Inorganic and Prepolymerized Filler Content Analysis of Four Resin Composites

By

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Dedication

To my father, Jesus Salazar, and my mother, Daisy Z. Lopez de Salazar, whose unconditional love, guidance, and support have made this accomplishment possible. Thank you for giving me the opportunity to follow my dreams and become the woman I am today.

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Background and Significance

The ultimate goal of dental restorative materials is to replace the biological, functional and esthetic properties of healthy tooth structure. Gold alloys and amalgam, which have a long record of clinical success have been used as dental restorative materials for more than a hundred years especially in posterior teeth, because of their mechanical properties, however, these metallic materials are not appealing to the human eye[1, 2].

During the last four decades, innovative improvements of direct restorative composite materials have been made, to allow their use as an aesthetic alternative to amalgam for posterior and anterior restorations. However, Bowen's chemistry formulation has remained relatively unchanged, therefore the mechanical properties of the most recent composites have not improved substantially. The formulation of methacrylate-based composites generally encompasses three main components: the inorganic filler particles, organic-resin matrix and the coupling agent. The inorganic fillers are typically created from silicon derivatives and consist of particles such as glass, quartz, pyrogenic silicon dioxide, and colloidal silica via a sol–gel process. The organic matrix consists of base monomers, photoinitiators, pigments, and stabilizers. Bisphenol-A glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA) are commonly used as dental-base monomers (Figure 1). The coupling agent, usually silane, which is widely used to bond the inorganic filler to the organic-resin polymer, enhances the mechanical properties of the weaker resin polymer matrix and facilitates stress transfer by forming a unitary material[3-5].
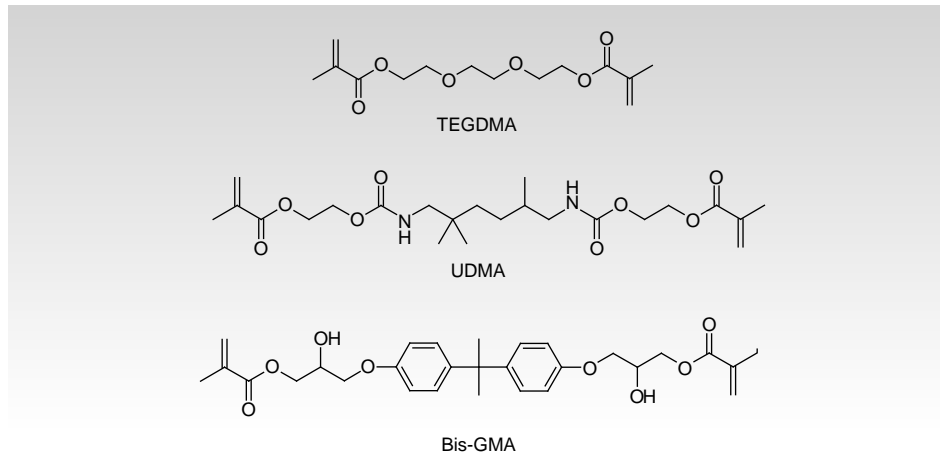
Figure 1. Methacrylate resin chemistry

The use of resin composite for large restorations is still controversial and fracture of restorations in the posterior region has been found to be a common caused for restoration failure[6].The two main reasons why today's methacrylate-based composites still have shortcomings that limit their application involves wear phenomena and polymerization stress[7]. During polymerization, shrinkage may stress the adhesively placed tooth-colored restoration while it functions within the complex oral environment through mastication and temperature fluctuations. With the passage of time, wear, fatigue, and internal stress–strain from thermal contraction and expansion may create plastic deformation and marginal leakage and subsequently increase the risks of cuspal deflection, secondary-caries formation, and pulpal inflammation [3, 7, 8].

Efforts to improve the clinical performance and to diminish external deformation and internal stress of methacrylate-based composites have been focused on the development of innovative monomers, and new filler technology [3, 5, 9]. Among the methods developed to modify the monomer matrix include the typical dimethacrylate monomers being replaced by methacrylates with reduced reactive groups (for example hydroxyl-free Bis-GMA) or the development of the urethandimethacrylate. Other approaches proposed for reducing polymerization

shrinkage include the development of liquid crystal monomers or ring-opening systems. One of these ring opening systems is the silorane-based composite resin whose matrix is formed by the cationic ring-opening polymerization of the silorane monomers. The "silorane" molecule represents a hybrid that is made of both siloxane and oxirane structural moieties[5]. Even though preliminary findings for the silorane-based matrix indicate significant polymerization shrinkage reduction (figure 2), research regarding the effect of the silorane monomers on the physical and mechanical characteristics of the cured composites has been limited[3, 10]. However, only a few of these newly developed monomers have been used in commercial composite materials and most of the conventional resin composite materials in use continue to be based on the dimethacrylate resins introduced in the 1960s and 1970s.
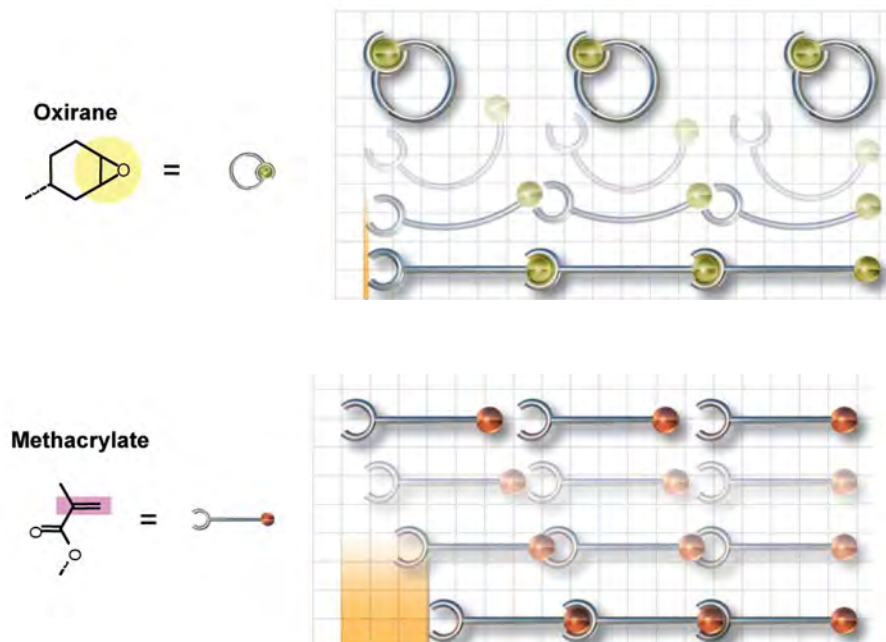
Figure 2. Reactive sites of silorane and methacrylates and corresponding shrinkage reduction after polymerization

Modifications in filler size, morphology and components have markedly affected the recent commercial composites. Barium glass has been added for radiopacity, amorphous silica has been introduced for improved handling and ytterbium has been added for an esthetic effect. Furthermore, particles have become spherical and smaller. The shape of prepolymerized filler particles has become more diverse, and various types of composites containing both prepolymerized and irregular-shaped filler particles have been developed[11-14]. One of the most important advances of the last few years in the field of dentistry is the application of nanotechnology to resin composites. Nanotechnology is known as the production and manipulation of materials and structures in the range of about 0.1–100 nanometers by various physical or chemical methods[15]. While the size of the filler particles lies around 8–30μm in hybrid composites and 0.7–3.6μm in microhybrid composites, recently, new fillers with size ranging from around 5–100 nanometers have been developed although 40 nm particles were already present in microfilled composites[14]. Therefore, these materials could be considered as precursors of nanofilled composites. Due to the reduced dimension of the particles and to a large size distribution, an increased filler load could be achieved with the consequence of reducing the polymerization shrinkage and increasing the mechanical properties such as tensile strength, compressive strength and resistance to fracture. These seem to be equivalent or even sometimes higher than those of universal composites and significantly higher than those of microfilled composites. On the other hand, the small size of the filler particles improves the optical properties of resin composites because their diameter is a fraction of the wavelength of visible light (0.4–0.8 μm) resulting in the human eye's inability to detect the particles. Furthermore, the wear rate is diminished and the gloss retention is better. As a consequence, manufacturers now recommend the use of nanocomposites for both anterior and posterior restorations[9, 16].

Despite all these efforts, due to the complexity of the materials, a clear and general valid classification of composites, especially in regard of their clinical success, could not be found. Researchers have suggested that filler content, size, and

morphology of the filler particles within a composite resin formulation has the potential to influence the mechanical performance of a composite resin. In addition, it has reported that, increasing the filler particle size will effectively modify not only the pattern of wear, but the rate of wear as well. It has also been stated that the greater the size of the particle, the greater the potential for wear[16-19]. Thus it would seem reasonable to expect more studies reporting classification of composites and correlations between wear and filler particle size. Perhaps the lack of some research is due to the difficulty in determining the exact size of the filler particles within a composite resin.

Testing mechanical properties of composites often correlates a physical property with filler loading. The filler content is often a mixture of organic and inorganic filler. When studies determine filler loading they often use one of three methods: 1. manufacturer's reported data; 2. thermogravimetric analysis (TGA); or 3. ashing in air. True filler content of both organic and inorganic particles is not captured using ashing in air or thermogravimetric analysis techniques since silane coatings and prepolymerized particles are often used in weight percentage filler contents reported by a manufacturer. The problems with ashing in air and thermogravimetric analysis are temperatures that are well above the decomposition points for silane and the organic matrix that comprise much of the prepolymerized particles.

No studies have concentrated on measuring filler content by weight or volume for current commercial composites using a technique, which preserves prepolymerized particles for the final filler calculation. There is no standard procedure for verifying a manufacturer's report of filler loading except the least expensive method of ashing in air. With ashing techniques, the temperature and time of exposure can vary greatly. Previous studies have used temperatures ranging from 570 to 1125°C and times of 20 to 60 minutes[14, 16, 19-24].

Scanning electron microscopy (SEM) often uses a dissolution technique with acetone or ethyl alcohol to remove the organic matrix from inorganic fillers[16, 20, 25]. According to some manufacturers the ashing in air technique can burn off some of the filler content of composites and thus give false results. To combat this problem a separation of the matrix and filler using acetone or ethyl alcohol needs to be explored. It is hypothesized that a solvent such as acetone will not break down prepolymerized filler, silane, agglomerates, or clusters from composite formulations.

Purpose:

The purpose of this study is to compare the filler content by weight reported by the manufacturer with ashing in air and acetone dissolution techniques and to determine if any differences exist between each technique. Secondary objectives include comparing the filler composite, morphology and size of each composite with SEM and EDS after dissolution with acetone.

Hypothesis:

Primary:

Ho_1:   There is no statistically significant difference in filler percent by weight content using ashing in air and acetone dissolution techniques.

Ha_1:   There is a statistically significant difference in filler percent by weight content using ashing in air and acetone dissolution techniques.

Secondary:

Ho_2:   The percent filler content by weight of selected composites using the ashing in air and acetone dissolution techniques is similar to manufacturer's data.

Ha_2:   The percent filler content by weight of selected composites using the ashing in air and acetone dissolution techniques are not similar to manufacturer's data.

Third:

Ho_3:   There is not significant difference of the filler composition, morphology and size of each composite with SEM or EDS

Ha_3:   There is significant difference of the filler composition, morphology and size of each composite with SEM and EDS.

Specific Aims:

The objectives of this proposed study are to:

1. Determine if there is a statistically significant difference in filler percent by weight content using ashing in air and dissolution by acetone techniques.

2. Determine if the filler by weight of selected composites using ashing by air and acetone dissolution are similar to the manufacturer's data.

3. Evaluate filler composition, morphology and size of each composite under SEM and EDS after dissolution with acetone.

Literature Review

Classification systems

      Lutz and Phillips[17] in 1983 published an article that reviews composite resin classification systems based on their components as well as some guidelines for the selection of the currently available composites resins. Resin-based restorative materials were defined as three-dimensional combinations of at least two chemically different materials with a distinct interface. A composite resin encompasses three phases: a) the organic phase (matrix); b) the interfacial phase (coupling agents) and c)the dispersed phase (fillers). Based on the manufacturing technique, fillers average size and chemical composition can be divided in three categories: 1. Traditional macrofillers, 2. Microfillers (pyrogenic silica), and 3. Microfiller-based complexes.

Figure 3. Composite classification based on types of fillers

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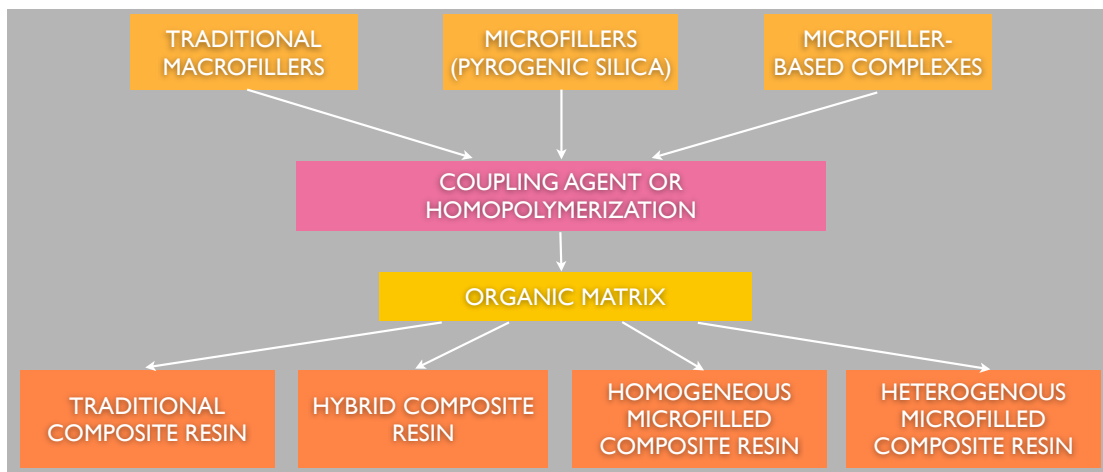
Figure 3. Composite classification based on types of fillers

Traditional microfillers are mechanically prepared from larger pieces of the material by grinding and/or crushing. The particles are purely inorganic, usually splinter shaped. The average particle size is generally between 1 to 5μm. Microfillers are derived chemically by hydrolysis and precipitation and consist of very finely dispersed radiolucent glass spheres. The commonly used primary particle size range is 0.05 to 0.1 μm. Microfiller-based complexes were developed to attain maximum inorganic loading with microfillers. There are three different types: 1. splintered prepolymerized microfilled complexes (1 to 200μm), 2. spherical polymer-based microfilled complexes (20 to 30μm) and 3. agglomerated microfiller complexes(1 to 25μm). The three types of fillers previously described represent the backbone of the classification. This classification in then oreganized into four major systems: 1. Traditional composite resins, 2. Hybrid composite resins, 3. Homogeneus microfilled composite resins and 4. Heterogeneous microfilled composites which fall into three different subclasses: a) those with splintered prepolymerized particles, b) those with spherical prepolymerized particles and c) those with agglomerated microfiller complexes. In general, hybrid composite resins can be considered an optimal combination of the well tried traditional and the new microfiller composite resin technology. The most promising anterior types, especially with regard to esthetics, consist of an extremely small (1 to 2 μm), rather soft, traditional macrofiller with a special size distribution placed into a reinforced organic matrix. If esthetics is the primary concern, then microfilled resin system particularly light-cured versions, are the materials of choice, especially the heterogeneous microfilled composite resins with splintered prepolymerized particles. As the filler particle size is reduced, the polishability, permanence of surface smmotheness, and esthetics improve. However, to achieve restorations of consistently outstanding quality, attention to technique sensitivity should be maintained, and certain modifications have to be made in the clinical procedures.

Lang, Jaarda and Wang[19] in 1992 thought that microstructure was one of the keys to understand material properties. In the past, investigators had relied, in part, on these classification systems to describe the filler particle contents of the

composite for the purpose of developing correlations between wear and filler particle size. The assumptions were two-fold: 1. that microfilled composites have smaller particles than traditional composites, and 2. the classification of the composites in question was accurate. To demonstrate the problems that exist, twelve composite resins were selected for this study, based on their published classification types, to examine the null hypothesis that: "There are no differences in the filler particle sizes between composites grouped according to their classification category as traditional, fine particle, or blends using the several classification systems". The twelve composite resins selected were: two microfilled composite resins (Heliomolar, and Distalite), seven fine particle composites (P- 10, Bisfil 1, Estilux Posterior, P-30, Visio-Fil, Ful-Fil, and Status), and three composites classified as blends (Herculite-Condensable, Sinter-Fil II, and Adaptic II). A 0.5 g sample of each composite was placed in 5ml of the solvent, Acetone, and centrifuged for 2 min at 1000 rpm to separate the solvent and matrix substance from the filler particles. This process was repeated three times using the acetone. The remaining composite mass was next placed in 5 ml of Chloroform for further washing and separation of the filler particles, which were clumped together as a result of the dissolution in acetone. The composite mass was again centrifuged for 2 min at 1000 rpm, and the chloroform and residual matrix substance was discarded. The second washing process was repeated three times. Finally, the remaining filler particles were suspended in 5 ml of absolute Ethanol, and the suspended solution and filler particles were smeared on a glass slide, for further SEM evaluation (2000x and 500x) to determine the range of filler particle sizes in each composite. After establishing the range of filler particle sizes in each composite using the SEM, the samples were photographed at a magnification of 125x under light microscopic examination and photo enlargement. Based on the filler particles sizes observed during the SEM evaluation, the 12 composite resins would appear to fall into four groups. The first group containing filler particles that range in sizes from submicron to greater than 25µm were: Visio-Fil, Heliomolar, Status, and Distalite, The second group with filler particles that range in sizes from submicron to approximately 10 µm were: P-10, P-30, Bisfil I, and Estilux Posterior. The third group of composite

with filler particles in the submicron to 5µm range were: Adaptic 11, Ful-Fil, and Siuter-Fil 11. The composite Herculite-Condensable was placed in the fourth group because it contains extremely small filler particles mostly in the micron to submicron range. Grouping composites on the basis of the filler particle sizes found after washing was easily correlated with wear and supported the suggestion that composites with smaller filler particles wear less. The results of this study would appear to indicate that classification systems for composite resins should be reviewed. If investigators cannot apply the classification systems to a composite and accurately and reliably verify that the composite is appropriately classified, then the utility of the system should be questioned. Certainly, using the system's classification nomenclature (fine particle, microfilled, etc.,) to report correlation with the physical properties of composites in general must be questioned according this project.

Ardu, Braut, Uhac, Benbachir, Feilzer, Krejci[18] in 2009 proposed a new classification of resin-based aesthetic adhesive materials according of their matrix and filler morphology. Eleven resin-based restorative materials were investigated in this study. In order to obtain the SEM micrographs which is used for filler characterization, 4 samples of each material were readied and their surface was dissolved in chloroform (Chloroform pro analysis, Meck KGaA, Germany) with a double step technique: 1) each specimen was rubbed with chloroform for 90 seconds, air dried and polymerized for 60 seconds with a LED light curing unit (L. E. Demetron II curing light, Kerr Corp, USA), and then again covered with several drops of chloroform for 5 minutes followed by the chloroform removal. Finally, specimens were dried at room temperature for 12 hours, gold sputtered and observed in the SEM (Phillips XL 20, Eindhoven, and NL, 400x magnification). According to the matrix composition, a general scheme of four different matrix systems, which characterize the material's level of hydrophobicity, was proposed. The subsequent SEM filler analysis showed a more complex scheme based on filler size and construction: 1)macrofilled composite (Concise, 3M Espe) filler size 2-5µm; 2)microfilled homogeneous composite (Isotit SR, Ivoclar Vivadent) filler size

