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Evaluation of inorganic particles of composite resins with nanofiller content

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SUMMARY

The purposes of this study were evaluate by energy dispersed X-ray (EDS) and scanning electron microscopy (SEM) the inorganic particles of three nanofilled composite resins, comparing particles sizes, shape and composition, and the filler weight content by thermogravimetric analyzes (TGA). Three composite resins classified as nanofilled were selected to this study: Esthet-X; Grandio; Filtek Supreme XT. The shade was standardized (A2) for enamel (E) or dentin (D). Ten samples with 20 mg (±10 mg) of each composite resin were submitted to thermogravimetric analyzes (TGA) in order to record the filler weight content (wt%). The amount of inorganic phase ranged from 75.75 to 87 wt%, to Esthet-X (D) and Grandio (D), respectively. The filler composition was analyzed by energy dispersed X-ray (EDS), and the size and shape were evaluated by scanning electron microscopy (SEM). The filler average size (µm) obtained by SEM were: Esthet-X (E) 1.16; Esthet-X (D) 1.39; Filtek Supreme XT (E) 0.6 (nanocluster); Filtek Supreme XT (D) 1.14 (nanocluster); Grandio (E) 2.05 and Grandio (D) 3.1. Silica (SiO_2), Ba and Al were observed through EDS. The shape of Esthet-X and Grandio fillers showed similar characteristics with high quantity of irregular inorganic particles and heterogeneous filler. However, Filtek Supreme XT showed spherical and regular particles with homogeneous distribution and sizes. Based in the analysis of nanofilled composites inorganic phase, inconsistencies of weight content, composition, shape and size can be stated between the literature and manufacturer's instructions.

Key words: dental materials, nanotechnology, fillers, composite resin.

INTRODUCTION

The fillers are incorporated into the composite resin, as the inorganic phase, due to insolubility on oral field, simple manipulation, moderate cost, ability to be bonded to dimetacrilates (1). The filler average size is used for composite resin classification (2, 3): macrofilled or traditional composites (to 50 µm), hybrid (8 to 30 µm), micro-hybrid (0.7 to 3.6 µm), microfilled (0.04 to 0.2 µm) (4), and, more recently, nanofilled (0.005 to 0.04 µm) (5). Filler particles are produced by three distinguish methods. The grinding and milling of quartz or glass that produces irregular particles between 0.1 to 100 µm size. The pyrolytic or precipitation process of colloidal silica results in particles of submicrometrical size (~0.04 µm) and the controlled growth of silicon dioxide up to 5 nm by nanotechnology introduced in dentistry in 2003 (6).

Besides size, the amount and distribution of these fillers also have influence on the classification (7). The colloidal silica fillers are used to minimize the interparticle spacing, increasing the filler weight content (wt%) and improving the mechanical behavior of composite resin (8). The introduction of nanofillers enhances aesthetics due to the size smaller than the wave length of visible light controlling a refractive index (9). The manufacturer's objective is develop nanofilled composites that could be used to either posterior and anterior teeth, getting high initial polishing and capability to maintain it, like microfilled composite resin, and support high stress bearing areas, like micro-hybrids (6, 10, 11).

Therefore, the aims of this study were to evaluate by energy dispersed X-ray (EDS) and scanning electron microscopy (SEM) the inorganic particles of three nanofilled composite resins, comparing particles

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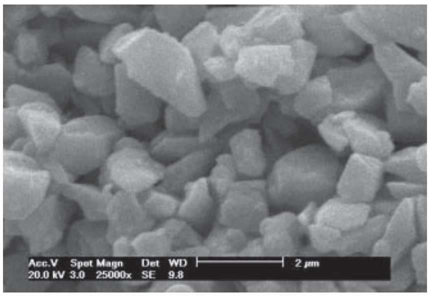

