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Original

EDX fluorescence analysis and SEM observations of resin composites

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Abstract: The purpose of this study was to evaluate the filler compositions of recently available light-cured resins. The composition of each resin paste was evaluated using an energy dispersive X-ray fluorescence spectrometer. Scanning electron microscopic observation of the polymerized resin pastes was also conducted. The main component of each resin composite was Si, while the other elements detected were Al, Ba, Sr, Zr, and K. These elementary compositions differed among the resin pastes used. Three different types of filler morphology were observed; splintered, prepolymerized and splintered, and spherical. The results of this study have thus characterized recently developed resin composites based on their filler elements and morphology. (J. Oral Sci. 46, 143-148, 2004)

Keywords: light-cured resin; filler composition; EDX analysis.

Introduction

Due to their improved esthetics and physical properties, light-cured resins are widely used in clinical dentistry (1). Light-cured resins are composed of a dispersion of fillers and base resin monomers. Mechanical properties, radio-opacity, and handling properties of resin pastes can be improved, while thermal expansion and volumetric shrinkage can be decreased, by incorporating inorganic fillers. To keep track of recently developed resin composites, several classification systems based on filler particle size and filler chemical composition have been proposed (2-4).

Recent improvements in resin composites have been affected by developments in resin monomers (5-7), fillers (8-10), and filler/matrix coupling agents (11-13). The mechanical properties as well as optical properties of resin composites have been affected by modifications in filler size, morphology, and components (14-16). Although the success of resin restorations depends on clinical factors such as handling properties of resin pastes and manipulation technique of each operator, filler morphology and their compositions are other important factors that should be investigated. The objectives of this study were: 1) to examine filler composition and morphology of the resin composites tested, and 2) to classify them in order to obtain a better understanding of the appropriate clinical selection of resin composites.

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Materials and Methods

Light-cured resins and curing unit

The light-cured resins employed in this study were; Beautifil (Lot No. 050253, Shofu Inc., Kyoto, Japan), Esthet·X (Lot No. 991018, Dentsply/DeTrey, Konstanz, Germany), Clearfil ST (Lot No. 2175025, Kuraray Medical, Tokyo, Japan), Filtek Supreme (Lot No. 2AM, 3M ESPE, St. Paul, MN, USA), InTen-S, (Lot No. D51032, Ivoclar

Vivadent, Schaan, Lichtenstein), Point 4 (Lot No. 211094, Sybron/Kerr, Orange, CA, USA), Solare (Lot No. 212171, GC Corp., Tokyo, Japan) and Solare P (Lot No. 212021, GC Corp., Tokyo, Japan).

The Optilux 501 (Demetron/ Kerr, Danbry, CT, USA) curing unit, which has a light intensity of over 600 mW/cm^2 as measured with a dental radiometer (Model 100, Demetron/Kerr, Danby, CT, USA), was used.

Elemental analysis of the resin composites

Elemental analysis of the resin composites was conducted using an energy dispersive X-ray fluorescence (EDX) spectrometer (Rayny EDX-900, Shimadzu, Kyoto, Japan) as shown in Fig. 1. The EDX spectrometer is an instrument that quantitatively determines the elements within a sample by irradiating the sample with X-rays and then analyzing the re-emitted fluorescent X-rays. The resin composites were condensed into the mold (6 mm in diameter and 2 mm in thickness), and cured for 30 s. After storage for 24 h in a darkroom, these specimens were put on the stage of the EDX spectrometer without any coating. Spectrometer analyses were performed at the center of the specimen using a 1.0-mm window, 300-s scans and 0% dead time. Data was automatically corrected for atomic number, absorbance and fluorescence excitation effects using the ZAF correction method for each element investigated.

Scanning electron microscopy

After EDX analysis, specimens were observed by scanning electron microscopy (SEM). Specimens were polished using abrasive discs and diamond pastes down to a particle size of 0.1 μm. The polished surfaces were subjected to argon-ion beam etching for 30 s under an ion beam (Elionix, Tokyo, Japan) with an accelerating voltage of 1.0 kV and an ion current density of 0.4 mA/cm^2 directed perpendicular to the polished surface. The surfaces were coated in a vacuum evaporator with a thin film of Au. The specimens were observed under an SEM (JSM-5400, JEOL, Tokyo, Japan) at an operating voltage of 15 kV.