0.04μm; 3)microfilled inhomogeneus composites (Durafill, Heraeus) with prepolimerized blocks of 5-30μm which are reinforced with microfilled particles of 0.4μm size; 4)coarse hybrid composite (Clearfill, Kuraray) filler size 1-2μm; 5)hybrid fine composite (Enamel plus HFO, Micerium) filler size 0.6-1μm; 6)micro hybrid homogeneous composite (Point 4, Kerr) ; 7)micro hybrid inhomogeneous composite with aggregated particles (Filtek supreme XT, 3M ESPE) ; 8)micro hybrid inhomogeneous composites with splinters (Tetric Evoceram, Ivoclar Vivadent) which is filled with crunched down pre-polymerized particles made out of the same type of composite: micro-hybrids 9)micro hybrid inhomogeneous composites with heterologous splinters (Gradia Direct, GC America) which is based on splinters made of another type of composite: microfill. All micro hybrid composites mean filler size ranges from 0.4 to 0.6 μm. The second level of classification, considering the matrix besides the filler morphology, are divided in: 1) compomer based composites (Dyract, Dentsply); 2) methacrylate based composites (all above composite materials); 3) ormocer based composites (CeramX, Dentsply); 4) silorane based composites (Filtek Silorane, 3M ESPE). This new classification for resin restorative materials proposed by this author, which takes in account not only resin matrix but also filler size, allows a better understanding of the mechanical and aesthetic characteristics of resin composites as well as compomers, ormocers and siloranes.
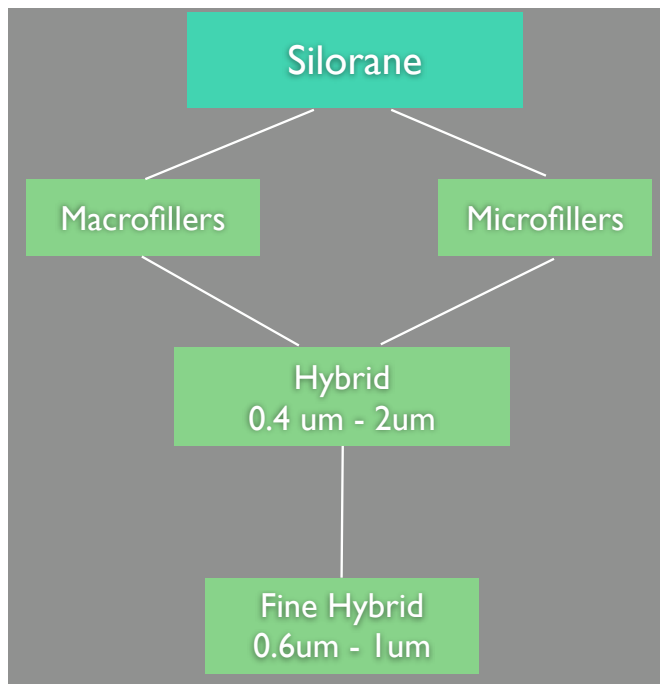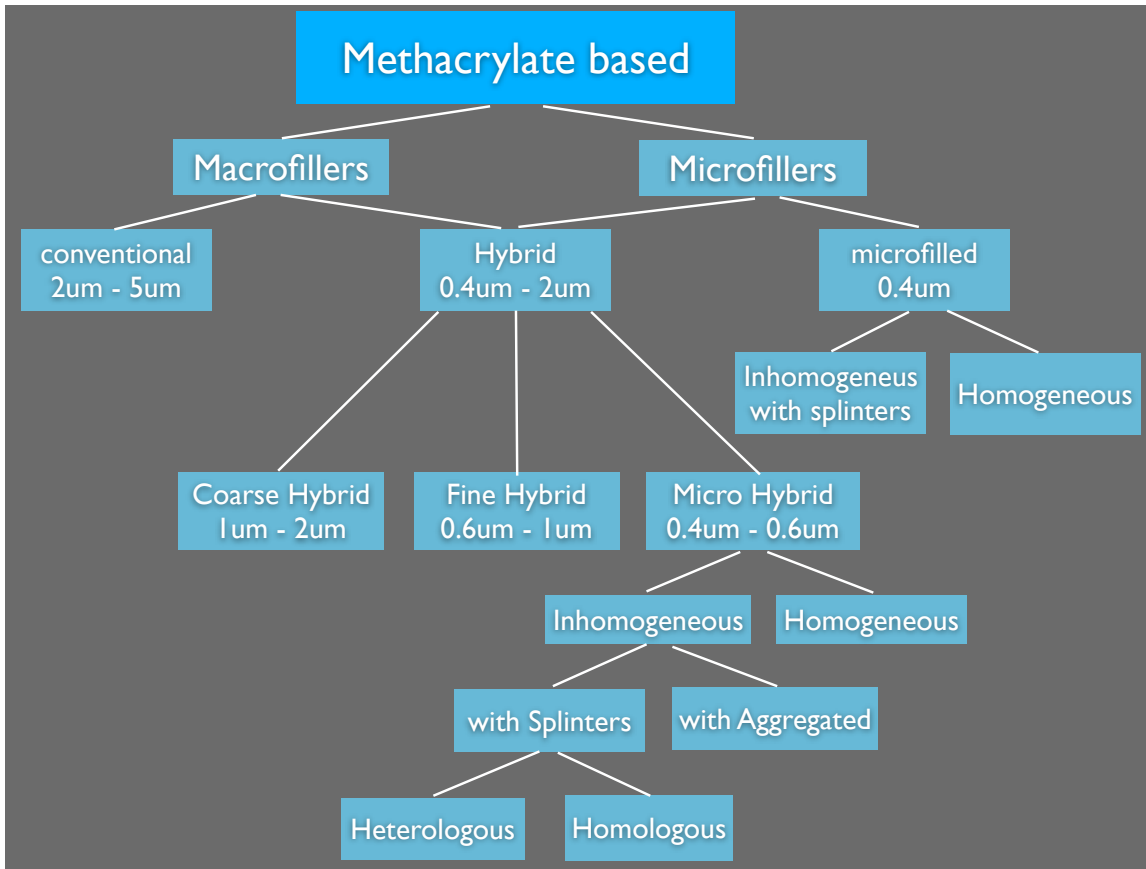
Figure 4. Classification of Methacrylate based (up) and Silorane based materials (down)

Physical properties

Rodrigues, Scherrer, Ferracane and Della Bona[26] in 2008 conducted a study that characterized the microstructure of two different composites, and also determined their influence on the physical properties and fracture behavior. The hypothesis to be tested were that differences in the properties between the two composites could be attributed to differences in their filler composition and extent of cure, and that fractography of unnotched specimens tested in flexure could be used to determine fracture toughness and result in similar values as the more commonly used single edge notch beam (SENB) method. Two composites were investigated: a microhybrid (Filtek Z250, 3M ESPE) and a nanofill (Filtek Supreme, 3M ESPE). The filler weight percentage was determined by the thermogravimetric ashing technique, by placing porcelain crucibles containing the composite in a furnace at 900^oC for a period of 1 hour. The weight of the filler fraction in the materials was considered to be the difference in weight before and immediately after ashing by using an analytical balance. For the analysis of filler morphology, composites were evaluated under the SEM (Quanta 200 MK2, FEI Company,OR) using the back scatter imaging mode at accelerating voltage of 15kV. A semi-quantitative elemental analysis was performed with electron disperse analysis (SwiftED model 6650, Oxford Instruments). A 100g load was applied using a knoop indenter with a 30s dwell time and a diamond indenter with a 136° included angle to determine material hardness. Degree of conversion (Fourier Transform Infrared Spectrometer), dynamic elastic modulus (ECALC and Sigview-F software) were also determined. Bar specimens were subjected to flexure loading and flexural strength was calculated. Fractographic analysis was performed to determine the fracture origin for calculation of fracture toughness, and these results were compared to those of from the single edge notch beam (SENB) method. Results were statistically analyzed using two-way ANOVA, Student's t-test and Weibull analysis. The filler weight percentage of Filtek 250 (78.7±0.5%) was significantly higher than that of Filtek Supreme (73.2±0.5%). The semi-quantitative analysis revealed similar

elemental composition between the composites. Hardness was significantly higher at the top surface of both composites. The degree of conversion of the microhybrid composite was similar at the top and bottom surfaces, while it decreased at the bottom surface of the nanofill composite. Elastic modulus was significantly higher for the microhybrid composite (25.5 GPa) then the nanofill (21.8 GPa). No statistically significant differences were found between fracture toughness values calculated by the fractographic approach or the SENB for both composites. With this paper the authors concluded that the procedures of characterization used in this study for a microhybrid and a nanofill composite revealed that different sizes of filler particles might result in different microstructures and filler contents. Among the factors evaluated, the filler content seems to be the most important factor in the determination of the properties of composites. On the other hand, the fracture behavior and the structural reliability seem to not be affected in the highly filled composites, so the initial hypothesis is rejected. Fractographic approach proved to be a reliable alternative for the determination of the fracture toughness of composites.

Shrinkage strain / Polymerization stress

Lu, Lee, Oguri and Powers[27] in 2006 conducted a study that compared polymerization shrinkage, wear resistance, and mechanical properties of a resin-based composite filled with spherical inorganic filler to other popular contemporary resin composites. Six dental resin composites were tested including: one submicron filled composite (Esthelite∑, Tokuyama Dental), one nano-composite (Filtek Supreme, 3M ESPE), two microfilled composites (Heliomolar- Ivoclar Vivadent; Renamel – Cosmedent) and two microhybrid composites (Esthet X improved-Dentsply; Tetric Ceram, Ivoclar Vivadent). Compressive strength, diametrical tensile strength, flexural strength, flexural modulus, generalized wear resistance and polymerization shrinkage were evaluated for the six materials. The surface of the specimens were light cured according to the manufacturers' instructions in their appropriate molds, stored and then tested on a universal material testing machine

(Instron 4465, Instron Corp, Canton, Ma, USA) at a crosshead speed of 0.5mm/min. Generalized wear resistance was tested with a Leinfelder-type wear tester for 400,000 cycles and the total wear-off volume was measured with a 3-dimensional profilometer (MTS, St Paul, MN, USA). Polymerization shrinkage (Volumetric shrinkage) was tested according to the Archimedes method at 1, 24 and 48 hours continually after polymerization. Data were analyzed by 1-way analysis of variance (ANOVA) to detect the influence of composite on properties. The results showed that Estelite performed similarly to nano-composite and microhybrid composites in mechanical properties and generalized wear resistance, while Estelite and Supreme had the lowest polymerization shrinkage among the materials tested. The two microhybrid materials had similar properties, while the two microfilled composites were different for most properties tested. In general, the microfilled composites had lower mechanical strength than other composites except Renamel for compressive strength. All the materials had a similar shrinkage pattern, in that about 99% of shrinkage occurred in less than 24 hours.

Condon and Ferracane[27] in 2000, studied the relationship between polymerization stress and marginal debonding on a variety of dental composite materials. Also, they explored the effect of a novel monomer in reducing polymerization stress. Eleven commercial composites were tested to determine their polymerization stress in a confined setting. They also tested an array of experimental composites containing a different monomer (methacrylated derivative of styrene-allyl alcohol, or MSAA) to evaluate the potential for reducing polymerization stress levels. A mechanical testing machine was used to evaluate polymerization stress tests of four microfills - Durafill VS, (Heraeus Kulzer), Epic TMPT, (Parkell), Litefil IIA, (Shofu), and Heliomolar, (Ivoclar-Vivadent), three minifills - Tetric, (Ivoclar-Vivadent), Charisma, (Heraeus Kulzer), and Herculite, (SDS Kerr) and three midifills - Fulfil, (DENTSPLY/Caulk), Estelite, (Tokuyama), and Prisma TPH, (DENTSPLY/Caulk). The self-cured composite Bisfil 2 was also tested to examine the effect of its different curing mode. A series of experimental composites, which incorporated MSAA, has been proposed as an adjunct to Bis-GMA. The MSAA

molecule consists of a carbon chain backbone with an average of six pendant methacrylate groups flanked by aromatic rings. Its addition has been found to yield improved compressive strength and degree of conversion of methacrylate groups. The high mobility of the functional ends could provide a flexible link by which internal stresses could be resolved within the growing polymer. Six composites were formulated by replacing MSAA with Bis-GMA at the level of 0, 20, 40, 60, 80 and 100 percent in a light-cured resin. The Bis-GMA/MSAA combination amounted to 50 percent by weight of the resin present. The thick monomers were diluted with TEGDMA, which made up the remaining 50 percent by weight of the resin phase. Silane treated filler particles (78 percent by weight [62 percent by volume]) were added to form a composite. They found a significant relationship between high filler volume and increased polymerization stress among the commercial materials. The introduction of MSAA produced a 30 percent reduction in polymerization stresses in the experimental composite material. The significance of this article is that higher levels of inorganic filler materials in a composite mix are more likely to produce lower levels of polymerization stress. These lower levels of stress could result in a reduction in postoperative sensitivity, marginal staining and recurrent caries.

Goncalves, Kawano and Braga[28] in 2010 evaluated the influence of filler fraction of experimental composites on the polymerization stress and its determinants as degree of conversion, volumetric shrinkage and elastic modulus and also they investigated the association between polymerization stress and the other variables. Eight experimental composites containing BisGMA, TEGMA, and barium glass at increasing concentrations from 25 to 60vol% (5% increments) were tested. Polymerization stress test was evaluated with a universal testing machine (Instron 5565, MA, USA) using acrylic as a bonding sustrate. Volumetric shrinkage was determined using a picnometer (5 cm^3, Brand Gbmh, Germany) and elastic modulus was obtained by three-point flexural test 15 min after photopolymerization in a universal testing machine (Instron 5565) with an 8-mm span between the supports at a crosshead speed of 0.5 mm/min. Degree of conversion was assessed by Fouirier-transformed Raman spectroscopy (RFS- 100/S

,USA). The results showed the polymerization stress and shrinkage showed an inverse relationship with filler content (R^2=0.965 and R^2=0.966, respectively). On the other hand, elastic modulus showed a direct correlation with inorganic content (R^2=0.984). Polymerization stress showed a strong direct correlation with shrinkage (R^2=0.982) and inverse correlation with elastic modulus (R^2=0.966). Degree of conversion did not vary significantly. In summary, high inorganic contents were associated with low polymerization stress values, which can be explained by the reduced volumetric shrinkage presented by heavily filled composites.

Satterthwaite, Vogel and Watts[29] in 2009 conducted a study to investigate the variations of filler particle size and shape on the shrinkage-strain accompanying polymerization of resin-composites. Twelve visible-light-cured experimental resin composites together with an established commercially available formulation (Tetric Ceram, Ivoclar Vivadent) were evaluated. The resin matrix in all composites was a mix of BisGMA, UDMA, and TEGMA with a dispersed phase of the same volume fraction (56.7%), which was treated with a silane coupling agent (methacryloxypropyltrimethoxysilane). The filler graded in size, and further were either spherical or irregular. The bonded disk method was used to determine shrinkage-strain. A resin-composite test specimen was placed in a brass ring situated upon a glass slab lightly grit-blasted with alumina to promote bonding to composite. Compression was achieved through the use of thick glass cover slip and a thick glass placed over the sample. A uni-axial LVDT (type GT2000 RDP Electronics) was positioned centrally over the cover slip and recorded displacement occurring due to polymerization during and following irradiation for 40s from QTH light-cure unit at 600mW/cm^2. The fractional volumetric shrinkage-strain was calculated and expressed as a percentage. Values were evaluated using two-way ANOVA and multiple pairwise comparisions using a Scheffé post hoc test to establish homogeneus subsets. The shrinkage-strain values were generally lower for those composites with spherical filler particles than those with irregular filler particles. For materials with spherical filler, the mean shrinkage-strain was 2.66% (SD 0.18) and for those with irregular filler it was 2.89% (SD 0.11). With regard to filler

particle size, the highest shrinkage-strain was seen in those composites with smaller filler particles.

Herrero, Yaman and Dennison[30] in 2005 were concerned about the availability of firmer and more packable composites that will ensure proper proximal contour and contacts as well as marginal seal. They evaluated polymerization shrinkage and depth of cure of five different packable composites: Surefil (Dentsply), Alert (Jeneric/Pentron), Solitaire (Heraeus/Kulzer), P60 (3M Dental Products) and Prodigy Condensable (Kerr). This study was divided in two phases: the first phase measured linear polymerization shrinkage and the second measured the composite hardness. For the first phase ten specimens of each composite in two different thickness (2mm thick and 5mm thick) were transferred to a glass slide which was coated with a separating medium to allow the composite to shrink free of surface adhesion. A flat aluminum target was placed on top of the specimen and the entire assembly was mounted in a vertical position. The target and the specimen were positioned at the required distance below a sensor connected to a measurement system or linometer (KµDATM, Kaman Instrumentation), which was calibrated prior to each measurement. Once positioned, the composite specimens were polymerized for forty seconds (Optilux 401 light, Demetron Research). For the second phase, ten specimens of each thickness for each material were prepared (n=100), and exposed for 40 seconds using the same light curing light. Three hardness measurements were made on the bottom and top surface of each specimen with a 200g diamond pyramidal indenter (Tukon tester, Wilson instruments). For shrinkage and hardness, the means and standard deviations were calculated for each group. A one=way analysis of variance (ANOVA) was used as well as Tukey multiple comparison test. For the 2 mm-thick specimens the volumetric shrinkage was: 0.2% for Alert, 1.2% for P60, 1.4% for Surefil, 1.8% for Prodigy and 2.1% for Solitaire. Hardness for the bottom surface at 5mm thickness showed that Alert (16.5) and P60 (16.3) had higher values than Surefil (8.9). Hardness for the bottom surface of the 2mm thickness showed that P60 (48.5) and Alert (42.6) had significant higher values than Solitaire (11.2). In

conclusion Solitaire had the most shrinkage and Alert the least at 2 and 5mm thickness. Also, the depth of cure was significantly compromised for all materials at a 5mm depth.

Filler vs. Wear

Lim, Ferracane, Condon and Adey[31] questioned the influence of microfiller particles on composite wear. Therefore, in 2002, they investigated the influence of filler volume fraction and filler surface treatment on the filler distribution in the resin matrix and wear resistance of experimental microfilled composites. Four series of experimental microfilled composites were created with a light cured resin (33% Bis-GMA/33% UDMA/33% TEGMA) and colloidal silica.

Table 1. Experimental microfilled composite resins used in this study

Experimental microfilled composite resins used in this study

Code	Filler (vol.%)	Filler treatment
A	20	F, NF,U
B	25	F, NF,U
C	30	F, NF,U
D	35	F, NF,[a]

The surface treatment of the colloidal silica in each group varied: Group F microfiller was treated with 10 wt % functional silane, group NF microfiller was treated with 10 wt. % non-functional silane, and group U microfiller was not treated at all. Silux plus served as a control. Specimens were made in steel molds and cured in a light-curing unit (Triad II) for 40 sec on each side. Abrasion and attrition wear were evaluated in an in vitro wear tester (OHSU oral wear simulator) with a abrasive slurry and human enamel antagonist (cycled 50,000 times). The composite wear patterns were analyzed with a diamond-tipped profilometer. The average of five specimens was computed and compared using an ANOVA/Tukey's test at $P \leq 0.05$. The surface of the wear patterns and the distribution of filler particles were

examined using SEM and digital imaging. The results showed that as filler volume increased, wear was reduced regardless of filler treatment. The amount of wear observed in specimens C (filler 30 vol %) and D (filler 35 vol %) were significantly lower than specimens A (filler 20 vol %) and B (filler 25 vol%). Composites in group F (with functional silane treated microfiller) produced significantly less wear than those in Group NF (with non-functional microfiller) at 30 and 35 vol. %, and less than the Group U (untreated microfiller) at 30 vol. %. SEM of specimens of group NF showed large filler agglomerates (size>1μm) in the resin matrix, while specimens of group F and U showed fewer agglomerates. Digital imaging analysis revealed small filler clusters (size ≤1 μm) in the resin matrix of all specimens. This result suggest that the addition of filler particles to the composite increases its wear resistance, but that optimal enhancement of wear resistance can be only achieved if the particles are well bonded to the resin matrix. The microfilled composite that possesses the highest percent of inorganic filler, the best homogeneous dispersion of filler, and the strongest chemical bond between filler and matrix should have the best wear resistance.

Flexural Strength

In **2007, Rodrigues, Zanchi, De Carvalho and Demarco[32]** conducted a study to assess the filler composition effect in different commercially available resin-based composites, including flexural strength and modulus of elasticity. Filler weight content was determined by heating each composite sample at 900°C for 30 minutes in an electric furnace to eliminate the organic matrix. The weight of each sample were measured before and after the heating process using an analytical balance (AG200, Brazil). Twelve specimens were made of each composite; Supreme, Esthet-X, Z250, Charisma, and Helio Fill with the dimensions specified by the ISO 4049 / 2000 specification (25 mm x 2 mm x 2 mm). The composite was cured for 40 seconds in three consecutive points, producing a partial overlapping with a light-curing unit with 450 mW/cm2 (Ultralux). Then, the specimens were stored in distilled water at room temperature for 7 days. They were submitted to a three-

point bend test with a universal testing machine (4411, Instron,Brazil) with a crosshead speed of 1 mm/min. Flexural strength and modulus of elasticity were calculated. The data obtained from the tests were analyzed using ANOVA and Tukey test. Pearson's correlation test was used to establish if there was any correlation between the filler wt% data and the mechanical properties. The statistical analysis showed significant differences between composites both for the flexural strength and the modulus of elasticity. The highest flexural strength was obtained with Z250, 168.87 (±15.36). The modulus of elasticity of Esthet-X, 6.93 (± 0.69) was similar to that of Z250, 6.40 (± 0.96) and significantly higher than that of others. A significant positive correlation was found between the filler weight and the mechanical properties flexural strength ($r = 0.591$) and modulus of elasticity ($r = 0.423$). It could be concluded that the filler content significantly influenced in the flexural strength and modulus of elasticity of the composites. This study showed the correlation between filler content and the mechanical properties of tested composite resins.

Consistency

Tyas, Jones, and Rizkalla[23] in 1998 evaluated a method for the assessment of the consistency of unset resin composite. Fourteen commercial resin composites were selected : Dyract (Denstply), Herculite XR (Kerr), Herculite XR Unidose (Kerr), P-50 (3M), Prisma-Fil (Denstply), Prodigy (Kerr), Silar A and B (3M Dental), Silux Plus (3M), Solitaire (Heraeus), Surefil (Denstply), Tetric (Ivocalar), TPH (Denstply) and Z-100 (3M). The range of consistencies were assessed subjectively. The material was placed in a cylindrical mold and the mold was placed on the base of a universal mechanical testing machine (Instron 1000, High Wycombe). A ground glass rod with a flat end was mounted beneath the cross-head and lowered slowly until it made light contact with the surface of the center of the composite. After a few seconds, the rod was driven into the composite for 6 sec at a rate of 24.4 mm min^{-1}; then the maximum load recorded was displayed using a data capture package (Labview v3.1.1, National Instruments). This test was repeated nine times. The mean maximum forced for each composite was calculated and the

values were compared for significant differences between materials using ANOVA followed by Duncan's multiple range test. The thermogravimetric analysis was performed to determine the weight percentage of inorganic filler, using a Perkin-Elmer TGS-2 analyzer. The mean wt% for each material was calculated and the values compared for significant differences using ANOVA followed by Duncan's multiple range test. The results showed that the consistency values ranged from 0.33 N (Silar A) to 31.3 N (Surefil), with the highest values being found for some of the recently introduced packable materials (Surefil, Herculite XR Unidose, Solitaire and Tetric Ceram). No correlation was found between consistency force and filler weight for the fourteen materials; The two materials with the highest filler content (P50, 84.6%w/w; Z-100, 81.6% w/w) exhibited much lower consistency forces than Solitaire (65.4%w/w), Prodigy (74.5% w/w) and Herculite XR Unidose (75.9% w/w), which have much lower filler content. The test method used for determining the consistency described in this study readily discriminates between a range of consistencies of the composites materials used in this investigation. Therefore, the consistency test described may prove to be useful as a standard test method for characterizing the handling consistency. Further work will be required to determine for stickiness.

