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## COMPOSITE FILLER CHARACTERIZATION BY SCANNING ELECTRON MICROSCOPY, IMAGE ANALYSIS AND THERMOGRAVIMETRY

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### Abstract

The morphological and compositional characterization of the filler particles in selected dental composites has been accomplished by a combination of backscattered electron imaging, digital imaging, energy dispersive X-ray analysis and thermogravimetry. Backscattered electron images provide excellent composition contrast between the filler and the matrix in this analysis. Qualitative energy dispersive spectroscopy was used to classify the filler composition in the composites studied. The digital imaging technique of feature analysis was utilized to quantitatively characterize the particle morphological parameters and their distributions. Several parameters were determined of which the particle area, breadth, height and Waddell diameter are emphasized. Particle size distribution histograms were also obtained. The filler contents in commercial composites were also determined by thermogravimetry. Thus a comprehensive method has been developed and applied to characterize filler morphology in particulate dental composites, which include both commercial and experimental systems. The commercial systems show variations in filler composition, filler size and distribution as well as filler loading levels. The experimental systems confirm variations in particle size and size distributions as a function of filler processing time.

**KEY WORDS:** composites, filler, morphology, backscattered electron imaging, feature analysis, energy dispersive spectroscopy.

### Introduction

Particulate composites have become an important choice of dental practitioners not only for anterior restorative applications because of aesthetic considerations but also for posterior fillings which may be subject to occlusal stress and wear during chewing cycles. It has been recognized in recent years that the properties of composites are greatly influenced by the composition, particle size and distributions of the filler as well as the volume fraction of the filler<sup>(1-2, 5, 6, 9)</sup>. While the importance of these parameters is recognized in previously published reports, only limited documentation exists on the methods to characterize the filler parameters. These efforts have focussed on the characterization of the extracted filler by microscopic and other techniques. There is a need to characterize the morphological details of filler particle parameters (e.g., mean particle size, size distribution, composition, as well as the filler volume fraction). There are several state of the art techniques available for such characterization. Scanning electron microscopy (SEM) using backscattered electrons (BSE) is well known for its ability to provide composition contrast based on atomic number differences of microscopic constituents. In recent years, this ability to differentiate composition contrast has been combined with digital imaging techniques to characterize the microscopic features of aggregate structures<sup>(3, 4)</sup>. The basis of this treatment is a computerized quantitative image analysis software procedure for investigating features in a microscopic image, developed by Rink<sup>(7)</sup>. This method provides information on morphological details of the features in the image. This can also be supplemented by energy dispersive spectroscopy (EDS) to identify composition differences between different features. In order to complete the range of information needed, the amount of filler can be quantified by thermogravimetry. The objectives of this investigation were:

- a) To characterize the filler particles by backscattered electron imaging (BEI).
- b) To evaluate the filler morphological details by image analysis of the BSE microstructures.
- c) To classify the filler composition differences of composites by qualitative EDS.

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d) To determine the total filler content in the composites by thermogravimetric analysis (TGA).

#### Materials and Methods

The materials studied included commercial and experimental composites. All commercial systems studied were popular light cured materials including small particle and hybrid systems. Table 1 lists the different commercial formulations studied. The experimental systems were barium glass filled composites. The filler was specially prepared in a commercial facility (Jeneric Pentron Inc., Wallingford, CT). The barium glass frit (T-3000) was obtained from Esschem Corporation (Essington, PA). The frit was processed by variable periods of wet grinding (0, 2, 4, 18, 24, 48 and 72 hours, respectively, as listed in Table 2) to yield different particle sizes and size ranges. The grinding, cleaning, and drying procedures of the filler were carried out according to the commercial practice in Jeneric Pentron Inc., Wallingford, CT. All the filler materials were silanated with  $\gamma$ -methacryloxypropyltrimethoxysilane by tumbling for a period of 6 hours at 175 rpm using a glass lined carboy. The silanated filler was then incorporated into a visible light cure (VLC) resin matrix containing 54.24% bisphenyl-glycidylmethacrylate resin (BisGMA), 44.38% triethyleneglycol dimethacrylate (TEGDMA), 0.23% diethylaminoethyl-methacrylate (DEAMA), 0.16% camphoro-quinone and 0.99% benzophenone. The selection of this composition was based on our previous unpublished studies and its composition is similar to commercial resin formulations. In order to remove entrapped air pockets in the composite, the paste was passed several times through stainless steel rolls in a rolling mill until a homogenous mix was obtained. The paste was stored in amber vials to avoid pre-polymerization of the VLC resin system.

Six mm diameter x 3 mm thick disk specimens of the composite were prepared for microstructural evaluation. They were carbon coated and examined in a Hitachi SEM S-2500 equipped with a retractable GW BSE detector. A Kevex imaging and microanalysis system (Delta Class -II with a Quantum detector capable of x-ray microanalysis of light elements down to boron) was used in this study. The BSE imaging of the SEM was combined with the advanced digital imaging, feature analysis and microanalysis capabilities of the Kevex system in this study. In addition, the filler content in the composite was determined by TGA in a Dupont thermal analysis system controlled by a computer data station (Thermal Analyst 2000). The decomposition of cured composite was followed by monitoring the residual weight percent as a function of temperature during a programmed thermal cycle from room temperature to 700°C at a rate of 25°C/min. The filler content was determined as percent of original weight remaining after the complete combustion of organic resin constituents giving a steady state value of residual weight percent in the thermal curve. A sample size of N= 3 was used.

