## The Effects of Nanofillers on Composite Materials Mechanical Properties

# ADRIAN ALMASI<sup>1</sup>, ANCA PORUMB<sup>1\*</sup>, ANGELA CODRUTA PODARIU<sup>2</sup>, LIANA TODOR<sup>1</sup>, SERGIU ALEXANDRU TOFAN<sup>2</sup>, RAMONA AMINA POPOVICI<sup>2</sup>

<sup>1</sup>University of Medicine and Pharmacy, Faculty of Dentistry, 10, 1 Decembrie Str.,410068, Oradea, Romania <sup>2</sup>Victor Babes University of Medicine and Pharmacy Timisoara, First Department of Faculty of Dentistry, 2 Eftimie Murgu Sq., 300041, Timiusoara, Romania

The goal study is benchmarking flexural strength FS of compressive strength CS, compression diametrical DTS (diametrically tensile strenght) and Vickers hardness for two nanocomposites experimental AD1 and AD3 achieved within the Research Institute in Chemistry Raluca Ripan Cluj Napoca and for the commercial product of the Kerr Premise company <sup>™</sup>. Electron microscopy aspects pre- and post-fracturing are also shown to highlight the structure of materials and spread

Keywords:Nanofillers, mechanical properties, mechanical fracture lines

Nanocomposites are a class of restorative material placed on the market in the last decade, with the aim of achieving and even exceeding the good mechanical properties of hybrid composites and aesthetic qualities and luster composites with microfilling [1-3].

The attractiveness of using the nanocomposites lies in using their biomechanical properties that manage to combine a good structural strength, lower polymerization shrinkage aesthetics, and exceptional luster due to their nanofiller [2-6].

One of the most important achievements of recent years is the application of nanotechnology in the field of composite resins [7]. While particle size is about 8-30im in hybrid composites and  $0.7-3.6\mu$ m in the micro hybrid [8], recently have been developed filler particles ranging in size from 5-100 nm [4]. The 40 mm particles that also existed in micro hybrid composites could have been considered as precursors of the nanocomposites.

The type and the filler proportion of inorganic particles, their size, and distribution play a decisive influence on the physical and mechanical properties of composite materials. The increasing filler level causes a strength increase for the compressive and a decrease in the absorption of water and a significant increase in wear resistance [9,10].

Laboratory testing of mechanical properties of nanocomposites is an essential step before their clinical use. With all the inherent limitations in simulating oral environment and different standards used by various manufacturers, it is necessary to find some test models as relevant as possible, taking into account the various interrelated physical parameters in material's behavior [11,12].

Masticatory forces applied to the teeth and to the restorative materials can produce different consequences for them: elastic deformation (depending on the degree of elasticity of each material), permanent deformation, and then a fracture [13].

*Droop strength* is the ability of material to resist bending until fracture [13,14]. The test is performed by applying a progressive force in the middle of rectangular bars, braced at the ends, producing tension on the underside of the specimen, respectively on the upper compression at the application of the force, until fracturing the material [15].

*Compression strength* measures the force supported by material before breaking [14]. Most intraoral masticatory forces are compressive, during which dental tissues and restorative materials are subjected to the greatest forces [13]. Compressive strength measurement is done by applying axial force on a cylindrical specimen [15].

The strength to diametrical compressive involves indirect assessment of the tensile strength by measuring the compressive strength of a specimen in the form of a disc, the diameter of the force being applied to the specimen; the test is easier to perform and more relevant than directly testing the tensile strength.

*Hardness* It is the property of a material to resist the destruction of its superficial layers under the action of another body. Vickers micro-hardness is measured by the effect of a compression ignition diamond pyramid of 136 degrees on the specimen surface [14].

## Experimental part

Material and method

Preparation AD1 and AD3 experimental nanocomposite was done by dispersing the organic phase of the inorganic filler bioactive silanized particles.

The organic phase is a dimethacrylate monomer mixture of the following: Bis-GMA (60%) synthesized in our own laboratory, TEGDMA (30%) (Aldrich) and UDMA (10%) (Merck).

