Journal of Oral Rehabilitation 2004 **31**; 1090–1101

Characterization of the inorganic fraction of resin composites

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SUMMARY **The purposes of this study were to determine the weight fraction of filler in thirty-nine resin-based materials including flowable and packable composites, and to examine the morphology of the filler particles. The percentages of inorganic fillers by weight were determined by Thermogravimetric Analysis and by ashing in air technique at 900 °C. The size and shape of the filler particles were examined using scanning electron microscopy (SEM) after dissolution of the organic matrix. The weight fraction of inorganic fillers ranged between 41·6 and 84·6%. Wide variations were found among materials of the same category. Values found in the present study were sometimes different from those given by the manufacturers. The SEM photomicrographs showed various shapes, and sizes of inorganic fillers. Compared with universal hybrid restorative materials, flowable composites have lower filler loading and packable resin composites did not show higher values as claimed by some manufacturers. Various factors may explain the observed discrepancies between the manufacturer's data and our 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.**

KEYWORDS: **composites, filler morphology, percentage of fillers, silanization**

Accepted for publication 08 July 2003

Introduction

Resin composites introduced in 1960 were initially used for anterior restorations. The growing demand of the patients for aesthetic restorations and their concern about mercury containing alloys, have promoted their use as a substitute for amalgam in posterior teeth.

The behaviour of the materials depends largely on their fillers: percentages, composition, dimensions and shape as well as the polymerization degree of the resin matrix. It has been shown that mechanical properties are highly correlated to the filler fraction of resin composites (1–4). Theoretically increasing filler content could also reduce the polymerization shrinkage. Percentage of fillers can be expressed by weight or by volume. In resin composites, inorganic fillers loading generally accounts for between 35 and 70 volume % or 50–85 weight % of the composite (5). Both volume and weight contents were used to study the influence of fillers loading on mechanical properties (1, 6–8). Although those two parameters are linked by the density of the fillers, in some cases it would be more relevant to determine the percentage of fillers by volume of resin composites. Percentage of fillers by volume can be measured through direct and indirect methods. The direct method using the picnometric technique showed wide variations and high standard deviations (V. Destoop, personal communication). The indirect technique uses a mathematical formulation including the percentage of fillers by weight and the density of the fillers. This procedure is not always simple, because if the percentage of fillers by weight is easy to measure, it is not the case with the density due to the wide variations of fillers morphologies and molecular compositions. This was in accordance with the findings of Kim *et al.* (9) who obtained for some materials, different percentages of fillers by volume than those reported by the manufacturers.

Other authors studied the effect of fillers size (8) and shape (9) on mechanical properties. The size and morphology of fillers greatly influenced filler loading which in turn affected the mechanical properties of the tested composites.

Lutz and Phillips (10) were the first to classify resin composites according to their filler size distribution. Later on, many authors ranked the resin composites according to their filler composition, size and percentage (11–15).

A few years ago, flowable and packable composites were put on the dental market. The former have a low viscosity and are suggested by the manufacturers for various indications: pit and fissure sealants, repair of marginal defects, liners in deep cavities, stress absorbers in the elastic cavity wall concept. The latter are recommended as posterior resin composites replacing amalgam, for improved condensation and contact point tightness. Moreover, some manufacturers were announcing better properties because of the incorporation of new kinds of fillers (for example: porous, alkaline).

More recently, Degussa and Voco introduced a new kind of restorative material, based on 'ormocer' (organically modified ceramics) technology: Definite and Admira. Ormocers® are hybrid polymer materials synthesized by the sol-gel process. Multifunctional urethane- and trioether (meth)acrylate alkoxysilyl groups of the silane allow the formation of an inorganic Si-O-Si network by hydrolysis and polycondensation reactions. The (meth)acrylate groups are available for photochemically induced polymerisation. These novel inorganic-organic oligomers partly replace, the conventional monomers in the composite.

Linking fillers of a composite to its resin matrix is of paramount importance. It is established by the silane coupling agent that bonds to both silicon-oxygen in the fillers and to methacrylate groups in the resin matrix (16). At high filler levels and small filler sizes, the silane coating of filler particles begins to rival the volume content of monomers in dental composites (17). This may be explained by the fact that the amount of silane is influenced by the morphology and the percentage of fillers. Consequently, in highly filled composites, the smallest the fillers the higher the quantity of silane.

The aims of this study were to determine the percentage by weight of the inorganic fillers and to examine the filler morphology by scanning electron microscopy (SEM) of some new composites. Two techniques for determining the percentage of fillers by weight will also be compared.

Materials and methods

Thirty-six commercially available light-curing and one chemically-cured resin composites were used in this study. Two resin based materials known as 'ormocers' were also included. By selecting this group of materials, all the available categories of resin composites on the market that can be used for direct restorative techniques were represented. A large group of universal hybrid composites with different percentages of fillers were compared with other categories as chemically-cured composites and microfine composites. The materials and their specifications are listed in Table 1.

The silane contents were determined for two types of fillers, SiO_2 and glass particles, according to the methods described in 'Percentage of fillers by Thermogravimetric Analysis' and 'Percentage of fillers by ashing in air' below. The silica and the glass fillers were provided by Hereaus Kulzer and were not extracted from the composites.

Percentage of fillers by Thermogravimetric Analysis

Thermogravimetric analysis (TG) 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 °C min^{-1} in a dynamic dry air purge of 30 mL min^{-1} from 30 to 900 °C. The software Pyris† was used to calculate the percentage weight loss corresponding to the organic part. The instrument was calibrated using ferromagnetic materials exhibiting known curve point transitions.

