Evaluation of composition and morphology of filler particles in low-shrinkage and conventional composite resins carried out by means of SEM and EDX

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Objective: *The aim of this study was to characterize the chemical elements and morphology of filler particles of conventional and low-shrinkage composite resins. The main components were identified by means of energy-dispersive X-ray spectroscopy (EDX) microanalysis; whereas filler particles were analyzed morphologically by scanning electron microscopy (SEM).* ***Methods:*** *Four composite resins were studied: two conventional ones (Heliomolar and Tetric N-Ceram, Ivoclar Vivadent™) and two low-shrinkage ones (Aelite LS, Bisco™; and Filtek Silorane, 3M ESPE™). The material (five samples of each resin) was immersed in organic solvents to eliminate the organic phase and was assessed by SEM and EDX.* ***Results:*** *Although EDX measurements showed a high content of silicon in all samples, there were differences in the elemental composition. Aelite LS composite resin contained spherical and irregular particles, whereas the other composites contained only irregularly shaped filler particles. Heliomolar composite resin had the highest particle size.* ***Conclusion:*** *All composite resins contained silicon, but the other components were also found. Resins differed in terms of filler particle size and morphology.* ***Keywords:*** *Composite resin. Polymerization shrinkage. Filler particles. SEM. EDX.*

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Introduction

Volumetric polymerization shrinkage of regular dental restorative composite resins after curing is approximately 3-5%. Polymerization shrinkage stress in resin-based material can cause damage at the resin-tooth interface, formation of marginal gaps, marginal staining, post operative sensitivity and, consequently, early failure of composite resin restorations.[1-4] In an attempt to reduce the effects of polymerization shrinkage, dentists place restorative composites by means of incremental techniques[5-8] and polymerize them by means of continuous, stepped, ramped, and pulse-delay techniques.[9-12]

Changes in the formulation of composite restorative material have also been made in order to eliminate or reduce volumetric shrinkage and contraction stress during polymerization.[4,13,14,15] Main changes have involved monomeric composition and filler particle characteristics. New monomers for resin-based restorative material were developed and incorporated into commercial composite resins, such as siloranes, dimer acid-based dimethacrylate, tricyclodecane (TCD) urethane, Bis-EMA, and organically modified ceramics (ormocers).[16-19]

Regarding the filler particle content, contemporary composite resins (microhybrid and nanofilled material) contain a higher amount of inorganic particles (in volume and weight) with reduced dimensions.[17,18,20] According to the filler particle size, composites are classified as nanofillers (mean particle size 0.001-0.01 μm), microfillers (0.01-0.1 μm), minifillers (0.1-1 μm), midifillers (1.0-10 μm), and macrofillers (10-100 μm). Most commercial products are hybrid, containing different types of particles, such as silica and glasses, with two or more sizes. The filler loading increased in the content of particles (up to 60% by volume), which reduced the monomeric phase and, consequently, the volumetric polymerization shrinkage.[20-23]

The aim of this study was to investigate the composition of the filler particles of traditional and low-shrinkage composite resins. To this end, energy-dispersive X-ray spectroscopy (EDX) was employed. In addition, the morphological characteristics of the filler particles were determined by means of scanning electron microscopy (SEM). The research hypotheses tested were that there are differences between traditional and low-shrinkage composite resins regarding inorganic composition and filler morphology.

"The examination of the filler particles by SEM showed morphological variations among composite resins."

Table 1: Material, manufacturers, composition and lot number of composite resins analyzed in the present study (information obtained from MSDS provided by manufacturers).