Anorganic filler consisting of a mixture of silanized particles with the following composition:

-glass particles (G1) with the following composition: 45% SiO<sub>2</sub>; 10% Al<sub>2</sub>A<sub>3</sub>; 17% B<sub>2</sub>A<sub>3</sub>; 20% BaO; 8% NaF-CaF<sub>2</sub>. The filling was achieved in our own laboratory by conventional methods of melting at 1350°C, followed by grinding.

-colloidal silica SiO,

-N1 nanoparticles composed of zirconium oxide and colloidal silica (SiO,-ZrO,)

-N2 nanoparticles consist of oxides of aluminum and zirconium (Al<sub>2</sub>A<sub>2</sub>-ZrO<sub>2</sub>)

N1 and N2 nanoparticles were obtained by sol-gel method in the laboratory.

 Table 1

 THE CHEMICAL COMPOSITION OF THE COMPOSITE MATERIALS USED

Composite materials	The organic phase (% mass)	ss) Inorganic filler (% mass)			ss)	
Premise™ (Kerr Corp.)	Bisphenol-A-ethoxylate dimethacrylate, TEGDMA, initiators, stabilizers,	16	Prepolymerised particles, 30-50 µm Barium glass 0.4 µm Silica 0.02 micrometres in total 84%			
			G1	N1	N2	SiO <sub>2</sub>
AD1 (ICCRR)	Bis-GMA, TEGDMA, UDMA, camforochinonă, dimetilaminometilmetacrilat	22	30	40	-	8
AD3 (ICCRR)		25	20	-	40	15

The connection between the anorganic filler and the organic silanization phase was done by acidified alcoholic solution with the particles in the three-metacriloiloxipropil-1-trimethoxysilane (A 174).

#### Specimens' preparation

For *flexural strength test* there were prepared for each of the three materials, ten specimens in the form of a rectangular bar with dimensions of  $25 \pm 2 \text{ mm} \log 2 \text{ mm} \pm 0.1 2 \pm 0.1 \text{ mm}$  in width and height as specified by ISO 4049 / 2000 [15].

The composites were placed with a spatula into a Teflon mold having the above shape, a transparent sheet and pressed by a glass slide, and then light cured on the upper surface of the halogen lamp XL2500<sup>®</sup>(3M ESPE) for 40 s on each quarter of the length of the specimen. Composite bars were then removed from the array, polymerized identically and on the underside and then finished with sandpaper grit 140 (fig. 1).



Fig. 1. Stages of the specimens for flexural strength testing

The specimens were stored in distilled water at 37°C for 24 h. After drying, the specimens were subjected to bending test (fig.2) in a universal test machine (Lloyd LR5K Plus / Lloyd Instruments Ltd, Fareham, England). Forward speed of the piston was 0.75 mm / min until fracture specimen, at which there was maximum force. The data were visualized and processed using PC software Nexygen (Lloyd Instruments Ltd).

The calculation formula used for flexural strength was as follows:

$$FS = 3FL / 2 BH^2$$
 (MPa)

where: F is the maximum force exerted on the sample (N); L is the distance between supports ( $\sim 20 \text{ mm}$  within  $\pm 0.01 \text{ mm}$ ; B thickness of the sample is measured before the test (mm) H height is measured before the test specimen (mm).

For *compressive strength testing* were prepared for each composite ten cylindrical specimens with a diameter of 4 mm and a height of 8 mm (according to ADA specification Sp.27/1993) [16]. The composite material was inserted into the Teflon matrix, a transparent sheet and pressed by a glass slide, then cured 40 s lamps halogen XL2500<sup>®</sup>(3M ESPE) (fig. 3). The specimen was removed from the mold and light cured same on the opposite side, and then finished with sandpaper grit 140.

The specimens were stored in distilled water at 37 ° C for 24 h. After drying, were subjected to a compressive force (fig. 4) in the universal test machine (Lloyd LR5K Plus) with a forward speed of the piston of 0.75 mm / min, the data being recorded by Nexygen PC software.