Percentage of fillers by ashing in air

The percentages of inorganic fillers by weight ($n = 3$) were also determined by the ashing technique (2) by comparing the difference in weight before and after ashing in air 0·5 g of each material at 900 °C. The crucibles were introduced in the furnace (Heraeus K

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Table 1. List of the tested materials

Material	Classification	Manufacturer	Batch and shade
A-110	VLC Microfine CS	3 M, St-Paul MN, USA	20000719 (A2D)
Admira	VLC 'Ormocer'	Voco, Cuxhaven, Germany	94545 (A3)
Admira-Flow	VLC Flow 'Ormocer'	Voco, Cuxhaven, Germany	20615 (A3)
Aeliteflo	VLC Hyb Flow CS	Bisco, Inc Itasca, IL, USA	039317 (A3)
Aeliteflo-LV	VLC Hyb Flow CS	Bisco, Inc Itasca, IL, USA	0008388 (A2)
Amelogen	VLC Hyb Univ CS	Ultradent products, UT, USA	2CPM (A2)
Arabesk-Flow	VLC Hyb Flow CS	Voco, Cuxhaven, Germany	82777 (A3)
Arabesk-Top	VLC Hyb Univ CS	Voco, Cuxhaven, Germany	81594 (A3)
Charisma-F	VLC Hyb Univ CS	Heraeus Kulzer, Wehrheim, Germany	23 (A20)
Clearfil Photo Posterior	VLC Hyb Univ CS	Kuraray, Osaka, Japan	0035A (UL)
Clearfil Photo Anterior	VLC Hyb Univ CS	Kuraray, Osaka, Japan	0024C (A3)
Concise	CC Conventional CS	3 M, St-Paul MN, USA	19970303 (U)
Durafill VS	VLC Microfine CS	Heraeus Kulzer, Wehrheim, Germany	030122 (A3)
Esthet-X	VLC Hyb Univ CS	Dentsply De Trey, Konstanz, Germany	0111000983 (U)
Filtek-Flow	VLC Hyb Flow CS	3 M, St-Paul MN, USA	20000809 (A3)
Flow-Line	VLC Hyb Flow CS	Heraeus Kulzer, Wehrheim, Germany	010021 (A2)
Inten-S	VLC Hyb Univ CS	Vivadent, Schaan, Liechtenstein	D58656 (A3)
Metafil-AP	VLC Hyb Pack CS	Sun Medical, Shiga, Japan	VG1 (A2)
Metafil-CX	VLC Microfine CS	Sun Medical, Shiga, Japan	71201 (A3,5)
Metafil-Flo	VLC Hyb Univ CS	Sun Medical, Shiga, Japan	VW2 (B2)
P-60	VLC Hyb Pack CS	3 M, St-Paul MN, USA	030998 (A3,5)
Pertac-II	VLC Hyb Univ CS	Espe, Seefeld, Germany	00634764 (A3)
Polofil-Molar	VLC Hyb Univ CS	Voco, Cuxhaven, Germany	63596 (U)
Point-4	VLC Hyb Univ CS	Sybron/Kerr, Orange, USA	003156 (A3)
Point-4 flowable	VLC Hyb Flow CS	Sybron/Kerr, Orange, USA	201656 (A2)
Prodigy	VLC Hyb Univ CS	Sybron/Kerr, Orange, USA	901683 (A3)
Prodigy Condensable	VLC Hyb Pack CS	Sybron/Kerr, Orange, USA	904665 (A2)
Pyramid Enamel	VLC Hyb Pack CS	Bisco, Inc Itasca, IL, USA	0009613
Quadrant Anterior	VLC Microfine CS	Cavex Haarlem, Holland	22C (A2)
Quadrant Posterior	VLC Hyb Pack CS	Cavex Haarlem, Holland	30C (A2)
Revolution Formula II	VLC Hyb Flow CS	Sybron/Kerr, Orange, USA	01252 (A2)
Silux-Plus	VLC Microfine CS	3M, St-Paul MN, USA	6DH (U)
Solitaire II	VLC Hyb Pack CS	Heraeus Kulzer, Wehrheim, Germany	VP150499 (A1)
Spectrum	VLC Hyb Univ CS	Dentsply De Trey, Konstanz, Germany	9608244 (A3)
Surefil	VLC Hyb Pack CS	Dentsply De Trey, Konstanz, Germany	980818 (A2)
Tetric-Ceram	VLC Hyb Univ CS	Vivadent, Schaan, Liechtenstein	900513 (A3)
Tetric-Flow	VLC Hyb Flow CS	Vivadent, Schaan, Liechtenstein	901232 (A3)
Z-100	VLC Hyb Univ CS	3 M, St-Paul MN, USA	19960229 (UD)
Z-250	VLC Hyb Univ CS	3 M, St-Paul MN, USA	030998 (A3,5)
Microglass silanized	Fillers	Heraeus Kulzer, Wehrheim, Germany	559
Microglass not silanized	Fillers	Heraeus Kulzer, Wehrheim, Germany	601
SiO_2 silanized	Fillers	Heraeus Kulzer, Wehrheim, Germany	2487
SiO_2 not silanized	Fillers	Heraeus Kulzer, Wehrheim, Germany	2537

VLC, visible light cured; CC, chemically cured; CS, composite; Flow, flowable; Pack, packable; Univ, universal; Hyb, hybrid.

1272[†], range of heating between 200 and 1125 °C) for an hour, after the temperature had reached 900 °C. The porcelain crucibles were weighted using an analytical balance (Mettler-Toledo AE260)[‡].

Filler morphology

For the SEM, the unpolymerized monomers were removed by a washing technique (13). A sample of 0·5 g of each material was dissolved in 4 mL of acetone and centrifuged for 5 min at 700 ***g***. This process was repeated three times using acetone and three other

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[†] Heraeus Kulzer, Wehrheim, Germany.

[‡] DeltaRange, Greifensee, Switzerland.

times with chloroform for a further washing and elimination of the unpolymerized resin. The remaining filler particles including the prepolymerized fillers were placed in 3 mL of absolute ethanol and the suspension of filler particles was smeared on a glass slide (7·5 × 2·5 cm) and dried at 37 °C during 6 h. A thin coating of gold was then sputtered on the filler bearing slides. Morphological examination was performed using a scanning electron microscope (Leica Stereoscan S-260)[§] operating at 20 kV.

Results

The inorganic filler content as percentages by weight, as well as standard deviations, of all the materials, are listed in Table 2. For the TG, they varied between 41·7% for the Metafil-CX and 85·2% for the Clearfil Photo Posterior. For the flowable composites, values ranged between 45·8 and 66·5%, for the packable composites between 65·5 and 79·8% and for the microfine between 41·7 and 59·8%. Universal hybrid composites showed values comprised between 69·7 and 85·2%.

Figure 1 shows typical TG thermal curve giving the weight per cent of the original sample versus temperature for different materials. As will be observed in this figure, the difference in the ordinate value (%) at the points immediately before and after the decomposition transition is assigned as the percentage weight loss corresponding to the organic part. The remaining part corresponds to the inorganic filler. The relative stability after 750 °C also allows to validate the ashing in air technique that used a temperature of 900 °C.

Using this latter technique, nearly all the materials showed similar values to those obtained by TG. In fact, the percentage of fillers of the materials tested by both techniques are highly correlated (regression analysis $r = 0{\cdot}99$ and $y = 1{\cdot}0083x - 0{\cdot}6481$ with $P < 0{\cdot}05$). Figure 2 shows the materials by categories, ranked according to their percentage of fillers by weight determined by ashing in air.