Material (manufacturer)	Composition	Lot number
Heliomolar (Ivoclar Vivadent™, Schaan, Liechtenstein)	Bis-GMA, UDMA, 1,10-decanediol dimethacrylate, camphorquinone, silicon dioxide, ytterbium trifluoride and prepolymerized filler (prepolymers) (46% vol.)	K35053
Tetric N-Ceram (Ivoclar Vivadent™, Schaan, Liechtenstein)	Dimethacrylates, additives, catalysts, stabilizer sand pigments, barium glass, ytterbium trifluoride, mixed oxide and prepolymerized filler (prepolymers) (56% vol.)	L48183
Aelite LS (Bisco Inc.™, Schaumburg, IL, USA)	Bis-GMA, Bis-EMA, TEGDMA, camphorquinone, glass filler, amorphous silica (74 vol%)	0900005990
Filtek Silorane (3M ESPE™, St. Paul, MN, USA)	Bis-3,4-epoxycyclohexylethyl-phenyl-Methylsilane 3,4 Epoxy cyclohexyl cyclopolymethyl siloxane, camphorquinone, iodonium salt and electron donor, silanized quartz, yttrium fluoride (55 vol%)	N205711

Abbreviations: bis-phenol A diglycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), ethoxylated bisphenol A dimethacrylate (Bis-EMA) and triethylene glycol dimethacrylate (TEGDMA).

Material and methods

Two traditional composite resins (Heliomolar and Tetric N-Ceram, Ivoclar Vivadent™, Schaan, Liechtenstein) and two low-shrinkage composite resins[24] (Aelite LS, Bisco™, Inc., Schaumburg, IL, USA, and Filtek Silorane, 3M ESPE™, St. Paul, MN, USA) were selected for this study (Table 1). For each material, five samples were prepared from 60 ± 1 mg of resin. The unpolymerized composite resins were dissolved in 6 mL of acetone (99.5%) and centrifuged for five minutes. This procedure was repeated three times at intervals of 24 hours. Chloroform (99.8%) was then used in the same manner.[22] Remaining filler particles were immersed in 6 mL of absolute ethanol for one day, followed by air-drying overnight at 37 °C.[24] The resulting samples were fixed onto plastic stubs and sputter-coated with

carbon (MED 010, Balzers, Liechtenstein) to eliminate charging effects. The samples were then observed by means of SEM and analyzed by EDX microanalysis.

EDX analysis was used to detect the main chemical components of the material analyzed. Chemical elements (organic and inorganic) were identified by means of a scanning electron microscope equipped with a Vantage EDX system (NORAN Instruments, Middleton, WI, USA). The EDX spectra were acquired for a 100-second lifetime (voltage 15 kV, dead time 20–25%, working distance 20 mm).

For morphological characterization of the filler particles, samples were observed by means of a scanning electron microscope (VP 435, Leo, Cambridge, UK). Five repetitions were performed for each composite resin. SEM images of the filler particles were recorded under magnifications of 1000x and 5000x (voltage 15 kV, beam width 25–30 nm, working distance 10–15 mm). Therefore five images under a magnification of 1000x and five images under a magnification of 5000x were obtained for each resin to be analyzed. The five images under a magnification of 5000x were used to calculate the size of the filler particles for each composite. Size measurement was performed by means of scale markers on the images.

Results

The chemical elements identified by SEM/EDX analyses are shown in Figure 1 and Table 2. The inorganic elements found in Heliomolar by EDX were aluminum, fluorine, ytterbium, calcium, and silicon (Fig 1A). For Tetric N-Ceram, the following were found: barium, aluminum, ytterbium, zirconium, and silicon (Fig 1B). Aelite LS contained aluminum and silicon in its inorganic composition (Fig 1C), and Filtek Silorane presented yttrium and silicon (Fig 1D). High amounts of silicon were detected in all composites. Two organic elements (carbon and oxygen) were detected in all types of material.