Fig. 1. SEM of Esthet-X enamel fillers

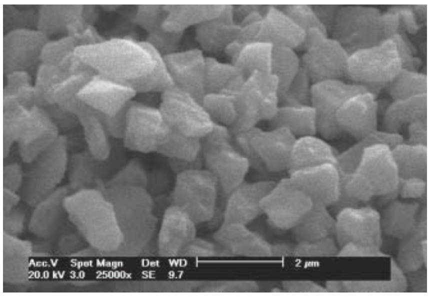

Fig. 2. SEM of Esthet-X dentin fillers

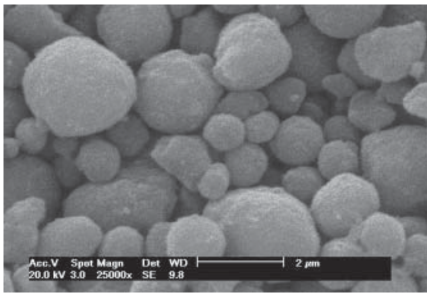

Fig. 3. SEM of Filtek Supreme XT enamel clusters

sizes, shape and composition, and the filler weight content by thermogravimetric analyzes (TGA).

MATERIAL AND METHODS

Three composite resins classified as nanofilled by manufacturers were used in this study: Esthet-X (Dentsply-Caulk, Milford, DE, USA); Grandio (Voco, Cuxhaven, Germany); Filtek Supreme XT (3M-ESPE, St. Paul, MN, USA). The A2 enamel and dentin shades were standardized for all samples (Table 1).

Thermogravimetric Analysis (TGA)

For each composite resin, 20 mg ($\pm$10 mg) were weighted on a precision balance AG 204 (Mettler/Toledo, Zurich, Schwerzenbach, Switzerland) and heated at 20ºC/min rate from 20 to 700ºC in TGA device – TGA 2050 (TA Instruments, USA). The organic matrix was completely eliminated when the stabilization of weight occurred. The difference between initial and final weight determinate filler weight content in percentage (wt%) (7).

Scanning-Electron Microscopy Analyzes (SEM)

Samples (0.5 g) were prepared using a single increment of each composite resin (11). The dissolution of organic matrix occurred with a dripping of organic solvent (acetone P. A., Klintex, Cachoeirinha, RS, Brazil). The process was repeated fifteen times to ensure a complete elimination of organic matrix, evidencing filler particles, that were stored during 6 hours at 37ºC (002 CB, Fanem, São Paulo, SP, Brazil) (11).

The fillers were observed by SEM (XL 30, Phillips, Eindhoven, Germany). Qualitative analysis was

Table 1. Table of materials used in the research

Group	Trademark	Batch#	Organic Phase	Filler composition	Filler average size (µm)	Filler shape	Filler Content (wt%)
Esthet-X D	Esthet-X (Dentsply, Caulk, Milford, USA)*	0509082	UDMA, Bis-GMA, TEGDMA	Barium boron fluoralumino silicate glass	0.6-0.8 space between them filled by nanoparticles (0.04)	Irregular	71.9
Esthet-X E	Esthet-X (Dentsply, Caulk, Milford, USA)*	0509141	UDMA, Bis-GMA, TEGDMA	Barium boron fluoralumino silicate glass	0.6-0.8 space between them filled by nanoparticles (0.04)	Irregular	71.9
Filtek Supreme XT D	Filtek Supreme XT (3M ESPE, St Paul, MN, USA)*	5AJ	Bis-GMA, Bis-EMA, UDMA, TEGDMA	Combination of aggregate zirconia/silicon cluster filler	0.005-0.02 (particle) 0.6-1.4 (clusters)	Spherical	78.5
Filtek Supreme XT E	Filtek Supreme XT (3M ESPE, St Paul, MN, USA)*	6BW	Bis-GMA, Bis-EMA, UDMA, TEGDMA	Combination of aggregate zirconia/silicon cluster filler	0.005-0.02 (particle) 0.6-1.4 (clusters)	Spherical	78.5
Grandio D	Grandio (Voco, GMBH – Cuxhaven – Germany)*	581271	Bis-GMA, TEGDMA	Silicon dioxide and fine particles of glass	0.02-0.05	Spherical	87
Grandio E	Grandio (Voco, GMBH – Cuxhaven – Germany)*	732242	Bis-GMA, TEGDMA	Silicon dioxide and fine particles of glass	0.02-0.05	Spherical	87

* According to the technical information of the product catalogs of the manufacturer (2007; 2005; 2005 respectively).