For some materials, our data were not in accordance with those given by the manufacturer, differences reaching more than 20%, in absolute values.

The isolated SiO_2 and glass particles (Heraeus Kulzer, Germany), showed variable weight loss ($n = 3$) (Table 3). Using the TG as well as the ashing in air techniques, the silanized SiO_2 microfillers had 9·2 and 9·7% of loss. The silanized glass particles showed 4·4% of loss. The unsilanized fillers showed only a small percentage of loss of 0·1 and 0·7% for the SiO_2 and 1·6% for the glass particles. Moreover previous dessication of the fillers at 105 °C during 10 h, in order to eliminate the adsorbed water on the surface, did not modify significantly the results.

The SEM photomicrographs of the fillers at 5000× magnification are shown in Figs 3–8. For clarity purpose, the 39 materials were divided in six different groups: universal hybrid composites, packable composites, microfine anterior composites, flowable composites, chemically-cured resin composites and ormocers. The filler shapes were either angular, rounded or spherical, depending on the product. The morphological character is not related to the material category. Some flowable resin composites (Fig. 4) contain, as well as some other universal hybrid composites like Arabesk-Top, Amelogen and Tetric-Ceram, irregular-shaped fillers. Microfine anterior resin composites (Fig. 5) show large filler aggregates of around 20 μm. Spherical filler particles are observed in Z-100, Z-250, P-60, Filtek-Flow and Point-4.

Discussion

Many methods can be used to study the filler concentration in percentage by weight. Thermogravimetry (TG) is a technique in which the mass of a substance is monitored as a function of temperature or time as a sample specimen is subjected to a controlled temperature programme. Nowadays, it is an important analytical tool in the various branches of chemistry, geology, ceramics and material science in general (12, 18). The curve patterns of the TG varied according to the material tested thus reflecting the variations in organic composition. Additional research on the analysis of the organic fraction is equally essential but not the purpose of this study. Thorough chemical analysis is complex and time consuming. For Surefil and Tetric-Ceram, our data were in accordance with those of Tyas *et al.* (18).

The TG technique was applied in our study to analyse the behaviour of different materials at higher temperatures than those used by different authors for the ashing in air technique. In fact this technique is 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 at a constant

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[§] Leica Cambridge Ltd, Cambridge, UK.

Table 2. Percentage of fillers by weight of the materials determined by Thermogravimetric Analysis and by ashing in air

Materials	% Fillers by TGA (s.d.)	% Fillers by ashing in air (s.d.)	% Fillers manufacturer	Range of fillers (mean)	Type of fillers
A-110	55·9 (0·9)	55·4 (0·2)	56	10–50 μm (0·04)	SiO_2
Admira	73·6 (0·4)	73·1 (0·1)	77	0·04–0·07 μm	Ba-Al-F-Si, SiO_2
Admira-Flow	61·0 (0·4)	61·2 (0·2)	63	(0·7 μm)	Ba-Al-F-Si, SiO_2
Aeliteflo	53·0 (1·7)	54·8 (0·2)	60	0·7 μm	Ba
Aeliteflo-LV	59·4 (0·3)	58·0 (0·2)	52	0·7	Ba
Amelogen	71·9 (1·0)	72·8 (0·2)	72	0·7 μm	–
Arabesk-Flow	61·6 (0·3)	61·5 (0·4)	64	0·7 μm	SiO_2, Ba, Borosilicate, Sr
Arabesk-Top	71·4 (0·4)	71·1 (0·8)	77	0·05–0·7 μm	SiO_2, Ba, Borosilicate, Sr
Charisma-F	74·7 (0·3)	76·1 (0·4)	75	0·02–2 μm (0·7)	AlF, Ba, SiO_2
Clearfil Photo Anterior	59·8 (0·2)	58·7 (2·0)	81	0·04–10 μm (2·8)	SiO_2, Glass, prepolymerized fillers
Clearfil Photo Posterior	85·2 (0·3)	84·6 (0·2)	86	0·1–20 μm (4)	SiO_2, Ba, Si
Concise	82·0 (0·3)	80·8 (0·5)	78	1–40 μm (9)	Quartz
Durafill VS	51·3 (0·5)	51·5 (0·3)	60	0·01–0·04 μm	SiO_2
Esthet-X	73·3 (0·6)	73·0 (0·1)	77	10 nm-0·8 μm	SiO_2, Ba-Al-F-Si
Filtek-Flow	65·3 (1·1)	65·9 (0·5)	68	0·01–6 μm (1·5)	SiO_2, Ba, TMTP
Flow-Line	59·4 (0·5)	59·4 (0·6)	62	0·7 μm	SiO_2, Ba-Al-B-Si-F
Inten-S	69·7 (0·6)	70·2 (0·2)	81·9		Copolymers, Ba, YbF_3
Metafil-AP	76·9 (0·6)	77·1 (0·6)	81	1–20 μm	SiO_2, Ba, TMTP
Metafil-CX	41·7 (0·3)	41·6 (0·2)	54	20 μm	SiO_2, TMTP
Metafil-Flo	61·2 (0·3)	61·8 (0·2)			
P-60	78·8 (0·6)	78·9 (0·3)	83 + silane	0·01–3·5 μm (0·6)	Zr/Si
Pertac-II	74·9 (3·2)	71·2 (2·7)	80	0·1–2 μm	SiO_2, Quartz, YtF_3
Polofil-Molar	78·6 (0·4)	78·6 (0·2)	84	0·05–25 μm	SiO_2, Ba, Borosilicate, Sr
Point-4	73·0 (0·1)	72·8 (0·4)	76	0·4 μm	SiO_2, Ba Al-Si,
Point-4 Flowable	66·5 (0·1)	66·3 (0·2)	70	0·4 μm	SiO_2, Ba Al-Si,
Prodigy	72·3 (1·9)	74·4 (0·3)	77	0·6 μm	SiO_2, Ba
Prodigy Condensable	77·0 (0·4)	77·4 (0·7)	80	0·6 μm	SiO_2, Ba
Pyramid Enamel	73·1 (0·6)	74·3 (0·7)	80	–	–
Quadrant Anterior	58·2 (0·2)	58·6 (0·0)	74	<0·1 μm	SiO_2, Ba-Al-F-Si,
Quadrant Posterior	65·5 (0·4)	64·9 (0·3)	66	0·1–10 μm	SiO_2,Ba-Al-F-Si, SrF2
Revolution Formula II	45·8 (1·9)	45·4 (1·8)	60	(0·6 μm)	Ba
Silux-Plus	57·7 (1·5)	54·5 (1·0)	56	10–50 μm (0·04)	SiO_2
Solitaire II	71·7 (0·7)	72·4 (0·1)	75	0·7–25 μm	SiO_2, Ba, Al, B-Si
Spectrum	75·0 (0·0)	75·1 (0·4)	77	0·04–5 μm	SiO_2, Ba, Al, B-Si
Surefil	79·8 (0·2)	79·0 (0·3)	82	0·04–0·1 (0·8)	Ba-F-Al-BSi
Tetric-Ceram	74·7 (1·2)	75·5 (0·2)	80	0·04–3 μm (0·7)	SiO_2, Ba-Al-F, YbF_3
Tetric-Flow	65·0 (0·2)	64·7 (0·6)	68·1	0·04–3 μm (0·7)	SiO_2, Ba-Al-F, YbF_3
Z-100	78·8 (1·1)	79·5 (0·2)	84·5	0·01–3·5 μm (0·6)	Zr/Si
Z-250	77·5 (0·4)	77·7 (0·3)	82 + silane	0·01–3·5 μm (0·6)	Zr/Si