**Table 1: List of commercial composites**

Sample Number	Brand	Manufacturer	Filler Type
1	Estilux	Kulzer, CA	Posterior, Hybrid
2	Herculite	Kerr, MI	Posterior, Small particle
3	Command Ultrafine	Kerr, MI	Anterior, Small particle
4	Occlusin	I.C.I. Gr. Britain	Posterior, Small particle
5	Pentrafill II	Pentron, CT	Anterior Small particle
6	Heliomolar	Vivadent	Posterior Hybrid

**Table 2: Filler particle processing time in experimental composites**

Particle size # (P.S.)	Filler grinding time in hours
1	0
2	2
3	4
4	18
5	24
6	48
7	72

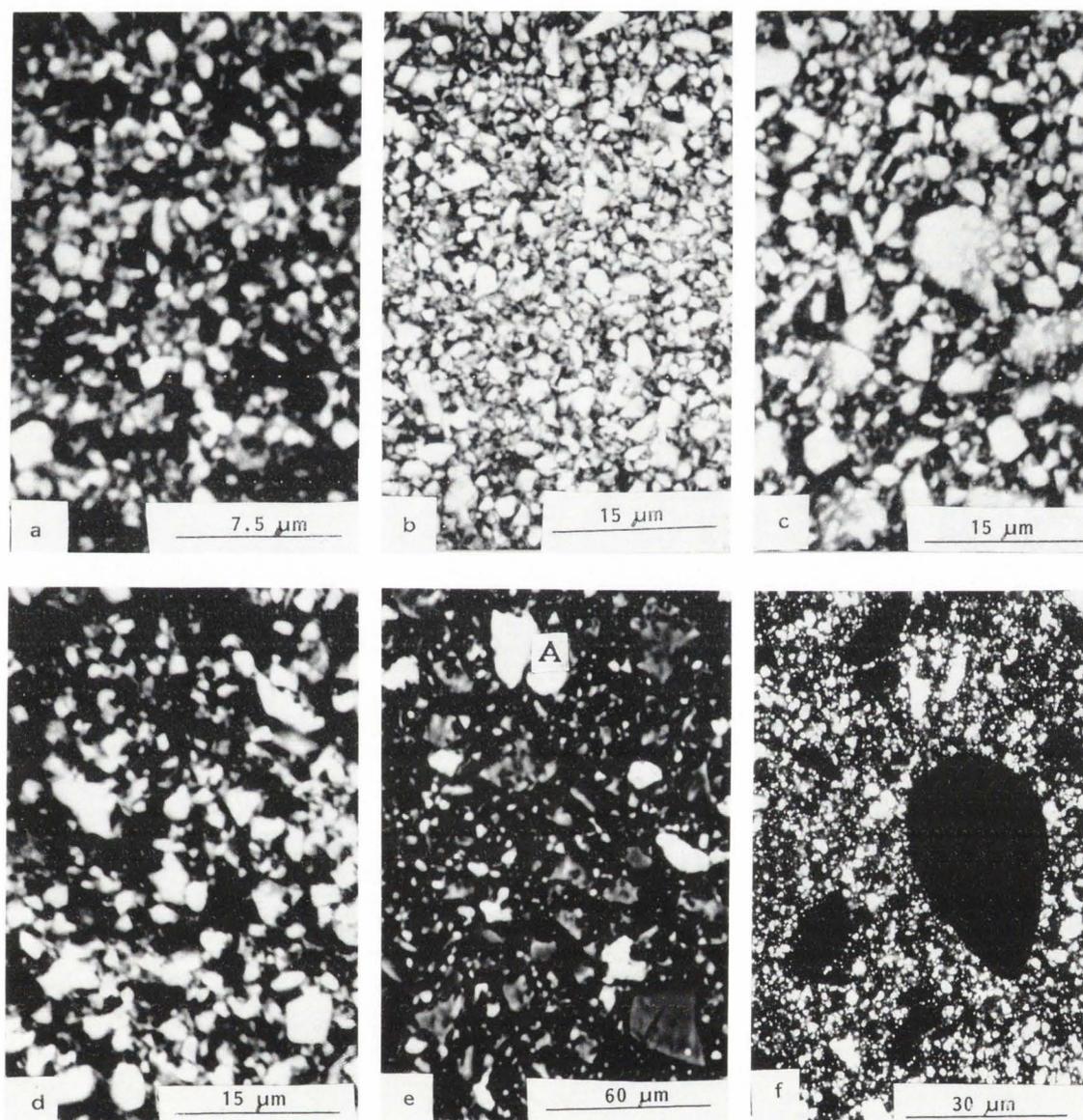
#### Results and Discussion

##### BEI and EDS Analysis

Figure 1 shows BSE microstructures of the commercial composites. A wide range of particle size differences are noted within and between the systems evaluated. The microstructures of the experimental composites are seen in Figure 2. The gradual particle size reduction in the filler is observed with increasing processing time used for particle size reduction.

Evaluation of the BSE microstructures of the commercial resins revealed that the filler particles generally appeared as white features against a black polymer matrix background. However, in two systems investigated (viz., Heliomolar and Estilux), two types of filler particles were observed with different shades or gray level ranges in their microstructures (Figures 1e and 1f). Qualitative spot mode EDS analysis of evaluation revealed composition differences between the filler particles of different gray level ranges. For example, EDS spectrum (Figure 3a) of the large particle of Heliomolar (see figure 1f) reveals peaks corresponding to Si and O