Results

Elemental composition of filler particles

The elements detected in the polished resin composites are shown in Table 1. Si was found in all the resin composites tested and was the main component of the fillers. Al was observed in all resin composites except for Filtek Supreme. Some composites contained Yb, Zr, and Sr, while Br was found in most composites that had splintered particles (Esthet·X, InTen-S, and Point 4).

SEM observation

Representative SEM micrographs (backscattered electron images) of the composites evaluated in this study are shown in Figs. 2 - 9. Prepolymerized filler particles were observed in the first resin composite group; Clearfil ST, Solare, and Solare P. Splintered particles (1 - 5 μm) in conjunction with round (1 - 5 μm) and splintered prepolymerized filler particles (5 - 10 μm) were observed in the first group. Splintered filler particles of different sizes were seen in the second resin composite group; Beautifil, Esthet·X, InTen-S, and Point 4. In Beautifil, most of these

Table 1 Composition of inorganic filler particles

Material	>50%	20 - 50%	5 - 20%	5% >
Beautifil	Si (50.5)	Sr (32.3)	Al (14.3)	P (2.0), Ti (0.6), Rh (0.3)
Esthet·X	-	Si (48.9), Ba (43.2)	Al (7.8)	Sr (0.1), Rh, Ti, Ce, I
Point 4	Si (60.9)	Ba (29.7)	Al (17.9)	Ca (1.0), Zn (0.2), Sr, Ti, Ce, I
Clearfil ST	Si (99.9)	-	-	Zr (0.05), Al, Rh
Solare	Si (75.8)	-	K (13.2), Al (10.8)	Zr (0.1), Rb (0.1), Fe (0.1), Rh
Solare P	Si (55.6)	Sr (22.6)	Al (17.4)	K (4.7), Ti (0.3), Rh, Y
InTen-S	-	Si (44.6), Ba (25.0)	Yb (16.6), Al (13.8)	Sr (0.1), Rh, I, W, Ni, Au
Filtek Supreme	Si (61.8)	Zr (20.8)	P (16.6)	P (0.5), Ti (0.1), Y (0.1), Rh

Values in parenthesis indicate % compositions of each filler particle.

particles were somewhat large (5 - 10 μm), while the remainder were 1 - 2 μm. Most filler particles in Point 4 were smaller than 0.5 μm. In the InTen-S specimen, different types of filler particles were observed as agglomerated particles that showed high electron density. Spherical filler particles of different sizes were observed in the third resin composite group; Filtek Supreme. Particle size was typically 1-2 μm, with the smallest particles being smaller than 0.1 μm.

Discussion

The EDX spectrometer is a powerful instrument for performing qualitative and quantitative elemental analyses of materials by measuring the characteristics of re-emitted X-rays (17). EDX is non-destructive and can therefore be used with a variety of materials in solid, powder, liquid

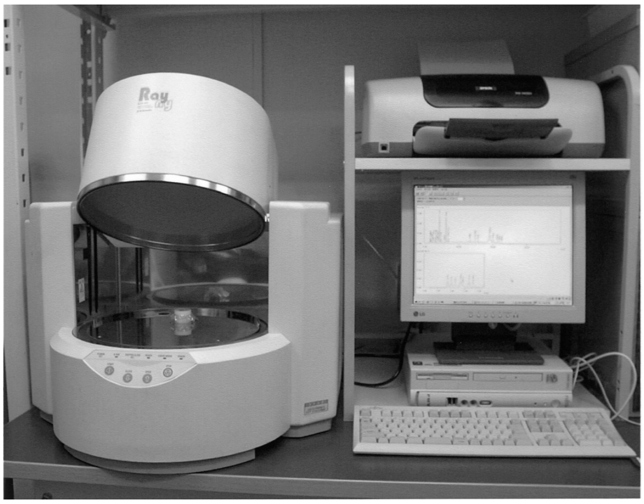

Fig. 1 Energy Dispersive X-ray fluorescence (EDX) spectrometer used in this study.

