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FRACTAL ANALYSIS OF SOME RESTORATIVE NANO-FILLED COMPOSITE MATERIALS MICROSTRUCTURE

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Abstract

Aim. The aim of the present study was to compare the microstructure of some commercially available resin-based restorative nano-composites using fractal analysis.
Materials and methods. 20 samples of two nanocomposites Filtek Supreme XT and Filtek Ultimate (3M ESPE) were examined by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Using element mapping, the filler particles were identified and their volume percentages and cluster particle size distributions were calculated. The fractal analysis was performed on microscopic images and the average fractal dimension was calculated for both type of materials.
Results. The SiO_2/ZrO_2 particle percent in volume was 45.73/12.61 (% vol.) for Filtek Ultimate composite resin and 48.65/9.66 (% vol.) for Filtek Supreme XT. The average of SiO_2/ZrO_2 cluster particle size was 0.26/0.20 µm for Filtek Ultimate composite resin and 0.36/0.21 µm for Filtek Supreme XT. The fractal dimension was 1.73 for Filtek Ultimate and 1.65 for Filtek Supreme XT.
Conclusions. Filtek Supreme XT composite resin presents a higher SiO_2 but a lower ZrO2 particle percentage in volume when compared to Filtek Ultimate composite resin. Both SiO_2 and ZrO_2 cluster particle size are higher in Filtek Supreme XT than in Filtek Ultimate. Filtek Ultimate microstructures have an increased fractal dimension when compared to Filtek Supreme XT, as an expression of a better particle-matrix adhesion surface.

Keywords: nanofilled composite, microstructure, Filtek Supreme XT, Filtek Ultimate, fractal analysis

Introduction

The enormous research on ceramic nanosized particles during the past years has led to numerous innovations. One of these was the development of nano-composite materials, which are a relatively new class of materials of ultrafine phase dispesion, typically ranged between 1 and 100 nm. Experimental studies showed that various types of nano-composites lead to new and improved properties when compared to their micro and macro-composite counterparts (1). Reports of particulate-based composites suggested that conductivity, dimensional stability, mechanical and other properties may be improved by incorporating small filler particles (2). Dental restorative composites generally consist of an organic polymerized matrix, inorganic fillers such as quartz, borosilicate, silica and silane-coupling agent, which connects the inorganic fillers to the organic matrix (3,4). The latest development in the field was the introduction of nanofilled materials, by combining nanosized particles and nanoclusters in a conventional resin matrix. Nanofilled materials offer excellent wear resistance, strength and ultimate esthetics due to their exceptional polishability and shinny appearance (5,6).
In the polymer reinforced materials, the adhesion between the reinforcing phase and the matrix is of great importance and it is controlled by the following factors:

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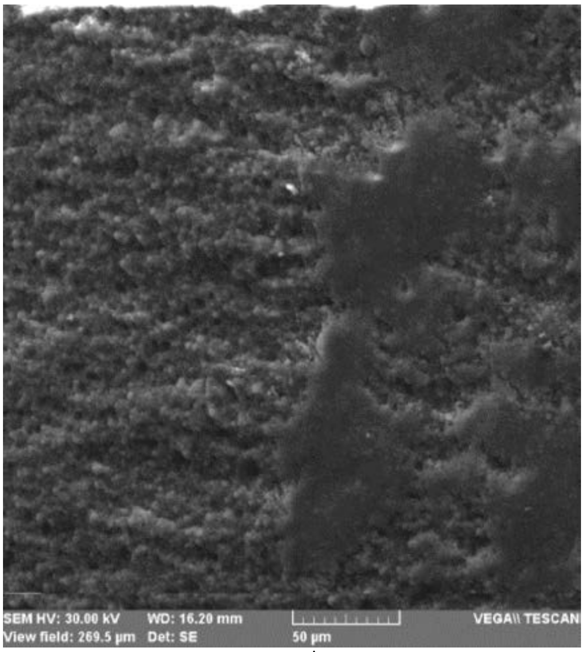
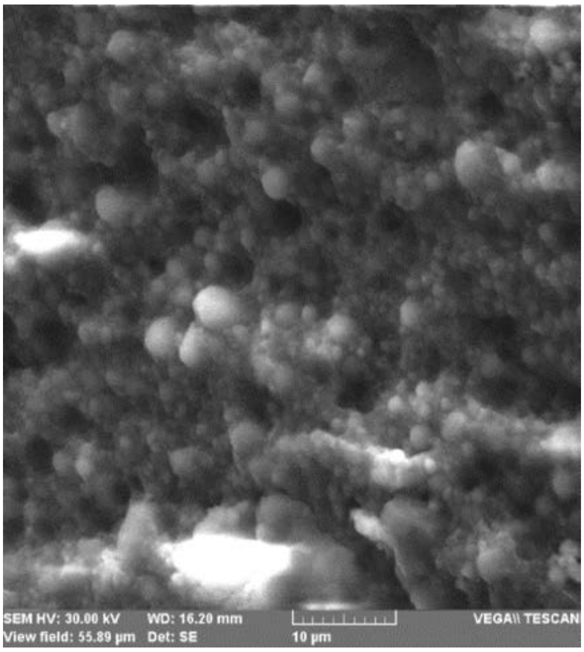
Table 1. Restorative material used in this study