Kaleem, Satterthwaite and Watts[33] in 2009 investigated the effect of variation in filler particle size and morphology within an unset model series of resin-composites on two stickiness parameters: maximum probe separation-force (F_{max}) and work of separation (W_s) and to assess the effect of temperature and speed of probe separation. The null hypotheses were that changes in filler particle size, morphology, speed and temperature have no effect on the stickiness of unset resin composite. Eleven experimental formulations, all light cured, were used in this study. All composites had the same matrix (Bis-GMA, UDMA and TEGMA, with 0.33% camphoroquinine) and the filler-volume fraction (56.7%), however filler particles varied in size and shape and were either unimodal or multimodal in size distribution. Each material was placed in a cylindrical mold held at 26 or 37° C. The maximum force (F_{max}) and work of probe-separation (W_s) were measured with a

texture analyzer (TA. XT2i, Stable Micro Systems). A flat-ended stainless-steel probe was mechanically lowered onto and into the surface of the unset sample, until a compressive force of 1N was reached, which was held constant for 1s. Then the probe was moved vertically upward at a constant velocity of 2 or 8mm/s. The tensile force produced on the probe by the sticky composite was plotted against displacement and the maximum value was identified. Data was analyzed by multivariate ANOVA and multiple pair-wise comparisons using a Tukey post hoc test to establish homogenous subsets for F_{max} and a Games-Howell was used for W_s. As potential measures of stickiness, F_{max} and W_s showed more coherent trends with filler size when measured at the lower of the two probe speeds, 2mm/s. For unimodal resin-composite F_{max} ranged from 1.04 to 5.11N and W_s from 0.48 to 11.12 Nmm. For the multimodal resin-composite they ranged from 1.64 to 4.13N and from 2.32 to 8.34 Nmm respectively. Temperature increase tended to slightly reduce F_{max}, although this trend was not consistent. W_s generally increased with temperature. In summary Filler particle size and morphology influences F_{max} and W_s of uncured resin-composite, which partly express the handling behaviors of resin-composites.

Surface Roughness

Marghalani[34] in 2010 evaluated the effect of different filler sizes ranging from 100 and 1500 nm and geometry (spherical and irregular) on the surface characteristics of experimental resin composites. The null hypothesis stated that: 1) There was no difference between surface roughness values of experimental composite series, and 2) there was no correlation between both vertical as well as horizontal surface roughness parameters and the increase in filler particle size. Eleven series of experimental resin composites on different particle size formulations (range of 100-1500nm) and two different geometries (spherical and irregular) were investigated.

Table 2. Experimental composite series formulations

Resin-composite series (Batch #)	Code	Filler Particles				Matrix
		Size (nm)	Shape	Wt%	Vol%	
RZD 102	S-100	100	Spherical	72.3	56.7	
RZD 107	S-250	250	Spherical	72.6	56.7	
RZD 106	S-500	500	Spherical	72.6	56.7	
RZD 105	S-1000	1000	Spherical	72.5	56.7	
RZD 114	S-100/250/1000	100:250:1000 (1:1:2)	Spherical	72.0	56.7	Bis-GMA, UDMA,
RZD 103	I-450	450	Irregular	76.4	56.7	TEGDMA
RZD 108	I-700	700	Irregular	76.4	56.7	
RZD 109	I-1000	1000	Irregular	76.4	56.7	
RZD 110	I-1500	1500	Irregular	76.4	56.7	
RZD 111	I-450/1000	450:1000 (1:3)	Irregular	76.4	56.7	
RZD 112	I-450/700/1000	450:700:1000 (1:1:3)	Irregular	76.4	56.7	

Thirty-three disc-shaped specimens were prepared in a split teflon mold, light-cured (450 mW/cm^2 for 40 s) at both top and bottom surfaces, finished, polished with 1500 SCI paper as well as aluminum oxide slurry pastes and stored for 3 months in distilled water. The surface roughness values in the form of surface finish-vertical parameter, maximum roughness depth and horizontal roughness parameter were recorded using a profilometer. The data were analyzed by one-way ANOVA and the means were compared by Scheffé post-hoc test (α=0.05). The results showed that the lowest surface roughness was observed in the composite with spherical filler particle shape and 100nm of size (0.079±0.013), while the roughest surface was noted in composites with irregular filler particle shapes and filler sizes 450:700:1000 (0.125±0.011) and 450:1000 (0.124±0.004). The spherical-shape series showed the smoothest surface finish compared to the irregular-shape ones with higher significant difference (p>0.05). The vertical surface roughness parameter values increased as the filler size increased. On the contrary, the filler size as well as the filler shape did not significantly affect the horizontal paramete. In summary, the filler particle's size and shape have a great

effect on the surface roughness parameters of the resin composites evaluated in this study.

Optical properties

       Mundim, Garcia Lda and Pires-de-Souza [35] in 2010 assessed the color change of three types of composite resins exposed to coffee and cola drink as well as the effect of repolishing on the color stability of these composites after staining. The tested null hypothesis was that there is no difference in the color stability of composites after immersion in staining solutions and repolishing. Three commercial composite resins currently indicated for esthetic anterior and/or posterior restorations were used in the study: Esthet-X, Denstply (microhybrid); Filtek Z-250, 3M ESPE (microhybrid) and Surefil, Dentsply (high-density hybrid). Fifteen specimens of each composite were fabricated and polished with aluminum oxide discs (Sof-Lex discs sequence, 3M ESPE). Color was measured according to the CIE (Commision Internationale de l'Eclairage) L*a*b* system relative to CIE standard illuminant D65, against a white background (Standard for 45/0 degrees; Gardner Laboratory) in a reflection spectrophotometer (PCB 6807 BYK Gardner). After baseline color measurement, the specimens were assigned to three groups (n=5), each one immersed in a different solution, and subjected to a new color measurement. Group 1 (control) was immersed in distilled water, Group 2 was immersed in coffee and Group 3 was immersed in a cola soft drink (Coca-Cola). After 15 days, specimens were cleaned properly before the second color measurement with spectrophotometer. Color stability was determined by the difference (ΔE) between the coordinates L*a*b* obtained from the specimens before and after immersion into the solutions and after repolishing. The means and standard deviations of color change were calculated and submitted to statistical analysis by 3-way repeated measure ANOVA and Tukey's test at 5% significance level. The results showed no statistical difference among the ΔE values for the different types of composites after staining or repolishing. For all composite resins, coffee produced more color change ($\Delta E>3.3$), than distilled water and the cola soft drink. After

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repolishing, the ΔE values of the specimens immersed in coffee decreased to clinically acceptable values (ΔE<3.3), but remained significantly higher than those of the other groups. In summary, no significant difference was found between composite resins or among color values before and after repolishing of specimens immersed in distilled water and cola. Immersing samples in coffee caused greater color change in all types of composite resins tested and repolishing contributed to decreased staining to clinically acceptable ΔE values.

Mechanical properties

Chung and Greener[21] understood that by increasing the content of the reinforcing filler and development of bulky and rigid monomer systems were the usual methods of producing dental composites for utilization as posterior restorations. Thus, in 1990, they correlated the degree of conversion, filler concentration and mechanical properties in highly filled dental composites. Seven commercially available composites were used in the study: Marathon - DentMat, Ful fill - L.D. Caulk, Estilux -Kulzer, Sinterfil - Teledyne Getz, Occlusin - Imperial and Bis-fil I - Bisco. The polimerization reaction of these composites was monitorized with a Fourier Transfrom spectrometer. The degree of convertion was calculated by comparing the absorvance ratio of the aliphatic C=C peak with the unchanged aromatic ring C=C peak for the pre- and post-polymerized resins. The inorganic filler content was determined by the gravimetric ashing technique, in which the difference in weight is compared before and after ashing at 700°C. The density of the filler was measured pycnometrically. The strength test was performed using an Instron universal testing machine with a crosshead speed of 0.1-inch min^{-1}. The Knoop hardness test was performed at 24±1°C under a 200 grams load on a microhardness tester (M12a metallurgical microscope), using a Knoop diamond indenter. Results were analyzed by ANOVA, Scheffe's test and Pearson's r-test. The degree of conversion of composites ranged from 43.5 – 73.8%. The weight fraction of filler obtained was 66.3 – 85.2%. The volume fraction varied from 58.2 – 74.2%.

The mean values of the compressive and diametral tensile strengths ranged from 242.3 - 324.7 MPa and from 39.8 – 62.6 MPa, respectively. The Knoop Hardness values ranged from 41.8 – 81.9. Significant correlations were observed between the volume fraction of filler and the diametral tensile strength, and between the volume fraction of filler and the Knoop hardness number. No correlation was found between the degree of conversion and any of the mechanical properties of the composite resins tested. Because of the correlations between the volume fraction of filler and the diametral tensile strength, and between the volume fraction of filler and the Knoop hardness numbers, it was concluded that the filler concentration plays a prominent role in determining the properties of contemporary posterior composite resins.

Modifications in the filler size, morphology, and components have markedly affected the recent development of composites in the market. Given that filler morphology affects the filler loading rate of composites, **Kim, Ong, and Okuno[14] in 2002** hypothesized that a)composites can be classified by their morphology, b)filler loading is dependent on filler morphology, and c)filler morphology and filler loading influence the mechanical properties of commercially available composites. Fourteen commercial composites were evaluated in this study: four composites with pre-polymerized particles (Metafil CX, Silux Plus, Heliomolar Radiopaque, Palfique Estelite), six composites with irregular-shaped particles (Aelitefil, Charisma, Herculite XR, Hipolite, TPH, Veridonfil), one composite with pre-polymerized plus irregular shaped particles (Photoclearfil) and four composites with round particles (Pertac-Hybrid, Z-100, Palique Toughwell). Scanning electron microscopy and elemental analysis (FE-SEM S-4200 Hitachi Co, Tokyo, Japan) were performed to evaluate three specimens per composite at X500 magnification. Filler weight content was determined in three specimens per composite by the standard ash method: the weight of each sample was measured with an analytical balance and later heated in a furnace at 600^oC for 30 min to burn out the organic matrix and then

re-weighted. The final weight consisted only of the inorganic filler, which was determined by the following formula:

$$\text{Filler wt\%} = \text{initial weight/final weight} \times 100\%$$

The filler volume fraction (vol%) of the inorganic filler was calculated as follow:

$$\text{Filler vol\%} = \frac{dr \times wt\%}{dr \times wt\% + df\,(100 - wt\%)} \times 100$$

where d_r is the density of the resin and d_f is the density of the filler. Four mechanical properties were investigated: flexural strength, flexural modulus, Vickers hardness, and fracture toughness. Flexural strength and flexural modulus were determined with a 3-point bending test in a universal testing machine (Model 4202; Instron Corp, Canton, Mass.) at a crosshead speed of 0.1 mm/min. to determine Vickers hardness, specimens from each composite were prepared in triplicates and a 200-g load was applied for 15 seconds (FM-7; Future-Tech Co, Tokyo, Japan). To determine fracture toughness, five single-edge notch specimens from each composite were fabricated and at a crosshead speed of 0.1mm/min, a 3-point bending test was performed in a universal testing machine. Each test parameter was evaluated with 1-way analysis of variance (ANOVA) and Duncan's multiple range test was used for post-hoc analysis ($P < .05$). The results showed that filler loading was influenced by filler morphology. Composites containing prepolymerized filler particles had the lowest filler content (25-51% of filler volume), whereas composites containing round particles had the highest filler content (59-60% of filler volume). The mechanical properties of the composites were related to their filler content. Composites with the highest filler by volume exhibited the highest flexural strength (120-129 MPa), flexural modulus (12-15 MPa), and hardness (101-117 VHN). Fractured toughness was also affected by filler volume, but maximum toughness was found at a threshold level of approximately 55% filler volume.

Ikejima, Nomoto and McCabe[36] in 2003, understood that the most appropriate kind of mechanical testing regime for evaluating restorative materials has not been agreed amongst the international community responsible for developing standard tests for composites products. Shear test has been advocated as it has certain advantages over more traditional compressive and flexural tests. The purpose of this study was to identify the effect of filler volume fraction, particle size and silanation on shear punch strength, flexural strength and flexural modulus of different types of resin composites. Fourteen model resin matrix dental composites manufactured by Shofu, Inc. Japan, were used in this study. Hybrid type glass with filler silanation (0 ± 65.2 vol%), composites without filler silanation (30.7 ± 51.0 vol%) and microfilled type (0 ± 13.0 vol%). The resin matrix was a blend of UDMA and EGDMA. For the shear punch test, 10 disc specimens were prepared for each composite and tested with a 3.2 mm diameter punch at 1 mm/min. Flexural strength (n=10) was measured by the three-point flexural testing performed at a test speed of 1mm/min and both flexural strength and flexural modulus were calculated. Data were analyzed using one-way ANOVA and Fisher's multiple-range test, t-test and test for correlation/regression. The results showed shear punch strength and flexural strength increased with increasing filler content up to 52.2% for hybrid composites and between 0 and 9.1% for microfilled composites. Shear punch strength and flexural strength decreased with increasing filler volume fraction for un-silanated composites. Flexural modulus for all materials increased with increasing filler volume fraction. Hybrid composites with silanated fillers have significantly higher values of flexural strength, flexural modulus and shear punch strength than equivalent materials with un-silanated fillers. According with these results filler silanation is an important factor for determining material strength and the addition of small quantities of microfillers appeared to have a greater effect on shear strength than similar amounts of hybrid filler. The shear punch test may prove beneficial for routine testing of composites as specimen preparation was simple, specimen quality was easy to maintain and the results were meaningful.

Beun, Glorieux, Devaux, Vreven and Leloup[16] in 2007 conducted a study that characterized the inorganic fraction and measurd the mechanical properties of nine commercial resin based composites. Furthermore, the degree of conversion of the photopolymerized materials was evaluated using halogen and LED units. Two microfilled (A11-3M ESPE and Durafill VS-Heraeus-Kulzer), three nanohybrids (Supreme-3M ESPE, Grandio-Voco, Grandio flow-Voco) and four universal (Point 4-Kerr, Tetric Ceram-Ivoclar-Vivadent, Venus-Heraeus-Kulzer, Z 100-3M ESPE) were the materials tested in this study. The weight percentage of fillers was determined using thermogrametric analysis (TGA/SDTA861, Metler-Toledo, Switzerland). Three samples of each material were analyzed. The weight changes were evaluated during a thermal program ranging from 30 to 900°C at the rate of 10°/min followed by air cooling to room temperature. The calculated ratio between the final sample weight and its initial weight is designated to the inorganic fraction. The filler morphology was determined using SEM. The washing technique was used to remove the unpolymerized monomers: 0.5g of each material was dissolved in 4ml of acetone and centrifuged for 5 min at 700rpm. This process was repeated three times and repeated three other times using chloroform for a complete unpolymerized resin elimination. The remaining fillers were suspended in ethanol, smeared on a glass slide and dried. After gold coating, fillers were observed by SEM (Leica Stereoscan S-260, /Cambridge, UK) at 5000 and 10,000 magnifications. Furthermore, five samples of each material were prepared and light cured using two conventional curing devices (XL 3000, 3M-ESPE, St. Paul, MN, USA, 650mW/cm^2 followed by mechanical properties measurements: 1) Dynamic modulus: measured by the impulse excitation technique, 2) Static modulus and flexural strength: measured using a three- point bending setup according to the ISO-4049, and 3) Vickers microhardness: which was carried out on the fractured samples obtained from a previous test with a Durimet microhardness tester (Leitz, Wetzlar, Germany). The degree of conversion was evaluated in composites samples polymerized with the XL 3000 (3M-ESPE, St. Paul, MN, USA) for 40s with an intensity of 650mW/cm^2 and with the Elipar Freelight 2 (3M-ESPE, St. Paul, MN, USA) for 10s. The degree of convertion was measured using the Raman spectrophotometry. The mean values of

the percentage of fillers by weight ranged from 51.3% for the Durafill VS to 84.1% for the Grandio. On the other hand, values varied between 71 - 79.7% for Universal hybrid composites, 51.3 – 54.9% for the microfilled composites and 71.9 and 84.1% for the nanofilled composites. The SEM microphotographs the Z-100, Supreme and Point-4 showed spherical particles. Irregular shaped particles were found in Grandio, Grandio flow, Tetric-Ceram and Venus. Microfilled composites contained large filler aggregates. Nanofilled resin composites showed higher elastic moduli than the universal or microfilled composites, except for the Z-100. For the overall mechanical properties evaluations, the microfilled composites exhibited the lowest values. The degrees of polymerization obtained with the halogen lamp were higher than the ones obtained with the LED lamp. The significance of this article is that nanofilled resin composites show mechanical properties comparable to the universal hybrid composites, so it can be expected they are able to resist stresses at least as well as the universal composites and could thus be used for the same indications and in anterior restorations due to their high aesthetic properties.

Ilie and Hickel[37] in 2009 analyzed in an laboratory test under standardized and simulated clinical conditions eight different materials categories of commercial composites. Seventy-two hybrid, nano-hybrid, micro-filled, packable, ormocer-based and flowable composites, compomers and flowable compomers were compared for flexural strength and modulus of elasticity, compressive and diametral tensile strength were evaluated. The following null hypotheses were tested: there are no differences in the mechanical properties between the eight material categories, and the behavior of the tested materials is similar in the three different loading conditions. The flexural strength and flexural modulus were determined in a three-point bending test (MCE 2000 ST, Germany) with a crosshead speed of 0.5 mm/min. The universal testing machine measured the force during bending as a function of deflection of the beam and the bending modulus was calculated from the slope of the linear part of the force-deflection diagram. The compressive strength and diametral tensile strength were determined with the universal testing machine and a compressive load applied axially at a crosshead speed of 0.5 mm/min. Data

were analyzed using one-way ANOVA, Tukey HSD post hoc test and the multivariate analysis. Large differences between the tested materials within the same material category were found. The hybrid (116.6 MPa), nano-hybrid (103.1 MPa), packable (105.9 MPa) and ormocer-based (104.3 MPa) composites do not differ significantly among each other as a material type, reaching the highest flexural strength values. Nano-hybrid composites are characterized by good flexural strength, the best diametral tensile strength but a low flexural modulus. The lowest mechanical properties were with the micro-filled hybrids. The flowable composites and compomers showed comparable result for all properties . Both flowable material categories do not differ significantly from the micro-filled composites for the most mechanical properties, showing only a higher diametral tensile strength. The filler volume had the most influence on the measured properties, inducing a maximum flexural strength and flexural modulus at a level of 60%, whereas such dependence was not measured for diametral tensile strength or compressive strength. The influence of the type of material on the mechanical properties was significant but very low, having the strongest influence on the compressive strength.

Mesoporous fillers

Samuel, Li, Mukherjee, Guo, Patel, Baran, and Wei[38] in 2009 studied the mesoporous fillers because of their potential for creating micromechanical filler/resin matrix interphase bonding which could eliminate the need for the silane treatment of the filler. They synthesized mesoporous by using the non-surfactant templating method. The porous silica used in this study contained interconnected pores and channels as opposed to porous fillers containing surface pores. Then light cured experimental resin composites were prepared. For comparision purposes, experimental dental composites were created using three types of fillers: A. mesoporous silica fillers, B. mesoporous and nonporous silica fillers (500nm) and C. 3- methacryloxypropyltrimethoxysilane treated nonporous spherical silica fillers (500 nm). Compression testing was performed to measure compressive strength, yield stress, and compressive modulus by using a servohydraulic machine (MTS

Mini-Bionix 2, Eden Prairie, MN) using a cross head speed of 1mm/min. Flexural strength and flexural modulus of the post cured composites were determined by a three point bending test. The results showed that composites containing a combination of mesoporous and monodisperse spherical fillers have a higher compressive modulus (8.1±0.5 GPa) when compared with composites that only contain mesoporous (5.7±0.14 GPa) or MPS silane treated nonporous spherical fillers (5.7±0.4 GPa). As expected, the yield strength increased with an increase in filler content. Composites containing a combination of mesoporous and nonporous spherical fillers had a significantly higher flexural modulus (10.3±0.8 GPa) when compared to the composites containing mesoporous fillers alone (6.7±0.5 GPa). The flexural strength however was not statistically significant. These results showed that porous fillers with interconnecting pores are promising materials to prepare stronger dental composites but further studies are needed to find the relationship between the extent of resin penetration and the final mechanical property of mesoporous filler based composites.

Filler analysis

Acharya and Greener[25] in 1972 studied the effectiveness of thermogravimetric techniques as a tool in the characterization of dental composites and to find the residual "ash" content on completion of a thermally induced weight loss. Also, the thermogravimetric technique was used to determine fluid absorption by polymeric materials and to characterize polymers on the basis of this parameter. The six commercially available composite resins investigated were designated as: CR1 (Adaptic, Johnson and Johnson), CR2 (Addent 12, 3M), CR3 (Addent 35, 3M), CR4-unfilled polymer (Addent XV, 3M), CR5 (Blendant, Kerr), and CR6 (Concise, 3M). The thermogravimetric apparatus consisted of a vertical cylindrical furnace that surrounded a pyrex hangdown tube that contained the platinum sample pan. The sample pan was hung on a thin platinum wire connected to the torque motor of the electrobalance. The furnace temperature was raised linearly in the range of 25

to 680 °C. The sample was hung about 10mm from the closed bottom end and samples were pyrolyzed essentially in their own gaseous environment. The composite samples were prepared according to the manufacturers' instructions. Samples from each of the brands were also immersed for 96 hours in Ringer's solution (NaCl, KCl, $CaCl_2$, $NaHCO_3$) at room temperature before being polymerized. The weight loss vs. temperature for all six resin composites was similar. The rate of weight loss went through a maximum in the temperature interval of 370 to 440 C. The similarity of the TG values of the six composites suggests that they are made of essentially the same resin system. The ashed weight, which was taken to be the filler weight, varied between 70% and 75% by weight. From pyrolysis and fluid absorption data, it was concluded that brands CR4 and CR6 are different from the other four composites.