Examination of the filler particles by SEM showed morphological variations among composite resins. Figures 2–5 show filler particles from Heliomolar, Tetric N-Ceram, Aelite LS, and Filtek Silorane composites, respectively. The SEM micrographs of Heliomolar composite resin showed small particles (around 1 μm in size) and many particles larger than 10 μm (Fig. 2). For Tetric N-Ceram (Fig 3) and Filtek Silorane (Fig 5), most particles were irregularly shaped, with sizes ranging from 0.5 to 1.5 μm; however, Filtek Silorane showed the most homogeneous particle size (the average size was 1 μm). Tetric N-Ceram also showed small

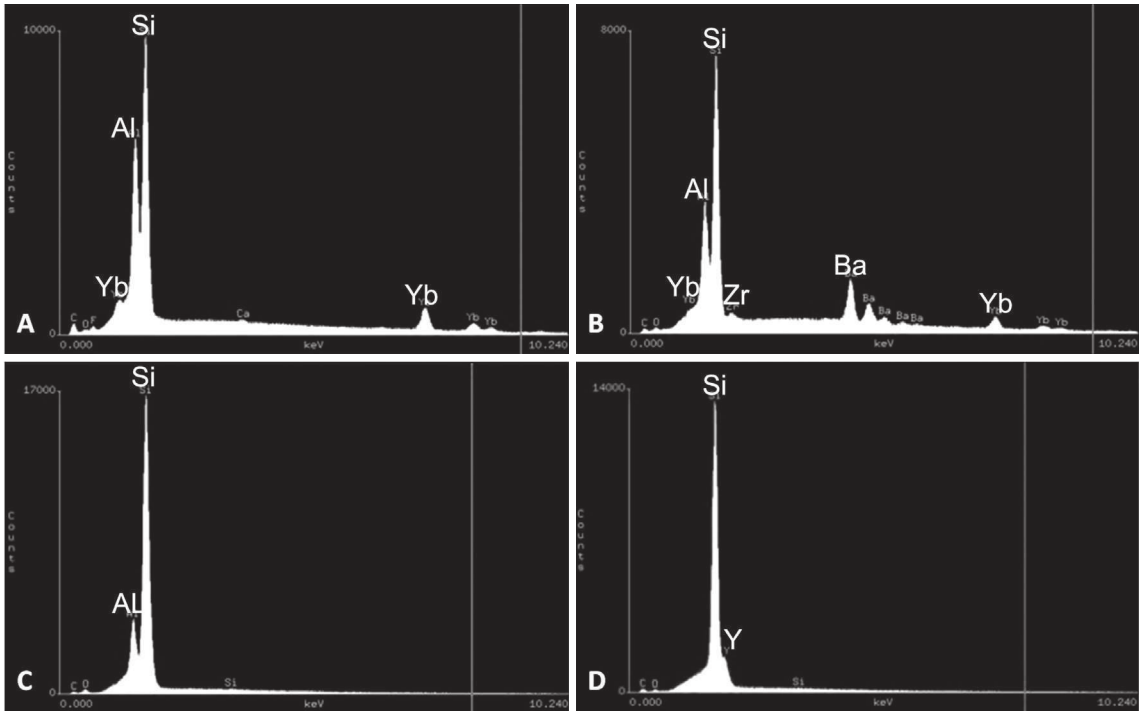

Figure 1: Elements identified by energy dispersive X-ray spectroscopy microanalysis for Heliomolar (A), Tetric N-Ceram (B), Aelite LS (C) and Filtek Silorane (D).

Table 2: Chemical elements identified by EDX analysis of the composite resins studied.

Composite resin	Chemical elements
Heliomolar	O, C, Al, Si, Yb, F, Ca
Tetric N-Ceram	O, C, Al, Si, Ba, Yb, Zr
Aelite LS	O, C, Al, Si
Filtek Silorano	O, C, Si, Y

Abbreviations: O (oxygen), C (carbon), Al (aluminum), Si (silicon), Yb (ytterbium), F (fluorine), Ca (calcium), Zr (zirconium), Ba (barium) and Y (yttrium).