Material	Matrix	Filler
Filtek Supreme XT	Bis-GMA, Bis-EMA TEGDMA UDMA	Silica and zirconia 0.01-3.5 µm, average size 0.6 µm 60% volume
Filtek Ultimate	Bis-GMA, Bis-EMA TEGDMA UDMA PEGDMA	Silica and zirconia 0.01-3.5 µm, average size 0.6 µm 60% volume

Bis-GMA: Bisphenol A diglycidylmethacrylate; Bis EMA(6): Bisphenol A polyethylene glycol diether dimethacrylate; UDMA: Urethane dimethacrylate; TEGDMA: Triethyleneglycoldimethacrylate; PEGDMA: poly(ethylene glycol) dimethacrylate



a)



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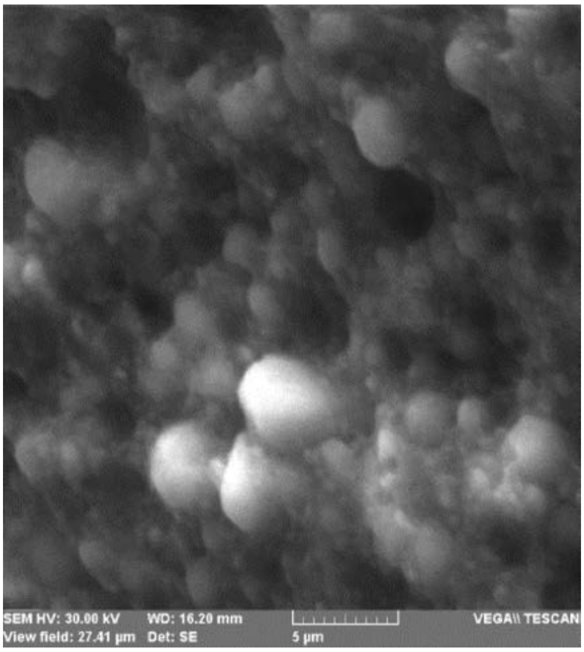

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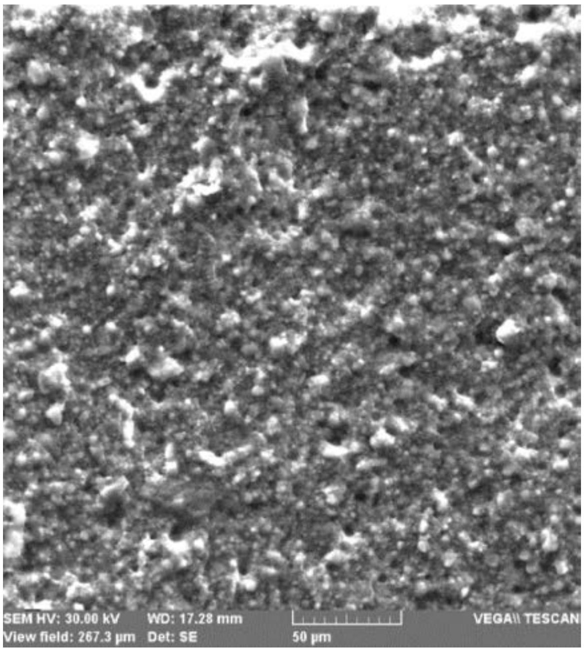

