Stomatologija, Baltic Dental and Maxillofacial Journal, 14:126-30, 2012

Evaluation of mechanical properties on three nanofilled composites

Rogério Simões Rosa, Carlos Eduardo Agostini Balbinot, Eduardo Blando, Eduardo Gonçalves Mota, Hugo Mitsuo Silva Oshima, Luciana Hirakata, Luis Antonio Gaieski Pires, Roberto Hübler

SUMMARY

The purpose of this study was to evaluate the mechanical behavior of three composites with nanoparticles Filtek Z350 XT (3M ESPE), Esthet X (Dentsply), Grandio (Voco) in enamel and body shades (A2) trough nanohardness, elastic modulus, compressive strength test, flexural strength test, diametral tensile strength, flexural modulus, weight filler content and Knoop microhardness. One sample of each material was submitted to nanohardness and elastic modulus. Five values of ten indentations were considered valids inside confidence intereval. Ten samples of each material were submitted to compressive strength, flexural strength and diametral tensile strength test at universal testing machine. The flexural modulus test was calculated based on flexural strength results. Ten samples of each group were submitted to knoop microhardness test. The results were submitted to ANOVA and Tukey statistical tests. The highest inorganic weight filler content for Grandio was registered after the organic mould decomposition. After statistical analysis Grandio showed the highest averages for nanohardness, elastic modulus, flexural modulus and knoop microhardness. For diametral tensile strength Grandio and Filtek Z350 XT obtained the highest averages. The tested composite resins ranged similar medias statistically for compressive strength. For flexural strength Filtek Z350 XT and Esthet X showed the highest averages. The results suggest that the weight filler content, the filler size and shape and the contact surface between nanofillers and organic phase has direct relation with composite resins with nanoparticles mechanical properties. Further studies should be carried out to improve the knowledge of composites with nanoparticles mechanical behavior.

Key words: composite resins, nanotechnology, in vitro, dental materials.

INTRODUCTION

During the last few decades, the increasing demands in esthetic dentistry have led to the development of resin composite materials for direct restorations with improved physical and mechanical properties, esthetics and clinical longevity (1, 2). The latest development in this field has been the introduction of nanofilled materials, by combining nanomeric particles and nanoclusters in a conventional resin matrix. The essence of nanotechnology is in the development and use of materials and devices at the level of atoms and molecules with sizes ranging from 0.1 to 100 nanometers, equivalent to half particles size of minifilled composite resins (3).

The objective of some authors have been to develop a composite dental filling material that could be used in anterior and/or posterior tooth restorations with high initial polish and superior polish retention, typical of microfills, as well as excellent mechanical properties, suitable for high stress bearing restorations typical of hybrid composites (3). Nanofilled materials are believed to have high filler content, easy handling and restoration sculpture maintainance for long time (4, 5). Because of reduzed nanofilled composite resins particles size and filler obtainance method, reducing polymerization shrinkage, a higher amount of filler content implies improved mechanical behavior, like diametral tensile strength, compression strength and fracture toughness, that is very important in areas with high functional stress in oral environment (6-8).

[*] *Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, Brazil*

***Rogério Simões Rosa**[*] – D.D.S., M.S., PhD*
***Carlos Eduardo Agostini Balbinot**[*] – D.D.S., M.S., graduate program student*
***Eduardo Blando**[*] – PHYS, M.S., PhD*
***Eduardo Gonçalves Mota**[*] – D.D.S., M.S., PhD, assoc. prof.*
***Hugo Mitsuo Silva Oshima**[*] – D.D.S., M.S., PhD, assoc. prof.*
***Luciana Hirakata**[*] – D.D.S., M.S., PhD, assoc. prof.*
***Luis Antonio Gaieski Pires** – D.D.S., M.S., PhD*
***Roberto Hübler**[*] – PHYS, M.S., PhD, assoc. prof.*

Address correspondence to Dr. Rogério Simões Rosa, Dental clinical, Mostardeiro, 333/602, Porto Alegre, Rio Grande do Sul, Brazil, ZIP: 90430-001.
E-mail address: rgsrosa@yahoo.com.br

The objective of this in vitro study was to comparate the mechanical behavior of three direct composites with nanoparticles in enamel and body shade (A2), trough nanohardness, elastic modulus, compression strength, diametral tensile strength, three-points flexural strength, flexural modulus, Knoop microhardness and weight filler content. The null hypothesis is that these tested materials will have similar behavior in relation to mechanical properties proposed in this study.