Data given by the manufacturers were included when available and expressed as percentage of fillers by weight, range of fillers (mean particle size) and type of fillers; '–' (not available).

temperature. Chung and Greener (2) ashed the materials at 700 °C, while other authors used different temperatures, sometimes quite inferior (11, 19, 20). Kim *et al.* (9) ashed the composites at 600 °C during 30 min. Results were similar to the present investigation for Metafil-CX, Clearfil Photo Anterior, Silux-Plus and Z-100. The stable patterns observed with TG curves after 750 °C allowed us to validate the ashing in air technique at 900 °C during 1 h.

The results obtained with both techniques (TG and ashing in air at 900 °C) are highly correlated (coefficient of estimation '*r*' and slope '*a*' are nearly equal to 1) and the percentages of fillers by weight for the Prodigy, the Tetric-Ceram and the Z-100 are similar to

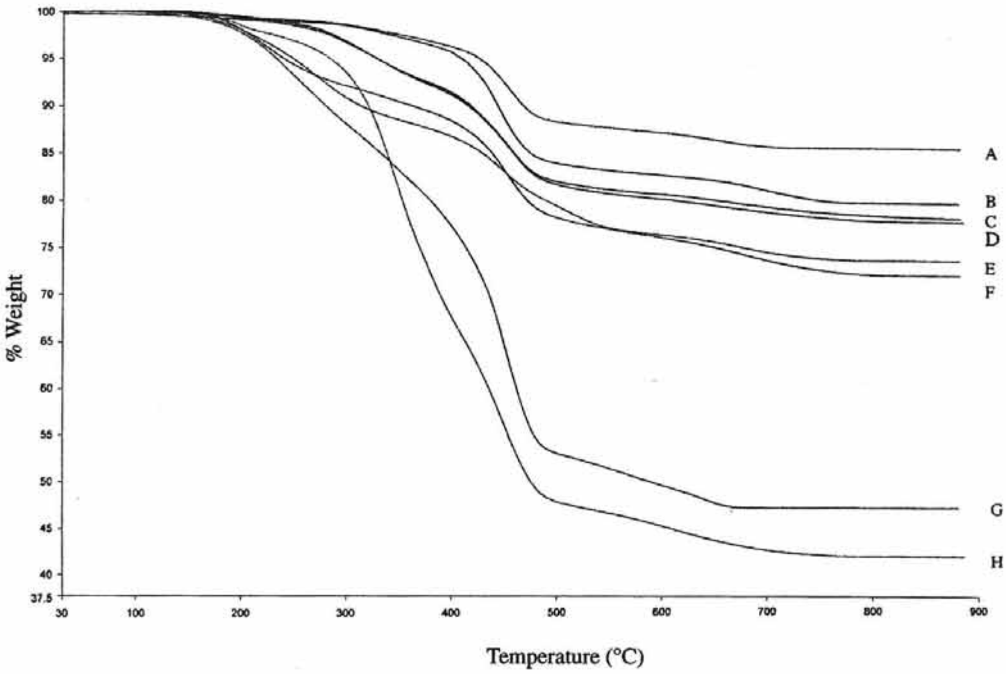


Fig. 1. Thermogravimetric Analysis curves of different resin composites. Note the difference in the residual percentage of weight and the stability after 750 °C. A: Clearfil Photo Posterior; B: Concise; C: P-60; D: Z-250; E: Admira; F: Amelogen; G: Revolution Formula II; H: Metafil-CX.

those reported in the literature (18, 20). Except for Pertac-II, the percentages of fillers by weight of all the investigated materials showed low standard deviations using both techniques. In fact, the Pertac-II contains among its fillers, Yttrium Trifluoride (YF_3). Previous analysis of Yttrium Trifluoride fillers, showed with both techniques, after 7 h, continuous loss of weight (nearly 18%). The unstable behaviour of the YF_3 fillers explains, at least partly, the high standard deviations observed with Pertac-II.

As illustrated by the histogram in Fig. 2, the percentages of fillers vary widely within the same category. Microfine and flowable composites have the same range of percentages of fillers by weight, but lower than those of all but one packable or universal hybrid composites. Point-4 flowable, had the highest percentage of fillers by weight compared with other flowable composites and was nearly similar to that of Quadrant Posterior, classified as packable composite. As shown in Fig. 6, this material as well as Solitaire II, have several fillers including particular porous filler that may be responsible for this low percentage by weight. The other packable composites did not show higher values than those of universal hybrid composites.

In some cases, differences were found between our data and those given by the manufacturers. Various explanations are possible. The first one is variable layer thickness and amount of silane. Silanization process plays a main role in the adhesion of the organic resin matrix to the inorganic mineral fillers. The most used silane coupling agent is the γ-methacryloxypropyltrimethoxysilane. Laboratories and manufacturers treat the filler-matrix interface according to their own original methods and use different ways of calculation of the percentage of fillers. Some manufacturers seem to assess the percentage of fillers by weight before the silanization process of the fillers, while others include the percentage of silane coating in their calculations. On the contrary, the surface area of fillers will affect the percentage of silane used; the smallest the fillers, the higher the quantity of silane. In fact, our observations fulfilled this statement; the use of silane treated fillers of SiO_2 and small glass particles, enhance the total percentage of fillers by weight of about 9 and 2·8% respectively (Table 3).

