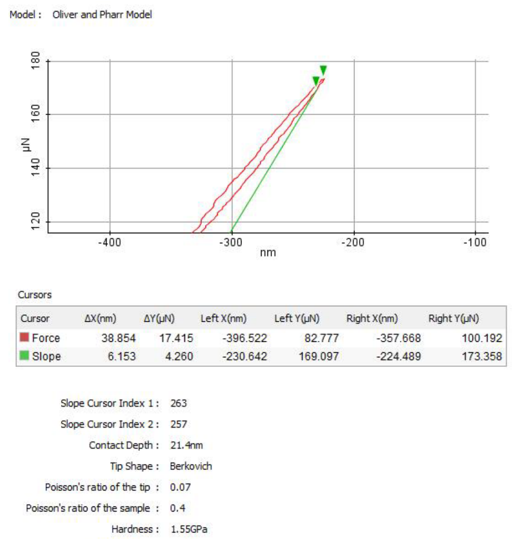

Fig. 6 Hardness of Vertise Flow dental material at 20^{0}C

The same experiment was performed for all investigated dental restorative materials and the hardness value and the indentation depths are presented in table 2 and figure 5.

Table 2 Hardness (GPa) of investigated dental materials at 20^{0}C

Material	Hardness [GPa]
Vertise Flow	1.55
Premise Packable	2.6
XRV Herculite	1.62
XRV Herculite Ultra	2.2

Modulus and hardness for each material were calculated using the Oliver-Pharr method [16] from the load-displacement curves during unloading. The Oliver-Pharr method was proven to be an efficient tool for mechanical characterisation of soft or hard dental materials [1; 4]. The Oliver-Pharr method is based on analytical solutions for other indenter geometries. It accounts for the curve in the unloading data and provides a method of finding the contact area at peak load using a determined depth and indenter shape function. They note that like the conical indenter, the Berkovich has a cross-sectional area which varies as the square of the depth of contact.

The obtained results from the nanoindentation tests confirm hardness value in the range of 1 to 3GPa of investigated dental material at the room temperature.

The measured mechanical properties of dental resins at ambient temperatures are in the same range of those reported with other studies taken from literature [1].

2.2.2 Nanoscratche test

Nanoscratch tests were performed using the scratch option available in the AFM XE 70 to assess the scratch resistance and deformation behaviour of our commercial dental composite resins which are presented in table 1.

Scratching was performed using a 60 deg conical diamond indenter with a 1µm tip radius (Berkovich diamond tip).

The technique involves generating a controlled scratch with a diamond tip on the sample under test. The tip is drawn across the surface under constant load.

The test protocol consisted of applying a normal load of 50 µN, holding at the peak load for 5 s, displacing the indenter tip laterally over a distance of 10 µm at a rate of 0,20 Hz, and than unloading. Material response was characterized by the normalized scratch force, and the scratch depth. After the scratch test, the indenter was lifted and moved back to the starting point. Then, the scratch track was scanned again under 2 µN at a rate of 1,00 Hz so that the ASP (after scracth) profile was obtained.

Remnant scratches were imaged by scanning probe microscopy AFM.

The normal forces used for the preceding scratch tests were selected based on the criterion that the sample deformation be well into the plastic domain of the test sample, so that can be analyzed remnant scratches using the XEI Software.

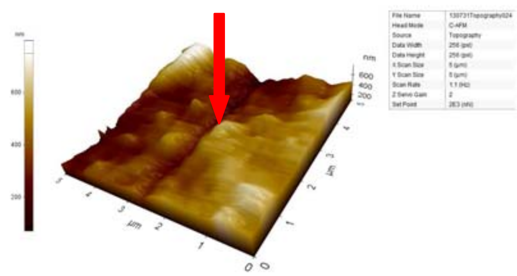

Fig. 7 Remnant scratches of Vertise Flow dental material at 20^{0}C with a force of 50µN

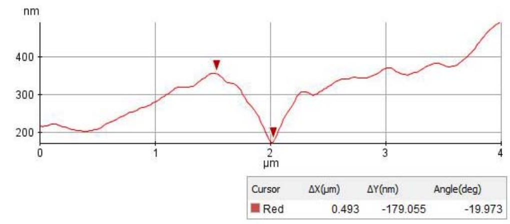

Fig. 8 Nanoscratch depths of Vertise Flow material at 20^{0}C with a force of 50µN

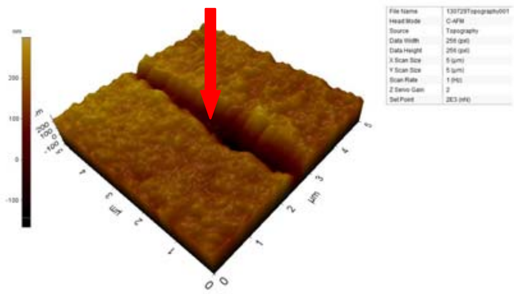

Fig. 9 Remnant scratches of Herculite Ultra dental material at 20^{0}C with a force of 50µN

Figure 7 and 9 shows constant load scratch profiles on the surfaces of the different dental materials (Vertise Flow, Herculite Ultra).