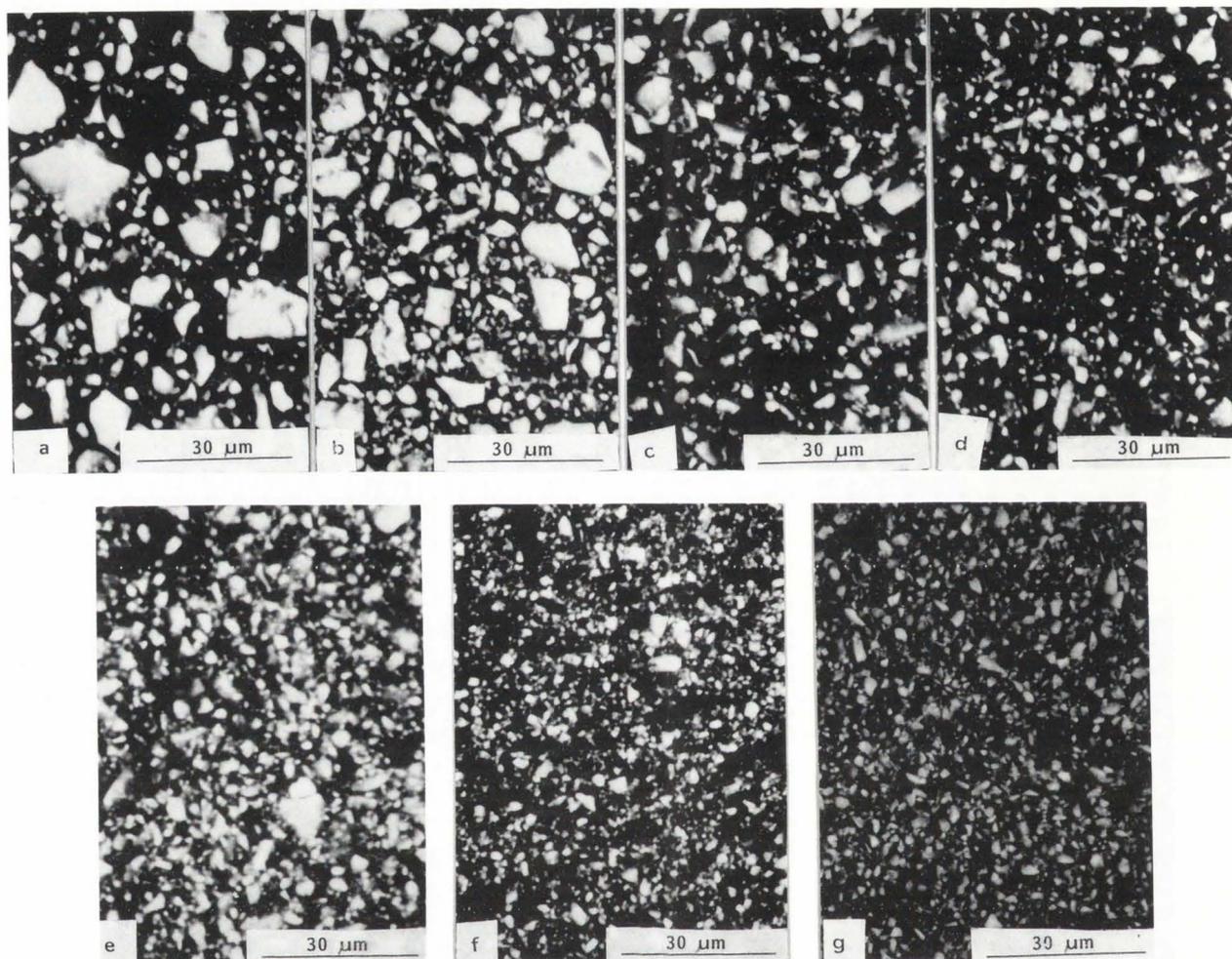
## Composite Filler Characterization



**Figure 1.** BSE microstructures of commercial composites (see Table 1): (a) Herculite, (b) Command, (c) Pentrafill II, (d) Occlusin, (e) Estilux, and (f) Heliomolar.

only, indicating that such dark features are the pre-polymerized aggregate particles (microfill particles) containing colloidal silica. The EDS spectrum (Figure 3b) of the bright particulate features in figure 1f showed peaks for ytterbium (Yb) and fluorine (F). These particles were identified as ytterbium fluoride added to the composite to make it radio opaque. In the case of Estilux also, two types of particles (Figures 4a and 4b) were observed. However, these particles appeared brighter than the matrix, but with two different gray level ranges that were adequate to differentiate them in the BSE image. The EDS spot spectrum (Figure 4a) of

the bright particle ('A' in Figure 1e) revealed the presence of Ba, Al, Si and O, indicating that these particles were barium boroaluminosilicate. A spot EDS spectrum (Figure 4b) corresponding to the other particles in Estilux appearing intermediate in gray level between the bright barium boroaluminosilicate particles and the dark polymer matrix (see feature 'B' in figure 1e) showed peaks corresponding to Si, Al and O. These particles were classified as lithium aluminosilicate particles, added by the manufacturer in order to keep the thermal expansion of the composite at a low value. Note that neither Li nor B can be detected by the quantum detector used in the Kevex system.



**Figure 2.** BSE microstructures of experimental composites (see Table 2): (a) P.S.# 1, (b) P.S.# 2, (c) P.S. # 3, (d) P.S. # 4, (e) P.S. # 5, (f) P.S. # 6, and (g) P.S. # 7. The nominal volume fraction in all experimental composites was 0.70.

All other composites (Occlusin, Command Ultrafine, Herculite, Pentrafill II and all experimental systems) revealed only filler particles of barium boroaluminosilicate.