The second explanation of the discrepancies, related to the microfine composites, is because of the presence of the 'organic filler' (pre-polymerized resin) as part of the filler content. In the so-called microfilled composites, pre-polymerized blocks of resin containing high loading of silica particles (0·04 μm), ground into particles of about 10–50 μm diameter are included (10). The ashing technique destroys the organic part of the blocks and measures only the real inorganic fillers. This could explain the differences observed between our results and the data given by the manufacturers for Clearfil Photo Anterior, Durafill VS, Metafil-CX and Quadrant Anterior.

Other hypotheses could be the presence of water and the evaporation of some inorganic component of the composite fillers. However, the presence of water can be excluded as no difference was observed before and

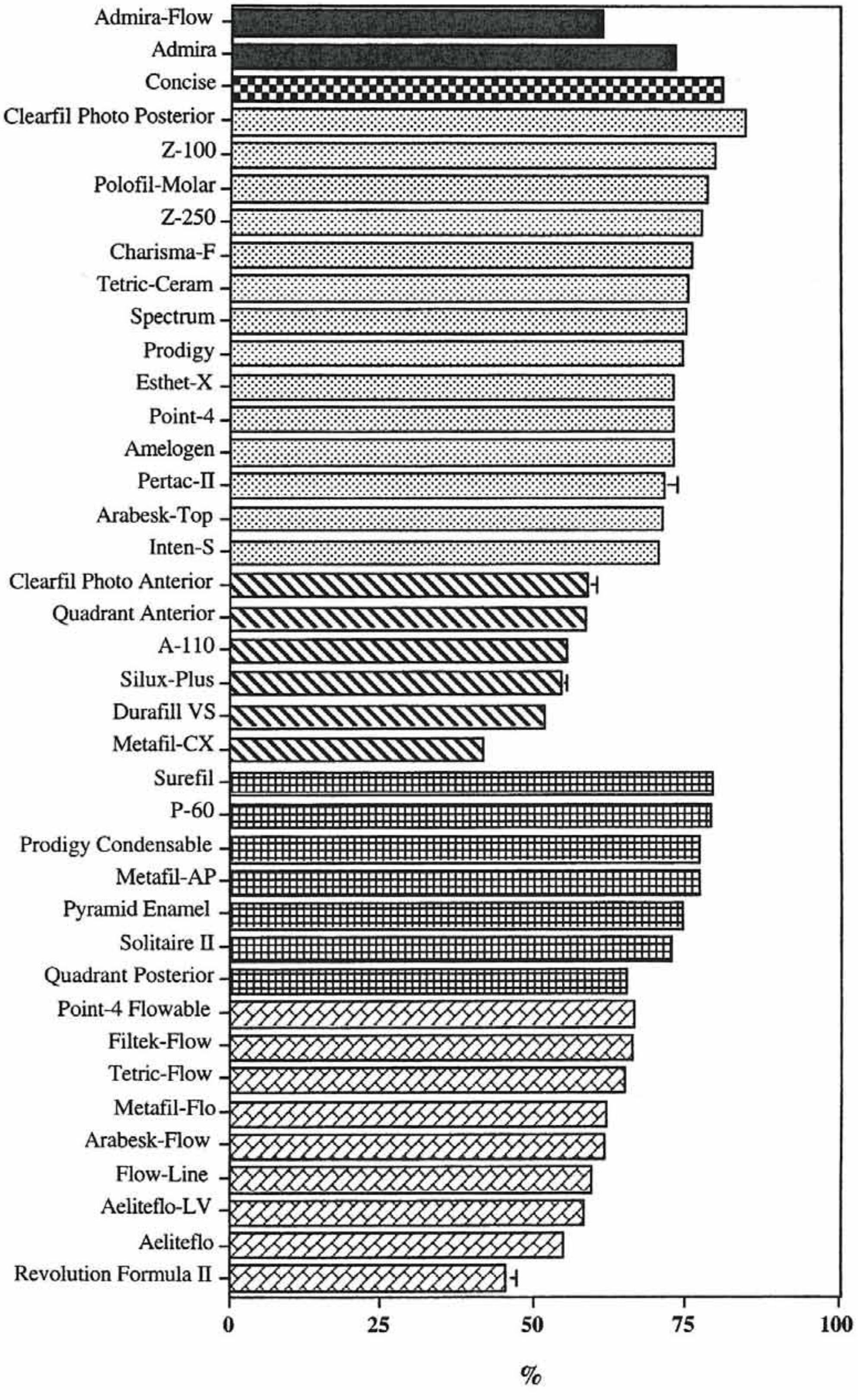
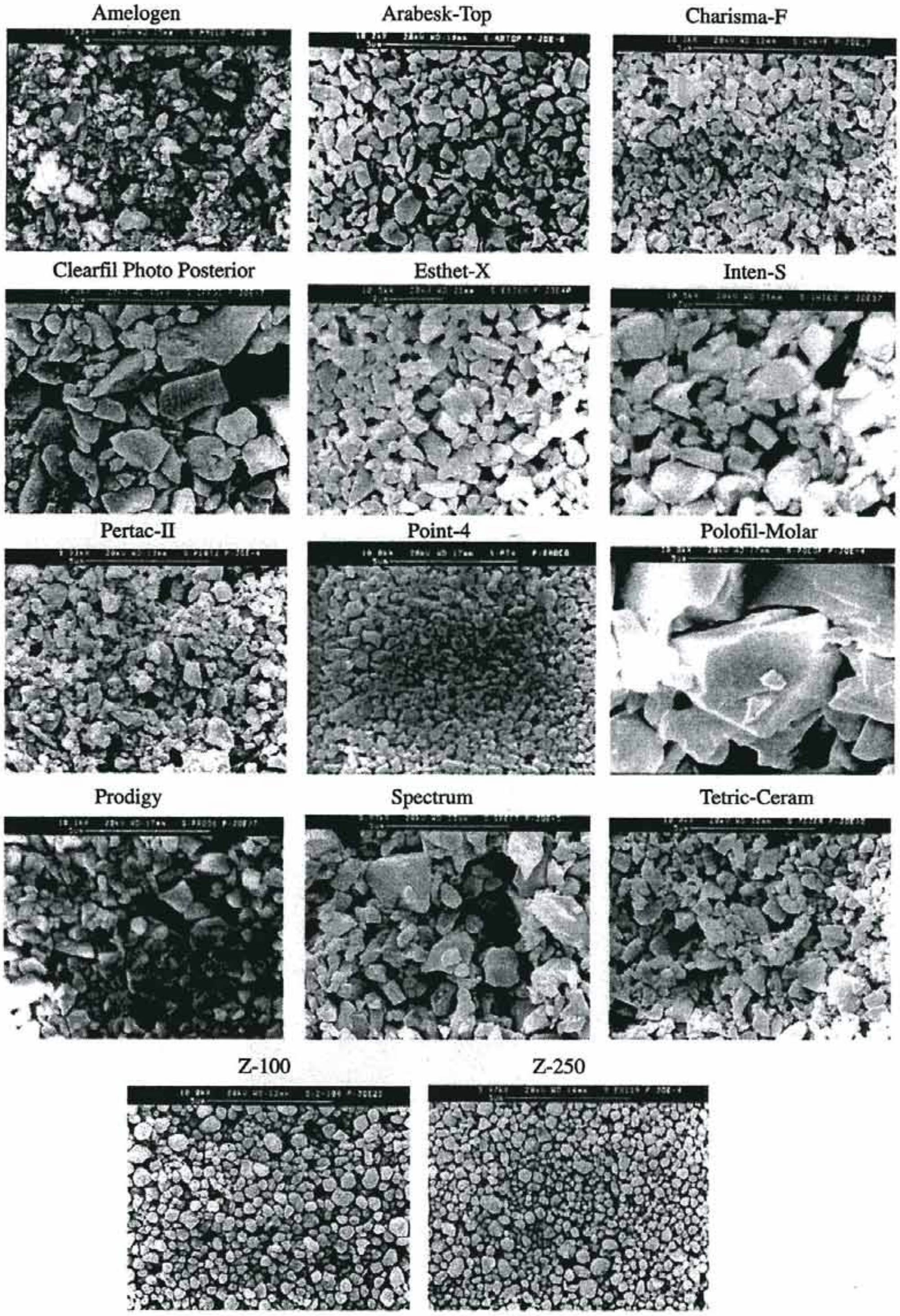