MATERIAL AND METHODS

The composites evaluated in this study are specificated in Table 1.

Nanohardness and Elastic modulus

One sample of each composite resin were made using a mould with diameter 8 mm and height 1mm central hole. The composite was packed into the central hole in three 2 mm increments with polymerization for 20 s (curing unit XL–1500, 3M-ESPE, Germany, Bavaria, Seefeld) and light intensity between 400-600 mW/cm², which was monitored by a radiometer (model 100, Demetron/Kerr, United States of America, *Connecticut*, *Danbury*). The samples were stored in individual light-protected plastic tubes with distilled water at 37˚C for 24 hours (9). After this step, the samples were tested in nanohardness equipment (Fischerscope HV 100, Fischer, Germany, Baden-Württemberg, Sindelfingen). Ten indentations were made in each sample with Berckovich indentator. However, were considered a minimal of 5 valid values into the confidence interval. A dynamic load-unload cycle, with load graduated increase and decrease, was applied in 40 seconds to each sample. The maximum load applied in samples was 500 mN. After the nanohardness test, the load and the corresponding deflection were recorded and used to calculate the elastic modulus (GPa) (10).

Compressive strength test

Ten samples (n=10) of each composite resin were made using a polytetrafluoroethylene (PTFE) mould (3 mm diameter and 6 mm height). The samples were placed in an universal testing machine (*Emic DL 2000*, *Emic*, *Brazil*, Paraná, São José dos Pinhais) at a crosshead speed of 0.50 mm/min. (9, 11). Data were obtained in kgf and transformed in MPa using the following formula: $RC=F\times 9.80/A$, where *RC* is the compressive strength (MPa), *F* is the recorded force (kgf) multiplied by the constant *9.80* (gravity), and *A* is the base area (7.06 mm²).

Flexural strength test

Ten samples of each composite system were made using a 25×2×2 mm metallic mould. After this step, were placed on a 25 mm-length supporting base and assembled in a universal testing machine. A customized device was adapted to the upper holder to allow vertical loading of the samples according to a three-point bending test design. Axial load was applied until failure at a crosshead speed of 0.5 mm/min. Flexural strength data were obtained in kgf and transformed in MPa using the formula: $s=3FL/2bh^2$, where *s* is the flexural strength (MPa), *F* is the recorded force (kgf), *L* is the length between the supporting points (21 mm), *b* is the width of the prism (2 mm), and *h* is the thickness of the prism (2 mm) (12). The load-deflection curves were recorded with computer software (MTest, EMIC).

Flexural modulus

Based on flexural strength data, flexural modulus was calculated using the following formula: $Ef= L^3F1\times 10^{-3}/4bfh^3$, where *Ef* – flexural modulus

Table 1. Specifications of the composites evaluated in this study

Group and Manufacturers	Filler	Organic mould	Color	Batch number
Filtek Z350 XT (3M ESPE, St.Paul, Minessota, USA)	Combination of aggregated zirconia/silica cluster with primary particle size (5-20 nm), and nonagglomerated silica filler (20 nm). 78.5 Wt%.	Bis-GMA, UDMA, TEGDMA and Bis-EMA	A2E, enamel	6BW
Grandio (VOCO, Cuxhaven, Low Saxony, Germany)	Ceramic glass fine particles (1μm), spherical silicium dioxide (20-60 nm). 87.0 Wt%.	BisGMA, UDMA and TEGDMA	A2, enamel	732242
Esthet X (DENTSPLY, Milford, Delaware, USA)	Barium boron fluoralumino silicate glass with particles sizes (0.6-0.8 μm) and silica nanofiller (0.04 μm). 77.0 Wt %.	Bis-GMA, Bis-EMA and TEGDMA	A2, body	070724

(GPa); *L*– support width (mm); *F1* – load (N) at convenient point that is in straight line portion of the trace; *f* – deflection of the test sample at load *F1* (mm); *b* – breadth of the test sample (mm); and *h* – height (mm) (13).

