The Study of Some Experimental and Commercial Nanocomposites Used in Dentistry

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The most appealing aspect related to nano-composites use, consists of their biomechanical properties; these properties succeed in giving good mechanical strength, a minimal polymerization contraction and an exceptional aesthetics and polish due to the features of the nano-filler. Investigating the effect upon both the filler level and the size of the filler particles on some experimental composites' mechanical and physico-chemical properties, some authors have come to the conclusion that by increasing the filler level can be obtain first of all an increasing of the compression resistance and secondly a significant decrease of water absorption. The vast majority of the investigated composites, based on borosilicate glass, are showing an important increase of their resistance to wear together with the increase of the filler level. In this particular study the resistance to traction and respectively to fracture and also the structure (SEM) for some experimental nanocomposites (produced in our laboratory) and for a commercial product (Premise - Kerr Corporation) has been determined. The samples of material were made according to the ISO 4049 specifications; they were tested with the use of the Instron Universal Lloyd apparatus and the Scanning Electronic Microscope (SEM - FEI).

Keywords: nanocomposites, physical properties, flexural strength, diametral tensile strength, SEM

The most appealing aspect related to nano-composites use, consists of their biomechanical properties; these properties succeed in giving good mechanical strength, a minimal polymerization contraction and an exceptional aesthetics and polish due to the features of the nano-filler. In the laboratory testing of the nano-composites' mechanical properties is merely an essential stage before their clinical use. Taking into account all the inherent limitations in the process of simulation of the oral medium and all the different standards used by various producers, it should be a necessity to discover new testing relevant patterns that can get the most interconnections of the diverse physical parameters characteristic to the material's behavior [1,2]. Filler content, particle size and distribution of the filler's particles, highly influence the physical and mechanical properties of the composite materials [3-5]. Recently, by introducing nanoparticles fillers, manufacturers try to achieve both high mechanical properties and the outstanding aesthetics for composites [19]. Nanocomposites are a recent development on the market of dental materials. They contain filler particles with sizes smaller than 100 nm (0.1 μm). Among all the mechanical stresses from the oral cavity the most frequent are compression and the stretching effort; due to these processes, evolves the greatest force the dental hard tissues are subjected to. The resistance to compression and, respectively to traction properly reflects the ability to the so-called "in vivo" endurance of the dental material, one of the aspect abrasion strength, given the fact that the diametral tensile strength is also a measure of the restoration's adhesion to the dental substratum [4,6,7]. The methods that are used for testing in such laboratory research do not totally succeed to simulate the concrete "in vivo" solicitation conditions. The results of the "in vitro" measurements on standard test sample represent only a comparative value.

The purpose of the study was to develop and evaluate a novel composite system for dental applications by a comparative evaluation of two experimental nanocomposites AD1 and AD3, obtained within the "Raluca Ripan" Chemistry Research Institute from Cluj Napoca, on one hand and on the other hand upon of commercial product (Premise - Kerr Corporation), especially the evaluation of their resistance to flexural strength (FS), compressive strength (CS) and to diametric tensile strength (DTS). Electronic microscopic images of the pre- and post- fractured samples are highly lightening the structure of studied composites and the propagation of crack under mechanical solicitation.

Experimental part

The nanocomposites (AD1-AD3) were prepared as a paste (table 1), by dispersing in the organic phase the silanized bioactive inorganic fillers with A-171 silane. The organic phase (fig.1) consists of a mixture of dimethacrylate monomers: Bis-GMA (60%), (synthesized in our laboratory)/TEGDMA (30%) (Aldrich) and UDMA (10%) (Merck) with camphorquinone (Merck) and *N,N dimethylamino methylmethacrylate* (Aldrich) as initiator/activator system.

The inorganic phase consists of silanized fillers based on a mixture between glass (G1), colloidal silica and some nanofillers (N1, N2) obtained through the sol-gel method in our laboratory. The above mentioned nanofiller was: N1-nanoparticles based on colloidal silica and zirconium oxides (SiO_2-ZrO_2); N2- nanoparticles of aluminum and