Fig. 2. Bar chart of the percentage of fillers by weight obtained by ashing in air of the resin based materials, ranked by categories in decreasing order.

Sample	% loss by weight after desiccation at 105 °C	% loss by weight without desiccation after ashing in air	% loss by weight without desiccation after TGA
SiO_2 silanized	9·6 (0·1)	9·7 (0·1)	9·2
SiO_2 unsilanized	0·6 (0·1)	0·7 (0·1)	0·1
Glass particules silanized	4·4 (0·1)	4·4 (0·1)	4·4
Glass particules unsilanized	1·6 (0·2)	1·6 (0·1)	1·6

Table 3. Percentage of loss by weight of glass and SiO_2 fillers with and without desiccation process, unpaired *t*-test showed non-significant difference between the two techniques ($P < 0{\cdot}0001$)



Amelogen; Arabesk-Top; Charisma-F; Clearfil Photo Posterior; Esthet-X; Inten-S; Pertac-II; Point-4; Polofil-Molar; Prodigy; Spectrum; Tetric-Ceram; Z-100; Z-250

Fig. 3. Universal hybrid composites. Fillers by scanning electron microscopy at 5000× magnification.

after dessication of the fillers at 105 °C during 10 h (Table 3) and, according to Weast *et al.* (21), the boiling temperature of some inorganic component of the composite fillers are higher than those used in our study with both methods.

Although dental composites used today contain different fillers, there have been few studies concerning their morphology (9, 11–13). When embedded in the resin phase, fillers are difficult to observe. Furthermore, in this condition, polishing techniques significantly alter the surface appearance of the composite (9, 12). In our study, the fillers were extracted from the composites using a solvent to obtain SEM images of only the isolated particles. For information purpose, the range and the mean size of the fillers according to the manufacturers are listed in Table 2.

Most fillers are of irregular shape with roughened surface. Spherical filler particles are observed in Z-100, Z-250, P-60, Filtek-Flow and Point-4. A spherical shape improves the packing of the particles and allows to increase the volume fraction of the filler in the composite (15). Smooth, rounded shape of the filler

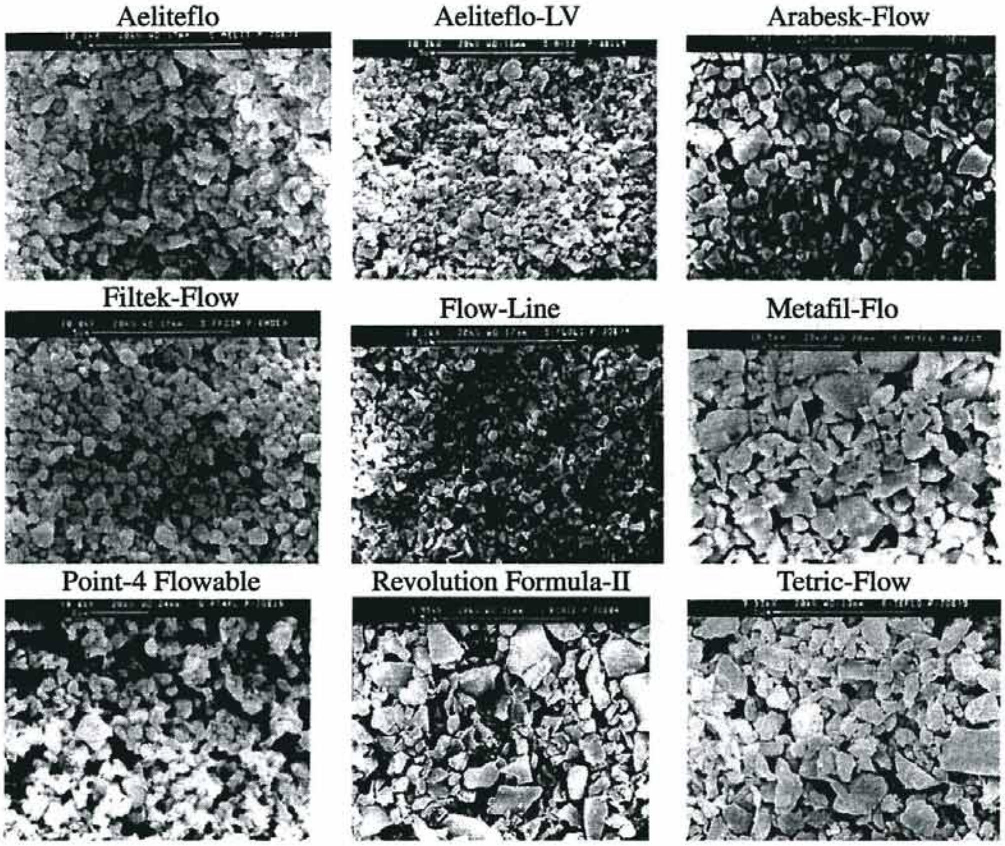


Fig. 4. Flowable composites. Fillers by scanning electron microscopy at 5000× magnification.