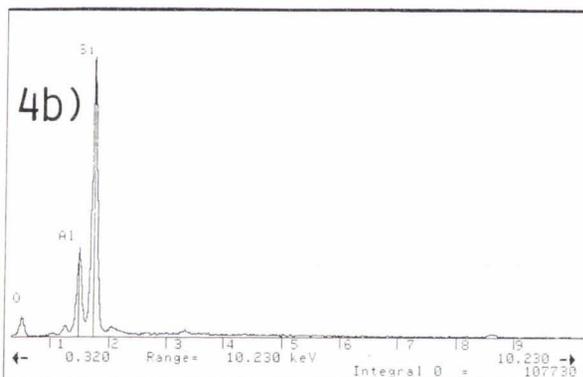
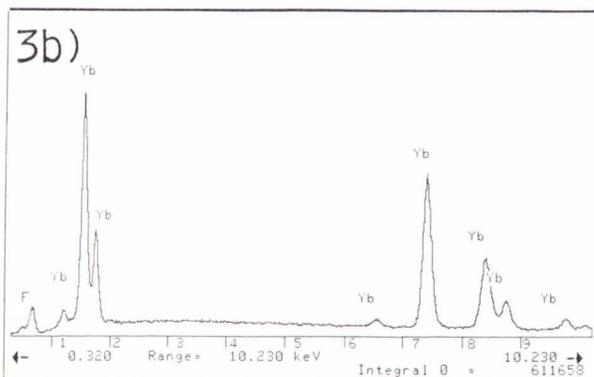
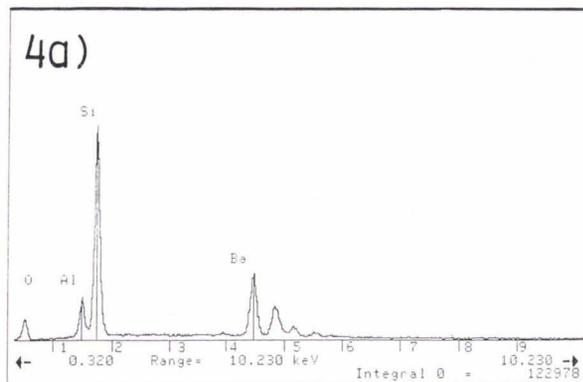
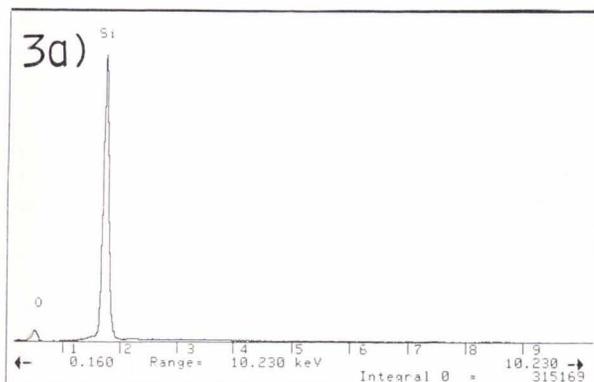
#### Filler characterization by feature analysis

BSE analog images from the SEM were first acquired as digital images by the Kevex imaging system. The gray level values of the image points in the analog image are digitized and stored during this acquisition. The acquisition is based on 512 x 256 pixels or picture elements, i.e., the digital image is an array of 131,072 numbers representing the gray levels of as many image points. The range of gray levels used is 256 from black (0) to white (255).

Figure 5 shows a typical hardcopy output of the acquired image of a commercial composite, Command Ultrafine. A histogram of the gray levels in such an image showed two peaks corresponding to the 'black'

polymer matrix and 'white' filler particles, as shown in Figure 6. By painting the white features, the filler particles can be highlighted in any selected color by the digital imaging technique. The painted image is then processed by identification, creating a binary image that can be processed further by the program software. The first step in the processing is a combination of erosion and dilation operations. In erosion, one pixel from each boundary point of the filler at the particle-matrix interface is removed. Noise artifacts can partially be eliminated in this way. In the subsequent dilation processing, addition of a pixel at each boundary point restores the true particles to the original size. The final feature processing marks the boundaries of the particles and determines the feature parameters both individually and overall. During feature processing, remaining noise artifacts (not eliminated by erosion) are ignored by pre-defining a lower limit for the number of pixels in the

Composite Filler Characterization



Figures 3a, 3b. EDS spot spectrum from large dark particle and bright particles in Figure 1f respectively.

Figures 4a, 4b. EDS spot spectrum from bright particles and less bright particles in Figure 1e respectively.

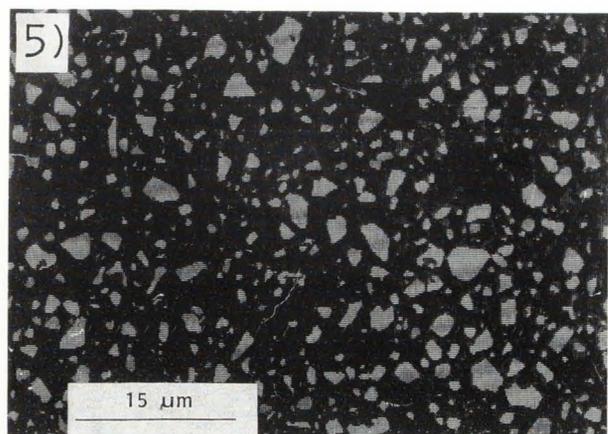


Figure 5. Hard copy output of an acquired image in the Kevex system.