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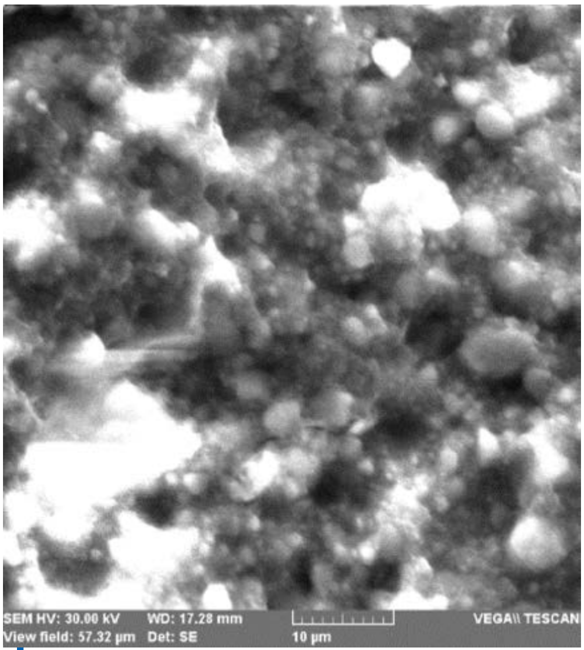

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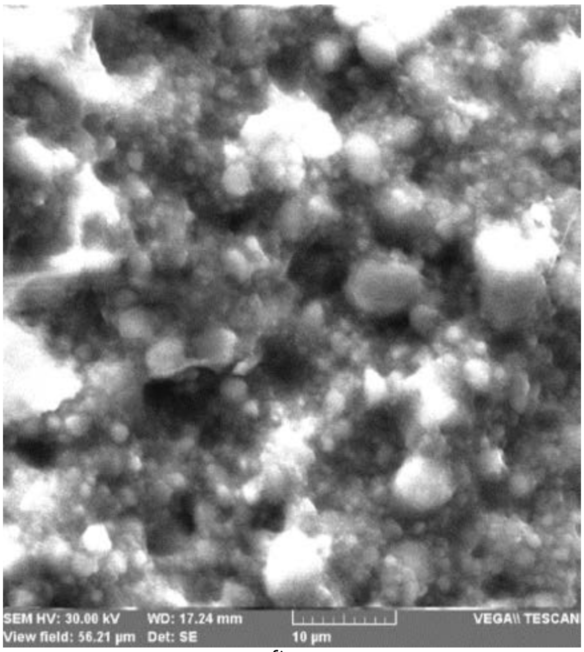