Hosoda, Yamada and Inokoshi[24] in 1990 examined composite resins by scanning electron microscopy (SEM) and by qualitative analysis (EDX) to obtain an understanding for the appropriate selection for composites resins for clinical use. Sixty-six commercially available composite resins were used, which included twenty-four chemically-cured resin composites, twenty-one light-cured anterior resin composites, three light-cured anterior and posterior composite resins, and eighteen light-cured posterior composites. The weight filler contents were determined for individual materials by ashing at 570°C in air. The surface of the composite resin specimens was analyzed with EDX (SED-880, Seiko EG&G) under 500 power magnification. When a few filler particles, different in shape and shade, were observed under the SEM, the energy spectra of elements present in the individual fillers were obtained under 3000 through 5000 power magnification. The composite resin specimens used for EDX analysis were re-polished to remove the carbon coating. After vapor-coating with gold, the polished surfaces were examined in the SEM with the back-scattered electron images under 500 power magnification. The results showed that the weight filler content of the traditional resins presented high inorganic contents ranging from 70% to 80%. The microfilled composite resins showed relatively looser quantities around 50%. The heavily filled composite resins

exhibited approximately 85% inorganic contents. The filler content of the other varied from 60% to 80%. The elements detected in the polished composite resin surfaces were Si, Al, Ba, Zr, La, Yb Zn and Ti. Only Si appeared in the traditional composite resin surfaces and the microfiller–filled composite resins. Al, Ba, Zr, La, Ti, Zn, and/or Yb appeared in the other resins. The filler particles having radiopacity contained Ba, Al, Zr, Zn, and/or Yb. The composition SEM images of the polished surfaces produced by using back-scattered electrons were divided in five groups according to the filler type and their distribution: 1. Angular quartz filler particles distributed in the matrix (traditional resin composites); 2. Angular-splintered microfiller complexes of various sizes incorporated in a microfiller-reinforced matrix; 3. Angular-splintered prepolymerized complexes making up spherical submicron-filler particles added to a submicron-filler reinforced organic matrix; 4. Angular-splintered prepolymerized or agglomerated microfilled complexes and the inorganic filler particles of various sizes are distributed in a microfiller-reinforced composite resin matrix; 5. Spherical microfilled complexes and the inorganic filler particles are observed in a microfiller-reinforced matrix. Based in these results, the authors proposed to divide the resin composites in five groups with two hypothetical categories:

1. Traditional composite resin: traditional macrofiller

2. Microfilled composite resin (0.06-0.04 µm)

3. Microfilled type composite resin:

   3. Microfiller (0.06-0.04 µm) splintered microfilled complex

   4. Microfiller (0.06-0.04 µm) agglomerated microfiller complex

4. Submicrofilled type composite resin: Submicrofiller (0.3-0.2 µm) splintered submicrofilled complex

5. Hybrid composite resin: traditional macrofiller microfiller (0.06-0.04 µm)

6. Hybrid type composite resin:

   a. Traditional macrofiller microfiller (0.06-0.04 µm) splintered microfilled complex

b. Traditional macrofiller microfiller (0.06-0.04 μm) spherical microfilled complex

c. Traditional macrofiller microfiller (0.06-0.04 μm) agglomerated microfiller complex

7. Semihybrid or heavily-filled composite resin
   a. Traditional microfiller (50-0.1 μm)
   b. Traditional small filler (6.5-0.1 μm)

Jaarda, Lang, Wang, and Edwards[15] in 1993 initiated a study to examine two methods that would qualify the filler particle content of a composite resin and quantify the number, size, and area occupied by the filer particle in composite resins. The experiment was divided in two parts: the first part examined qualitatively the size of the filler particles contained in the three composite resins with the SEM. The second part of the project used the SEM plus digital imaging to qualitatively measure the number, size, and area occupied by filler particles in composites samples. Three fine-particle composites resins, BIS-Fil I (BISCO), Visio-Fil (ESPE-Premier) and Ful-Fil (L.D. Caulk) were the materials selected for this study. For part one, samples were prepared, suspended in acetone, centrifuged for two minutes at 1000rpm to separate the filler particles from the matrix followed by SEM evaluation. The acetone washing process was repeated three times. After the SEM analysis, the remaining filler particles were placed in chloroform for further washing and centrifuged for two minutes at 1000rpm and later examined by SEM. This chloroform washing was repeated three times. Finally the remaining filler was suspended in absolute ethanol followed by SEM evaluation. For the second part samples were prepared and embedded in EXAKT 7200 Technovit medium (EXAKT-Kulser, Germany) and prepared with a series of sandpaper disks and the EXAKT machining system. Then the surface was carbon-coated for SEM examination (AMRAY 1000-B SEM, Bedford, Mass.) and digital imaging (Princeton GammaTech 4 Plus digital imaging system) at 500X and 5000X. To characterize the filler particle content of the composites studied, seven groups were established with specific

filler-particle size groupings and an eight category for the matrix was added to provide a measure of the percent of fill of the composite resin: Group I: 0.11-0.5μm (0.0094≤0.2μm²), Group II: 0.5-1.0μm (0.2≤0.8μm²), Group III: 1.0-2.0μm(0.8 ≤3μm²), Group IV: 2-5μm(3≤20μm²), Group V: 5-9μm(20≤60μm²), Group VI: 9-20μm(60≤300μm²), Group VII: 20μm(300≤μm²), Group VIII: matrix. The results demonstrated that the range of particles sizes and the individual filler particle size differences are dramatically different for each composite. The total mean number of particles were 7991 for Ful-Fil, 6850 for Visio-Fil, and 5033 for Bisfil I composite resins. Ful-Fil was the most highly filled composite followed by Bis-Fil I and Visio-Fil. No filler particles smaller than 0.11μm in diameter were found in the three composites. When the seven groups were combined with the matrix, the data indicated that the percentage of fill for each composite was 55.26% fill for the Viso-Fil composite, 36.49% for Bis-Fil I, and 32.14% for Full-Fil composite. The mean particle size was 2.31μm² for Visio-Fil composite, 2.08 μm² for Bis-Fil I composite, 1.15 μm² for Ful-Fil composite. It can be concluded that the three composites were significantly different in the mean number for filler content and in the mean area occupied by the filler particles. The conventional classification as fine particle composite resin could not be justified for the three materials, and the validity of such systems as a selection guide for the clinician is questioned. Characterizing the filler particle content of a composite resin by using the profile map proved to be a much better method than the previously used conventional methods of classification as microfilled, fine particle, and blends. SEM and digital imaging are valid and reliable methods to evaluate composite resins qualitatively and quantitatively for filler particle numbers, sizes, and the area occupied by the particles.

In 2004, Sabbagh, Ryelandt, Bacheries, Biebuyck, Vreven, Lambrechts, and Leloup[20] conducted a study to determine the percentage by weight of the inorganic fillers in thirty-nine composite materials (flowable and packable) and to examine the filler morphology by SEM (scanning electron microscopy). One commercially light-cured, one chemically cured resin composites and two resin based materials

known as Ormocers were the materials used in this study. The thermogravimetric analysis was used to determine the percentage of fillers by weight using a thermogravimetric analyzer (Perkin- Elmer TGA-7). Three specimens of each material were heated at a rate of 30℃ min^{-1} from 30 to 900℃. The percentages of inorganic fillers by weight (n=3) was also determined by the ashing technique by comparing the weight difference before and after ashing in air 0.5 g of each material at 900℃. The samples were introduced into a furnace for an hour and then weighted using an analytical balance. For the SEM, the unpolymerized monomers were removed by a washing technique. Each sample was dissolved in acetone and centrifuged for 5 min at 700g. This process was repeated three times using acetone and three other times with chloroform followed by washing and elimination of the unpolymerized resin. The remaining filler particles including the prepolymerized fillers were placed in ethanol and the suspension of filler particles was smeared on a glass slide and dried at 37° for 6 hours. Then, a thin coating of gold was sputtered on the filler bearing slides. Morphological examination was performed using a scanning electron microscope operating at 20 kV. The results showed that the weight fraction of inorganic fillers ranged between 41.6% and 84.6% and a wide variation was found among materials of the same category. In some materials, the values recorded were different from those given by the manufacturers. The SEM photomicrographs showed various shapes, and sizes of inorganic fillers. When comparing universal hybrid materials with flowables composites, the flowables have lower filler loading and packable resin composites did not show higher values as claimed by some manufacturers. Some factors could explain the observed discrepancies between the manufacturer's data and their results. The silane treatment as well as the incorporation of organic material as part of the fillers of the composite could be responsible for those differences.

New technology in Resin–based composites

Nanocomposite

Mitra, Wu and Holmes[9] in 2003 conducted a study that reported the development of a new dental nanocomposite, Filtek Supreme Universal Restorative (3M ESPE Dental products) that has the esthetic properties required for cosmetic restorations and the mechanical properties necessary for posterior restorations. They measured the nanocomposite properties and they were compared with those of several commercial composites. They synthesized two types of nanofiller particles for this investigation: nanomeric particles and nanoclusters. The nanomeric particles are monodisperse nonaggreagted and nonagglomarated silica nanoparticles. The silica particles were treated with the coupling agent 3-metacryloxypropyltrimethoxysilane or MPTS to make the filler compatible with the resin before curing to prevent agglomeration or aggregation. Two types of nanoclusters were synthesized: Zirconia silica particles whose particle size ranged between 2-20nm with spheroidal particles with and average size of 0.6μm. The other type of nanocluster filler was a silica particle of 75nm with another broad particle size with a 0.6μm average. The resin system used was the same proprietary mixture used in Filtek Z250 Universal restorative composite (3M ESPE). Using statistically designed experimentation methodology, many combinations of nanocluster and nanomeric fillers were studied to determine an optimal formulation. The commercial materials tested were Filtek A110 (3M ESPE), Filtek Z250 (3M ESPE), TPH Spectrum (Denstply Caulk), EsthetX (Denstply Caulk), Point 4(Kerr), Filtek Supreme standard (3M ESPE), and Filtek Supreme Translucent (3M ESPE). The properties they studied were compressive strength and diametrical tensile strength (Instron 4505), in vitro three-body wear (Profilometer), Flexural strength (three-point bending), fracture toughness, polish retention (micro-tri-gloss instrument, BYK-Gardner, Columbia, Md) and surface morphology after toothbrush abrasion (SEM analysis). The statistical analysis was performed by an analysis of variance, or ANOVA/Tukey-Kramer paired analysis at a ninety-five percent

confidence interval.   The compressive and diametral strengths and fracture resistance of the nanocomposite were equivalent to or higher than those of the other composites tested. The three-body wear results of the nanocomposites sytems developed were statically better than those of the all other composites tested. The nanocomposite showed better polish retention than the hybrids and microhybrids tested for all the brushing periods. After extended tooth brush abrasion, the dentin, body and enamel showed polish retention similar to that of the microfill tested, while translucent shades showed better polish retention than the microfill. In summary, combinations of these two types of nanofillers resulted in the best combination for an improved physical property. With the combination of superior esthetics, long-term polish retention and other optimized physical properties, it is expected that this novel nanocomposite system would be useful for all posterior and anterior restorative applications. Further clinical studies will be needed to confirm these in vitro findings.

New resin-based composites with nanofillers have been commercialized the last decade. While manufacturers make claims of improved clinical performance and characteristics little evidence is available that suggests these materials show improvements over other materials already in the market. **Yesil Z, Alapati S, and Johnston,[39] in 2008** evaluated the relative wear resistance of 2 nanofilled composites (Filtek Supreme, Premise) with the traditional microfilled (Heliomolar RO) and microhybrid (Point 4) resin composites. Six specimens of each composite material were subjected to a 3-body wear tests using the Oregon Health Sciences University Oral Wear Simulator to produce abrasive wear and attrition. The enamel cusp is forced into contact with the composite specimen through a layer of foodlilke slurry. The cusp imparts an initial 20-N load to the composite and is slid across the surface over an 8 mm linear path. At the end, a static 70-N load is applied to produce localized attrition wear with a sequence of 1.0 Hz for 50,000 cycles. The amount of abrasion and attrition was measured using a profilometer (Surfanalyzer; Mahr Federal, Inc, Providence, RI). Profilometric tracing were performed at 1 mm increments from the head of the wear pattern to the tail. To determine the average

roughness of wear facet, an additional profilometric tracing was made along the entire length of the wear facet. 1-way ANOVA and Tukey multiple range test compared the wear and surface roughness data. The size of the wear facets was assessed to determine the relative wear of the antagonist enamel cusps. SEM images were made to qualitatively assess the surface characteristics after testing. The results indicate that the composite resin type did not influence the overall attrition wear rate of the material, but did significantly affect abrasive wear. The microfill material exhibited significantly less abrasive wear than the nanohybrid material. Also, no significant difference was found in the average size of the opposing enamel wear facet generated by the different composites materials. The microfilled material resulted in a significantly rougher surface within the wear facet than either nanohybrid or microhybrid composites but was not significantly different than nanofilled composites. In conclusion, the incorporation of nanofillers did not result in significantly improved in vitro abrasive or attrition/wear in the materials tested.

Chen[40] in 2010 reviewed recent studies of the development of dental nanocomposites and their clinical applications. Nanocomposites allow for increasing filler loading and a reduced amount of resin matrix, thereby reducing polymerization shrinkage while providing esthetics and strength. Many nanocomposites are in the market, and some of them are: Filtek Supreme (3M ESPE), Premise (Kerr/Sybron) and Ceram-X (Denstply DeTrey). Nanocomposites can be strengthened by the addition of reinforced fillers with nanofibers, short E-glass fibers, and TiO_2 nanoparticles. Ion-releasing nanocomposites can also be used to increase the mineral content of dental caries lesions by the use of nano-DCPA whiskers or TTCP-whiskers for releasing Ca and PO_4 ions, by the use of calcium fluoride nanoparticles for fluoride release, or by the use of both calcium fluoride and DCPA for F, Ca, and PO_4 release. Polymer-kaolinite nanocomposites can also release fluoride, and C (Kacrylamide) might be a useful material for caries prevention. Nanocomposites with a ring-opening resin matrix can reduce polymerization shrinkage by the use of epoxy-polyols, or by the use of Silorane (3M-ESPE), which is generated by the cationic ring-opening polymerization of the cycloaliphatic oxirane

moieties, or by the use of epoxy resin ERL 4221 or SSQ monomers. Different approaches have been used to prevent nanoparticles from forming microscopic aggregation during processing. The same silica fillers are coated with MPTS (3-methacryloxypropyltrimethoxysilane) to avoid particles aggregation and promote interfacial adhesion through covalent and H-bonding. Silica fillers can be modified by OTMS (n-octyltrimethoxysilane), a non-reactive aliphatic silane, to interact through weak Van Der Waals forces. The silane structure used for the silanization of nanosilica has an effect on solvent absorption and the solubility of composites. The composite containing UDMS (3-[(1,3(2)-dimethacryloyloxypropyl)-2(3)-oxycarbonylamido]prop-yltriethoxysilane) showed the highest amount of absorved water, the composite with OTMS showed the highest solubility in both water and ethanol/water. GPS (γ-glycidoxypropyl trimethoxysilane) can be used as a couplin agent in nanocomposites with epoxy resin matrix. ATES: (organosilane allytriethoxysilane) increase the dispersion and linkage of TiO_2 nanoparticles within the resin matrix. There are several commercial nanocomposites that have good strength after 1 day of immersion in water. However, their strength can decrease by more than 50% after just a couple of months of immersion; therefore, strength durability is an important issue, especially in ion-releasing composites. Overall, the development of nanocomposites has led to significant improvements in dental materials and their clinical applications. However, more improvement in the properties of nanocomposites needs to be done, so it is worthwhile to continue further research.

Silorane

Ilie and Hickel[10] in 2006 conducted a study to examine the characteristics of a silorane-based composite material in terms of degree of cure and mechanical properties as a function of different curing conditions and compare them with those of well known methacrylate based composites when examined under equivalent curing conditions. The curing behavior of a silorane based composite (Hermes, 3M ESPE) shade A3 was evaluated by assessing the degree of cure and variation of

hardness and modulus of elasticity with depth after polymerizing the material with 16 curing regimes comprising one halogen and three LED-curing units. One increment of composite in a mold 2 mm high and 4 mm diameter and 3 increments in a 6 mm high mold were used to evaluate the degree of cure. Measurements were made in real time with an FTIR spectrometer with an ATR accessory for 20 minutes at the bottom of the samples. To analyze the polymerization quality hardness and modulus of elasticity profiles the middle of the samples were measured and calculated for each group as a curve-fitted line, based on data from five samples (300 measuring points). Results were then compared using a one-way ANOVA and Tukey's HSD post hoc test. The results showed highest irradiance was measured for the halogen curing unit, Astralis 10 (1857 mW/cm2), whereas LED curing units, MiniLED, Freelight 2, and Blue phase, with a narrow band spectral output, achieved irradiances of 1141 mW/cm2, 1226 mW/cm2, and 1435 mW/cm2 respectively. Highest decrease rate of irradiance with distance was observed for the halogen curing unit, whereas that of the LED curing unit, MiniLED, was less than a quarter of Astralis 10's in the first five millimeters. No significant differences (p<0.05) were found among the curing units regarding the degree of cure at 2-mm depth - with the exception of MiniLED Pulse regime. At 6-mm depth, no significant differences in the degree of cure were observed for the 10-second polymerization time. However, with the 20-second and 40second regimes, curing units with a turbo tip yielded significantly lower DC than the curing units with a standard tip. The mechanical properties tended to decrease with depth. However, no significant differences were observed between 2-mm and 6-mm depths within one regime, or between different curing regimes. At 2 mm, no such correlation was found between polymerization time and mechanical properties, and that irradiance did not correlate with any measured property. At 6-mm depth, the influence of polymerization time on the degree of cure and mechanical properties increased. A silorane composite and a representative commercial methacrylate-based composite (Tetric Evo Ceram) were cured under the same conditions. No differences were registered between the two categories of material in terms of hardness. However, modulus of elasticity of the silorane material was slightly lower and the creep resistance higher when compared

with the methacrylate-based composite. The study presented appropriate sample sizes for each group. The methodology should provide more details on the comparison of silorane and methacrylate based composites. In addition, the hypothesis and clinical significances should be addressed.

Lien and Vandewalle[3] in 2010 realized that the introduction of a silorane-based composite opens new ideas in the quest to reduce polymerization shrinkage and to balance volumetric stress caused by the behavior of polymerization contraction. The purpose of their study was to determine and to distinguish the unique physical properties of a new-silorane based restorative material in comparison to five methacrylate-based restorative materials consisting of a compomer, giomer, nanocomposite, hybrid, and micro-hybrid. Six restorative materials were selected: Filtek LS - 3M ESPE (silorane-based), Beautiful II – Shofu (giomer), Dyract Extra – Denstply (Compomer), Esthet X – Denstply (Microhybrid), Filtek Supreme – 3M ESPE (Nanocomposite), and Filtek Z250 – 3M ESPE (Hybrid). Diametral tensile strength (universal testing machine and crosshead speed of 1.0 mm/min), compressive strength (universal testing machine and crosshead speed of 1.0 mm/min), flexural strength and flexural modulus (three-point bending test using universal testing machine, crosshead speed of 0.25 mm/min), fracture toughness (single-edge notched-beam method, UTM and crosshead speed of 1mm/min), knoop microhardness (diamond indenter, LM 300AT Leco, with a 200g load and a 10s dwell time), and polymerization shrinkage (video-imaging device, AcuVol, Bisco) were the properties examined. The mean and standard deviation were determined per group and one-way ANOVA/Tukey was performed per property. The results showed that the hybrid material had the highest compressive strength, which was not significantly different from the nanocomposite, and the silorane–based composite had the lowest compressive strength. There was no significant difference between any of the restorative materials for the diametral tensile strength test. The hybrid resin-composite had the highest flexural strength, which was not significantly different from the silorane-based composite. The micro hybrid had the lowest flexural strength. The giomer and the silorane materials

showed the highest flexural modulus. On the other hand, the nanocomposite and microhybrid had the lowest flexural modulus. None of the materials showed a significant difference related to the fracture toughness except the compomer, which had the lowest value. The hybrid material had the highest micro-hardness followed by the hybrid composite and the giomer material. The materials with the lowest micro-hardness values were the compomer and microhybrid composite. Finally, for the volumetric shrinkage property, the composite materials that showed the lowest shrinkage were the silorane and nanocomposite, and the composite materials with the highest shrinkage values were the microhybrid and compomer.

Marchesi, Breschi, Antoniolli, Di Lenarda, Ferracane and Cadenaro[41] in 2010 were concerned about the volumetric shrinkage and subsequent contraction stress arising during the polymerization reaction of the resin-based tooth colored restorative materials. They measured the contraction stress of a silorane-based material and a new low-shrinkage nanohybrid composite compared to three conventional dimethacrylate-based resin composites during photo-polymerization with a halogen curing light using a universal testing machine provided with a feedback system and stress analyzer with no feedback. The hypotheses tested were: 1.The silorane-based and the low-shrinkage nanohybrid composites develop lower contraction stress during photo-polymerization than conventional dimethacrylate-based restorative materials irrespective of the stress testing method and 2.Testing system affects the measured stress values. The materials tested were Filtek Silorane LS - 3M ESPE (silorane), Venus Diamond - Heraeus Kulzer (low shrinkage nanohybrid), Tetric EvoCeram - Ivoclar Vivadent (nanohybrid), Quixfil - Dentsply DeTrey (packable), and Filtek Z250 - 3M ESPE (universal microhybrid). Shrinkage stress was assessed using a stress-strain analyzer consisting of two opposing attachments, one connected to a load sensor and the other fixed to the device, or a system fixed to a universal testing machine with an extensometer as a feedback system. All specimens were polymerized with a quartz-tungsten halogen curing light for 40s; the contraction force generated during polymerization was continuously recorded for 300s. Contraction stress (MPa) was calculated at both 40s and 300s.