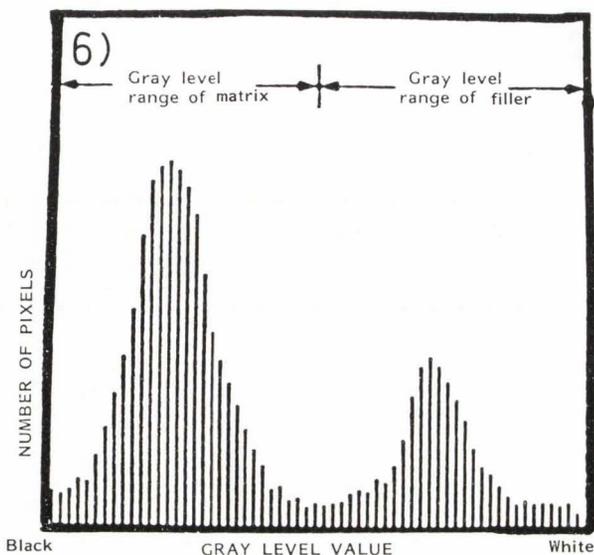
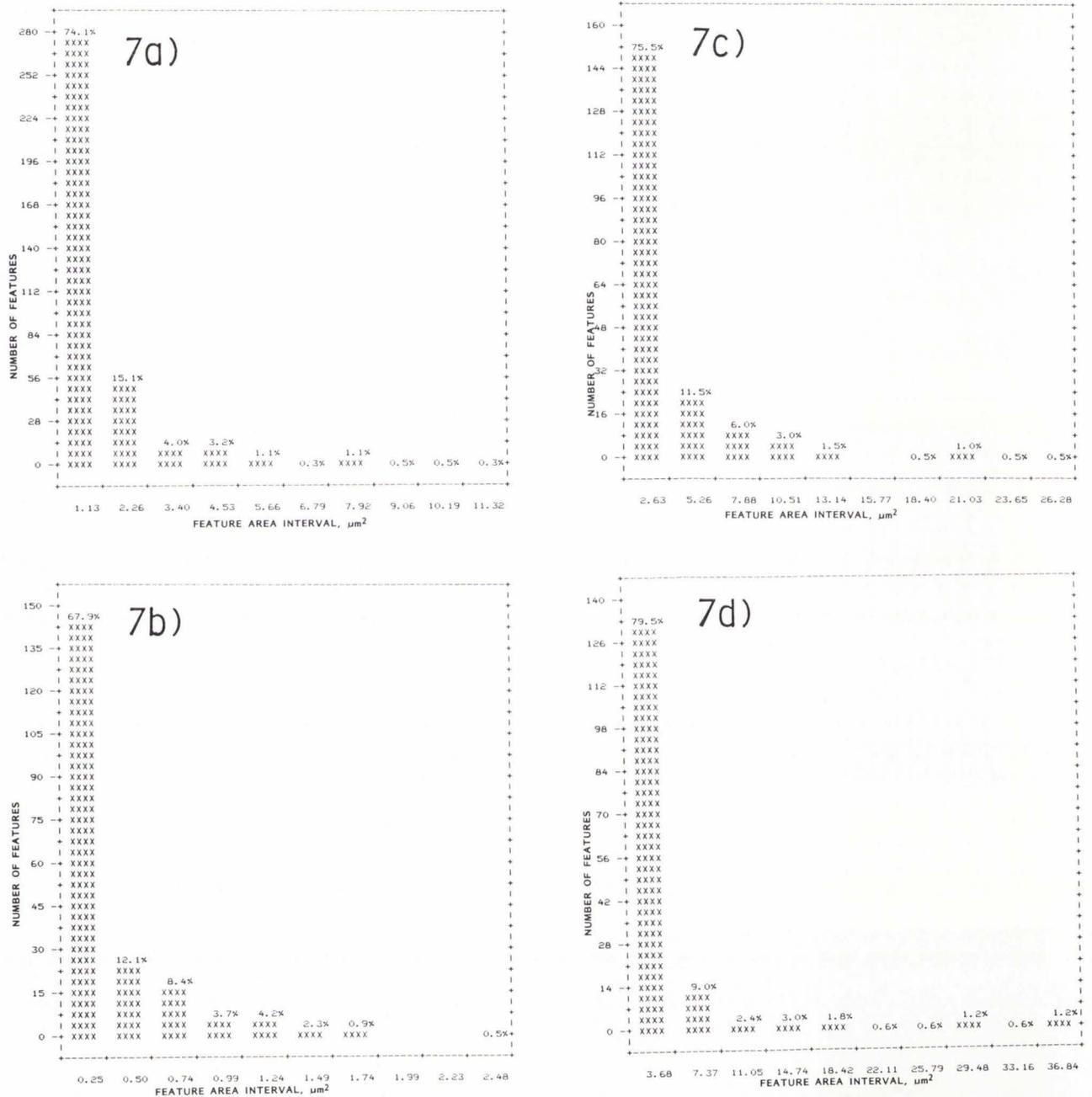


Figure 6 (at right). Gray level histogram corresponding to the microstructure in Figure 5.



**Figure 7.** Histograms of feature areas in different composites; (a - d above; e - h on the facing page): (a) Command; (b) Herculite; (c) Pentafill II; (d) Occlusin; (e) Estilux, Lithium aluminosilicate particles; (f) Estilux, Barium borosilicate particles; (g) Heliomolar, 'Microfill' particles; and (h) Heliomolar, Ytterbium Fluoride particles.

feature before they are recognized as features. Figures 7a to 7h show typical hardcopy outputs of data histograms and Tables 3 and 4 are the summary of the data output obtained after the feature processing.