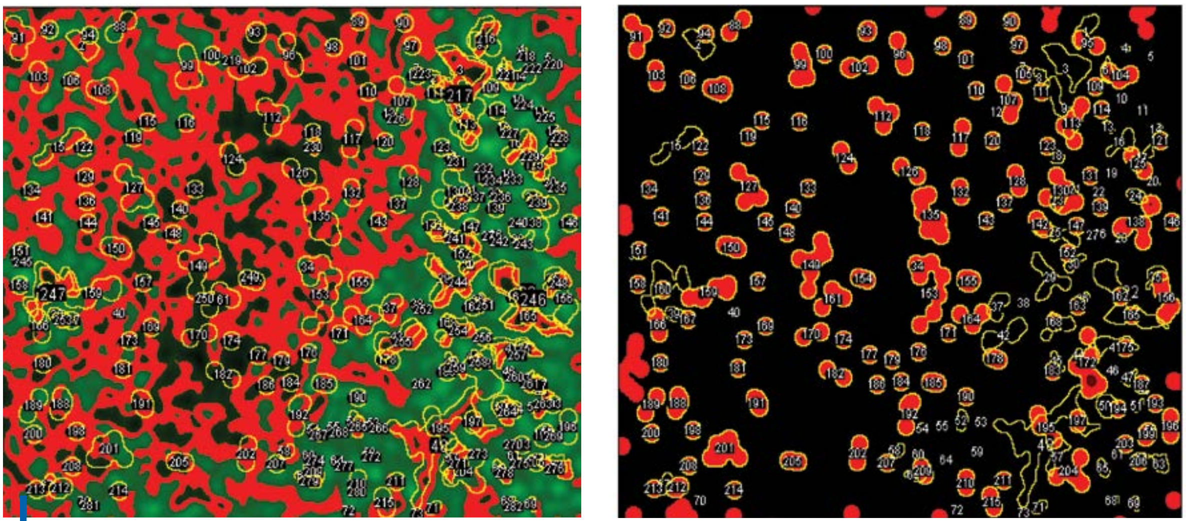
f)

Figure 1. Microstructures of Filtek Supreme XT (a-c) and Filtek Ultimate (d-f) at various magnifications: 1000× (a,d), 5000× (b,e), and 10000× (c,f)

i) the particles surface on which chemical bonds are formed with the functional groups of the matrix; ii) the particle surface roughness which extends the effective area for physical contact with the matrix.
It is known that the micro- and nanosized particle surfaces have a fractal nature that can be characterized by the fractal dimension and other fractal parameters. The geometry of the interface between matrix and filler particle can be used to compute the interfacial fractal dimension, D. The smoothness or straightness of a curve can be expressed by the fractal dimension, D, where $1 \leq D = 2$ [7]. A perfect smooth line has D=1, while a highly irregular line has D=2. Similarly, the surface irregularities and roughness are also characterized by the fractal dimension, with $2 \leq D \leq 3$, where D=2 corresponds to a perfectly smooth surface, while D=3 to a highly disordered one. Thus, the interface between the filler particles and polymeric matrix can be quantified (8).
Several specialized software were developed to perform fractal analysis. Generally, they express a fractal dimension called the box counting fractal dimension or DB. The DB is the slope of the regression line for the log-log plot of box size (or scale) and count from a box counting scan. The ratio quantifies the increase in detail with increasing magnification or resolution seen in fractals but also in microscopy. It is measured by the ratio of increasing detail with increasing scale (ε).
The aims of the present study were to evaluate and compare the microstructure of two commercial resin based restorative nano-composites using the fractal analysis.

Experimental technique and materials

Two commercially available composite resins: Filtek Ultimate and Filtek Supreme XT (3M ESPE) were selected for this study (9,10). The compositions of the studied composite according to the producer's specifications are presented in Table 1, where similar dentin shades (A3) were used. Twenty cylindrical samples of each material of 5 mm in diameter and 2 mm in width were prepared by placing them in cylindrical ringed-shaped anti-sticking pre-molds. The specimens were polymerized using the high intensity LED mdium emmitance unit with the emitted wavelengths between 440 and 460 nm (Optilight LD Max, Gnatus, Ribeirao Preto, Sao Paulo, Brasilia). The photo-polymerization time was 40 seconds.
The samples were studied by scanning electron microscopy (SEM) using Vega Tescan LMH II equipment. The SEM images were taken in secondary electrons (SE); the acceleration voltage was equal to 30 kV, and the emission current was between 0,5pA and 500nA. The energy dispersive detector for X-rays (EDX), QUANTAX - Bruker equipment was used for chemical composition measurements. From element mapping, the filler particles were identified and their volume percentages and cluster particle size distributions were calculated.
Using microscopic images the fractal analysis was performed and the average fractal dimension was calculated for both types of materials. Firstly the microscopic images were converted in binary format and then they were analyzed using the routine FracLac in Image J (11). Several grids of decreasing caliber (box size) are placed over an



a) b)

Figure 2. Particles identification from element mappingin Filtek Ultimate: a) SiO_2; b) ZrO_2