Data were statistically analyzed by three-way ANOVA and Tukey's multiple comparison test. The results showed that Venus Diamond exhibited the lowest stress under both experimental conditions. Stress values scored as follows: Venus Diamond<Tetric EvoCeram<Filtek Silorane LS<Quixfil<Filtek Z250 ($p<0.05$). Stress values measured with the stress-strain analyzer were significantly lower than those measured with the universal testing machine with feedback. The hypothesis was partially rejected because only Venus Diamond exhibited the lowest stress values among the tested materials. Contraction stress was higher for all composites when measured in a test system with a feedback. This study confirms that simply reducing the shrinkage does not ensure reduced stress development in composites.

Ormocer-based composites

Leprince, Palin, Mullier, Debaux, Vreven and Lepoud[42] in 2010 were concerned information of a new inorganic-organic resin type that was developed many years ago for the polymer industry and has subsequently been adapted for dental use, known as ORMOCER-based composite was not widely reported. Ormocer technology consist of an organic reactive species which is bound by the in situ formation of a inorganic (Si-O-Si) network, which may result in reduced shrinkage ranging from 1.46 to 2.64 vol%, depending on the material and measurement method. The aim of this study was to characterize the inorganic fraction of materials belonging to each type of composite and to compare their mechanical properties. Eight resin composites were included in this study: two Ormocers (Admira and an experimental Ormocer V35694), one silorane (Filtek LS) and five metacrylate-based composites (Filtek Supreme XT, Tetric EvoCeram, Grandio, Synergy D6 and one experimental material V34930). Inorganic fillers were quantified by thermogravimetric analysis and morphologically characterized by SEM. The mechanical properties measured were: dynamic modulus, static modulus, flexural strength and Vickers microhardness. Dynamic modulus was determined by an impulse excitation technique, static elastic modulus and flexural strength by a three-point bending method and Vicker microhardness with a Durimet microhardness

tester and 200-g load. The results were analyzed using ANOVA tests ($P < 0.05$) and linear correlation. Grandio (84.3 vol%), V34930 (86.7 vol%) and V35694 (86.5 vol%) exhibited significantly higher filler mass fractions. Both dynamic and static moduli of Grandio (24.9 GPa and 9.2 GPa respec.) and V34930 (25.7 GPa and 9.0 GPa respec.) were significantly higher than the other materials ($P < 0.05$), although no significant difference in flexural strength was observed between material type ($P > 0.05$). From the present findings, it was suggested that V35694 and Filtek Silorane exhibit comparable properties to conventional methacrylate-based composites, although clinically the cavity type and location must guide material choice. Under high occlusal load, the use of Grandio and V34930 might be favored. For small cavities, alternative technologies could be preferred as the need for mechanical resistance is lower and the potential for stress generation is greater.

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CHAPTER II

Abstract

Objectives*:* To determine the filler content by weight percentage of four resin composites and to examine the morphology, size and elemental distribution of the filler particles.

Methods and materials: Four commercially available light-cured resin composites (Kalore, Filtek LS, Aelite LS and IPS Empress Direct) were evaluated for filler content by weight using ashing in air and acetone dissolution techniques. Ten specimens, 0.5 g each, were analyzed for each material and technique. Specimens for ashing were heated to 650°C for 30 min. For the acetone dissolution, the specimens were dissolved, centrifuged and decanted. In addition, SEM evaluation and Energy Dispersive X-ray Spectroscopy (EDS) analysis were performed to determine morphological characteristics and elemental distribution, respectively. Filler percentages were compared against manufacturer's data and statistically analyzed by one way-ANOVA, Pearson Correlation, Tukey Multiple Comparison and Independent t-tests.

Results: Filler percentage by weight for Aelite LS, Filtek LS, Empress Direct and Kalore from ashed in air were: 86.44%, 77.86%, 72.17 and 70.62%, and from acetone dissolution were: 85.05%, 75.56%, 78.88% and 77.73%, respectively. Mean values for all materials were significantly different for both ashing and acetone dissolution. Aelite LS had significantly higher filler content for both techniques. Kalore had significantly lower filler content for ashing (70.62%) and Filtek LS for acetone dissolution (75.55%). Manufacturer reported filler content for Aelite LS (88%) and Filtek LS (76%) approximated the study results for both techniques, while Kalore (82%) and IPS Empress Direct (79%) were only similar for acetone dissolution, indicating higher content of prepolymerized particles. Morphological examination showed spherical shaped particles for Aelite LS and splintered and irregular shaped particles for all other materials.

Conclusions: Aelite LS had the highest filler content for both ashing and acetone dissolution. Values for filler content by weight using the acetone dissolution were closer to manufacturer reported values.

Introduction

The development of resin composite technology for restorative dentistry was one of the most significant contributions to dentistry in the last century. Initially, they were widely used by dentists for restoring anterior teeth. However, the growing demand of the patients for aesthetic restorations and their concern about mercury containing alloys, has promoted their used as a substitute for amalgam in posterior teeth[1, 2].

Since the very first dental resin composites were developed, many efforts to improve their clinical performance have been undertaken. Researchers have suggested that filler content, size, and morphology of the filler particles within a composite resin formulation, has the potential to influence the strength, elastic modulus, wear resistance, color matching and polymerization shrinkage of a composite resin[3-8]. In addition they have reported that increasing the filler particle size will effectively modify not only the pattern and rate of wear, but the restoration's polishability as well. It has also been stated that the greater the size of the particle, the greater the potential for wear, which in turn affects mechanical properties of composites [3, 8-10]. Thus it would seem reasonable to expect more studies reporting correlations between mechanical properties and filler particle morphology and size. Perhaps the lack of some investigations is due to the difficulty in determining the exact size of the filler particles within a composite resin[11]. Furthermore, attempts to improve clinical performance and to decrease polymerization stress of methacrylate-based composites have been focused in the development of new monomers, such as ring-opening silorane chemistry[12-14]; and a new filler technology, such as nano-sized particles[7, 15, 16].

Several methods have been suggested to determine the filler loading in resin-based composites. Ideally, filler loading should not vary with the different test methods. However, different results have been reported by varying the test method among resin-based composite materials. Factors like organic matrix and inorganic fillers as well as silane coating and prepolymerized particles have been reported to influence the filler content results of these materials. Actually, the most routinely used methods are: 1. manufacturer's reported data; 2. thermogravimetric analysis (TGA); or 3. ashing in air[8-10, 17-19].

No studies have reported measuring filler content by weight or volume for current commercial composites using a technique, which preserves prepolymerized particles to determine filler content. There is no standard procedure for verifying a manufacturer's report of filler loading except the least expensive method of ashing in air. With ashing techniques, the temperature and time of exposure can vary greatly. Previous studies have used temperatures ranging from 570 to 1125°C and times of 20 to 60 minutes[3, 8-10, 20]. From this data, it could be concluded that the organic resin matrix can be effectively burned off at a temperature of 650°C in 30 minutes.

Scanning electron microscopy (SEM) often uses a dissolution technique with acetone or ethyl alcohol to remove the organic matrix from inorganic fillers[3, 8-10, 20-23]. According to some manufacturers ashing in air technique can burn off some of the filler content of composites and thus give false results. To combat this problem a separation of the matrix and filler using acetone or ethyl alcohol needs to be explored. It is hypothesized that a solvent such as acetone will not break down prepolymerized filler, silane, agglomerates, or clusters from composite formulations.

Purpose: The aim of this study was to determine the filler percentage by weight of four different resin composites using ashing in air and acetone dissolution and to examine the morphology of the filler particles with SEM and EDS analysis. The null

hypotheses tested were that there was no difference in filler percent by weight content using ashing in air and acetone dissolution techniques, the percent filler content by weight of selected composites using the ashing by air and acetone dissolution techniques were similar to manufacturer's data and that there was not significant difference of the filler morphology and size of each composite under SEM.

Materials and Methods: Four commercially available light-cured resin composites (listed in Table 1) were chosen based on their filler content by particle size, and evaluated in this study for filler content by weight percentages. In addition, EDS analysis and SEM morphological characterization were performed on the filler particles. Ten specimens (n=10) were analyzed for each material and technique. Filler percentages obtained were compared against manufacturer's data.

Table 1. Composites examined in this study

Brand name	Filler type	Manufacturer
Kalore	Nanohybrid	GC America
Filtek LS	Microhybrid	3M ESPE
Aelite LS	Microhybrid	Bisco
IPS Empress Direct	Nanohybrid	Ivoclar

1.Percentage of fillers by weight using ashing in air

The filler contents of the selected composites were determined by using an ashing in air technique. Ten (n=10) 0.5g specimens of each composite were placed in a burn out furnace at 1200^oF (Neymatic 101, JM Ney Company, Bloomfield, CT). All crucibles were cleaned with cavicide wipes. Each crucible was weighed empty and then weighed after specimen loading. The crucibles (high alumina, 10 mL,

Cole-Palmer Instrument Co., Golden, CO) loaded with specimens were introduced in the furnace after the temperature reached 650°C and then they were left to ash for 30 minutes. The crucibles with the ashed specimens were weighed on an analytical scale (Analytical Standard, AS200-S, O'Haus, Florham Park, NJ). Crucibles were allowed to cool for 15 minutes prior to weighing. The formula that was used to determine percentage by weight of the specimens was as follows:

$$\textbf{Weight Percent} = \frac{\textbf{Wt after ashing – Wt of crucible}}{\textbf{Initial Wt of sample}} \textbf{ X 100}$$

2. Percentage of filler by weight using dissolution with Acetone

The percentages of organic and inorganic fillers by weight (n=10) were determined using acetone in a dissolution process. A specimen of 0.5 g of each material was mixed with 10 mL of acetone (electronic grade, Fisher Chemical, Fair Lawn, NJ) in a test tube (Pyrex 50 mL, Fisher Scientific, Hanover Park, IL). All tubes were weighed initially empty and then weighed again following loading with the 0.5 g specimen. Tubes were covered with aluminum foil to prevent light exposure. All specimens initially were agitated (Maxi-mix 1, Thermolyne, Dubuque, IA), until all solid was dissolved and verified visually. Aggitation continued with a gyrotory shaker (G10, New Brunswick Scientific, New Brunswick, NJ) within a controlled temperature chamber (Norlake Scientific, Hudson WI) at 37⁰C for 1 hour. Specimen tubes were centrifuged (Centrifuge 5810R, Eppendorf, Hamburg, Germany) for 15 minutes at 4000 rpm and then decanted twice (5 mL pipette, Novamed Inc, Lawndale Skokie, IL) for a total of 9.5 mL.   The specimens were left to dry overnight in the temperature-controlled chamber to ensure all acetone evaporated and weights of the specimens were measured to the nearest 0.001-gram the following morning. The entire process was repeated twice to ensure dissolution of the organic matrix. The calculation of filler percentage by weight was the same as the ashing technique except that residual material might include prepolymerized

fillers, clusters, and possible silane contents. The formula to determine percentage by weight of the specimens after acetone dissolution was as follows:

$$\text{Weight Percent} = \frac{\text{Wt after dissolution} - \text{Wt of tube}}{\text{Initial Wt of sample}} \times 100$$

3. Filler morphology using SEM evaluation

The specimens from ashing in air and dissolution with acetone techniques were collected for each composite and stored in separate 50 mL polystyrene conical tubes (Blue Max Jr., Becton Dickinson, Franklin Lakes, NJ). Residual fillers from ashing in air tests were mixed with 10 mL of acetone to produce a suspension, which was smeared on an aluminum SEM stub, and allowed to dry. Morphologic evaluation was done using a Scanning Electron Microscope, (FEI Quanta 200 3D Focussed Ion Beam Workstation and Environmental Scanning Electron Microscope, Tokyo, Japan) with inspections at magnifications of 20,000X and 40,000X at 20 - 30 kV beam acceleration voltage.

4. Elemental Analysis with EDX Analysis

The same areas of the samples utilized for SEM observation (with different magnification) were additionally x-ray scanned using a FEI Quanta 200 3D SEM/FIB Microscope (Figures 1-4) with an EDXA-EDX system for qualitative and semi-quantitative analyses to determine the elemental distribution profile. After the identification of all peaks on the EDX spectrum, X-ray color mapping was performed on each mounted sample to detect all the elements present in each composite.

Figure 1. FEI Quanta 200 3D Focussed Ion Beam Workstation and Environmental Scanning Electron Microscope
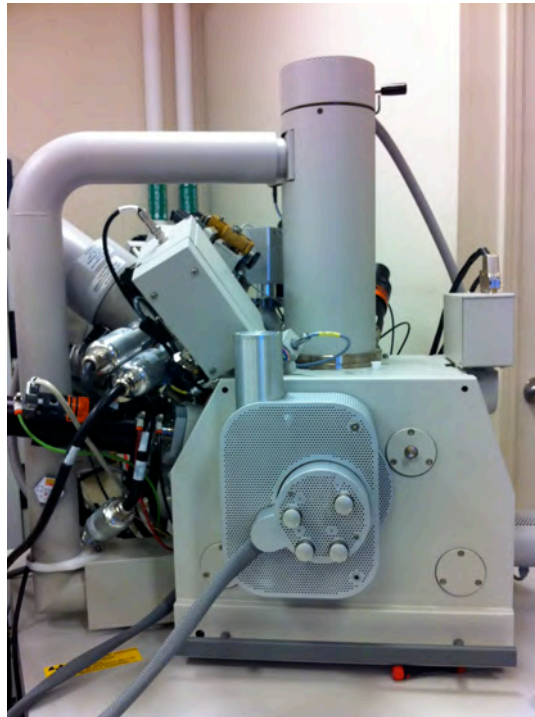
Figure 2. FEI Quanta 200 3D Focussed Ion Beam Workstation and Environmental Scanning Electron Microscope
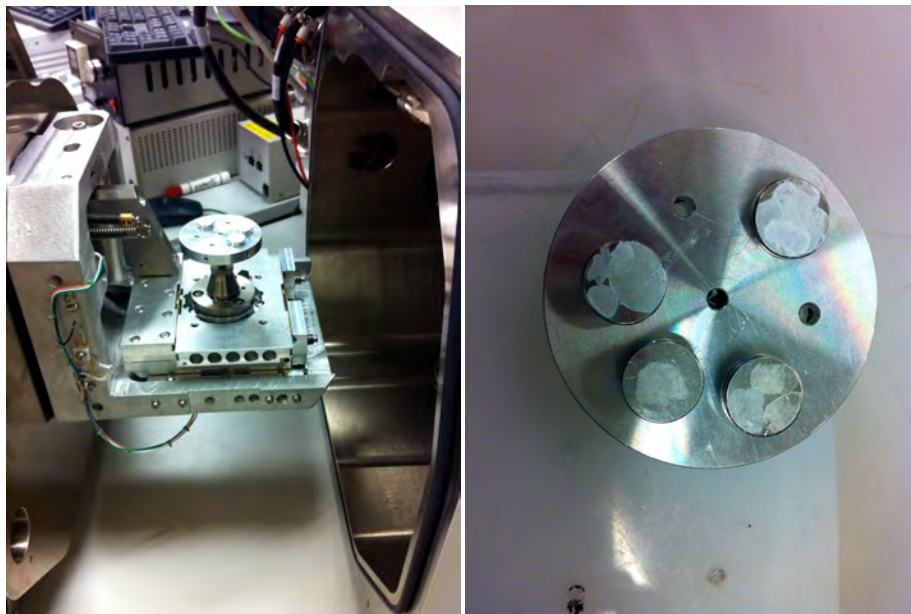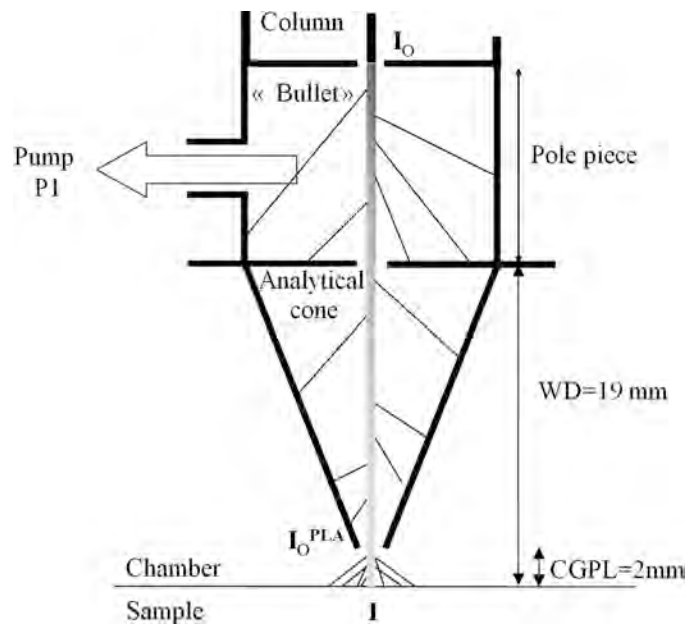
Figure 3. FEI Quanta 200 3D Focussed Ion Beam Workstation and Environmental SEM Chamber (top) with sample mounted in Aluminum wheel (right and left bottom)

Figure 4. FEI Quanta 200 3D Focussed Ion Beam Workstation and Environmental Scanning Electron Microscope. Screens displace sample location (right) and element analysis (left).

Statistical analysis

The results for each individual test were analyzed for difference between materials by using one-way analysis of variance and Tukey's test for making multiple comparisons between means. A Student's t-test was also used to compare differences between procedures for each material to determine statiscally significantly differences. All analyses were at $p < 0.05$ level of significance.

Results

Four commercially available light-cured resin composites, GC Kalore, Filtek LS, Aelite LS and IPS Empress Direct were evaluated for filler content by weight. Ten specimens (n=10) for each composite were evaluated for percentage filler analysis using ashing in air and acetone dissolution methods. SEM morphological characterization of the filler particles was also performed.

Figure 5 and Table 2 show the means and standard deviations of the materials evaluated with both techniques. Weight percent of inorganic fillers from ashed specimens ranged from 70.62 to 86.44%. Weight percent of fillers from

acetone dissolution specimens ranged between 75.56 and 85.05%. Mean values for all materials were significantly different for both ashing and acetone dissolution. When comparing techniques, there was a significant difference for each material ($p<0.05$). Kalore and IPS Empress Direct had higher values for acetone dissolution and Filtek LS and Aelite LS had slightly higher values for ashing in air.   Aelite LS and Filtek LS showed closer results for percentages by weight to manufacturer reported data when using ashing and acetone technique. On the other hand, Kalore and IPS Empress Direct, showed results closer to manufacturer reported data when using acetone dissolution for weight measurements. Aelite LS had a significantly higher loading than the others for weight percentage by both ashing in air and acetone dissolution. Comparisons of filler by weight after each acetone dissolution are shown in **Table 3.**

    Table 4 shows the correlation between ashing in air and acetone dissolution tecniques. Both techniques were highly correlated (r=0.72).
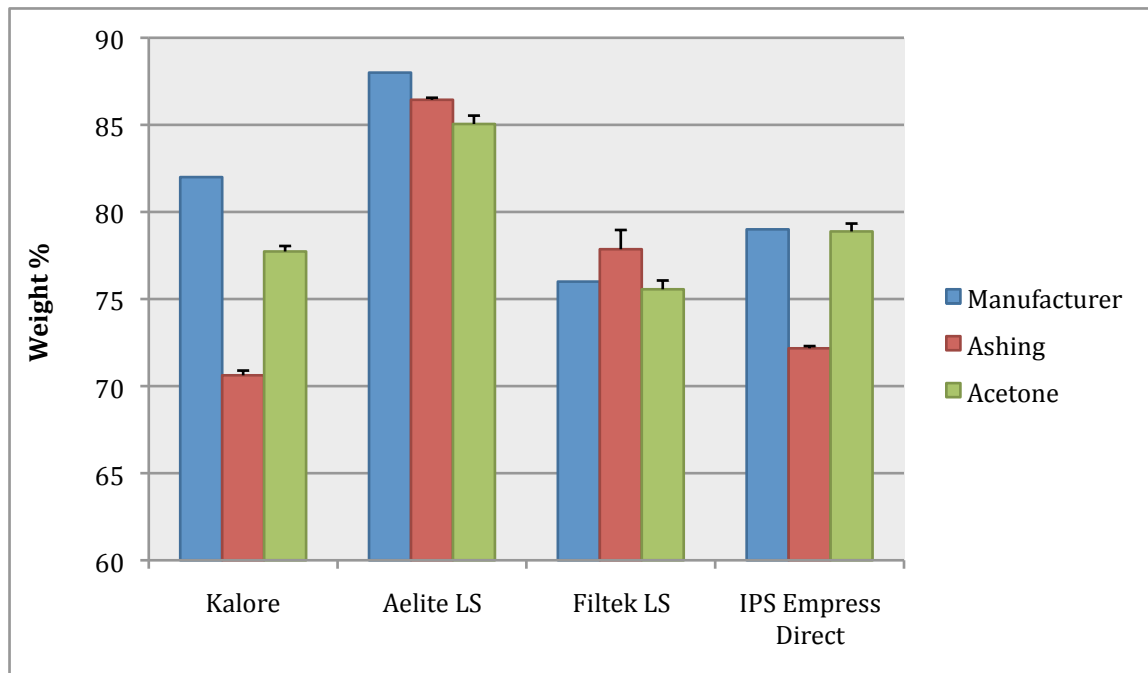
Figure 5. Comparison of filler content measurement techniques

Product	Reported filler by Wt. %	Filler by Wt.% after Ashing in Air	Filler by Wt.% after two Acetone dissolutions	Significance (Independent t-test)
Kalore	82	70.62 (0.3)	77.73 (0.3)	p<0.001
Aelite LS	88	86.44 (1.1)	85.05 (0.5)	p=0.003
Filtek LS	76	77.86 (0.1)	75.56 (0.2)	p<0.001
IPS Empress Direct	79	72.17 (0.1)	78.88 (0.5)	p<0.001