Compressive strength (CS) was calculated according to the formula:

$$CS = F / \pi r^2$$
 (MPa)



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Fig. 2. Schematic representation of the flexural strength test (a) and part of the experiment(b)





where:



where: F is the maximum force exerted on the sample (N); r radius cylindrical sample is measured before the test (2mm).

For strength testing to diametrical compressive there were prepared from each composite specimens ten cylinder with the diameter of 6 mm and 3 mm, according to the norm ADA Sp. 27/1977 [164]. The composite was inserted in the mold of Teflon coated with clear and light cured (lamp halogen XL2500<sup>®</sup>) For 40 s (fig. 5) After removing the specimens from the mold, they were polymerized on the opposite side too and finished with 140 sandpaper grit.



Fig. 5. Stages of specimens' implementation for the strength test to diametrical compressive

The specimens were stored in distilled water at 37°C for 24 h. After drying, the specimens were subjected to a compressive force applied vertically on the side portion of the cylinder (fig.6) by the piston with the forward speed of 0.75 mm / min of the universal test machine (Lloyd LR5K Plus). The recorded data were visualized with Nexygen PC software.

Diametrical reduction strength resistance (DTS diametrically tensile strength) was calculated using the formula:



Fig. 3. CS composite application in mold (a) followed by curing (b

## $DTS = 2F / \pi dl$ (MPa)

**F** is the maximum force exerted on the specimen when fractured (N); **d** is the diameter measured before the test sample (6 mm) and **l** is the length of the sample measured before the test (3 mm).

For Vickers hardness testing there have prepared three specimens of each composite cylinders with a diameter of 6 mm and 3 mm, similar to those for STD testing. The composite was inserted in the Teflon mold, coated with a clear sheet and lamp cured (XL2500 halogen lamp /3M ESPE) for 40 s. After removing the specimens from the mold, they were polymerized on the opposite side too and finished with 140 s and paper grit. The specimens were stored in distilled water at  $37^{\circ}$ C for 24 h. After drying with the air jet, the specimens were subjected to Vickers hardness test, according to STAS 6300-64, achieved with a device of Carl Zeiss Jena's company, equipped with a microscope Neophot 21 that allows the diagonally print measurement with an accuracy of 0.5%.

To determine the Vickers hardness, samples were subjected to a force F = 0.02 kgf. The penetrator was applied with a travel speed of  $20 \,\mu\text{m}$  / s, perpendicular to the surface of the test tube. The maintaining penetrator duration under test load on the specimen surface was 15 sec. After 15 s the charge was removed and has brought the intersection point of network, to coincide with the corner of the print square. With bolt centering eyepiece ranged and have read the appropriate divisions (one division equals 0.2312  $\mu$ m), which was calculated the angle d = no. div x 0.2312  $\mu$ m.

Vickers microhardness (HV) was calculated using the following formula:

$$HV = 1854.4F / d^2 (Kg / mm^2)$$

where: HV is Vickers' microhardness; F is strength in kgf and d is the diagonal length in  $\mu$ m.

Electron microscopy. When analyzing electronic microscope SEM Philips, is observed comparatively the structure of the materials before and after fracturing (test DTS).

*Statistical processing* The obtained data were statistically processed [17] using ANOVA and Scheffe PostHoc for comparing averages of the three composites.



Fig. 7. Schematic representation of the Vickers hardness test

http://www.revistadechimie.ro

The significance threshold (p) was 0.05. For statistical processing was used PASW Statistics 18.0 software.

#### **Results and discussions**

Resistance bending values, compression, diametrical compression and Vickers microhardness, for the two experimental nanocomposites AD1 and AD3 were compared with corresponding values for the composite material Premises. They were plotted the mean standard and the deviation of the four tests was carried out (fig. 8)

ANOVA test results reveal that between average values (denoted Media) of the three nanocomposites exist, statistically significant differences (p < 0.0001) on flexural strength (MPa). PostHoc Scheffe test shows which are the nanocomposites pairs between the differences of the medium values are statistically significant (table 2).