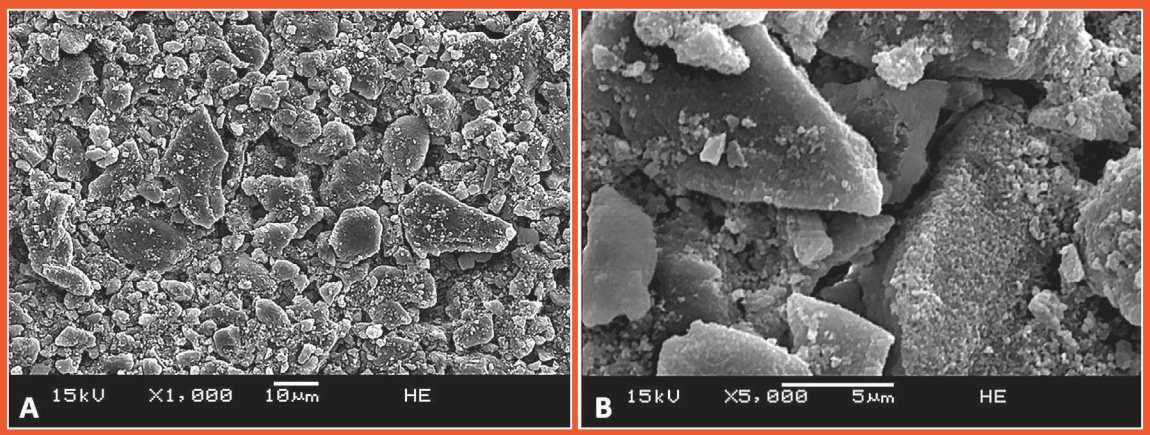

Figure 2: SEM micrograph of Heliomolar composite resin; magnification 1.000X (A) and 5.000X (B).

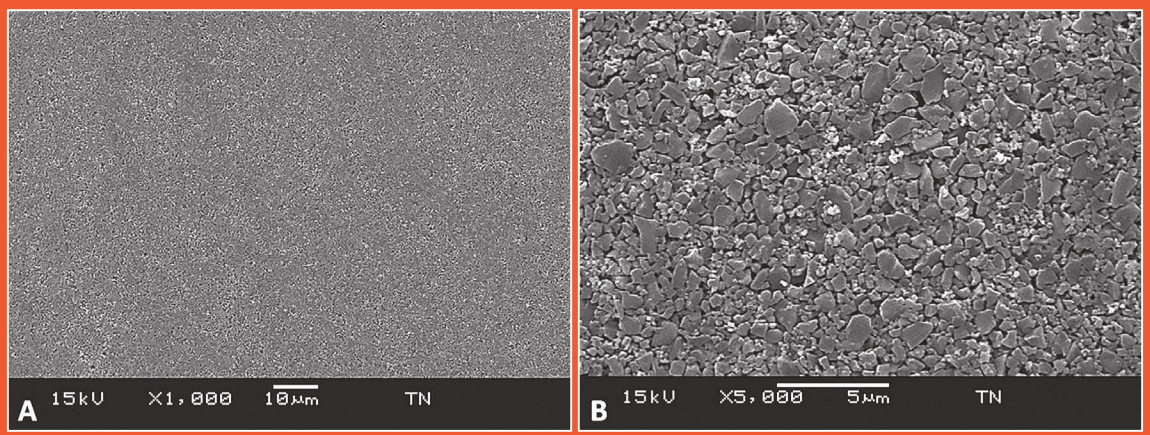

Figure 3: SEM micrograph of Tetric N-Ceram composite resin; magnification 1.000X (A) and 5.000X (B).