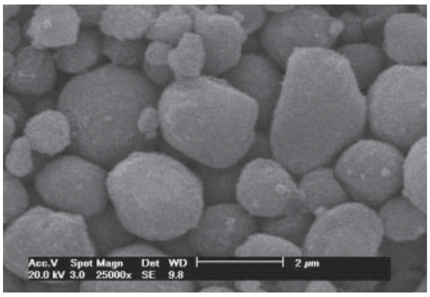

Fig. 4. SEM of Filtek Supreme XT dentin clusters

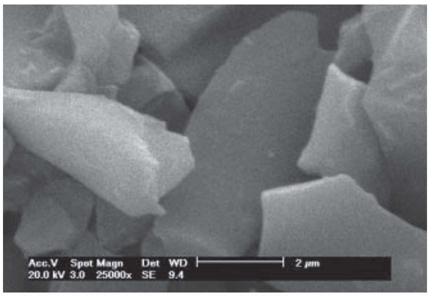

Fig. 5. SEM of Grandio enamel fillers

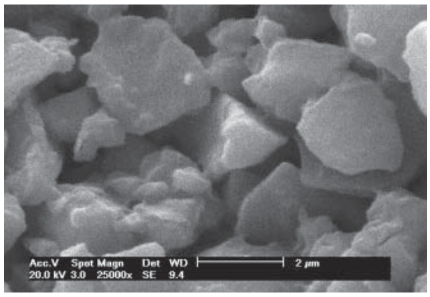

Fig. 6. SEM of Grandio dentin fillers

performed in order to classify the fillers according to shape and homogeneity. Quantitative analyze of particles size (μm) was also observed with introduction of images on Image Pro Plus 4.5.1 software (Media Cybernetics, Inc., MD, USA). Data were submitted to ANOVA, followed by Tukey test with significance of 5%. Furthermore, the filler composition was analyzed by the energy dispersed X-ray (EDS).

Table 2. Descriptive table of filler weight content (wt%) evaluated by Thermogravimetric Analysis (TGA)

Composite resin	wt%
Esthet-X D	75.75
Esthet-X E	76.8
Filtek Supreme XT D	76.54
Filtek Supreme XT E	76.22
Grandio D	86.89
Grandio E	87

Table 3. Descriptive table of observed elements by Energy Dispersed X-ray Spectrum (EDS)

Groups	Ba	Al	O	Si
Esthet-X E	37.56	6.15	23.37	32.92
Esthet-X D	37.00	6.05	17.42	39.53
Filtek Supreme XT E	–	–	40.79	59.26
Filtek Supreme XT D	–	–	37.38	62.62
Grandio E	–	10.38	36.93	52.70
Grandio D	5.18	10.12	33.27	51.42

– not recorded.

Table 4. Descriptive table of mean size (μm) of inorganic particle and clusters of particles and standard deviation

Composite resin	μm	Standard deviation
Grandio D	3.10 A	2.27
Grandio E	2.05 AB*	2.39
Esthet-X D	1.39 B	0.44
Esthet-X E	1.16 B	0.41
Filtek Supreme XT D	1.14 AB*	1.19
Filtek Supreme XT E	0.60 B	0.74

* Averages followed by different letters differ at the 5% significance by analysis of variance and Tukey.

RESULTS

When samples were analyzed by thermogravimetry (TGA), it was observed that weight contents of filler varied between composites ranging from 75.75 to 87 wt%, to Esthet-X (D) and Grandio (E) respectively. However, no relevant differences were recorded between enamel and dentin shades to the same composite resin trademark (Table 2).