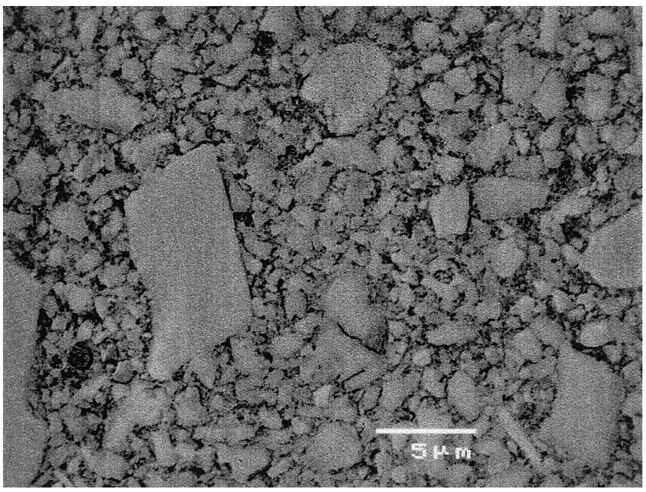

Fig. 2 SEM photographs of ground surface of Beautifil (× 3,500).

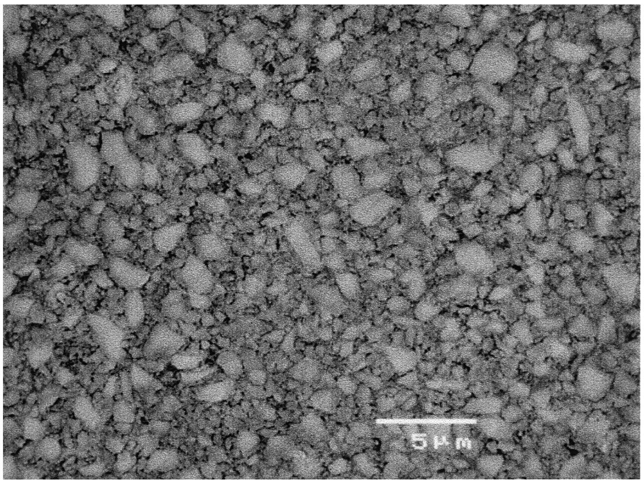

Fig. 3 SEM photographs of ground surface of Esthet·X (× 3,500).

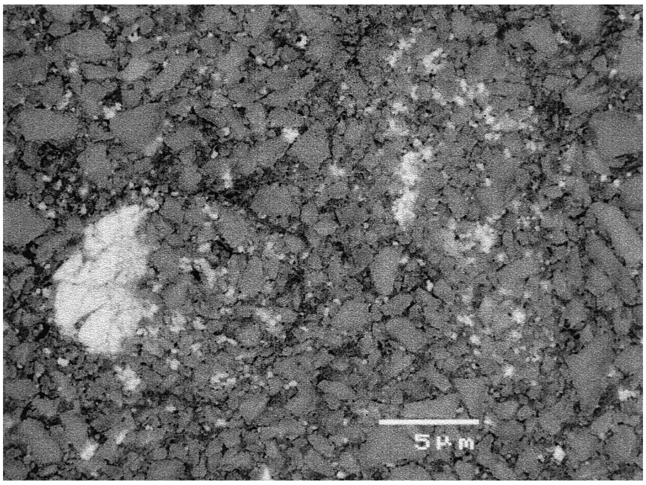

Fig. 4 SEM photographs of ground surface of InTen-S (× 3,500).