Diametral tensile stength

Ten samples of each material were made using a PTFE split mould (6 mm diameter and 3 mm thickness). After that, were mounted in a universal testing machine and tested with 1.00 mm/min of cross-head speed. The diametral tensile strength (MPa) was converted using the following formula*:* (2×p)/(¶×d×t). Were *p* is the ultimate tensile strength (N), *d* is the diameter (6 mm) and *t* is the thickness (3 mm).

Knoop microhardness

Ten samples (n=10) of each composite resin were made using a PTFE split mould (6 mm diameter and 3 mm thickness). Each sample was submitted to one indentation at knoop microhardness tester (Shimadzu HMV, Shimadzu, Japan, Kansai, Kyoto) using a load of 100 g for 15 s. The results of each previous test were analyzed by ANOVA and Tukey`s test (α= 0.05).

Weight filler content

One sample with 20 mg was made to each composite resin group. After this step, were inserted in platine crucible and submitted to temperature heating between 20-700 °C/min inside of machine for calculate the weight filler content (TGA 2050 dispositive, *TA Instruments* representative, USA, Delaware, New Castle*)*. The organic matrix decomposition temperature and weight filler content were registred. When stabilized sample weight, the inorganic content (Wt%) was registred (14, 15).

RESULTS

The results are summarized in Tables 2-4. A significant difference was observed when composites with nanoparticles nanohardness (p=0.00, Grandio enamel > Filtek Supreme XT enamel > Esthet X Improved enamel) and elasticity modulus results (p=0.00, Grandio enamel > and Filtek Supreme XT enamel = Esthet X Improved enamel) were compared. The weight filler content (wt%) results were, in decrease order, 87.00 (Grandio enamel), 76.80 (Esthet-X Improved enamel) and 76.54 (Filtek Supreme XT enamel). The compressive strength results weren`t statistically different applying ANOVA (p=0.87, Filtek Supreme XT enamel = Grandio enamel and = Esthet X body). A significant difference was observed when flexural strength (p=0.02, Filtek Supreme XT enamel > Grandio enamel and = Esthet X body), diametral tensile strength (p=0.03, Filtek Supreme XT enamel = Grandio enamel and > Esthet X body), flexural modulus (p=0.00, Grandio enamel > Filtek Supreme XT enamel > Esthet X body) and knoop microhardness (p=0.00, Grandio enamel > Filtek

Table 2. Nanohardness, elastic modulus and weight filler content of the tested composite resins

	Nanohardness (MPa)		Elastic modulus (GPa)		Weight filler content (wt%)
	Mean	SD	Mean	SD	
FILTEK Z350 XT (Nanofilled)	474.79[b]	21.77	12.77[b]	0.89	76.54
GRANDIO (Nanohybrid)	727.01[a]	21.55	19.78[a]	1.51	87.00
ESTHET X (Nanohybrid)	392.94[c]	25.88	12.30[b]	0.40	76.80

Means followed by different letters are statistically different (p<0.05).

Table 3. Compressive strength, flexural strength and flexural modulus of the tested composite resins

	Compressive strength (MPa)		Flexural strength (MPa)		Flexural modulus GPa)	
	Mean	SD	Mean	SD		
FILTEK Z350 XT (Nanofilled)	184.67[a]	57.18	123.29[a]	21.92	8.50[b] 2.02	
GRANDIO (Nanohybrid)	181.83[a]	47.77	103.23[b]	14.32	11.53[a]	1.36
ESTHET X (Nanohybrid)	173.55[a]	39.73	106.51[ab]	11.52	6.46[c] 1.39	

Means followed by different letters are statistically different (p<0.05).

Supreme XT enamel > Esthet X body) of composites with nanoparticles where compared.

DISCUSSION

The milling procedure used to make filler particles usually cannot reduce the filler particle size below 100 nm. The nanotechnology manufactures smaller filler particles with average size of 40 nm or 0.04 μm (1 μm is equal to 1000 nm in scale). The same filler size has been reached by microfilled composites since 70's. However, the real innovation that implies better mechanical behavior is the nanofiller's possibility to improve the load of the inorganic phase in 80 Wt% when compared to microfilled composites 50 Wt% for example (16).

Restorations in functional areas are exposed to attrition and wear, then the hardness may determine the abrasion resistance. As the filler is very small, nanohardness was applied in order to record the behavior in a minor area. This test was realized with Fischerscope equipment that permits realization of indentation dynamic tests in 0.4 to 1000 mN load scale with possibility of 1 to 999 load steps number, allowing load test speed variation. The knoop microhardness (KHN) observed for Esthet X comply with 54.45 (±1.47) previously registered in the dental literature validating the used methodology (17). However, for Supreme XT the average 54.40 (±2.40) was previously registered in the dental literature (18).