Table 2. Filler by weight with two different techniques

Note. Mean values for all materials were significantly different for both ashing and acetone dissolution (one-way ANOVA, p<0.001; Tukey Multiiple Comparison Test, p<0.001)
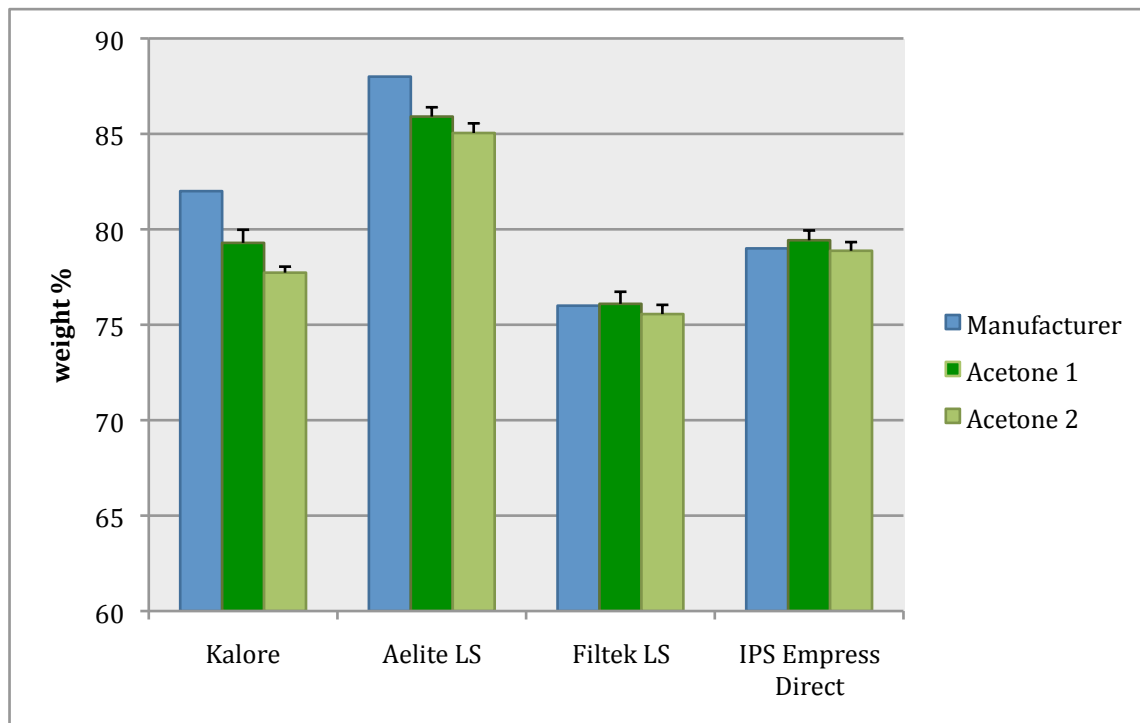
Figure 6. Comparison of filler by weight after each dissolution with acetone

Table 3. Filler by weight after each dissolution with acetone

Product	Reported filler by Wt. %	First dissolution Wt. %	Second dissolution Wt. %
Kalore	82	79.29 (0.7)	77.73 (0.3)
Aelite LS	88	85.91 (0.5)	85.047 (0.5)
Filtek LS	76	76.10 (0.6)	75.56 (0.2)
IPS Empress Direct	79	79.43 (0.5)	78.88 (0.5)

Note. Second dissolution values were significantly different from first dissolution values for all materials (paired t-test , $p < 0.05$).

Table 4. Correlation for combined materials between ashing in air and two-acetone dissolutions

Correlation = 0.72

Representative SEM photomicrographs (backscattered electron images) of the composites evaluated in this study at 20,000X and 40,000X are shown in Figs. 7 - 14. Irregular particles (3.96 μm) in conjunction with spherical (32.03 nm - 2.22 μm) filler particles of different sizes and agglomerated particles were observed in Aelite LS (Figure 7). Overall, Aelite LS was the material that showed the biggest (3.96 μm) and smallest filler particles (32.03 nm) (Figure 8). Irregular and splintered filler particles of different sizes were seen in Filtek LS, Empress Direct and Kalore. In Filtek LS, most of these particles were somewhat larger (598 nm - 2.74 μm), while the remainders were between 212.77nm – 321.61 nm (Figure 10). Kalore showed the most irregularly shaped filler particles among all composites evaluated, with a

mix of medium (631 nm - 1.85 μm) and small (48nm - 157 nm) size particles (Figure 11 and 12). Most filler particles in Kalore were smaller than 0.5 μm. On the other hand, in Empress, a more regular shape-pattern in the filler particles was observed, with particles typically ranging from 1.28 μm to 1.77 μm, and the smallest particles being around 56.62 nm (Figures 13 and 14).
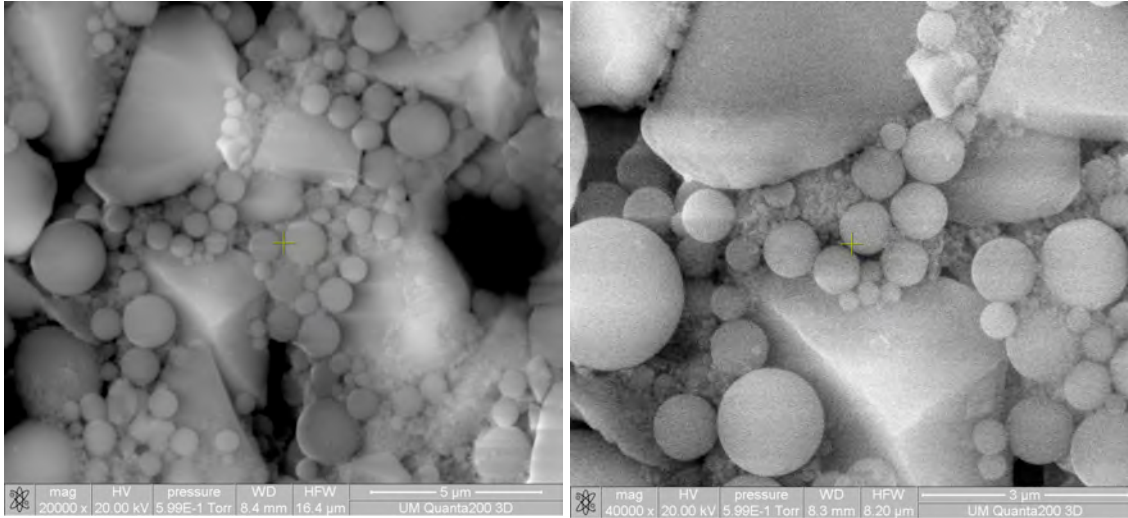
Figure 7. SEM photomicrographs of Aelite LS after acetone dissolution at 20,000X (left) and 40,000X (right) magnification
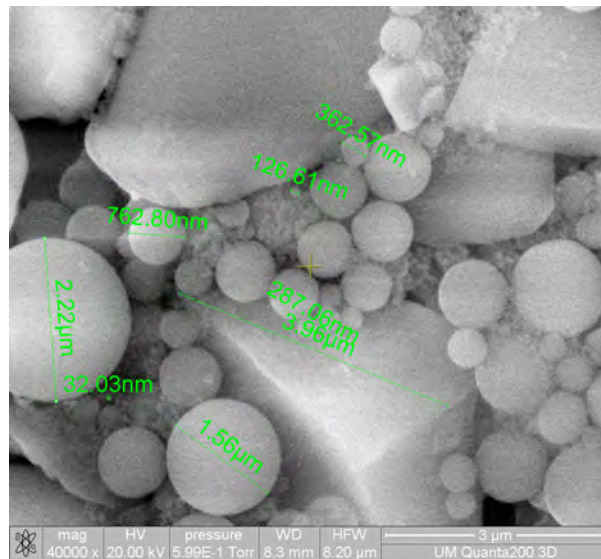
Figure 8. SEM photomicrographs and filler measurements of Aelite LS after acetone dissolution at 40,000X magnification with particle sizes noted
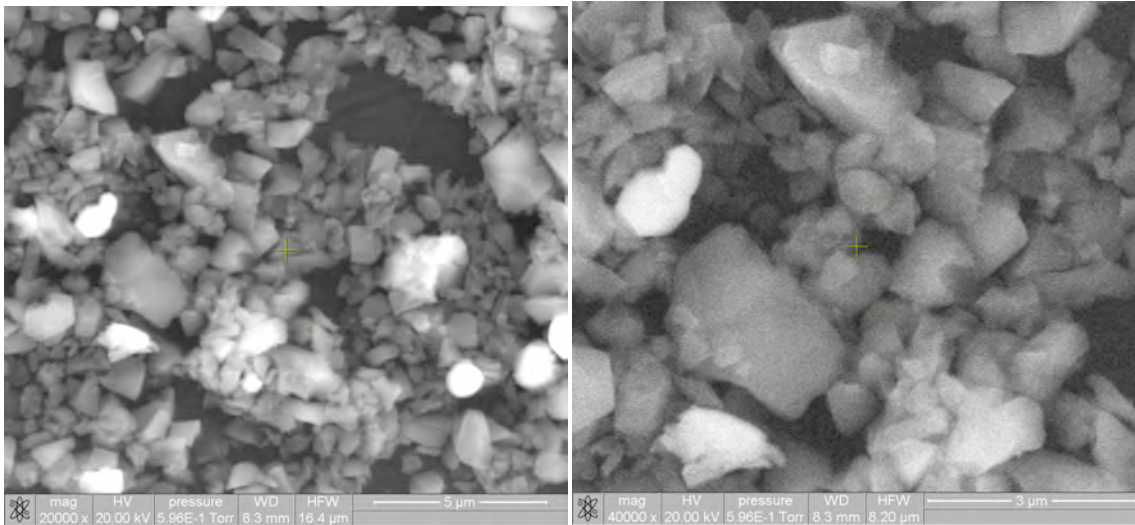
Figure 9. SEM photomicrographs of Filtek LS after acetone dissolution at 20,000X (left) and 40,000X (right) magnification
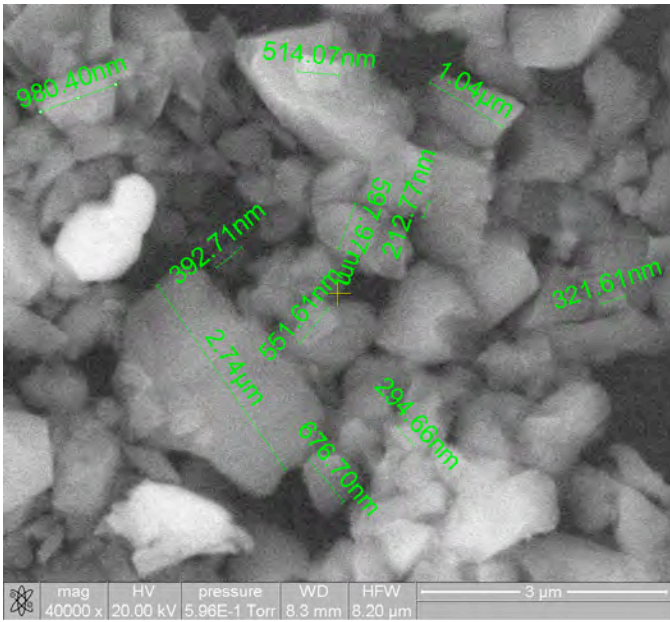
Figure 10. SEM photomicrographs and filler measurements of Filtek LS after acetone dissolution at 40,000X magnification with particle sizes noted
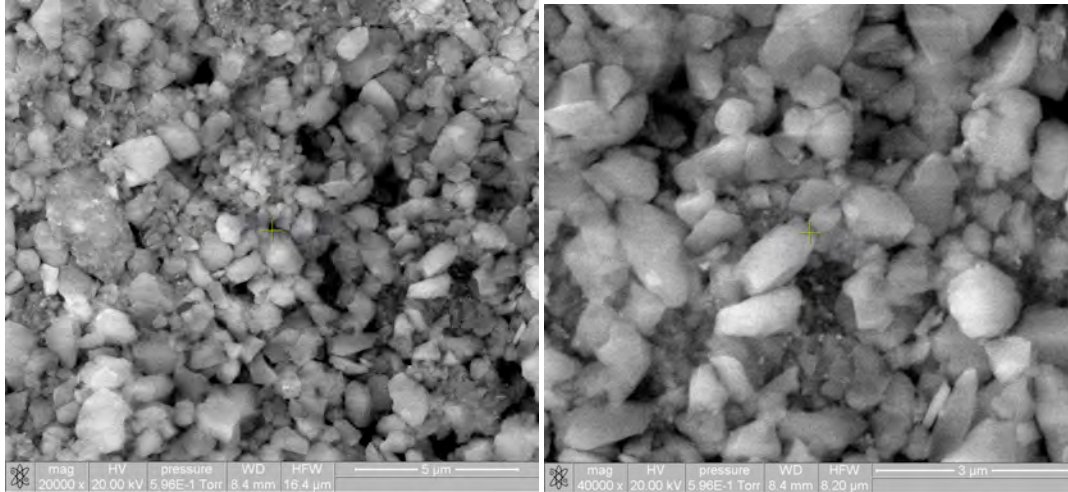
Figure 11. SEM photomicrographs of Kalore after acetone dissolution at 20,000X (left) and 40,000X (right) magnification
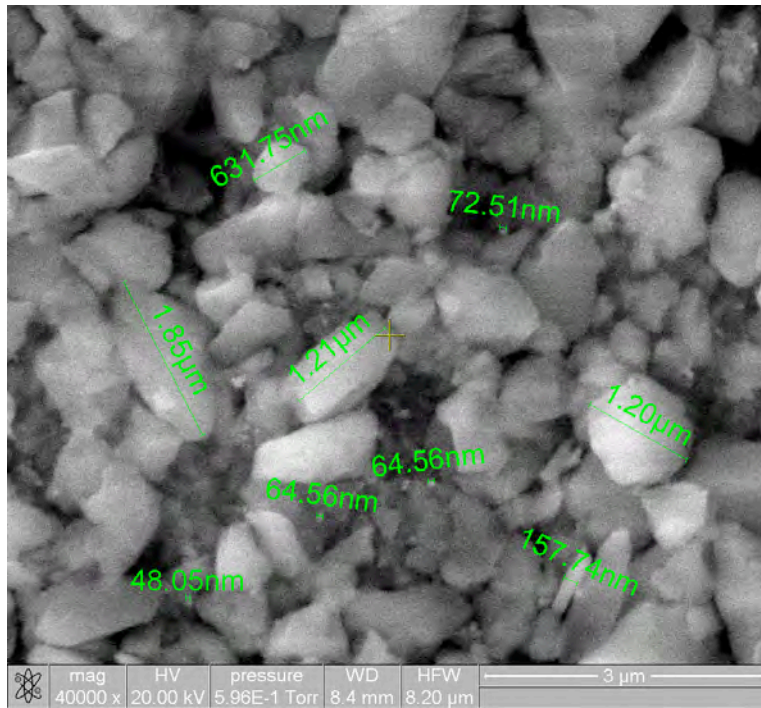
Figure 12. SEM photomicrographs and filler measurements of Kalore after acetone dissolution at 40,000X magnification with particle sizes noted
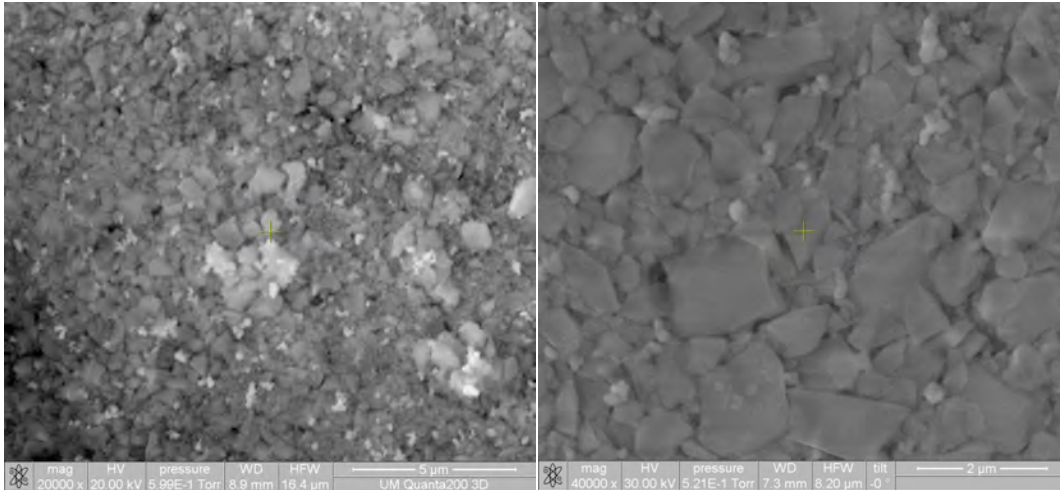
Figure 13. SEM photomicrographs of Empress Direct after acetone dissolution at 20,000X (left) and 40,000X (right) magnification
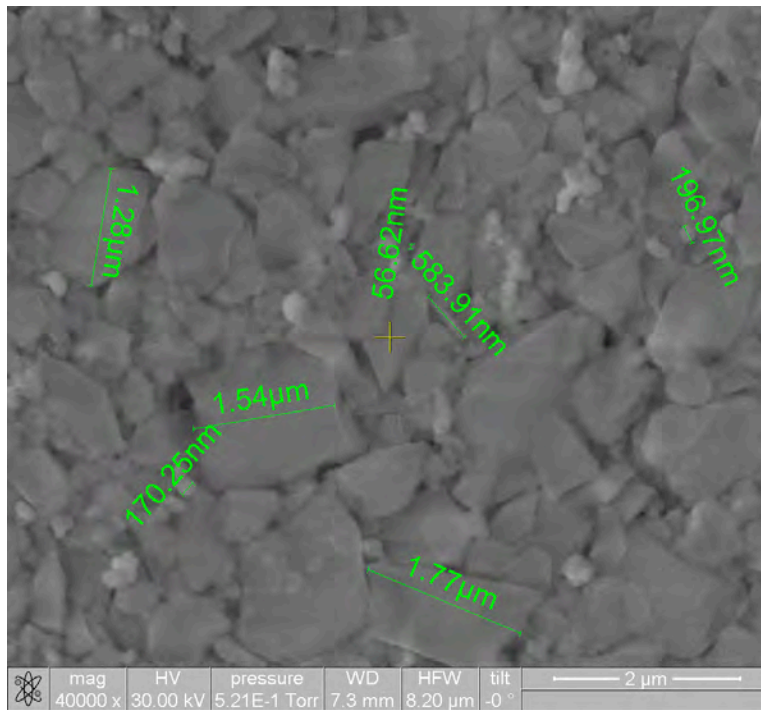
Figure 14. SEM photomicrographs and filler measurements of Empress Direct after acetone dissolution at 40,000X magnification with particle sizes noted

The elements and elements' concentration detected in the resin composites are shown in Table 5 and Figures 15 to 26. In general, the Energy dispersive spectroscopic (EDS) analysis done in Aelite LS, Filtek LS, Kalore and Empress Direct showed the following elements: Si, Al, Sr, Na, Ba, Y, Mg, F, Yb, O and Zr. Si, Al and O were commom elements for all the resin composites tested (Table 5). Empress was the material that presents the greatest variety of elements, followed by Kalore, Filtek and Aelite with the least amount of different elements in its composition. Ca was only found in Aelite LS, which is the only material with spherical filler particles.