Table 2: Filler loading, average of particle size and fractal dimension for filtek ultimate and Filtek Supreme XT

	Filtek Ultimate	Filtek Supreme XT
ZrO_2 particle percent (% vol.)	12,612	9,669
SiO_2 particle percent (% vol.)	45,732	48,658
Average SiO_2 cluster particle size (μm)	0.26±0.02	0.36±0.02
Average ZrO_2 cluster particle size (μm)	0.206±0.003	0.218±0.004
Fractal dimension	1.7365	1.6578

image and the number of boxes that contain pixels is counted for each grid (boxes containing pixels correspond to the number of parts or detail). Data are collected for each box of every grid (grid size is specified by the user or calculated automatically). The DB is based on the calculation of a scaling rule or fractal dimension using [8],

$D_B = -\lim[\log(N_\varepsilon)/\log(\varepsilon)]$ (1)

The count refers to the number of grid boxes that contained pixels in a box counting scan. Epsilon is the scale applied to an object. In FracLac, the scale refers to box size relative to image size, where image size means the boundary containing the pixelated part of an image.

Results and discussions

In Fig. 1 the typical microstructures of Filtek Supreme XT and Filtek Ultimate are given for different magnifications. Uniform particles distributions are observed and micro-segregates of silica and zirconia particles. Using the chemical structure obtained by EDX measurements of the materials tested, from the element mapping (for more details see (12)) it is possible to identify the SiO_2 and ZrO_2 particles using the ImageJ software [11]. Some typical results are given in figs. 2a, b for Filtek Ultimate. Moreover, from the ratio between particle area and total image area, the filler particle content can be calculated in volume percentages.