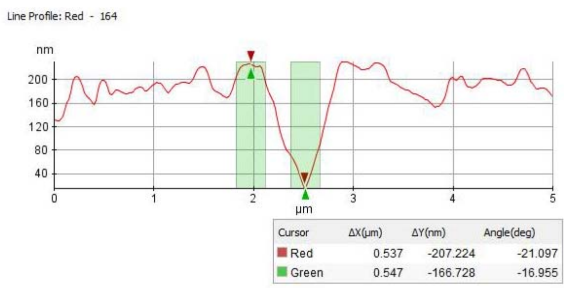

Fig. 10 Nanoscratch depths of Herculite Ultra dental material at 20^{0}C with a force of 50µN

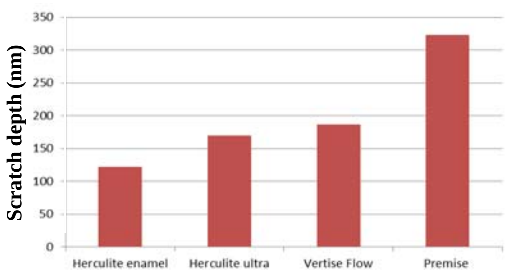

Fig. 11 Scratches depths for restorative dental materials material at 20^{0}C with a force of 50µN

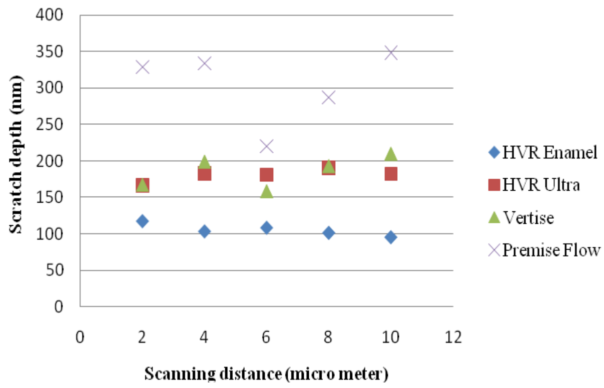

Fig. 12 Scratch curves under constant loading.

The difference between ASP (after) and BSP (before) represents the depth of the scratch groove remaining on the sample surface after the scratch tests. It is termed as scratch depth in this study, which reflects the permanent damage caused by the scratching. For each scratch test, a set of surface profiles along the track was measured, including the track profile before scratch and after scratch. In Figure 12 is shown scratch curves under constant loading. DSP (during scratch) profile being the recorded depth profile during scratch track under 50 µN constant load along 10 µm track.

3. CONCLUSIONS

Investigations of the mechanical and tribological properties at micro/nano-scale using the atomic force microscope can provide insights into failure mechanism of dental material.

Nanoindentation is an attractive method for measuring the mechanical behaviour of small specimen volumes in dental hard tissue and dental fillings. Using this technique, the mechanical properties of four resins dental material were investigated. This technique evaluates only the mechanical properties of a very shallow surface region of a specimen that may have undergone damage associated with mechanical preparation required to achieve a satisfactory flat sample for testing. The technique is also very surface sensitive with a fine-polished surface as a prerequisite. In addition, the inhomogeneous and anisotropic nature of the dental materials add further complications that, to date, have barely been addressed.

The nano characterisation verified that the XRV Herculite Ultra resin material has the highest hardness and modulus of all materials tested.

Nanoscratch data, in conjunction with in-situ SPM images, provides a wealth of information concerning a materials behavior under simultaneous normal and lateral stresses.

Nanoscratch tests suggested that the XRV Herculite Enamel resin material is more wear resistant than other materials tested.

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Investigatii nanomecanice ale materialelor dentare pe baza de rasina utilizand microscopia de forta atomica.

Rezumat: Smaltul dentar este cea mai dura suprafata a dintilor. Durata de viață a dintilor depinde de proprietățile mecanice si tribologice ale acestuia. Aceste proprietăți sunt influențate de condițiile de masticație, inclusiv de efectele produse de umiditate, temperatura şi abraziune. Scopul lucrării este de a analiza proprietățile mecanice ale materialelor dentare pe baza de rasina folosind tehnici avansate de testare prin utilizarea microscopului de forță atomic AFM XE 70 prevazut cu modul de nanoidentare. Nanoidentarea şi nano zgârierea oferă informații despre duritatea, modulul de elasticitate, rezistență, de asemenea, despre fluaj şi conformitatea, astfel asigurându-se o soluție completă de testare a caracteristicilor tribomecanice ale suprafetei fără nici un compromis. Aceste tehnici de caracterizare mecanica relativ non-distructivă pot ajuta în a înțelege mai bine comportamentul mecanic al materialelor dentare şi astfel să faciliteze obtinerea lor cu excelente proprietati mecanice si tribologice.

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