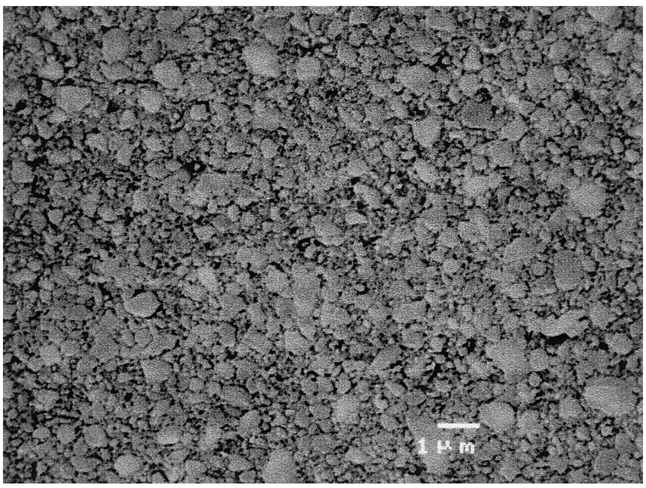

Fig. 5 SEM photographs of ground surface of Point 4 (× 7,500).

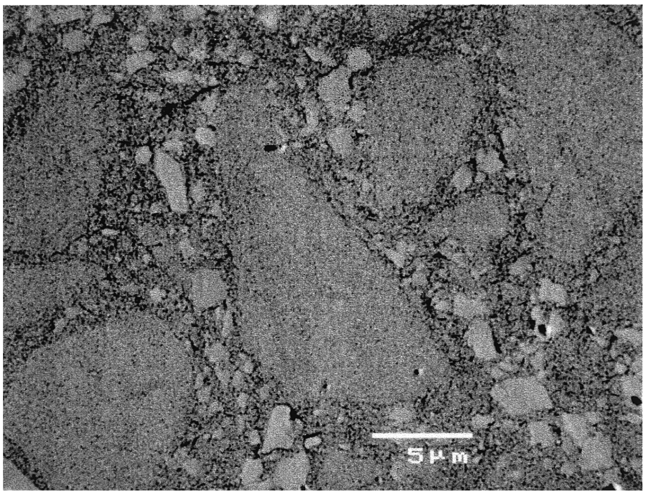

Fig. 6 SEM photographs of ground surface of Clearfil ST (× 3,500).

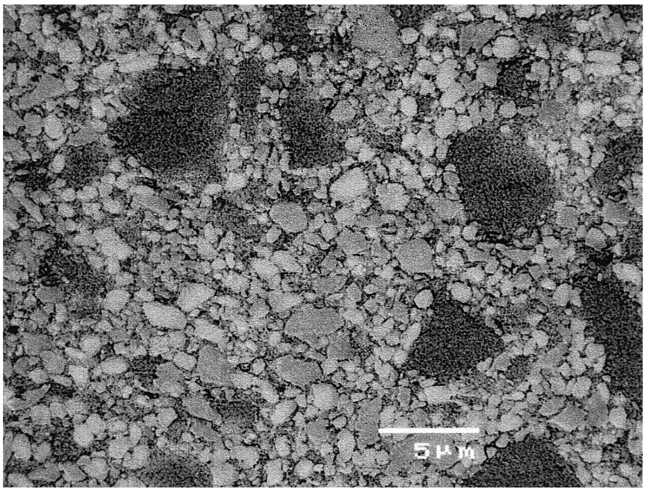

Fig. 8 SEM photographs of ground surface of Solare P (× 3,500).

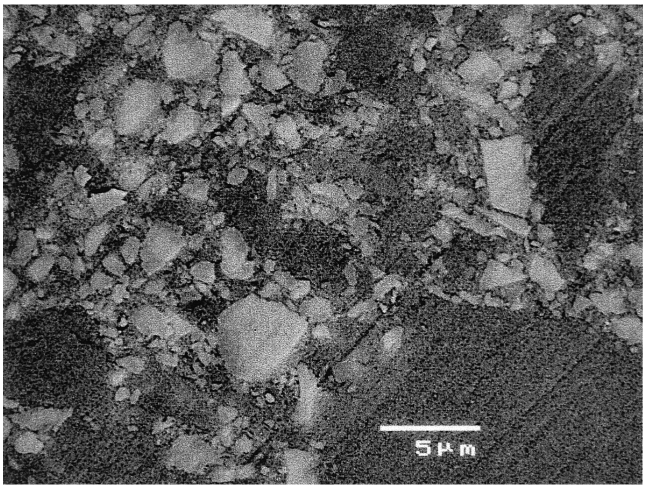

Fig. 7 SEM photographs of ground surface of Solare (× 3,500).