Table 5. Type, elements detected and filler content of resin-based composites

Brand name	Type	Elements detected	Weight filler content (%)
Kalore	Microhybrid	Si, Al, O, Mg, F, Yb Sr, Y	82%
Aelite LS	Nanohybrid	Si, Al, O	88%
Filtek LS	Nanohybrid	Si, Al, O Mg, F, Y	76%
Empress Direct	Microhybrid	Si, Al, O, Mg, F, Yb, Zr, Na, Ba	79%
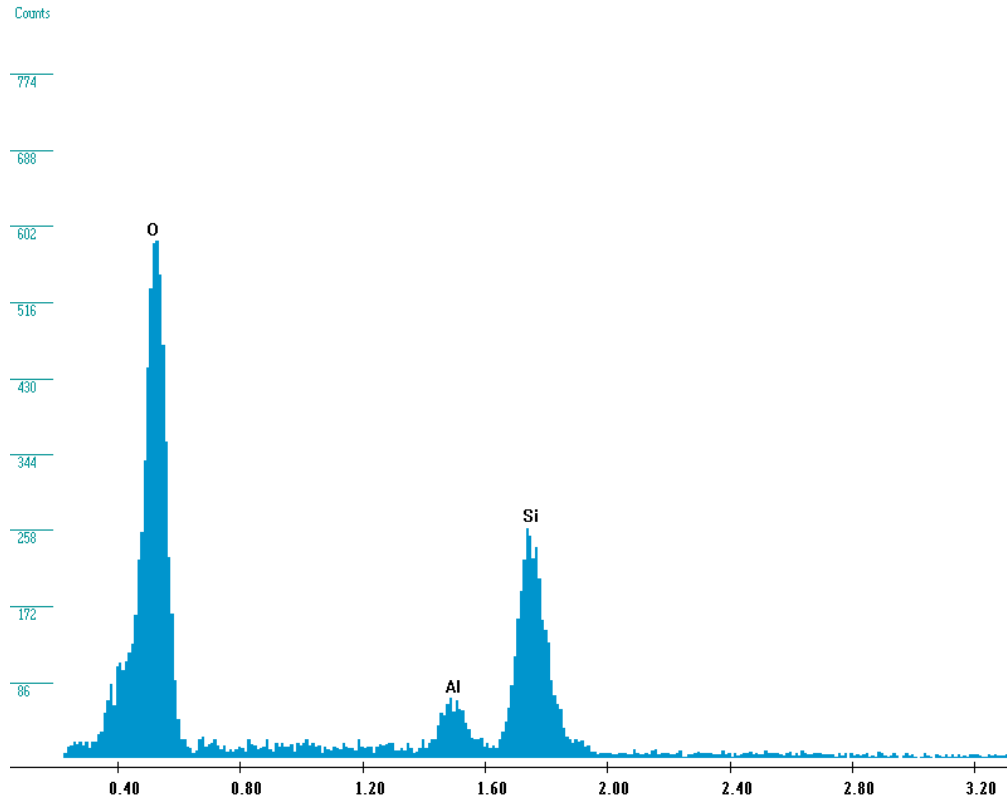
Figure 15. Energy dispersive spectroscopic analysis of the filler particles in Aelite LS after acetone dissolution
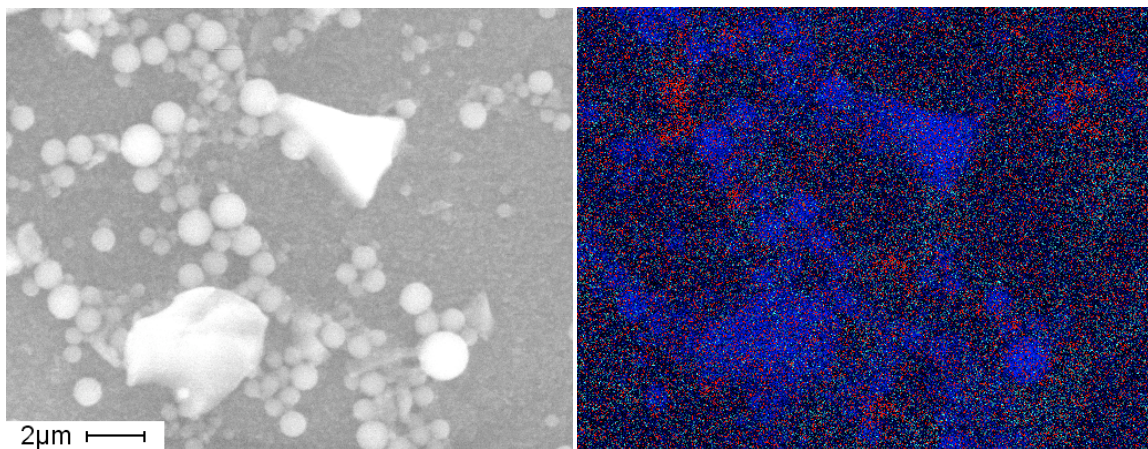
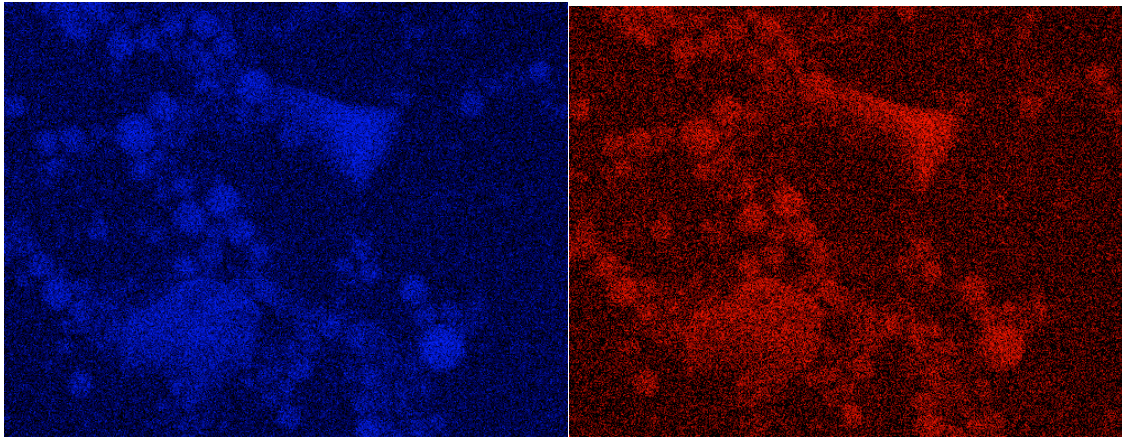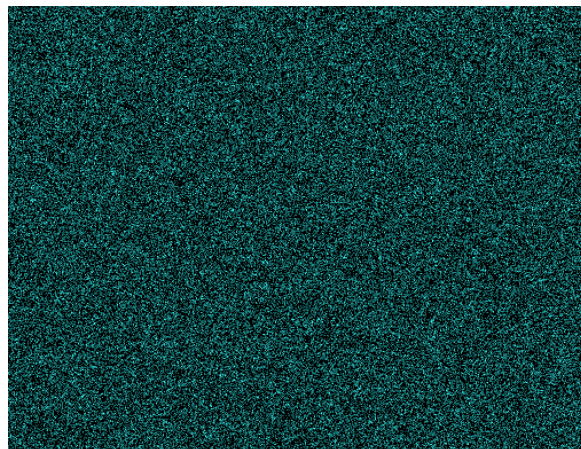**Figure 16.** SEM photomicrographs used for EDS analysis (left) and EDS color mapping overlay (right) on Aelite LS

Si (Blue)   Al (Red)

O (Light blue)

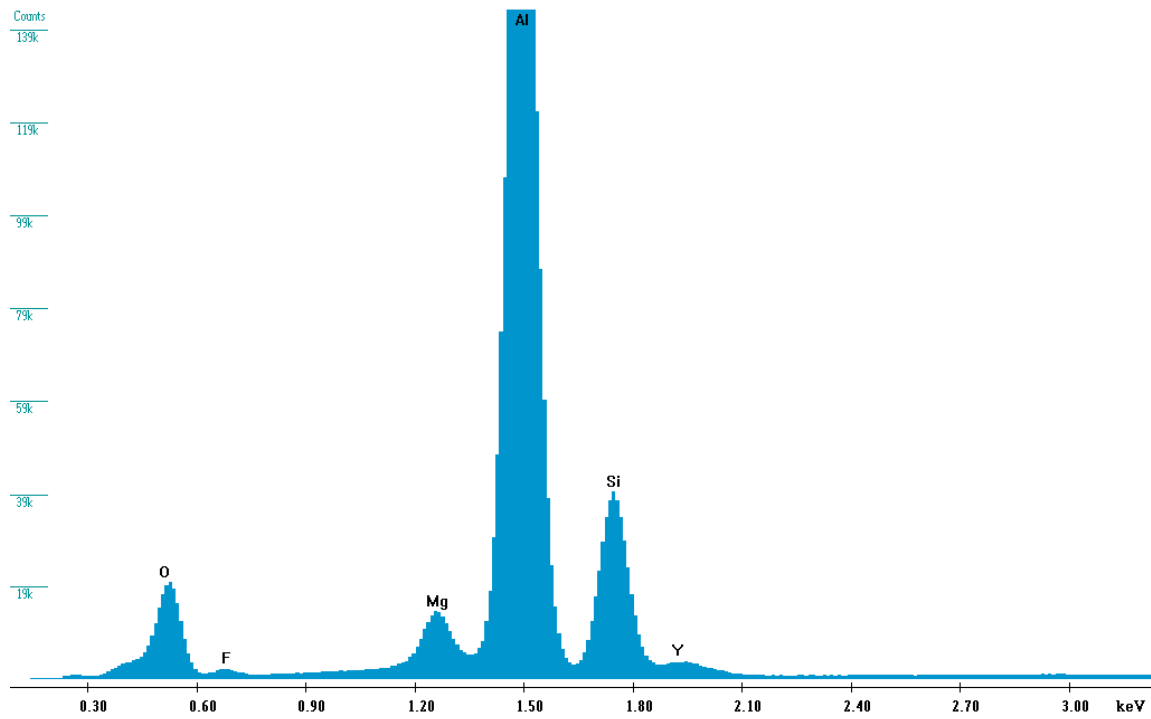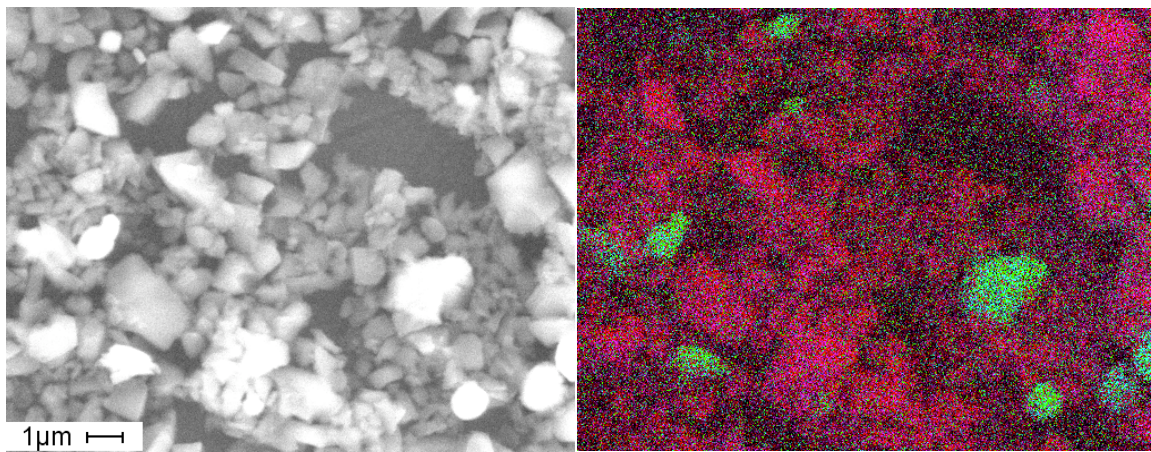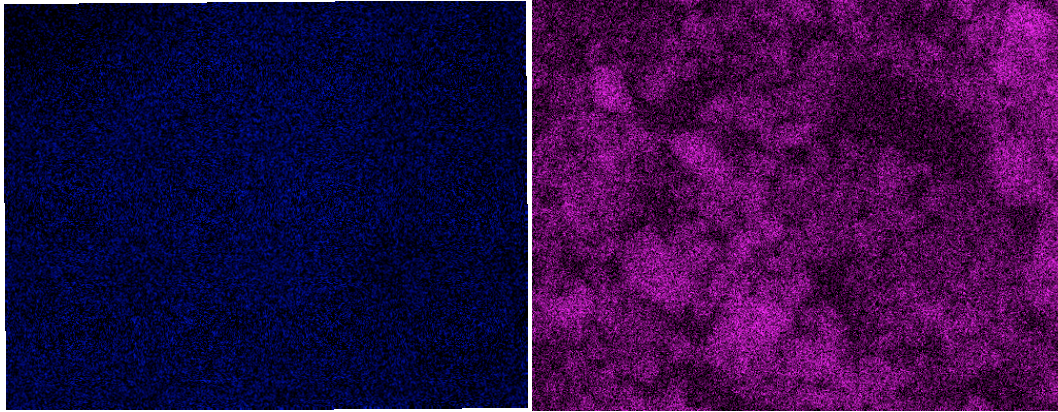**Figure 17.** EDS color mapping of Si, Al and O distribution for Aelite LS

Figure 18. Energy dispersive spectroscopic (EDS) analysis of the filler particles in Filtek LS after acetone dissolution
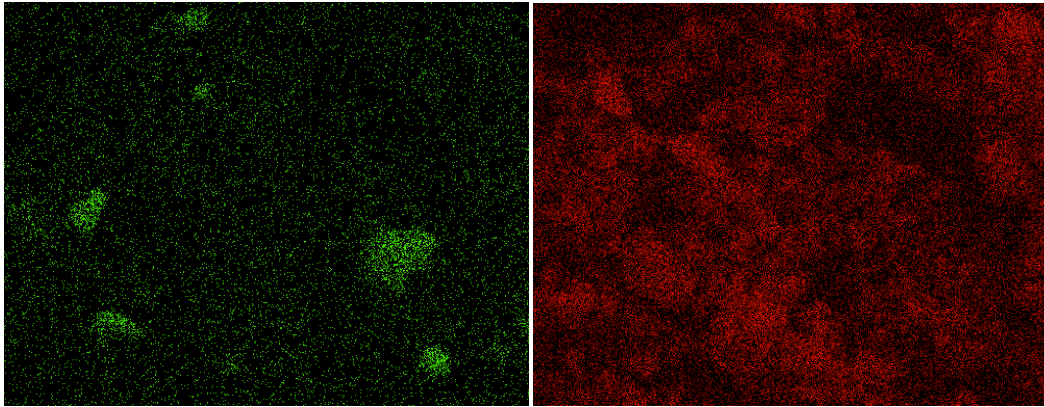

Figure 19. SEM photomicrographs used for EDS analysis (left) and EDS color mapping overlay (right) for Filtek LS
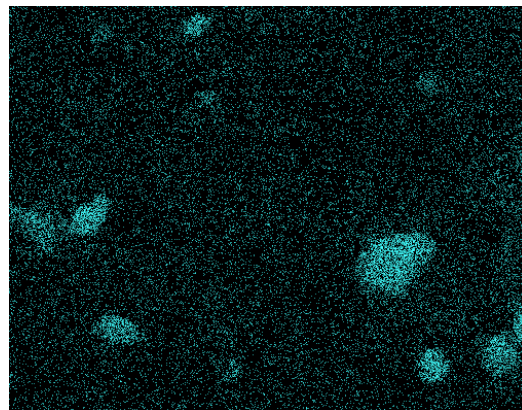
Mg (Blue)

Si (Pink)

F (Green)

O (Red)

Y (Light Blue)

Figure 20. EDS color mapping of Mg, Si, F, O and Y distribution in Filtek LS
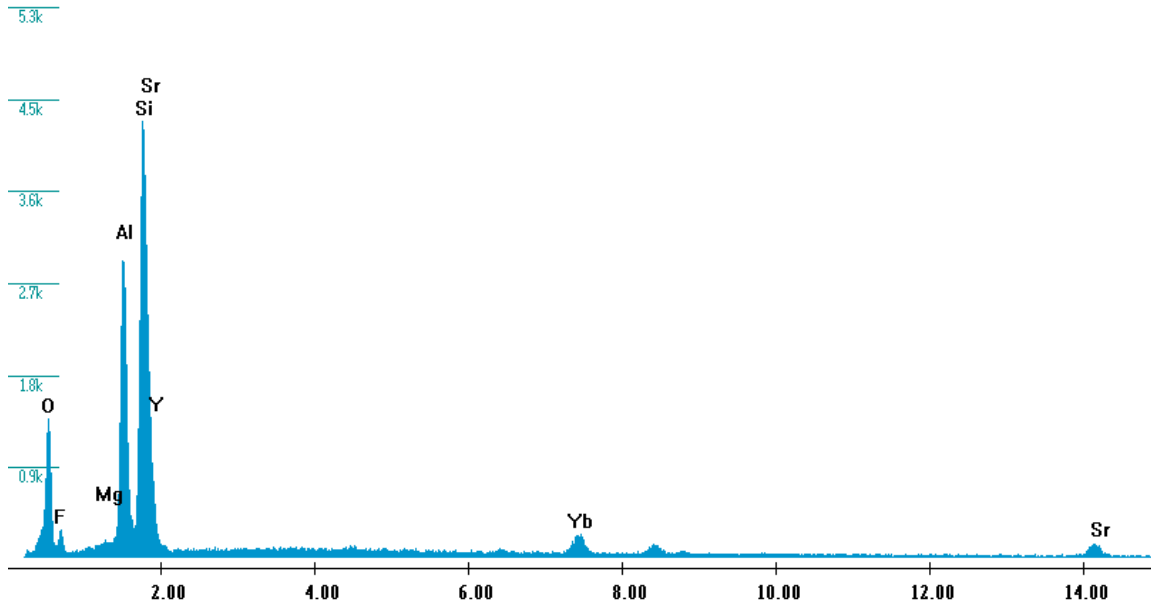
Figure 21. Energy dispersive spectroscopic (EDS) analysis of the filler particles in Kalore after acetone dissolution
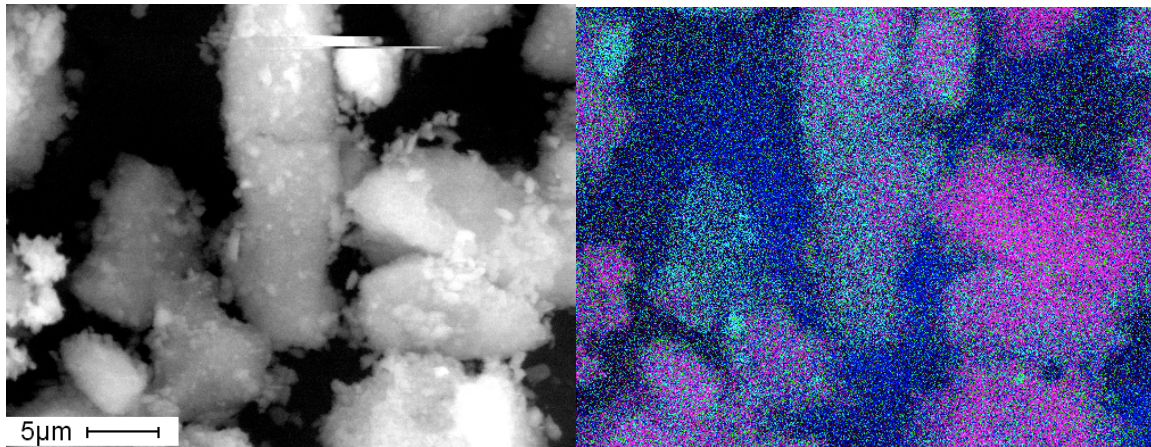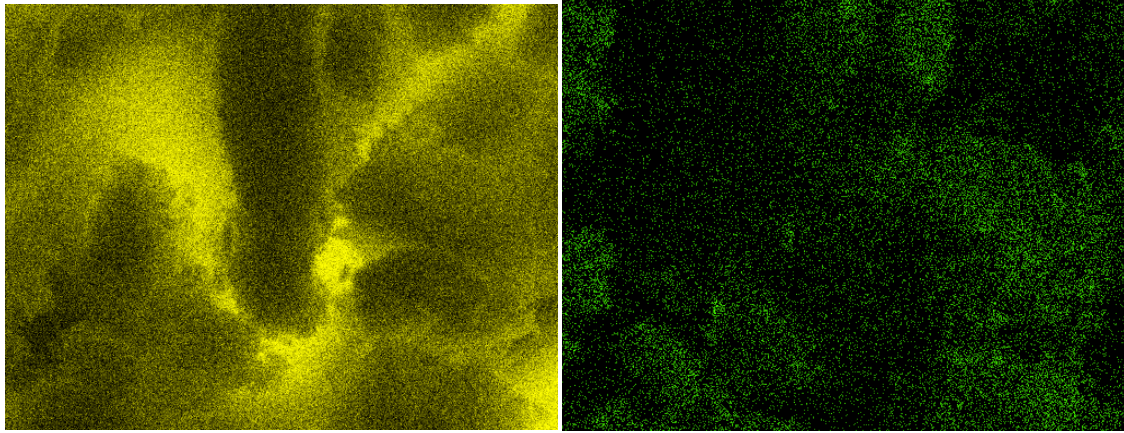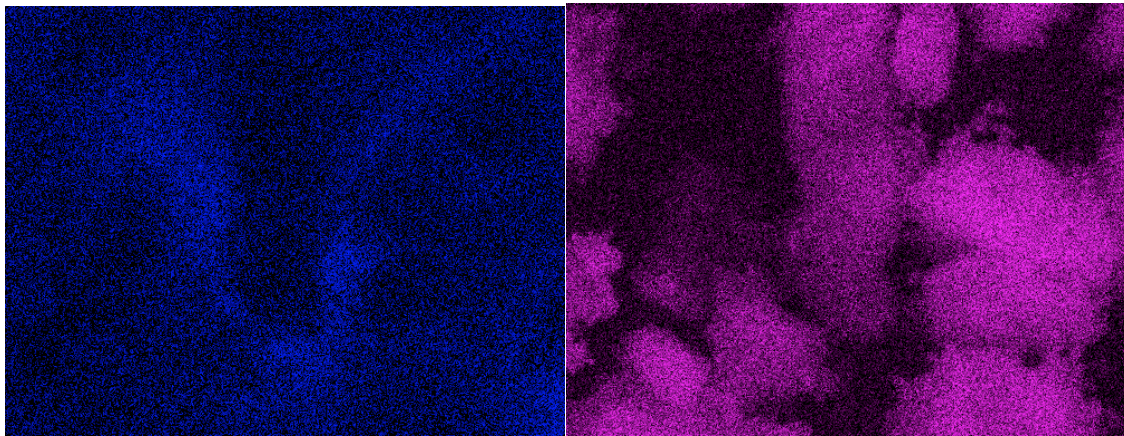

Figure 22. SEM photomicrographs used for EDS analysis (left) and EDS color mapping overlay (right) for Kalore

O (Yellow)

F (Green)

Mg (Blue)

Si (Pink)
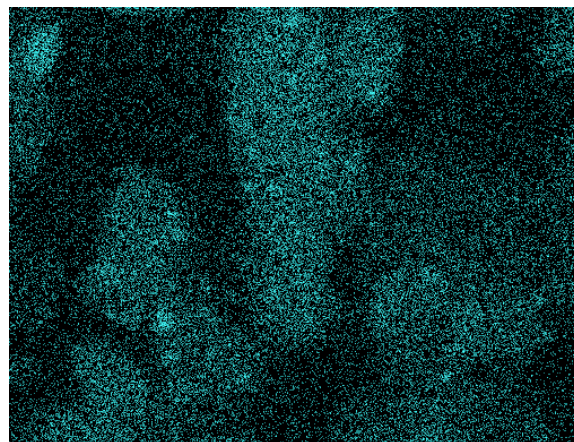
Yb (Light Blue)