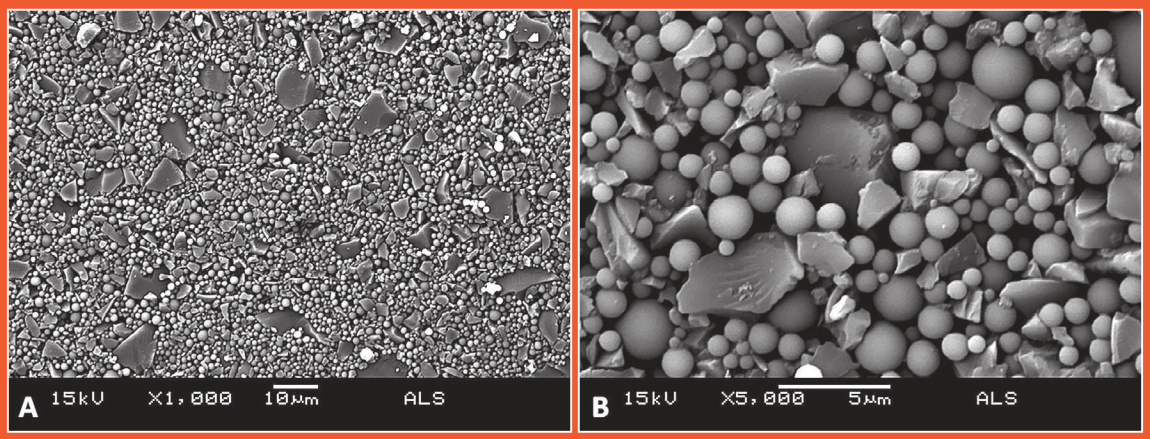

Figure 4: SEM micrograph of Aelite LS composite resin; magnification 1.000X (A) and 5.000X (B).

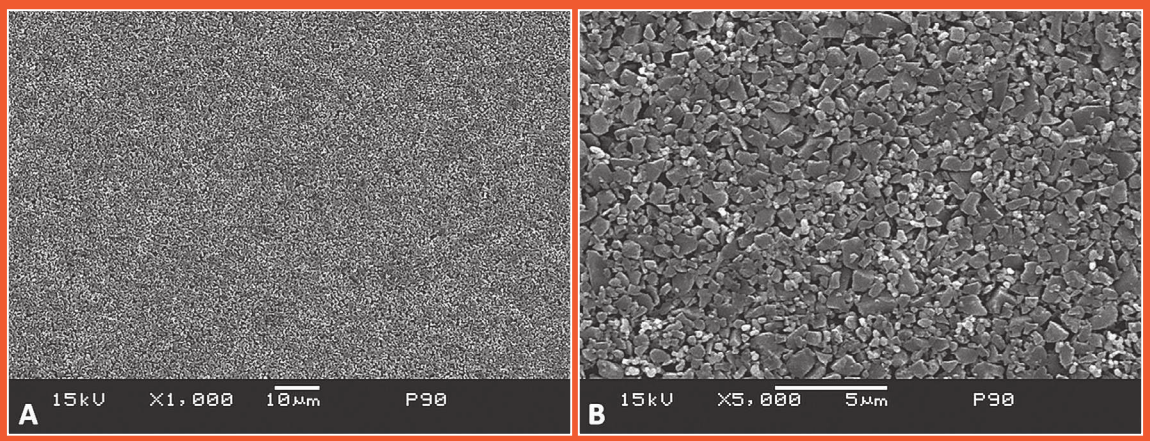

Figure 5: SEM micrograph of Filtek Silorane composite resin; magnification 1.000X (A) and 5.000X (B).

spherical particles (Fig 3B). Irregularly shaped and spherical particles could be observed in Aelite LS (Fig 4A and B). This low-shrinkage composite presented irregularly shaped filler particles with size ranging from 5 to 10 μm, and spherical particles ranging from 0.5 to 3 μm.

Discussion

The hypotheses that there are differences between traditional and low-shrinkage composite resins regarding inorganic composition and morphological characteristics of the filler particles were accepted. The two low-shrinkage composite resins investigated in this study are designed for using in posterior teeth only. The changes that were made in the composition of these composites to reduce volumetric polymerization shrinkage compromise their esthetic properties, limiting their indication for anterior teeth.