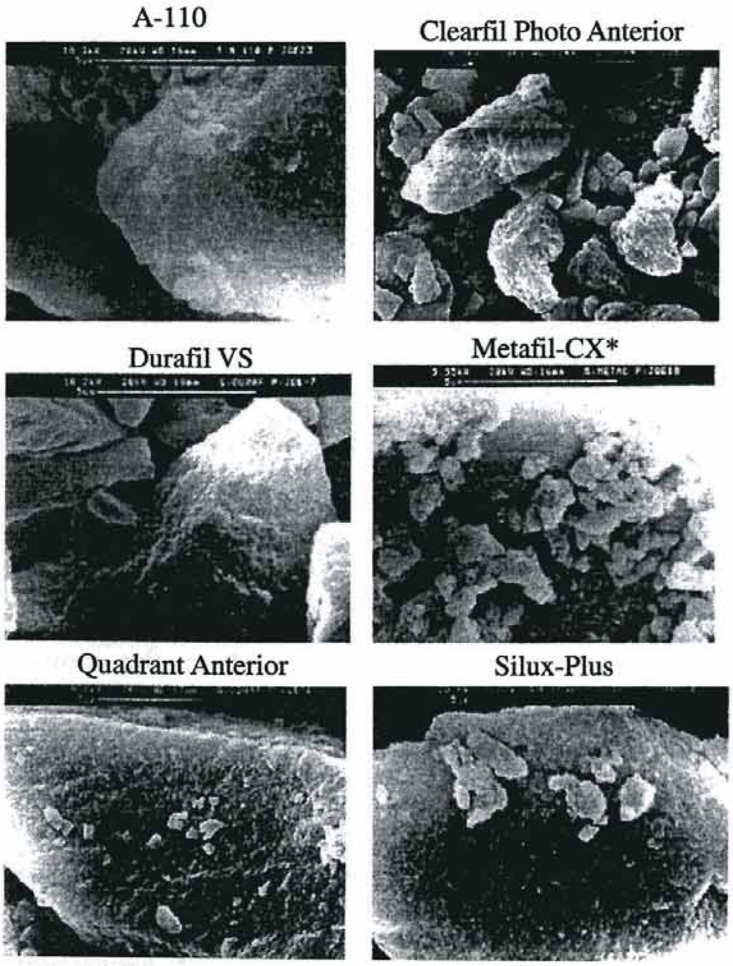


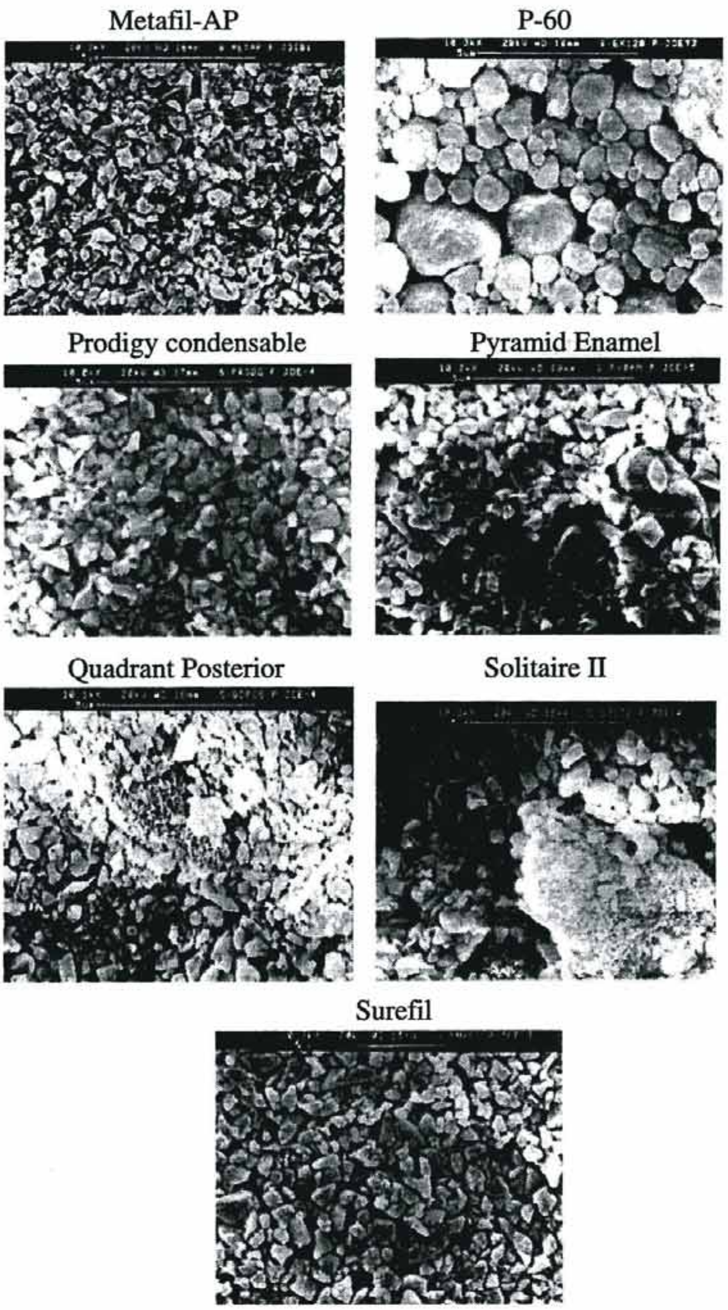
Fig. 5. Microfine anterior composites. Fillers by scanning electron microscopy at 5000× magnification. *As mentioned in the discussion, Metafil-CX fillers were extracted without using chloroform.

also enhances the fracture strength of the material. Indeed, as mechanical stress tends to concentrate on irregularities of the filler/matrix interface, angles and protuberances of filler particles are zones where cracks initiate promptly (16, 22).

Clearfil Photo Posterior and Spectrum (Fig. 3) showed a wide range of filler sizes that is in accordance with the manufacturers data (Table 2).

Packable resin composites (Fig. 6) have different filler shapes. Solitaire II as well as Quadrant Posterior, contain a mixture of small particles and large porous aggregates. According to the manufacturer, this design enhances the linkage between the filler and the matrix providing 'an entangling effect'. Prodigy Condensable, Pyramid Enamel and Surefil have rather the same irregular filler's shape while P-60 shows rounded particles.