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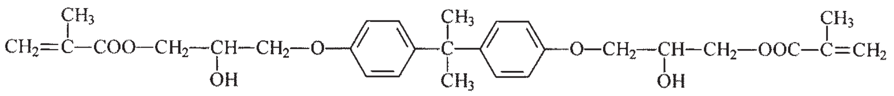
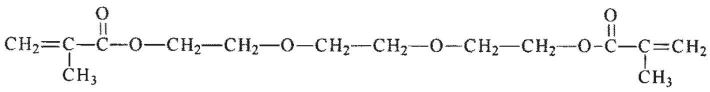
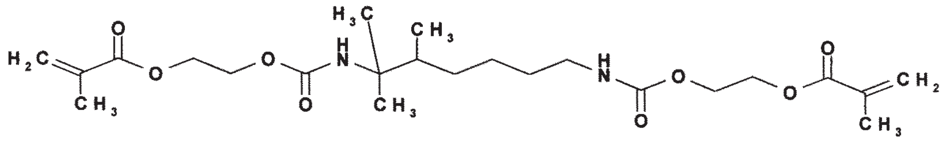


Bis-GMA- *2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane*



$CH_2{=}C(CH_3)-C(=O)-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-C(=O)-C(CH_3){=}CH_2$

TEGDMA – *triethylene glycol dimethacrylate*



UDMA - *1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane*

Fig. 1. Formula of monomers

Table 1

CHEMICAL COMPOSITION OF THE EXPERIMENTAL DENTAL COMPOSITES [wt%]

Composites	**Organic phase**	**Inorganic phase**			
Premise	Ethoxylated bis-phenol-A dimethacrylate; Triethylene glycol dimeth-acrylate (TEGDMA)	Prepolymerized filler (PPF) with 30 to 50 μm; Barium glass with 0.4 μm; colloidal silica with 0.02μm			
		G1	**N1**	**N2**	**SiO_2**
AD1	22	30	40	-	8
AD3	25	20	-	40	15

zirconium oxides (Al_2O_3-ZrO_2). The chemical composition (G1) and the condition for synthesis in our laboratory are: 45% SiO_2; 10% Al_2O_3; 17% B_2O_3; 20 % BaO; 8% NaF–CaF_2; obtained through the conventional melting method at 1350°C. The chemical bond between the organic and inorganic phases was provided by silanization of the fillers from an acidulated ethanol-water with *3*-methacryloyloxypropyl-1-trimethoxysilane (A-174).

Characterization of the composites.

The tests for the mechanical properties such as compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS) were performed with a universal mechanical testing instrument from the LOYD Company, at 23°C. The samples, were obtained in Teflon moulds (6 mm diameter and 3 mm) thick for DTS; (3mm diameter and 6 mm) thick for CS; (2×2×25 mm) for FS where the composite resins were polymerized with a 3M XL 2500 Lamp for 40 s, from several directions. After the polymerization process, the samples were kept into distilled water at a temperature of 37±1°C for 24h. The calculation formulae for mechanical properties are:

Flexural Strength

The flexural strength was determined by using the equation $FS = 3Fl/2bh^2$ [MPa]; where: F is the maximum force to falling, being exercised on a sample [N]; L is the distance measured in mm, between the supports, with an error of ± 0,01 mm; b is the thickness of the test tube, measured before the concrete testing [mm]; h is the height of the test tube, measured before the concrete testing [mm].

Compressive strength

The compression strength was calculated from the equation $CS= F/\pi r^2$ [MPa] where: F is the force applied to the sample by the piston [N]; r is the ray of the cylinder sample, measured before the concrete testing [2 mm].

Diametral tensile strength

The diametral tensile strength was determined by the relation $DTS = 2F/\pi dl$ [MPa]; where: F is the force applied on the sample when breaking [N]; d is the sample diameter, measured before the concrete testing [6 mm]; l is the length of the sample, measured before the concrete testing [3 mm].

Results and discussion

The complexities of the oral environment and the diversity of dental composite make it difficult to define clinical failure processes and associate routinely measured mechanical properties with composite performance. Fracture propagation studies (SEM) attempt to overcome these difficulties by addressing more realistic stress environments and considering more fundamental mechanical properties.

The properties of dental composites depend also on the degree of conversion of the monomers, the strength of the obtained materials increasing with the degree of conversion [11, 12]. The degree of conversion is increased also with the increasing of monomers ratio. The fracture mechanics approach to the study of composite mechanical properties has been taken into consideration in an attempt to understand the fundamental energetic of crack propagation and failure of experimental nanocomposites (fig.3-5).