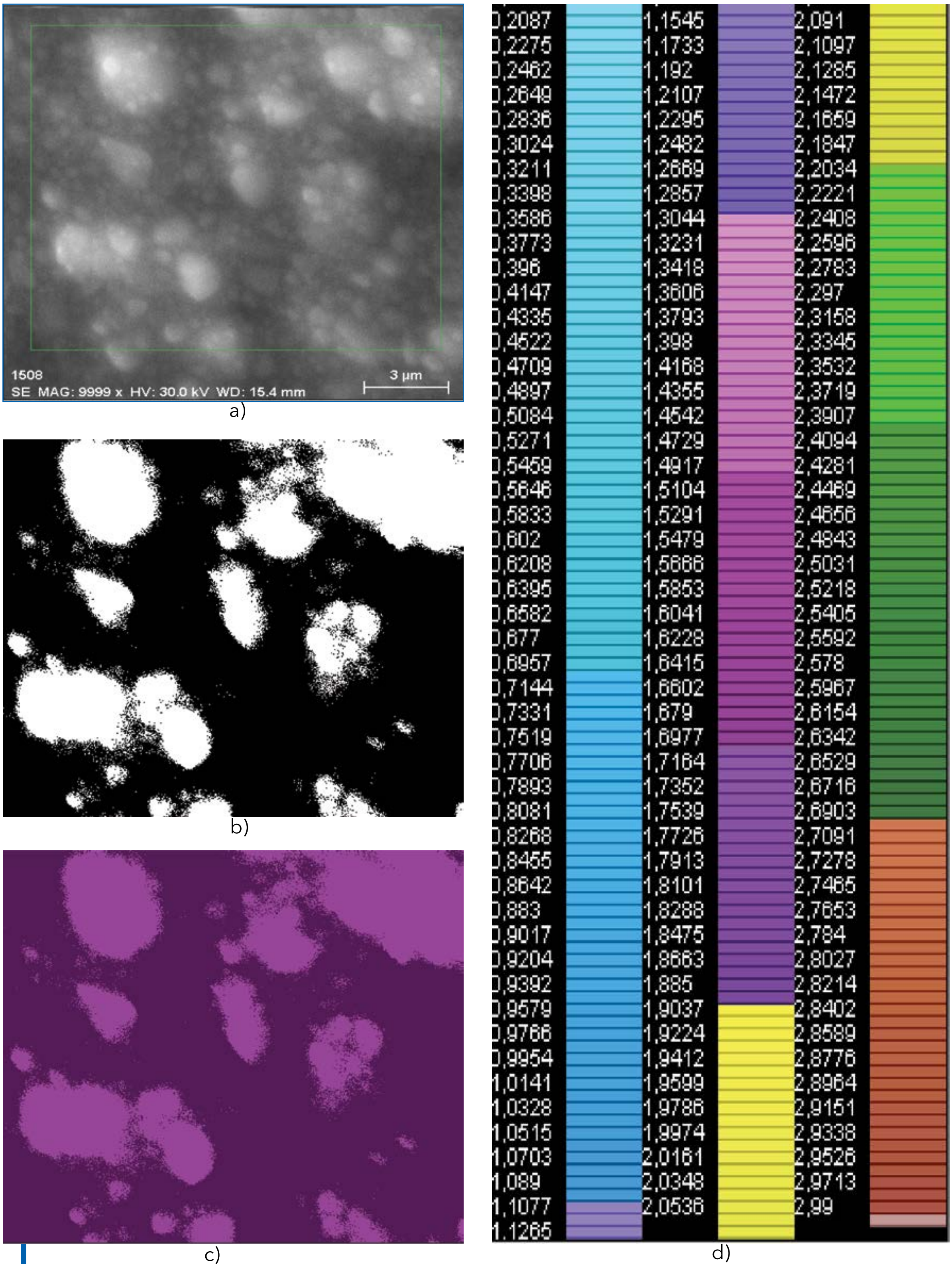


Figure 3. Typical fractal analysis of Filtek Ultimate nanofilled composites: a) microscopic image; b) binary conversion, c) regions of similar fractal dimension as given by the colour codes (d)

The results of filler loading and filler size evaluation were presented in Table 2. The results showed almost the same filler loading for Filtek Ultimate and Filtek Supreme XT, i.e. about 59 volume %, the values being in keeping with the producer specifications. We noted a slightly higher percent of zirconia particles in the case of Filtek Ultimate than for Filtek Supreme XT (for more details see [12]).

Examples of microscopic images converted in binary format are presented in Fig. 3 a,b) for Filtek Ultimate.The results of FracLac in Image J evaluation of these samples are presented in Figure 3 c-d. In Fig. 3b the regions with similar

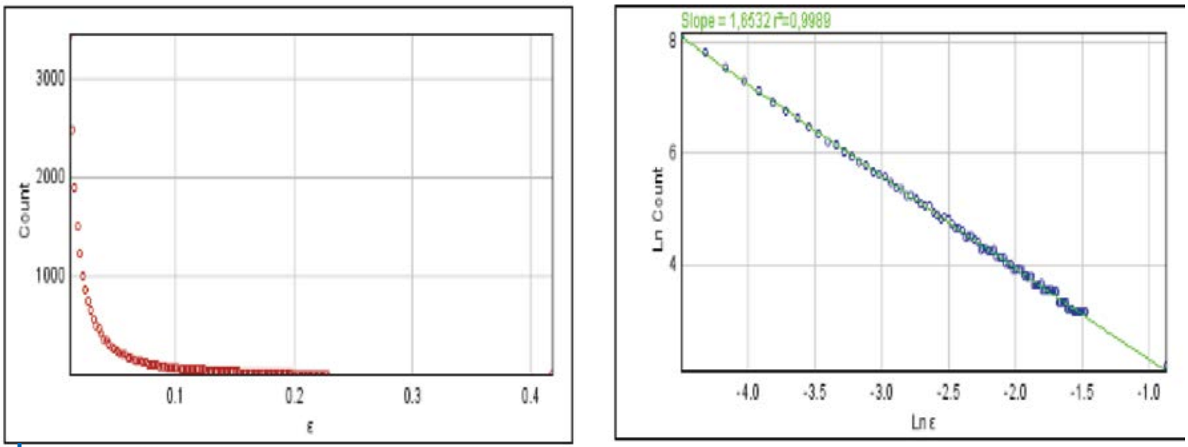


Figure 4. The (Nε)- (ε) and log(Nε) - log(ε) plots which give the fractal dimension for Filtek Ultimate

fractal dimension are plotted, where the coulour codes are given in Fig. 3 c. The fractal dimension results from the slope of log(Nε) - log(ε) plot (Fig. 4 a, b,) as being 1.6532 with a error r2=0,9989, i.e. a good accuracy of the results.