Nanohardness test give little information about the bulk of the material, because of the limited depths of penetration and the small loads applied. Thus, elastic modulus values must be examined in conjunction with the microstructure of the material's surface (19). The results (GPa) obtained in this study for elastic modulus are similar to the average previously recorded as 12.40, 12.70 for Supreme XT and 20.20, 20.40 for Grandio (20, 21). Besides, the media previously recorded ranged from 9.31 to 12.54 GPa for spherical fillers model dental resin-composites and from 14.09 to 17.03 GPa for irregular fillers (19). However, different averages has been reported as 8.2 (±1.00), 5.76 (±1.49) for Supreme XT, 14.10 (±1.50) for Grandio enamel and 6.93 (±0.69) for Esthet X (7, 16).

Composite resins would suffer a "barrel" effect when submitted to a compressive test and expand until plastic deformation occurs (22). The results (MPa) obtained for Mitra *et al*. (2003) methodology and Filtek Z350 XT manufacturer were different than the obtained in this study (3).

The diametral tensile strength is a mechanical property used to understand the behavior of brittle materials when exposed to tensile stress commonly observed in anterior restorations. The results (MPa) obtained in this study are similar to the average previously recorded as 44.42, 58.00 for Supreme XT, 49.24, 54.6 for Grandio enamel and 42.87 for Esthet X (17, 23, 24). All tested composite resins obtained higher averages than ADA specification n. 27 for direct filling resins (25).

The results (MPa) obtained in this study for flexural strength, that realize simultaneously tensile, compression and shear tensions, are similar to the average previously recorded as 118.00 (±12.00), 119.43 (±18.68) for Supreme XT, 107.00 (±12.00) for Grandio enamel (7, 16). However, different results were obtained as 173.70 (±30.40), 154.40 (±29.80) for Supreme XT (18, 22) and 145.67 (±13.96), 119.48 (±2.10) for Esthet X (16, 24).

The flexural modulus determines the composite resins relative stiffness. The results (GPa) obtained in this study are similar to the average previously recorded as 8.20 (±1.00), 8.80 (±0.70) for Supreme XT, 14.10 (±1.50) for Grandio enamel and 6.93 (±0.69) for Esthet X (7, 16, 22).

The null hypothesis was rejected. The results suggest that the weight filler content has direct relation with composite resins with nanoparticles mechanical properties. The results (Wt%) obtained in this study are similar to the manufacturers information. Weight filler content results of some authors could explain the different averages between groups (15, 26). From our results a high contact surface observed between nanofillers and organic phase improving the material hardness. These data coincide with other results (17). Besides, nanoparticles have a higher surface energy. It is necessary to chemi-

Table 4. Knoop microhardness, diametral tensile strength and weight filler content of the tested composite resins

	Knoop microhardness (KHN)		Diametral tensile strength (MPa)	
	Mean	**SD**	**Mean**	**SD**
FILTEK Z350 XT (Nanofilled)	123.10[b]	3.51	50.26[a]	6.66
GRANDIO (Nanohybrid)	172.52[a]	76.22	42.29[ab]	9.37
ESTHET X (Nanohybrid)	54.42[c]	1.46	41.50[b]	6.94

Means followed by different letters are statistically different ($p<0.05$).

cally inactivate the surface of nanoparticles in order to enable their isolation. The filler size and shape of composite resins seemed to be a fine tuning factor for the determination of elastic modulus. It has been found that the larger filler sizes tend to render the material stiffer and irregular filler shapes result in higher modulus values than resin composites with spherical fillers (19).

CONCLUSIONS

According to the methodology used, it may be concluded that:

The weight filler content has direct relation with composite resins with nanoparticles mechanical properties.

High contact surface observed between nanofillers and organic phase improving the material hardness.

The larger filler sizes tend to render the material stiffer and irregular filler shapes result in higher modulus values than resin composites with spherical fillers.

Further studies should be carried out to improve the knowledge of composites with nanoparticles mechanical behavior.

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Received: 11 07 2011
Accepted for publishing: 21 12 2012