The level of fracture toughness enhancement is considerably lower 2 – 3 times the one observed in the dental nanocomposites, implying the presence of an additional toughening mechanism. Since crack deflection and interface crack growth are the observed fracture mechanisms, the finding suggests that the fracture toughness enhancement originates from increases in the interface toughness resulting from the use of coupling agents silanization during the composite fabrication process. Silanization is beneficial for interface toughness because it helps to establish Si-based bonds between the

Table 2
MECHANICAL PROPERTIES OF DENTAL COMPOSITES AND FOR THE COMMERCIAL COMPOSITES

FS [MPa]			CS [MPa]			DTS [MPa]		
AD1	AD3	PREMISE	AD1	AD3	PREMISE	AD1	AD3	PREMISE
98	85	111	165	185	167	53	42	65
89	89	88	181	200	189	58	54	57
93	90	115	170	192	178	51	55	67
95	87	102	190	214	197	45	51	54
91	91	116	170	224	180	49	53	61
Average value								
93.2	**88.4**	**106.4**	**175.2**	**203**	**182.2**	**51.2**	**51**	**60.8**

matrix and the particles [13-19]. Since fracture of both the dental nanocomposites is dominated by interface fracture, it appears that the interface bonds are not sufficiently strong to induce particle fracture. The nano-sized particles appear to enhance fracture toughness of the nanocomposites in two ways: - the large surface to volume ratio that aids to improve interface bonding and consequently the interface toughness, and - the high strength of the nano-sized particles that helps to prevent particle fracture during interface cracking. The results obtained with the use of the previously mentioned formulae are shown in table 2.

The flexural strength of a material allows it to resist as thin layers within unconstrained areas of the obstruction, where the flexural forces act and react. However, the flexural modulus must be located in a convenient zone not to make the material too breakable. ISO 4049:2000 [8] requests a minimum of 80 MPa, minimum satisfied by all three tested materials [9,10]. Flexural strength of samples AD 1 and AD3 have values close to the value of the commercial composite. All samples satisfy the ISO requirements for flexural strength (a minimum of 80 MPa).

The compressive strength (CS) represents the compressive force to which the composite breaks. It is a well-known fact that the dental composite material does not break this way within the oral cavity, and the resistance to compression does not belong to the ISO 4049 specifications, but this test is often used in order to verify the correct silanization of the filler and to make sure whether the composite paste is uniform and without air bubbles or other kinds of imperfections [9, 18]. Sample AD3 have a very good compressive strength, higher than the value of the commercial composite material. The best results related to compressive strength have been obtained for the sample AD3, while CS for sample AD1 is very close to the one for commercial composite. DTS for the samples AD1 and AD3 have the same value being close to the value of the commercial material. The average value for FS, CS and DTS are shown in figure 2.

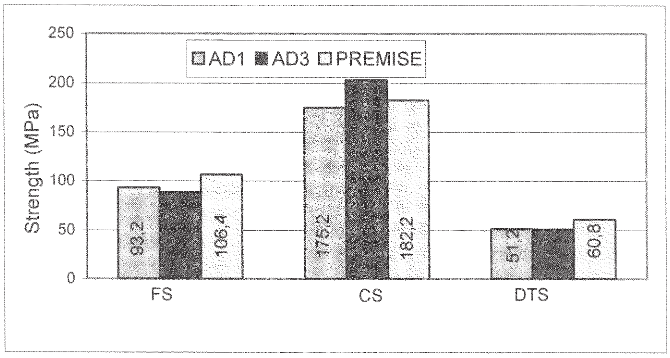


Fig. 2. Average value for FS, CS and DTS for experimental and commercial dental composites