The values of fractal dimension for Filtek Supreme XT and Filtek Ultimate, as a average of all 20 samples evaluation are given in Table 2. Higher value of fractal dimension for Filtek Ultimate was obtained when compared to Filtek Supreme XT.

Fractal analysis is used for objectively analyzing complexity and heterogeneity, as well as some other measures of binary digital images: to measure difficult to describe geometrical forms where the details of design are as important as gross morphology (13-16). It is suitable for images of biological cells and other biological structures, including branching structures and textures, as well as for known fractals (17). Patterns can be easily extracted from many types of images and converted to binary digital images that can be analyzed (18-21).

Two different commercial composite resins were evaluated in the present study. Filtek Supreme XT is a nano-filled composite, having non-agglomerated nanoparticles and clusters of agglomerated zirconia/silica. In Filtek Ultimate Universal Restorative (10) the resin system is slightly modified from the original Filtek Supreme resin. The resin contains bis-GMA, UDMA, TEGDMA, and bis-EMA (6) resins. To moderate the shrinkage, PEGDMA has been substituted for a portion of the TEGDMA resin in Filtek Supreme XT restorative. The fillers are a combination of non-agglomerated/non-aggregated 20 nm silica filler, non-agglomerated/non-aggregated 4 to 11 nm zirconia filler, and aggregated zirconia/silica cluster filler (comprised of 20 nm silica and 4 to 11 nm zirconia particles).

The main objective of the present study was to observe a connection between the fractal dimension and microstructure. As the fractal dimension is increasing the higher are the irregularities at the matrix-filler particles interface, so the adhesion between those two components becomes stronger. This fact is influenced, in the case of the studied nanocomposites, by the clusters particle size.It was observed that the decreasing of the clusters dimension defines an increased fractal dimension. Similar studies made possible to understand the fracture behavior of the composites, and also confirmed the good potential of fractal analysis to explain complex mechanisms such as those involved in the fracture of brittle materials (14,15,18). Thus, the great potential of such method becomes more obvious.

4. Conclusions

Filtek Supreme XT composite resin present a higher SiO_2 but a lower ZrO_2 particle percent in volume when compare to Filtek Ultimate composite resin. Both SiO_2 and ZrO_2 cluster particle size are higher in Filtek Supreme XT then in Filtek Ultimate. Filtek Ultimate microstructure have an increased fractal dimension when compared to Filtek Supreme XT, as an expression of a better particle-matrix adhesion surface.

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Questions

Regarding the present study:

- ❑ a. Two micro-hybrid composites resins were analyzed
- ❑ b. A micro-hybrid and a nano-composite resin were analyzed;
- ❑ c. Two restorative nano-composites were analyzed;
- ❑ d. Two macro-filled restorative composites were analyzed;

The restorative composites used in the present study have the following filler load:

- ❑ a. Silica and zirconia 30% vol.
- ❑ b. Borosilicate and zirconia 60% vol.
- ❑ c. Silica 60% vol.
- ❑ d. Silica and zirconia 60% vol.

Regarding the fractal analysis, the fractal dimension, D, has the following value:

- ❑ a. D=1, for a highly irregular line;
- ❑ b. D=2, for a perfect smooth line;
- ❑ c. D=3, for a perfect smooth surface;
- ❑ d. D=2, for a highly irregular line.

Particle-matrix adhesion is not controlled by:

- ❑ a. The particle surface on which chemical bonds are formed with the functional groups of the matrix
- ❑ b. The particle surface roughness which extends the effective area for physical contact with the matrix.
- ❑ c. Silane-coupling agent, which connects the inorganic fillers to the organic matrix
- ❑ d. The filler particle size.