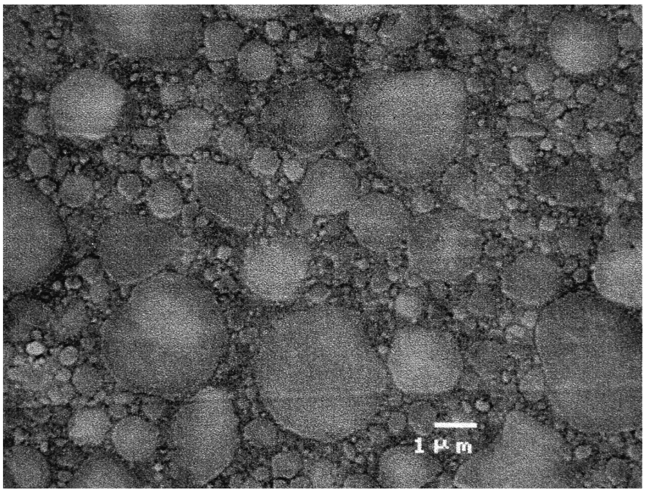

Fig. 9 SEM photographs of ground surface of Filtek Suprime (× 7,500).

or wafer states. The basic components of EDX can be summarized as (a) an excitation source; (b) a geometric arrangement for collimation and monochromatization of primary radiation; (c) an X-ray detector; and (d) software for operation of the instrument, data acquisition and spectral deconvolution to determine the elemental concentrations. When a sample is excited by X-rays, the individual elements comprising the sample re-emit their own characteristic X-rays, and these can be quantitatively analyzed to confirm which elements are present in the material.

Results from EDX spectroscopy analysis of the inorganic fillers revealed a great variety in the composition of different types of fillers. In order to delineate the restorations against dentin and enamel, radiopaque additives, such as Ba glass, are used to enhance the radiopacity of resin composites (18). Other additives used for this purpose are Sr, Zr, Yb and La. Since these elements have higher atomic numbers, the translucency to visible light of the resin composites is restricted. Incorporating a larger percentage of radiopaque fillers leads to a mismatch in the refractive index between the filler and resin. 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 (19). It is important to balance the optical and mechanical properties of resin composites with the incorporation of filler particles.

The addition of inorganic particles has been the main factor studied in the development of new resin composites. The mechanical properties of dental composites are known to depend on the concentration and particle size of the filler (20). Elastic modulus, which is defined as the ratio of stress to the corresponding strain in a material under loads below the elastic limit, is one of the basic properties that is of interest in many manufacturing and research applications. Materials should have a modulus appropriate for their usage. The elastic modulus of resin composites should be dependent on the maximum particle packing fraction and on the ratio of true particle volume to the apparent volume occupied by the particles, which is determined by particle shape and size distribution. The most appropriate elastic modulus for a composite resin would be comparable to, or preferably higher than, that of dentin (21).

Generally, resin composites containing splintered fillers with higher loading exhibit higher mechanical properties and elastic modulus. The sizes of the resin composite fillers examined in this study were not uniform. SEM observations suggest that the shape of prepolymerized filler particles has become more diverse, and three out of eight resin composites contained both prepolymerized and splintered filler particles (Clearfil ST, Solare, and Solare P). To improve the polishability of the resin composites containing splintered fillers, their filler sizes have been reduced (Esthet·X, InTen-S, and Point 4). The filler particles of Filtek Supreme exhibited a range of spherical shapes and clusters that were loosely agglomerated collections of nanoparticles. These filler particles would create a resin composite that combines mechanical strength with high polishability.

The mechanical properties of resin composites are related to various factors, which do not individually provide them with all the desirable characteristics, such as esthetics. Further development and modification of resin composites should be conducted in order to meet clinical requirements.

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