Figure 23. EDS color mapping of Mg, Si, F, O and Y distribution in Kalore

Figure 24. Energy dispersive spectroscopic (EDS) analysis of the filler particles in Empress Direct after acetone dissolution

Figure 25. SEM photomicrographs used for EDS analysis (left) and EDS color mapping overlay (right) for Empress Direct

Ba (Blue)

Si (Yellow)
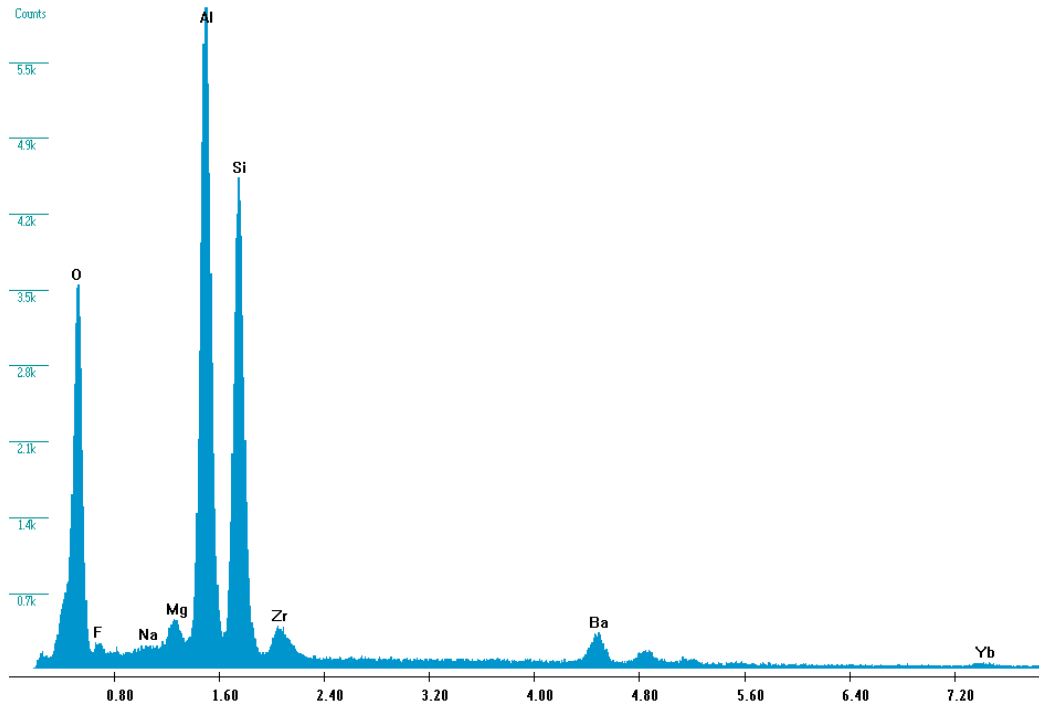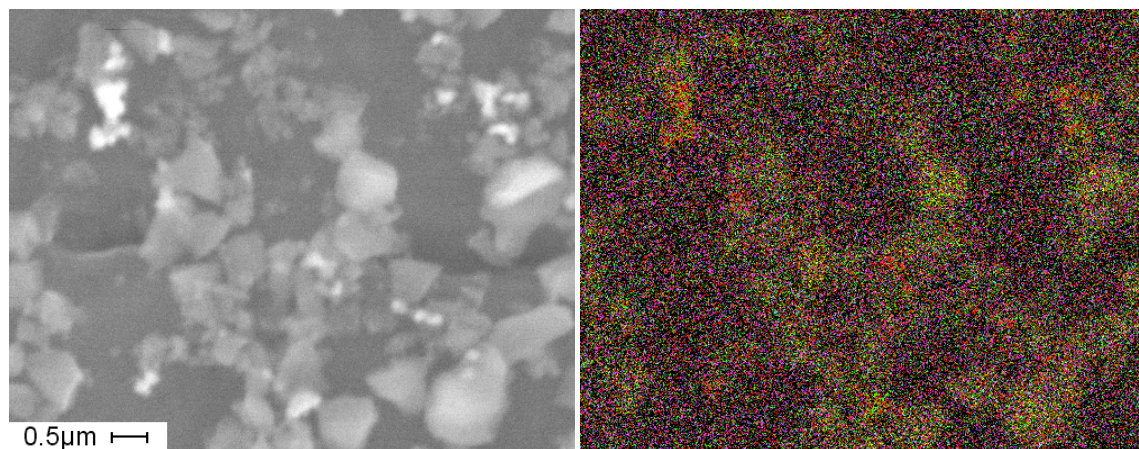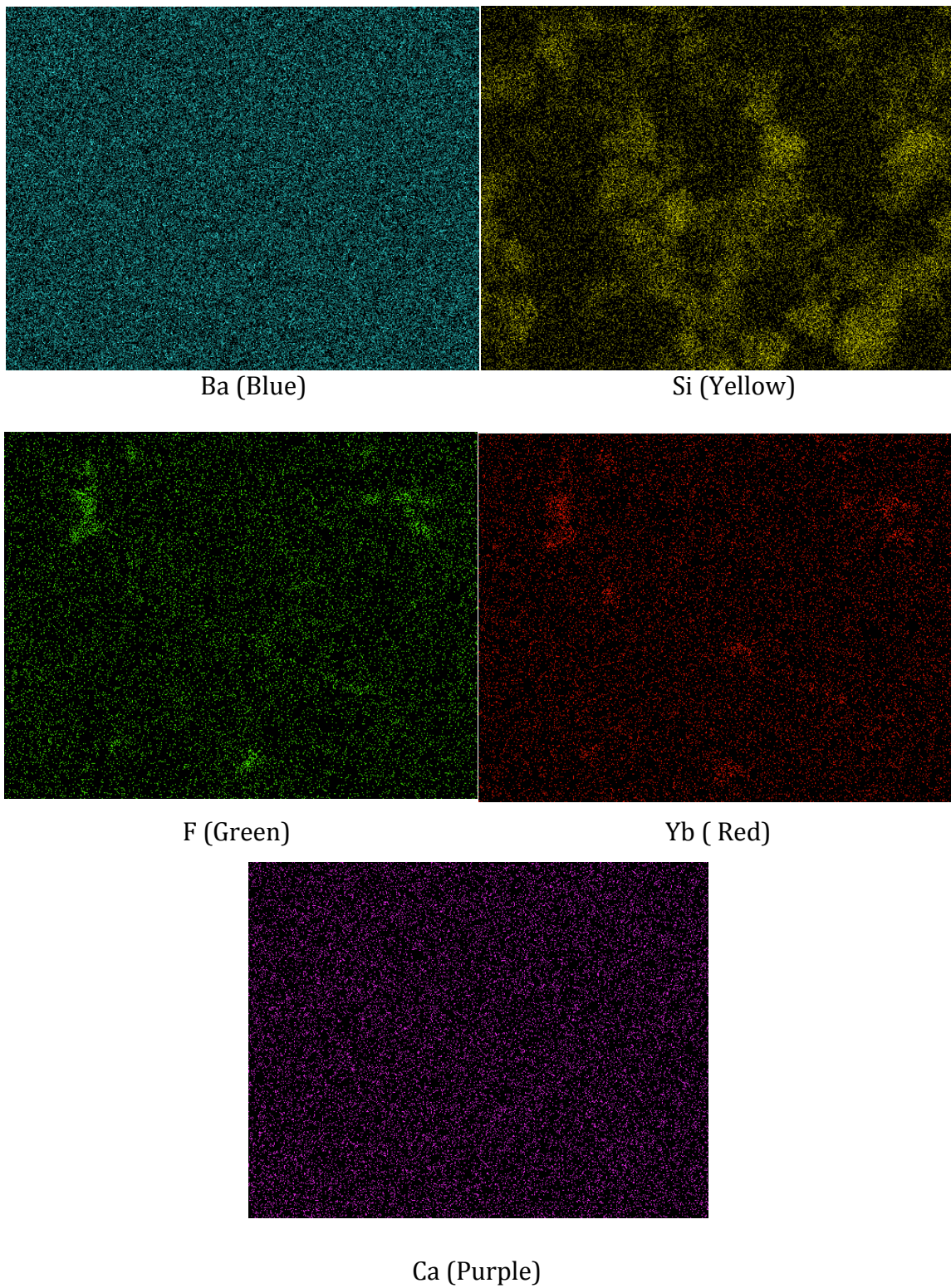

F (Green)

Yb (Red)

Ca (Purple)

Figure 26. EDS color mapping of Ba, Si, F, Yb and Ca distribution in Empress Direct

DISCUSSION

Filler Mass Fraction

Many methods could be used to study the filler concentration by weight. Thermogravimetry is a technique in which the mass of a material is monitored as a function of temperature and time as a sample specimen is subjected to a controlled temperature program[11, 19, 24]. The thermogravimetry curve pattern varied according to the materials tested, thus reflecting the variations in organic composition. Ashing in air, on the other hand, is the technique most frequently used to determine the percentage of fillers by weight. It is based on the elimination of the organic fraction of the resin composite by heating the composite to a constant temperature. Some authors, like Kim and Chung, ashed the materials in an electric furnace at temperatures that ranged between 600-700°C, respectively, for 30 minutes[3, 8-10]. Aelite LS (86.44%) and Filtek LS (77.86%) composites showed the highest amount of inorganic content after being ashed in the furnace. When comparing these results with the manufacturer's reported data, the microhybrid materials are the composites that showed closer results when using ashing in air technique. On the other hand, the nanohybrid composite's (Kalore and Empress Direct) results after ashed technique were different than the manufacturer's data.

The difference within these composites could be explained by the definition of filler content. The filler content reported by manufacturers, sometimes includes the inorganic filler particles and anything organic is vaporized in the ashing in air technique. Prepolymerized particles in many composites use the organic matrix and inorganic filler particles which are first cured into solid blocks and then milled or ground down into sizes ranging from 17 to 60 um[1, 25]. Then the milled particles are added to a non-polymerized resin along with inorganic particles and dispersed aggregates to increase loading. Pre-polymerized fillers are relatively large fillers with less surface area, enabling greater weight filler loading and thereby resulting in

less volumetric shrinkage. These larger fillers also prevent the resin matrix from moving as a result of friction between the resin and the pre-polymerized filler surface during curing, thereby reducing shrinkage[26].

Prepolymerized particles present different shapes and sizes, and they can have as much as 50% organic content[10, 11, 19, 20, 22, 26, 27]. It is of interest as to what constitutes filler content with different companies. Empress Direct and Kalore have prepolymerized particles in their filler composition. During ashing in air, organic matrix as well as prepolymerized particles can be vaporized which can result in significantly lower percentage by weight values (Table 2). Prepolymerized particles with organic content were included in the filler calculation of Empress Direct and Kalore, giving a difference of 7% for both materials. Empress Direct manufacturer reports 50.2% of barium-aluminum-fluorosilicate glass and 19.6% of prepolymerized particles in its total filler percentage by weight of 79%. On the other hand, Kalore reported a higher filler content, with a total of 82% of fluoroaluminosilicate and strontium glass and prepolymerized, which could be related to a higher percentage of prepolymerized particles with a higher organic content. So, Kalore and Empress Direct are directly related in how their filler percentages by weight were calculated. The nanohybrid composites results after acetone dissolution were closer to the filler by weight manufacturers' reports and the small differences may be due to some particles lost during each acetone pipette decantation step. However, these small differences were not seen when using ashing in air technique instead of acetone for the same measurement. Kalore had the smallest filler by weight percentage after ashing in air (70.62%), and this may be due to a higher amount of silane and prepolymerized particles with a high organic matrix in its composition. According to their manufacturer, Aelite LS and Filtek LS, do not have prepolymerized particles incorporated in their filler composition, which resulted in the smallest difference between ashing in air and acetone dissolution techniques. The microhybrid manufacturers' reports were very close to the results obtained in this study and the small differences could be due to loss of some particles during handling of samples from furnace to analytical scale after ashing

technique or loss of particles during the decantation step in the acetone dissolution technique. Aelite LS had the highest percentage of filler content by weight for both techniques while Filtek LS had the lowest percentage of filler by weight after acetone dissolution (75.56%).

Filtek LS is claimed by the manufacturer to be a low-shrinkage composite based on a silorane organic matrix, which consists of siloxane and oxirane functional moieties[14, 16]. The siloxane determines the hydrophobic nature of the siloranes, and the cycloaliphatic oxirane functional groups are claimed to be responsible for the decreased shrinkage of siloranes compared to methacrylate-based composites. Oxiranes, which are cyclic ethers, polymerize via a cationic ring-opening mechanism, whereas typically methacrylates polymerize via free radical mechanism. The volumetric shrinkage and polymerization stress have been decreased with the new silorane organic matrix because the ring opening mechanism results in expansion whereas the free radical mechanism caused shrinkage.

Others factors could explain differences found between our data and those given by the manufacturers. The first one is the variable amount of silane. Silanation process plays a main role in the adhesion of the organic resin matrix to the inorganic mineral fillers[34]. Manufacturers and laboratories treat the filler-matrix interface according to their own methods and use different ways to calculate the percentages of fillers[8]. Some manufacturers seem to evaluate the percentage of fillers by weight before the silanization process of the fillers, while others include the percentage of silane coating in their calculation. In addition, the surface area of the fillers will affect the percentage of silane used, the smaller the fillers, the higher the quantity of silane.

Furthermore, samples from each composite were dissolved in acetone to evaluate the filler content by weight using a technique that preserves the prepolymerized particles. Previous studies had evaluated filler structure and size[8, 10, 11, 20, 22], but no studies in the literature have determined filler percentage by

weight using the acetone dissolution technique. With the new generation of composites, it will be necessary to evaluate these materials considering their prepolymerized particles. A pilot study was done to determine the amount of cycles of acetone dissolution necessary to obtain a stable percentage by weight. No significant differences were found between second and third dissolution, therefore, two cycles of acetone dissolution were chosen as a standard procedure. Kalore showed the highest difference in filler content by weight for the acetone dissolution technique (77.73%) . A similar increase was seen with Empress Direct when comparing ashing in air (72.17%) and acetone dissolution (78.88%). Aelite LS and Filtek LS showed a decreased weight percentage when using acetone dissolution, which may be related to residual nanoparticles suspended in the acetone after centrifuge sedimentation that are lost during pipette aspiration.

Filler Morphology and Size

For the filler morphology analysis, the samples dissolved in acetone where collected and dissolved a third time for mounting purposes. On the SEM evaluation, all composites showed an irregular to splintered shape except for Aelite LS, which is the only composite in this study that contains spherical particles mixed with irregular-shaped particles. A spherical shape is known to have many advantages such as to allow an increased filler load for composites and also to enhance their fracture strength, surface roughness and shrinkage strain since mechanical stresses tend to concentrate on the angles and protuberances of the filler particles[3, 8, 10, 28, 29]. The spherical particles had different diameters that ranged from 32nm to 2µm while the bigger irregularly shaped particles presented an average size of 4µm. This composite showed the biggest filler particles among all resin composites. The SEM images showed some nanoclusters and dispersed nanoparticles surrounding the bigger filler particles.

For Filtek LS, the SEM images confirmed a distinct filler morphology of irregularly shaped fillers. Filtek LS's manufacturer claimed that the radical change in

the shape of the fillers, among the filtek composite varieties, is related to the specific characteristic that the silorane–based organic matrix needs in its composition. Silorane is known to contain quartz particles, which cannot be processed by a sol-gel technique and may explain the more irregular morphology compared with other materials provided by the same manufacturer. According to the manufacturer, the average size range was from 40 nm to 1700 nm; however the SEM images in this study showed particles that range from 200nm to 3μm in size. In addition, the images showed a more homogeneous size pattern (average size 470nm) when compared to Kalore, the other microhybrid material.

Still, there is not a clear explanation on the positive effect of a certain particle size and shape (spherical or irregular) on the physical and mechanical properties. Even the comparison of experimental composites has resulted in unclear results[30,31]. Some studies have speculated that the filler loading is the main factor for determining elastic modulus properties, while filler size and shape should be considered as secondary factor that will affect material properties.

According to the manufacturer, Kalore contains 60% filler content by weight of 400nm nano-sized modified strontium glass and 20% filler content by weight of 100nm of lanthanoid fluoride. Prepolymerized nanoclusters of fillers, inorganic fillers and mono-dispersed particles, contained in this specific nanohybrid composite present size ranges between 16 nm to 17 μm. When the samples were evaluated under SEM, the images showed irregular-shaped filler particles, whose bigger particles range from 630nm to 1.85μm and small particles range from 48nm to 158nm. Among all materials, Aelite LS (32 nm) and Kalore (48 nm) are the materials that had the smallest filler particles in their structure. As well as Kalore and Fitek LS, Empress Direct also showed irregular shaped particles with large fillers that range from 1.28μm- 1.77μm and smaller aggregates particles with sizes from 56.62nm to 196.97nm.

In this study, prepolymerized particles were not evaluated for elemental analysis because the components of each composite material were disrupted during the acetone dissolution technique; therefore, further studies should be done keeping the organic matrix of each resin-based composite.

EDS analyis

EDS (X-ray Energy Dispersive Spectroscopy) is a microanalytical technique that is based on the characteristic X-ray peaks that are generated when the high-energy beam of the electron microscope interacts with the specimen. Each element yields a characteristic spectral fingerprint that may be used to identify the presence of that element within the sample. The relative intensities of the spectral peaks may be used to determine the relative concentrations of each element in the specimen. The X-ray signal is detected by a solid-state silicon-lithium detector and the construction and efficiency of this detector sets a lower limit on the atomic number that may be detected. Generally elements heavier than carbon are detectable[20].

The first resin composites in the market were based on pure glass or quartz, but due to the hardness of this material, it was difficult to provide small particles, therefore the finishing and polishing outcomes were poor. To improve the hardness problem, other elements like aluminum and lithium have been added to the composition. In addition barium, zinc, boron and yttrium are used to impart radiopacity. Radiopacity is obtained through the incorporation of elements with a high atomic number into the inorganic filler phase. If excessive incorporation of such elements occurs, a reduction in the translucency of these materials may result[25]. Silane coupling treatment, which enhances bonding between the filler and matrix resin, can also lead to decreases in translucency. Another disadvantage with incorporating large percentages of radiopaque fillers is chemical degradation caused by water immersion. It has been reported that the barium and strontium containing fillers leaked more Si than quartz- containing resin composites[34]. It is important to balance the optical and mechanical properties of resin composites with

the incorporation of filler particles. Other elements like Ytterbium fluoride have been incorporated to create new fluoride releasing composites[25]. Results from EDX spectroscopy analysis of the inorganic fillers revealed a great variety of elements in the composition of different types of fillers[23]. The elements detected were Silica (Si), Aluminum (Al), Strontium (Sr), Y (Yttrium), Magnesium (Mg), F (Fluorine), Yb (Ytterbium), O (Oxygen), Zr (Zirconium) and Barium (Ba). Si, Al and O were the common elements in the composition, but according to each element spectral peak emission, Al showed the highest concentration among all materials, followed by Si with the second highest concentration.

Filler content related to physical properties

The addition of inorganic particles has been the main factor studied in the development of new resin composites. The physical properties of dental composites are known to depend on the concentration and particle size of the filler. Volumetric polymerization shrinkage is mainly determined by, composition of the material, such as the type and amount of the resin matrix used, the iniatiation system and the filler loading[3, 9, 32]. According to Chang's evaluation on the same composites, Filtek LS showed significantly lower volumetric shrinkage (0.45%) than the other materials. Aelite LS (1.59%), Kalore (1.65%) and Empress Direct (1.83%) have statistically similar shrinkage values[33]. These results indicated that the low shrinkage silorane chemistry proclaimed by the manufacturer reflected the high shrinkage reduction seen in this new line of Filtek composites.

Aelite LS, being the resin-composite with the highest filler content, showed similar shrinkage values to the composites with lower filler content. The rounded filler geometry on Aelite LS, filler particle size and the prepolymerized particles contained in the nanohybrid composites, did not seem to influence the degree of volumetric shrinkage in these materials. For the Knoop surface hardness evaluation, Aelite LS (114.55 KHN) demonstrated the greatest surface hardness followed by Filtek LS, Kalore and Empress Direct (36.59 KHN) with the lowest.

These values were better correlated with the percentage of filler content, since Aelite LS was the composite with the statistically significantly higher filler content by weight when compared to the other materials. In the other physical properties evaluated, Aelite LS and Filtek LS were significantly greater in Vickers surface hardness and flexural strength than Kalore and Empress Direct. This significant difference could be associated with the difference in the proprietary matrix composition of the low-shrinkage materials when compared to the metacrylate-based resin composites. Regarding physical properties and filler particle size correlation, the materials with the largest filler particles embedded in their composition, Aelite LS and Filtek LS, were the composites with the most ideal physical properties; however, further SEM imaging across the surface of each sample needs to be microanalysed.

Conclusions

- Mean values for all materials were significantly different for both ashing and acetone dissolution.
- Aelite LS had the highest filler content for both ashing and acetone dissolution.
- Values for filler content by weight using the acetone dissolution were closer to manufacturer reported values.
- Manufacturer reported filler content for Aelite LS (88%) and Filtek LS (76%) approximated the study results for both techniques, while Kalore (82%) and IPS Empress Direct (79%) were only similar for acetone dissolution, indicating higher content of prepolymerized particles.
- Kalore had significantly lower filler content for ashing (70.62%) and Filtek LS for acetone dissolution (75.56%).
- Morphological examination showed spherical shaped particles for Aelite LS and splintered and irregular shaped particles for all other materials.
- The elements detected were Silica (Si), Aluminum (Al), Strontium (Sr), Y (Yttrium), Magnesium (Mg), F (Fluorine), Yb (Ytterbium), O (Oxygen), Zr (Zirconium) and Barium (Ba), with Si, Al and O the common elements in the composition of all four resin-composites evaluated.

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