In the present study, some pairs of resin composites (universal versus a packable or a flowable) issued from the same manufacturer were compared (Z-100/P-60, Spectrum/Surefil, Tetric Ceram/Tetric Flow, Arabesk Top/Arabesk Flow, Metafil-AP/Metafil-Flo…). For each pair of composites, at least one feature, the shape, the percentage of fillers or the composition of the organic matrix was modified. Although having nearly the same percentage of fillers by weight, P-60 showed larger filler particles than Z-100. Spectrum showed a lower percentage of fillers by weight (75·1%) compared with



Metafil-AP

P-60

Prodigy condensable

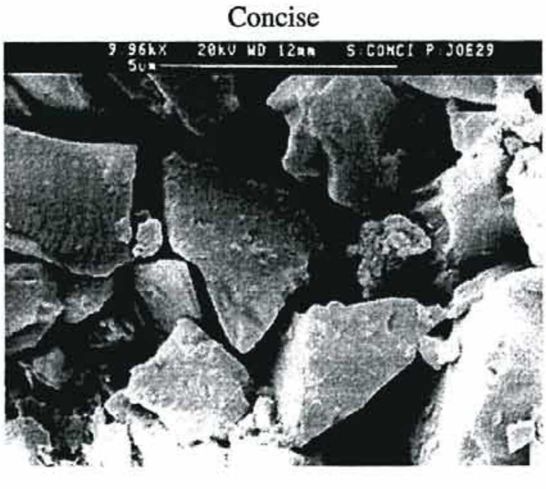
Pyramid Enamel

Quadrant Posterior

Solitaire II

Surefil

Fig. 6. Packable resin composites. Fillers by scanning electron microscopy at 5000× magnification.



Concise

Fig. 7. Chemically-cured composite. Fillers by scanning electron microscopy at 5000× magnification.

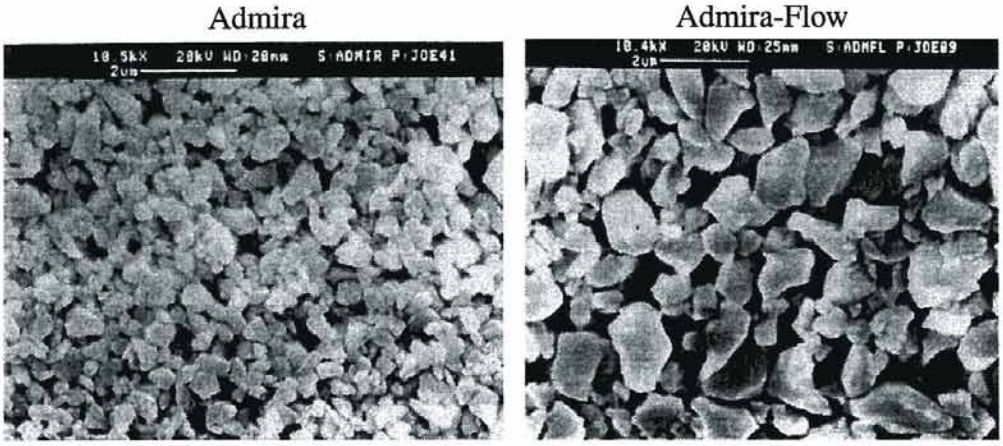
Surefil (79·0%) but with larger irregular fillers. Prodigy and Prodigy Condensable had the same filler shapes but different percentages of fillers.

The flowable resin composites, when compared with universal ones from the same manufacturer, had lower percentages of fillers but similar filler shapes as shown in Figs 3 and 4, (Arabesk-Top/Arabesk-Flow, Charisma-F/Flow-Line, Prodigy/Revolution-II, Tetric Ceram/Tetric Flow and Z-250/Filtek-Flow). As for the 'ormocers', some differences concerning the size of the fillers were noticed. Interestingly, the Admira-Flow showed a lower percentage of fillers by weight but larger fillers than the universal ormocer Admira (Fig. 8). Nevertheless, their fillers (percentages and morphology) were not different than those of universal resin composites.

The large fillers observed in the microfine anterior composites (Fig. 5) are issued from the prepolymerization of silica microfillers (0·04 μm) embedded in an organic matrix. The Metafil-CX based on urethane dimethacrylate resin matrix, contains in addition to the colloidal silica fillers, organic fillers of trimethylol propane trimethacrylate (TMPT). While the manufacturer claims that Metafil-CX contains large particles (20 μm), our photomicrographs showed small agglomerated fillers (data not shown). One hypothesis could be that during the washing technique, the chloroform known to be a strong solvent, has dissolved those large organic fillers into smaller. In order to test this hypothesis, we dissolved the Metafil-CX according to the procedure described previously, but we only used three baths of acetone without any chloroform. As described by the manufacturer, large particles of about 20 μm, were observed. So we could assume that the chloroform is held responsible of this particles fragmentation or dissolution of the TMPT matrix.

The traditional chemically cured resin composite (Concise) contains large particles that are, according to the manufacturer, fillers of quartz (1–40 μm) (Fig. 7).

New formulas of resin composites such as A-110, Aeliteflo-LV, Z-250, marketed earlier as Silux-Plus, Aeliteflo and Z-100, seem to contain the same kind of fillers regarding the shape and the percentages of fillers by weight except for Aeliteflo-LV. Although it is supposed to have a lower viscosity, Aeliteflo-LV had a slightly higher percentage of fillers by weight then Aeliteflo. Consequently, we could suppose that the chemistry of the composite is responsible, at least partly, for achieving some variations of viscosity.



Admira

Admira-Flow

Fig. 8. 'Ormocers'. Fillers by scanning electron microscopy at 5000× magnification.

Conclusion

Using two standardized procedures, the percentage of fillers by weight has been determined. For some materials, the results obtained were not in accordance with those given by the manufacturer. Different factors can influence the data obtained, as well as the technique used. Microfine and flowable composites although having the same range of percentage of fillers, showed different types of fillers. Packable resin composites did not show higher filler levels than universal hybrid composites. Some flowable composites contain nearly 20% less fillers than other universal resin composites. As the percentage of fillers is a very important factor that influence the mechanical behaviour of resin composites (4), the data given by the manufacturers must be considered with precaution as no standardized procedure exists for determining the percentages of fillers by weight.

Acknowledgments

The authors would like to thank the manufacturers for supplying materials.

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