The mode values of flexural strength for the mercantile Premise nanocomposite (106.40 MPa) were significantly higher compared with the experimental composites AD1 (93.20 MPa) respectively AD3 (88.4 MPa). The differences were statistically significant (p = 0.0001) between and among AD1 and AD3 Premises. There were no statistically significant differences between AD1 and AD3 (fig.9)

For compressive strength resistance (MPa), ANOVA test results reveal that between the average values of the three nanocomposites, there are statistically significant differences (p < 0.0001). PostHoc Scheffe test shows which are the nanocomposites pairs between which the differences of the medium values are statistically significant (table 3).

The highest value of compressive strength had it the AD3 experimental nanocomposite (203 MPa), and was



Fig. 8. Comparative graphical representation of mechanical test results

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		AD1	AD3	Premise
		Na	nocompozit	

Fig. 9.Graphical representation (median, 25-75% percentile, minimum, maximum) of the flexural results for the three nanocomposites used

The nanocomposites		Mode ± star		
Lot 1	Lot 2	Lot 1	Lot 2	р
AD1	AD3	93.20 ± 4.29	88.4 ± 2.41	184
AD3	Premises	88.40 ± 2.41	106.4 ± 8.46	0.0001
Premises	AD1	106.40 ± 8.46	93.2 ± 4.29	0.0001

Table 2THE MODE AND STANDARDDEVIATION FOR FLEXURALSTRENGTH (FS). N1=N2=N3=10

 Table 3
THE MODE AND STANDARD
DEVIATION OF THE REDUCTION
 STRENGTH (CS). N1=N2=N3=10

The nanocomposites		Mode ± star		
Lot 1	Lot 2	Lot 1	Lot 2	р
AD1	AD3	175.20 ± 13.14	203.00 ± 13.55	0.0001
AD3	Premises	203.00 ± 13.55	182.20 ± 12.70	0.209 -
Premises	AD1	182.20 ± 12.70	175.20 ± 13.14	0.501



Fig. 10. Graphical representation (median, 25-75% percentile, minimum, maximum) of the flexural results to reduction for the three tested nanocomposites

The nanocomposites		Mode ± star		
Lot 1	Lot 2	Lot 1	Lot 2	Р
AD1	AD3	51.20 ± 4.10	51.00 ± 4.00	995
AD3	Premises	51.00 ± 4.00	60.80 ± 5.14	0.0001
Premises	AD1	60.80 ± 5.14	51.20 ± 4.10	0.0001



Table 4THE MODE AND STANDARDDEVIATION FOR THE DIAMETRALSTRENGTH REDUCTION (CS).N1=Ne=N3=10

Fig. 11. Graphical representation (median, 25-75% percentile, minimum, maximum) of the results for the compresive diametrical strength of the material tested

The nanocomposites		Mode ± standard deviation			
Lot 1	Lot 2	Lot 1	Lot 2	р	Table 5 VICKERS IICROHARDNESS
AD1	AD3	67.91 ± 0.51	68.56 ± 0.70	205	MODE AND STANDARD
AD3	Premises	68.56 ± 0.70	86.55 ± 1.04	0.0001	DEVIATION. N1=N2=N3=10
Premises	AD1	86.55 ± 1.04	67.91 ± 0.51	0.0001	

statistically significant (p <0.05) higher than that of the material Premise (182.20 MPa). Compressive strength value for experimental nanocomposite AD1 (175.2 MPa) was statistically significant (p = 0.0001) lower than for AD3, but did not differ significantly (p = 0.501) compared to the Premise (fig.10).

ANOVA test results reveal that between average values (denoted Media) of the three nanocomposites exist, statistically significant differences (p < 0.0001) on flexural reduction strength (MPa). PostHoc Scheffe test shows which are the nanocomposites pairs between which the

differences of the medium values are statistically significant (table 4).