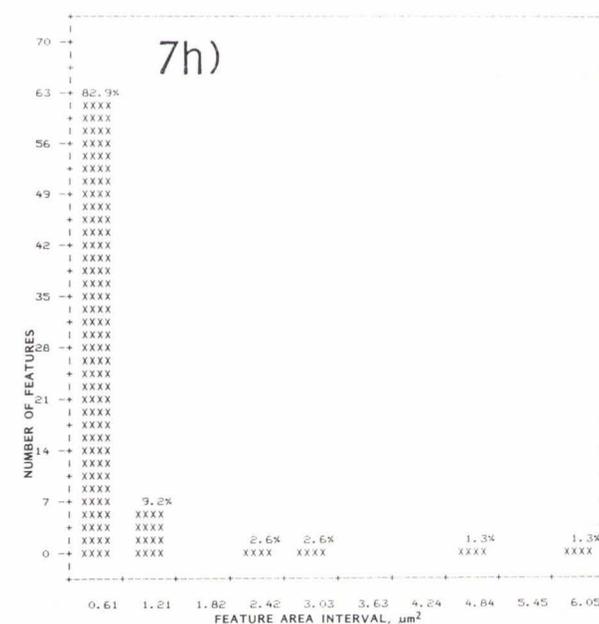
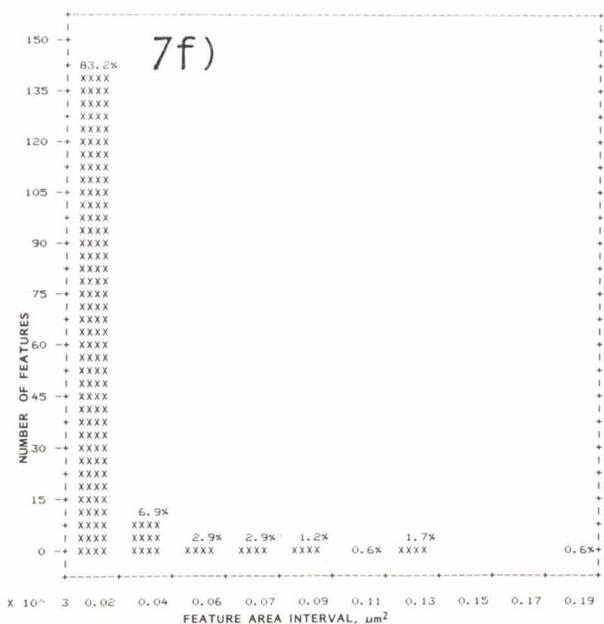
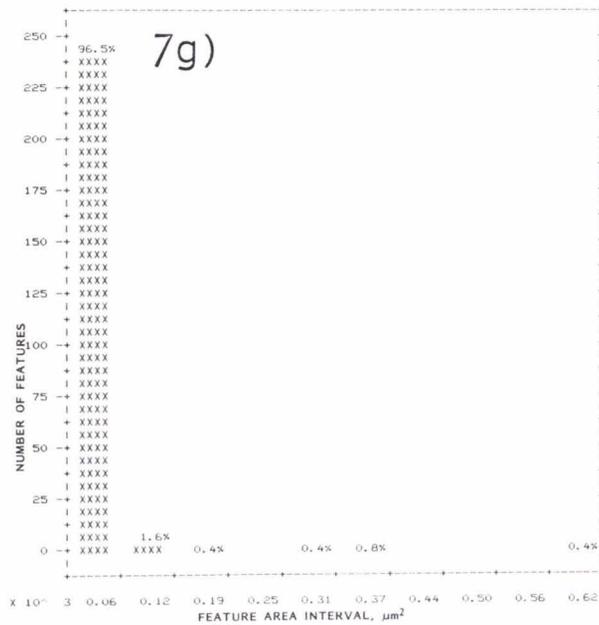
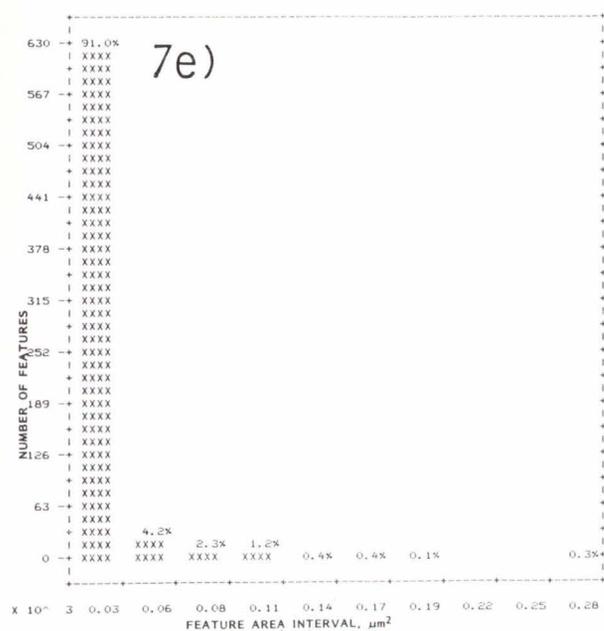
Figures 8 and 9 are bar graphs of the mean values of the filler parameters (e.g., feature area, breadth, height and Waddell diameter, which is defined as the diameter of a circle of equivalent area). Note that the

data generated comprises a wide range of particle parameters; only selected parameters and their distributions are reported here for brevity. Thus, feature analysis and BSE imaging can be combined to completely and quantitatively characterize the feature morphological details.

**Filler content determination by thermogravimetry**

Because of the high filler loading levels, it was necessary to eliminate particle agglomerates during the

## Composite Filler Characterization



above feature analysis. For this reason, the amount of filler in the commercial composites was determined by thermogravimetry. Figure 10 is a typical hardcopy output of a TGA thermal curve. The filler content in the composite is determined at the steady state value of weight percentage after the resin is completely burnt off. Figure 11 is a bar graph of the filler contents in the different commercial composites.

### Conclusions

Commercial and experimental dental composites were characterized by combining the techniques of BEI,

digital imaging, EDS and thermogravimetry. The results indicate that the filler composition, morphology, weight fraction and distribution can be characterized both qualitatively and quantitatively by appropriate selection of the techniques used.