Using energy dispersed X-ray (EDS), the composition of fillers was recorded for each group by weight of each element (wt%). It was observed that oxygen and silica are the main elements in all composite resins. Barium and aluminum were also observed in exception of barium in Grandio (E) (Table 3).

The SEM analysis showed that Grandio (D) presents the higher average of filler size (3.14 μm) in comparison to Filtek Supreme XT (E) (0.6 μm). Significant differences of filler size were recorded between the nanofilled composites when data were submitted to ANOVA and Tukey ($p<0.05$) (Table 4).

Morphological aspects of filler, observed in SEM, showed similar morphology and size of Esthet-X and Grandio inorganic particles, without qualitative differences when enamel and dentin shades were compared. For those composites, a majority of micro-hybrid irregular fillers are interposed with small amount of nano particles. The Filtek Supreme XT showed particles shape and sizes completely different form the other two composite resins. Round and homogeneous nanosized particles associated in clusters could be recorded without differences between enamel and dentin shades (Figures 1-6).

DISCUSSION

Thermogravimetry is a technique used to evaluate filler concentration in percentage by weight, comparing the difference in weight before and after complete elimination of all organic content through heating up to 700ºC (12). In comparison to manufacturer's instructions (Tabel 1), the filler weight content recorded in this study is in agreement to Grandio (87%) and an augmentation could be detected to Esthet-X from 71.9% to 76.8% (E) and 75.75% (D) as observed in this study. However, a slight reduction in filler weight percent was observed for Filtek Supreme XT from 78.5% according to the manufacturer to 76.22% (E) or 76.54% (D). Using the same methodology, a previous study recorded the same amount of inorganic phase for Grandio and Supreme (11), while an increasing for Esthet-X was also recorded (12). Such differences could be partially explained by the heterogeneous nature of composites, as it is an association of non miscible organic and inorganic materials.

The filler weight content has a direct and positive correlation with mechanical behavior (13). Significant improvement of diametral tensile strength and knoop microhardness was recorded for Grandio in comparison to Supreme and Esthet-X in a previous study (14). This difference can be explained by the high amount of inorganic phase observed for Grandio (87%).

The composite resin with nanofiller was developed as a material to be used either anterior or posterior teeth, with high initial polish and superior polish retention as well as excellent mechanical properties suitable for high stress bearing restorations (6). This mechanical behavior is directly associated to the inorganic filler of composites. Observation of particles by SEM with different magnification was used to analyze shape and size. Using this method and a qualitative analyzes, it could be obtained an adequate classification to clinical utilization (4). According to the mean size of particles observed in this study and following the classification purposed by Ferracane (4), Grandio and Esthet-X could be assorted as nanohybrid. However Filtek Supreme XT showed smaller, rounded and homogenous fillers grouped in clusters (0.6 µm) that could be the only classified as a nanofilled composite in accordance to previous studies (6, 11). About the morphology observed in SEM, Esthet-X presented irregular particles with homogenous sizes (12) as well as Grandio (11).

The common nanofiller composition is based on barium, aluminum and silica (15). The recorded elements described in this study (Table 3) are in accordance to a previous study (15) with similar amounts of these components. However, no zirconium was observed for Supreme XT. This distortion might be explained by technical limitation of EDS that analyses surfaces at maximum 6 µm deep. Higher radiopacity is expected for Esthet-X (enamel and dentin) followed by Grandio (dentin) due to the presence of barium. This physical property allows the long term radiological evaluation for secondary decays.

Based on the limitations of this study's analysis, it must be carried out further studies with TGA and EDS due to disagreements between literature and manufacturers.

CONCLUSION

According to the methodology applied, Filtek Supreme XT (3M ESPE) is the only tested composite that is in agreement to the manufacturer and literature references. Between the tested composites, it can be stated that Filtek Supreme XT is the only composite capable to be classified as a nanofilled. The other two tested composites, Esthet-X and Grandio, should be classified as nanohybrid resins highly filled with nanosized particles.

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