The highest average value was obtained by Premise (60.80 MPa), being significantly higher (p = 0.0001) than for AD1 (51.2 MPa) and AD3 (51 MPa). Between the average values of the two experimental materials have not resulted in significant differences (p > 0.05) (fig.11)

ANOVA test results reveals that between the average values of the three nanocomposites, exist statistically significant differences (p < 0.0001) on Vickers hardness (kg / mm<sup>2</sup>). PostHoc Scheffe test shows which are the



Fig. 12. Graphical representation (mediam, 25-75% percentile, minimum, maximum) results for Vickers microhardness of the material tested

Fig. 13. Nanocomposites SEM micrographs of the tested materials (1000x)
Background before (a) and after fracturing (b)
AD1 before (c) and after fracturing (d)
AD3 before (e) and after fracturing (f)

nanocomposites pairs between which the differences of the medium values are statistically significant (table 5).

The highest average value was obtained by Premise  $(86.55 \pm 1.04 \text{ kg} / \text{mm}^2)$  being significantly higher (p = 0.0001) than for AD1 (67.91 ± 0.51 kg / mm^2), AD3, respectively (68.56 ± 0.70 kg / mm^2). Between the average values of the two experimental materials have not resulted in significant differences (p > 0.05) (fig.12)

The micrographs obtained by scanning electron microscopy (SEM) at a magnification of 1000x, shows the appearance of the inorganic filler particles and homogeneity of the three nano-composite before and after fracturing, at the DTS test (fig.13)

Nanoscale inorganic filler particles (40-100 nm) are not an innovation in dental composites, microfiller composites being incorporated since the 70s, with particles of 40 nm. Improvements brought by the new class of nanocomposites relates mainly to the possibility of significantly increase the percentage of inorganic fillers. While microfiller composites were having 50% by weight filler, the nanocomposites can exceed 80%, resulting in an improvement of mechanical properties [18-20].

Among the mechanical loads from the oral cavity, the reduction and tensile stress prevails, which develops during the high forces which are subject to dental hard tissues. The strength reduction and tensile strength, respectively, reflects the ability of resistance *in vivo* of the restorative composite material including the abrasion resistance, the tensile strength being a measure of the dental adhesion restoration to the substrate. The used methods for such determinations in the laboratory, entirely fail to simulate actual conditions of stress *in vivo* [21-23].

The bending flexural strength of a restorative material allows it to withstand the unsupported thin layers of fillings in areas where flexural forces act. However, flexural modulus must be in a convenient area, for preventing the brittle material. The resistance bending test in three-point is recommended for specification ISO 4049/2000 and is conducted by comparative studies [24-26]. ISO requirements provide a minimum of 80 MPa, satisfied by all three tested materials [27]. Flexural strength bending values for the two experimental materials AD1 and AD3 are not statistically significantly different from each other, but both are significantly lower than for commercial premises material taken as control (table 2).

Matrix organic incorporation of resin nanoparticles composites resulted in increased bending resistance as long as the nanoparticles are isolated, to a decrease in mechanical properties with the aggregation of nanoparticles [29] other studies underlining the importance of nanoparticles silane for their uniform distribution and increaseing the bending and wear resistance[29-31]. In this study, the lower percentage of inorganic filler in experimental composites AD1 and AD3 could explain their lower resistance to bending composite material Premise.

The reduction strength is the reduction force to which the composite fails catastrophically. It is admitted that the composite dental material does not yield so in the oral cavity and, compression strength is not part of the ISO 4049 specifications, but this test is often used to verify the correct silane filler and if the paste composite is uniform and without bubbles air or other imperfections [28,30,31]. Common values reported in studies range from 250-400 MPa, to those obtained in our testing being lower for all three materials (table 3).

Recently, by micromanipulation techniques, Curtis et al. (2009) tested the reduction resistance of the nano-units particles from certain nanocomposites structure, noting that nano-aggregates tend to present multiple fractures compared with inorganic conventional fillers, which could alter the mechanical strength of the overall nanocomposite [33].