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**Table 3:** Particle size range in commercial composites

Composite	Area, $\mu\text{m}^2$	Breadth, $\mu\text{m}$	Height, $\mu\text{m}$	Waddel diameter, $\mu\text{m}$
Pentrafill II (PF)	0.064-26.3	0.267-8.38	0.240-10.2	0.286-5.78
Estilux 1 (Barium borosilicate) (ES1)	1.60-187	0.891-18.7	1.20-28.2	1.43-15.4
Estilux 2 (Lithium aluminosilicate) (ES2)	1.60-275	0.891-23.6	1.20-26.4	1.43-18.7
Occlusin (OC)	0.064-36.8	0.178-9.36	0.240-9.35	0.286-6.85
Herculite (HRC)	0.0214-2.48	0.134-2.41	0.120-3.06	0.165-1.78
Command (COM)	0.0071-5.95	0.059-4.34	0.08-4.34	0.095-2.75
Heliomolar Yb (HMYb) (ytterbium fluoride)	0.137-6.05	0.107-3.28	0.096-4.12	0.132-2.78
Heliomolar Si (HMSi) (Microfill)	1.03-625	0.713-33.2	0.959-28.8	1.14-28.2

**Table 4:** Particle size range in experimental composites

Particle size number	Area, $\mu\text{m}^2$	Breadth, $\mu\text{m}$	Height, $\mu\text{m}$	Waddel diameter, $\mu\text{m}$
1	0.712-463	0.594-41.9	0.399-41.9	0.952-24.3
2	0.712-278	0.594-21.4	0.799-27.6	0.952-18.8
3	0.712-178	0.594-29.4	0.799-24.4	0.952-15.0
4	0.712-38.9	0.594-11.0	0.399-12.0	0.952-7.04
5	0.712-60.0	0.594-14.3	0.799-12.0	0.952-8.74
6	0.712-30.1	0.594-7.43	0.399-9.19	0.952-6.19
7	0.475-19.2	0.297-9.21	0.399-6.39	0.777-4.95

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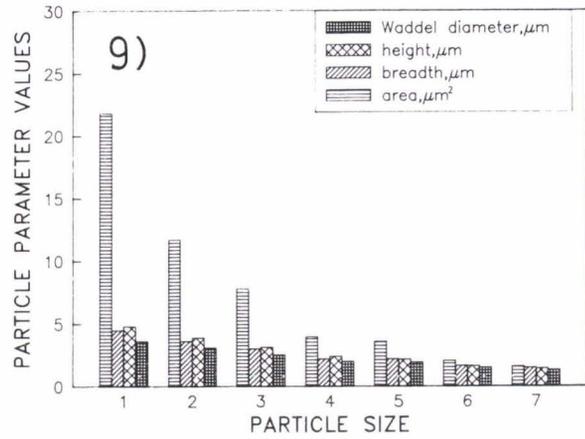
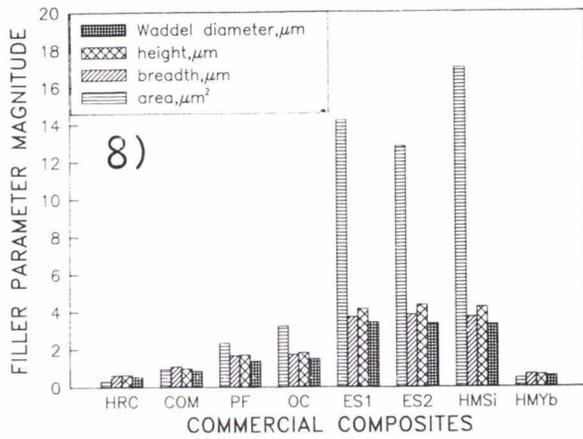
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#### Discussion with Reviewers

**K.-J. Soderholm:** The values in Tables 3 and 4 are suspicious. By assuming a spherical shape with a diameter of 41.9  $\mu\text{m}$  (particle size # 1), the surface should have a magnitude of  $3.14 \times 20.95 \times 20.95 \mu\text{m}^2$  rather than the maximal value of 463  $\mu\text{m}^2$ . Please discuss this discrepancy as well as the reliability of the technique.

**Authors:** The discrepancy is in the proposed calculation, rather than the technique. The implication of Dr. Soderholm's calculation is that the identical values of

## Composite Filler Characterization



Figures 8 and 9. Bar graph of filler parameters in commercial composites (Figure 8), and of feature parameters in experimental composites (Figure 9).

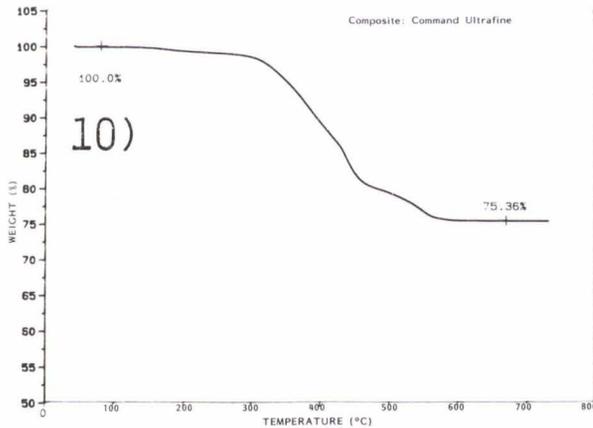


Figure 10. A plot of TGA thermal curve showing residual weight percent with temperature and the steady state value representing the amount of the filler in the composite Command Ultrafine.