Silorane-based composites polymerize by a cationic ring-opening process which is different from the polymerization reaction of traditional methacrylate-based material. The result of this cationic ring-opening mechanism is a significantly lower volumetric shrinkage (< 1%) than in methacrylate-based composites. Whereas in Filtek Silorane the monomer matrix was changed, in Aelite LS the filler particle content was increased to 74% by volume in order to reduce polymerization shrinkage.

According to its manufacturer, Aelite LS low-shrinkage composite resin shows 1.4% volumetric shrinkage and 0.5% linear shrinkage. This composite is highly filled and is considered a hybrid restorative material because it contains irregular shape and spherical filler particles of different sizes (ranging from 0.5 μm to 10 μm). The particles are composed of aluminum glass and amorphous silica. In Figure 4B, it is possible to observe that a higher amount of spherical filler particles has been incorporated into the organic matrix than would be possible for irregular filler particles of the same size. A spherical shape improves the packing of particles in the matrix[20] and therefore allows an increase in volume fraction of the filler in the composite,[26,27] which tends to reduce the monomer content and, consequently, polymerization shrinkage.[28,29] However, such an increase in filler volume fraction has a limit, since a high filler loading can lead to a decrease in mechanical properties.[14,30]

Filtek Silorane contains quartz and yttrium fluoride as filler particles, with a uniform particle size distribution and an average size of 1 μm (Fig 5B). Quartz is twice as hard as glass and more resistant to dissolution. However, a limitation on its use is that quartz is radiolucent. To overcome this limitation, the manufacturer has added yttrium fluoride as a radiopaque constituent. In this study, both silicon (from quartz) and yttrium were identified by EDX analysis.[20,31]

Although Heliomolar is considered a microfilled composite, small particles (around 1 μm) and many particles larger than 10 μm were found in this material (Fig 2). EDX analysis detected aluminum, silicon, ytterbium, fluorine, and calcium in the samples of this composite. According to the manufacturer, the filler particles present in Heliomolar consist of silicon dioxide, ytterbium trifluoride, and a prepolymer.

The ytterbium trifluoride particles serve as a radiopacifier and fluoride release agent.[22,27] The prepolymer particles are prepolymerized microfiller particles that show the same properties as the matrix. They increase the filler content and enhance the consistency and physical properties of the material. Calcium and aluminum may be constituents of these prepolymer particles. The manufacturer does not provide information about the composition of these particles; however, the manufacturer's information suggests that some type of glass containing a calcium fluoroaluminosilicate may form part of the microfiller particles.

Tetric N-Ceram is a hybrid composite resin and most of its filler particles were irregularly shaped, with sizes ranging from 0.5 to 1.5 μm. Small spherical particles were also seen and, according to the manufacturer, these are nanoparticles with a size less than 100 nm. The filler particles represent 56% by volume of the product and consist of barium glass, ytterbium trifluoride, mixed oxides, and prepolymerized filler. Among the chemical elements identified by EDX analysis, aluminum, barium and silicon may be constituents of the barium boroaluminosilicate glass filler. Zirconium and silicon are related to the mixed oxide particles. The name of this composite suggests that it includes ceramic fillers, such as porcelain, quartz or zirconia. Fluorine was not detected, possibly because of overlap of peaks of the elements detected or because of a low concentration of the element.

The elements carbon and oxygen are constituents of the resin monomers used in all composite resins. Some of these monomeric fractions may have remained adhering to the filler particles even after organic-solvent dissolution or under filler particles on the surface of the samples analyzed. Another source of carbon and oxygen were prepolymerized fillers which represent powder of polymerized resin incorporated to the two composites tested. Oxygen from silicon dioxide or colloidal silica particles and carbon from sputter-coating could also been detected.

Conclusion

The examination of filler particles by SEM in this study showed morphological variations among the composite resins investigated. EDX microanalysis also detected differences in inorganic composition, although the element silicon was always present. In general, inorganic components were in accordance with the information provided by the manufacturers.

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