AD3 nanocomposite showed the highest value of reduction strength, statistically significant (p < 0.05) higher than that presented by commercial Premises material, namely the experimental AD1, while the average values of the latter not having statistically significant differences. N1 inorganic filler comprises a mixture of zirconium oxides and silica, with a greater weight for silica, while the N2 filler comprises a mixture of aluminum and zirconium oxides with a high percentage of aluminum oxides. The presence of aluminum dioxide in a high proportion in the N2 nanofillers may take to increased reduction strength of the AD3 composite, because the reduction strength of the aluminum oxide is 2600 MPa while for the silica is only 1108 MPa [34].

Diametrical reduction strength is a common and accepted tested for composite materials, for understanding the behavior of fragile materials exposed to tensile stress, the most frequently observed in previous restorations [35,27]. The resistance to diametrical reduction is also relevant to the conversion degree and the to the double density bonds determined by the monomer composition, the polymerization degree and light duration and content filler in the matrix. Values obtained by us are generally accepted within the range of 30-55 MPa. The average values of diametrical reduction strength are not statistically different (p > 0.05) between the two experimental composite AD1 and AD3 but are both significantly lower (p = 0.0001) than those of the composite Premise. DTS value given by the producing company for Premise is 56-59 MPa, very close to the values obtained in the present study [36]

Recently, fracture mechanics concepts have been applied to the study of dental nanocomposites to characterize the behavior of these materials for cracks and defects. Elucidating the fracture mechanisms is performed by atomic force microscopy, electron microscopy transmission and scanning electron microscopy [30]. The results of Chan et al. study (2007) indicates that the main mechanisms of fracture in nanocomposites are crack deflection by nanoparticle, respectively the fracture evolution along the interface particle / organic matrix. Nanoparticles increase the fracture resistance of composite materials by increasing the particle-matrix interface adhesive due to a larger surface area per volume and due to increased resistance of the particles [30].

Composite materials must have a high hardness in addition to high values of properties that define normal strength and rigidity. The hardness determines the resistance to abrasion, tearing and the ability to maintain the original shape under stress. The factors influencing the hardness of a composite material are the nature, the proportion of the filler and the interfacial adhesion composite / inorganic filler, the conversion to curing, the degree of surface processing [37, 38]. The micro-hardness of the composite materials is significantly less than that of enamel or amalgam [39]. Lower hardness of composites obtained AD1 and AD3 could be due to a lower percentage of inorganic fillers.

In this study, scanning electronic microscopy specimens allows comparison of the structural layout before and after fracturing (for testing the diametrical reduction strength): examining the photomicrographs for Premise composite (Fig.14a and b) prior to the fracturing revealers a uniform structure, with a continuous distribution of the particles without pores and cracks. After fracturing there is a fracture line with rectilinear direction without branching trend, advocating for a good homogeneity of inorganic material filler. The composite AD1 (fig.14 c, and d) has a uniform morphology with fine particles, but after polymerization, in the structure of specimens few pores and cracks appeared. After fracturing there is a fracture line with the trend of branching. These may advocate fort the lower reduction strength and for diametrical reduction of this composite. In the case of AD3 composite, photomicrographs showed higher filler particles in the inorganic matrix (fig.14. e and f), this composite showing the highest reduction strength.

#### Conclusions

Knowing by the internship the mechanical properties of diacrylic resins with nanofiller is important for using them as universal direct restorative materials, as indicated the manufacturing companies.

The present study led to the following observations:

Mechanical properties of nanocomposites are influenced by the extent and type of inorganic filler and silane and correct distribution of nanoparticles in organic phase

The flexural strength of the AD1 composite has an intermediate value between the lowest AD3 composite, and the highest of Premise composite, the differences being statistically significant between both experimental materials and commercial material taken as control. However, all the tested materials are conform to the ISO 4049/2000

The compressive strength of the composite AD3 is significantly higher than the AD1 and Premises, possibly due to nanofiller aluminum oxide from AD3

Vickers micro-hardness of the Premise composite is significantly higher than the experimental composites AD1 and AD3

The two experimental nanofiller composite tested materials AD1 and AD3 - show good mechanical properties, similar to those of the composite Premise

The mechanical properties of the two experimental composite AD1 and AD3 fall within the generally accepted rules and allow the use of these materials for direct coronary restorations.

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Manuscript received:21.06.2016