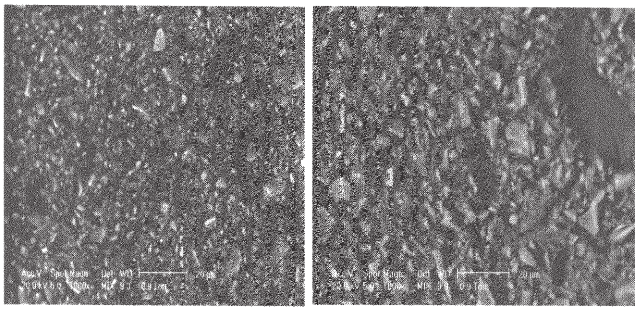


Fig.3. SEM micrographs for sample AD3 before and after the fracture

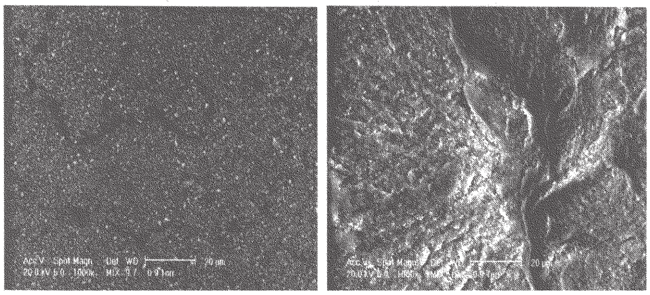


Fig.4. SEM micrographs for sample AD1 before and after the fracture

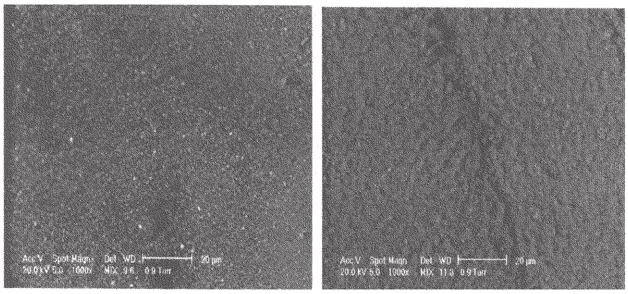


Fig. 5. SEM micrographs for PREMISEcomposite sample, before and after the fracture

DTS for the experimental dental composites is slightly smaller than the resistance of commercial composite. Our results integrate themselves within the generally admitted limits of 30 to 55 square meters. The diametral tensile strength through compression is a widely accepted test, an ordinary one as far as the composite materials are concerned; it fully relevant for the conversion degree, as well as for the density of the double links provoked by the monomer composition, the light intensity and its duration to polymerization and the filler content in matrix. Comparing the values of FS, CS, DTS we can conclude that the composition of the nanofiller does not influence the FS and DTS, or the influence is very small, being in the range of experimental errors. The presence of Al_2O_3 in sample AD3 improves the compressive strength with almost 14 %.

The value obtained for CS for the experimental dental composite obtained in our laboratory is higher than the value determined for the commercial composite, in the same conditions. Because the main difference between the experimental dental composites is the nanofiller composition, the compounds N1 and N2 contain ZrO_2, but N1 contains more SiO_2 and N2 contains more Al_2O_3 we presume that the presence of Al_2O_3 in sample AD3 can influence mechanical properties of the composite. The presence of Al_2O_3 improved the compressive strength. The improvement of compressive strength with the increasing of Al_2O_3 content can be explained by the properties of this material. Compressive strength of Al_2O_3 is about 2600 MPa, while for SiO_2 is much smaller (1108 MPa) [16]. FS decreased for sample AD3, while DTS has the same value for both samples.

The increasing of Al_2O_3 quantity can lead to the increasing of mechanical properties of composite materials, but Al_2O_3 has a higher coefficient of thermal expansion than SiO_2, [16], leading to the decreasing of dimensional stability. Using the SEM, one can notice and compare the structure of the materials before and after their fracture (in DTS testing) (figs. 3-5).

Recently the concepts of fracture mechanics have been applied to a number of problems in dental materials. Fracture mechanics characterizes the behaviour of materials with cracks or flaws. Flaws or cracks may arise naturally in a material or nucleate after a time in service. In generally any defect weakens a material, and, as a result, sudden fractures can arise at stresses below the yield stress. Examining the SEM micrographs one can see that the commercial composite (fig.5) was the most uniform.The particles have uniform sizes and distribution and the sample was continuous, without pores or cracks. AD1 sample has a uniform morphology, fine particles, but during polymerization in the structure of the samples some pores and crakes were formed. The imperfections of structure (fig.3) do not influence the mechanical properties of sample AD1. In the case of sample AD3 SEM micrographs (fig.4) revealed the existence of bigger particles embedded in the polymeric matrix. Nevertheless the mechanical properties were very close for all the studied materials despite of the differences related to the morphology of the samples. More than that, compressive strength was higher for the sample AD3, the sample with bigger particles. This more rigid morphology imparts a high tensile strength to these nanocomposites, yet leaves them less elastic and highly susceptible to damage upon contact with liquids. Investigating the effect of both the filler level and the size of the filler particles on some experimental composite mechanic and physico-chemical properties, some authors have come to the conclusion that by increasing the filler level one can obtain on one hand an increasing of the resistance to compression and on the other hand a significant decrease of water absorption. The vast majority of the investigated composites, based on borosilicate glass, are showing an important increase of their resistance to wear together with the increase of the filler level.

Conclusions

Dental composites were obtained and characterized, studying the influence of the nanofillers on mechanical and morphological properties of the composite. All the obtained composites have good mechanical properties, close to the ones of a commercial material. The increased content of Al_2O_3 for one of the samples determined the increasing of compressive strength, while flexural and diametric tensile strength were not influenced.

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