## TGA ANALYSIS OF COMMERCIAL COMPOSITES

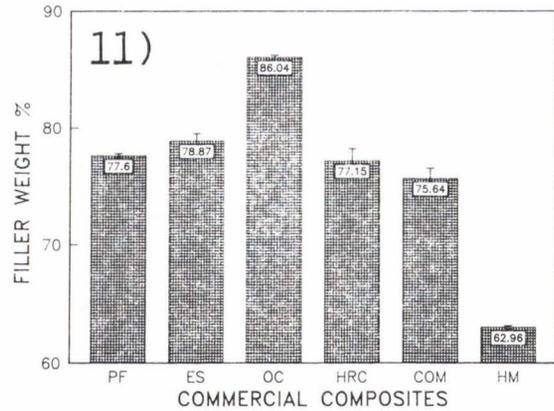


Figure 11. Bar graph of the filler weight percent in different commercial composites.

maximal height and width ( $41.9 \mu\text{m}$ ) of the particle can be used to define an equivalent diameter of the assumed sphere. The problem in this approach is that the maximum height and breadth reported are not generally associated with the same particle, but rather different particles. Therefore, these maximum values cannot be used to define an equivalent diameter of the same particle. Also, the particles are highly irregular in these composites.

**K.-J. Soderholm:** Can the authors supplement this technique with measurements generated by the BEI? This can be done on the experimental materials.

**Authors:** The feature analysis procedure involved a calibration using a standard grid of  $17.5 \mu\text{m}$  spacing. During this stage, BEI and KeveX monitor values of the grid spacing were measured and matched to avoid possible errors. The suggestion of the reviewer is not a standard

procedure and involves the risk of carrying over possible magnification errors in SEM to the measured data. Also, the measured data in command Ultrafine and Herculite composite system were close to the values reported by the manufacturer.

**K.-J. Soderholm:** Another closely related question is whether the depth of the electron probe can reach adjacent to the filler edges. I suspect that due to a certain depth penetration ability, information from filler particles located just under the surface is registered. This could result in an analytical error. Please discuss.

**Authors:** This a very important question. The particle size in the composite is typically in the micrometer level. The probe depth of penetration of interest in BSE imaging is of the order of a few hundred angstroms. Therefore, it is unlikely that particles from the subsurface regions directly under the surface particles will be

detected. However some subsurface particles in the lateral vicinity of the surface particle will show up in the image, if they are located within the probe depth of interest. However, this problem is identical to the agglomeration problem already discussed in the text. The agglomerates are generally easy to locate by their morphological appearance. Simple two-particle agglomerates can be cut through software routine, prior to feature analysis. More complex agglomerates are discarded by manual elimination routine in the software.

**J.L. Ferracane:** Is it possible to quantify the filler volume fraction, a much more meaningful parameter than filler weight fraction, using feature analysis? If not, why?

**Authors:** The quantification of the filler volume fraction is normally possible using the feature analysis method. However the presence of fused silica which cannot be resolved is a complicating factor. A combination of feature analysis and TGA should be successful in most cases. Some difficulties are encountered when composites with heavy loading are analyzed. The problem here is that of agglomeration. Simple agglomerates can, however, be cut using software routines. These steps do introduce some errors. However, the method outlined can be refined to improve accuracy by using calibration for volume fraction calculation. We are presently examining this aspect in a separate investigation.

**J.L. Ferracane:** What are the resolution limits of this technique? How critical is the selection of the appropriate gray levels for including and excluding apparent particles?

**Authors:** The resolution of the BEI is at least an order of magnitude smaller than the measured quantities. Therefore, BEI probe limitation may introduce only negligible errors, if any. The resolution of the gray level histogram peaks is however critical. The gain and brightness can be adjusted both in the SEM and the KeveX firmware in order to separate the gray level peaks. The peak separation is best accomplished using the entire gray level range of 0 to 255 when possible. The BSE image can provide a wide separation between the filler and matrix gray level ranges; secondary electron images were, however, found to be unsatisfactory for the gray level differentiation. If the gray level peaks are adequately separated as in the histogram illustrated in Figure 6, the measured data should be considered accurate.

**J.L. Ferracane:** Can you discuss why occlusin appears in the micrograph to be least dense although your results indicate that it has the maximum filler fraction? Is this because of the presence of fused silica which cannot be resolved in SEM?

**Authors:** A single micrograph used to illustrate particle size morphology cannot be used to compare how dense the filler distribution is. The particular illustration was selected in a rather less dense area to avoid agglomera-

tion problems in particle size characterization. However, Dr. Ferracane is correct in pointing out that fused silica cannot be determined by the feature analysis technique alone. The BEI resolution will not discriminate these particles. A combination of feature analysis and TGA can be used to characterize the filler fractions. Once the weight fractions are determined for each filler type, the volume fraction determination involves only the knowledge of densities of the filler components and the composite.

**R.P. Kusy:** Do the results imply that greater particle size of a hybrid resin, such as Estilux, provide any advantages over a small particle filled resin, such as Occlusin?

**Authors:** No, absolutely not. We have not evaluated the structure-property relationships in this investigation. The method proposed is simply to characterize the particle size of the filler.

**R.P. Kusy:** How do the TGA results compare with the compositional literature available?

**Authors:** The values are close to the reported data in the literature. For example, The mean filler weight percentages obtained for Occlusin and Heliomolar were 86.04 and 62.96 respectively compared to 85.6 and 60 reported by Ruyter and Oysaed (text reference 8) after combustion at 575°C.

**R.P. Kusy:** Are there any correlations between clinical results of other research groups and the analytical results in this study?

**Authors:** We have not examined this correlation, if any. We are also evaluating other properties of the composites studied and comparison with clinical results is more appropriate after completion of the above work.

**H.J. Mueller:** Regarding TGA, was a steady state condition reached at the same temperature for the different composites studied? Were similar curve shapes obtained with the composites?

**Authors:** While the shapes are somewhat similar, temperatures of decomposition was primarily dependent on resin composition and not on the filler. This aspect will be reported separately in a different article.