

A New Classification of Resin-Based Aesthetic Adhesive Materials

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ABSTRACT

The purpose of this article is to illustrate a new classification of resin based aesthetic materials laying on the characterization of their matrix and their filler morphology. Four samples per material have been prepared for SEM evaluation. Each sample has been treated with chloroform to dissolve its matrix in order to evidence the filler morphology. A general schema of four different matrix systems which characterize the material's level of hydrophobicity can be put in evidence. The subsequent filler analysis individuates a more complex schema based on filler size and construction. A new classification based on matrix nature and filler morphology has been proposed. Based on this concept mechanical and aesthetic characteristics of the materials can be presumed.

Key words: SEM, filler morphology, matrix

Introduction

Resin based restorative materials are used worldwide due to their good aesthetic characteristics and their relatively low price. Furthermore, their coupling with adhesive systems allows for the advantages of adhesive restorations such as minimally invasive treatment. Direct bonded composite restorations provide optimal conservation of sound tissue, potential reduction of microleakage and prevention of postoperative sensibility, together with a good aesthetic outcome. Furthermore composite restorations are considered a cost-effective approach when compared to a prosthetic intervention.

From the early 1970s on, resin based restorative materials have been dramatically improved by their manufacturers in regard to mechanical and aesthetic behaviour. This has been mainly achieved by continuous attempts to change their particle morphology. Particularly, the latest developments in nanotechnology have radically changed their particles' size and behaviour. As consequence contemporary composite materials are very different from those of the 1970s. Due to continuous changes from the 1980s on, composite classifications based on average particle size, manufacturing techniques, and chemical composition of the fillers have been introduced¹⁻⁵. All these classifications show the dramatic changes that

have taken place: barium glass has been added for radiopacity, amorphous silica has been introduced for improved handling, ytterbiumfluoride has been added for enhanced radiopacity, and particles have become spherical and smaller, reaching nanodimensions⁶. On the other hand, not only fillers have changed with time, but matrix components have also been modified. This is why ancient classifications do not sufficiently reflect the properties relevant for a clinical choice of present restorative material. In this study, an attempt is made to propose a new classification which characterizes current resin based restorative materials on their morphological basis.

The aim of this study was to classify composite materials, describing the differences of their basic components (i.e. matrix and fillers).

Materials and Methods

Table 1 lists 11 materials investigated in this study which are representative of all types of resin based restorative materials present nowadays on the market.

In order to obtain the SEM micrographs which were used for filler characterisation, approximately 2 g of each

TABLE 1
LIST, BATCH NUMBER AND EXPIRATION TIME OF THE COMPOSITES TESTED

Product	Manufacturing	Lot	Expiration period
Dyract	Dentspy De Trey GmbH 78467 Konstanz Germany	K106.251/3	2008–07
Concise	3M Espe St Paul, MN 55144-1000 USA	20070829	2008–11
Isosit SR	Ivoclar Vivadent Liechtenstein	980423	not available
Durafill VS Email A2	Heraeus Kulzer GmbH D-63450 Hanau	010207	2010–02
Clearfill PP	Kuraray Medical Inc. Okayama, 710-8622 Japan	00214A	2009–05
Enamel Plus HFO GE2	Micerium Via Marconi 83 Avegno (ge) Italy	2006105325	2011–08
Point 4 A1	Kerr Corporation Orange, CA 92867 USA	29876	2010–05
Filtek Supreme XT A2E	3M Espe St Paul, MN 55144-1000 USA	6CC	2009–02
Tetric Evoceram A3	Ivoclar Vivadent Liechtenstein	H09256	2008–07
CeramX E2	Dentspy De Trey GmbH 78467 Konstanz Germany	0709002059	2010–02
Filtek Silorane A3	3M Espe St Paul, MN 55144-1000 USA	7KP	2010–02
Venus Diamond A3	Heraeus Kulzer GmbH D-63450 Hanau	010022	2012–02

material were readied and their surface was dissolved in chloroform (Chloroform pro analysis, Merck KGaA, 64271 Darmstadt, Germany) by using a double-step technique: First each specimen was rubbed with chloroform for 90 s by means of a microbrush, air dried and polymerized for 60 s with a LED light curing unit (L.E. Demetron II curing light, Kerr Corp., Middleton, USA) at a light intensity of 1200 mW/cm², than again covered with several drops of chloroform for 5 minutes and finally, after the removal of chloroform, dried at room temperature for 12 hours, gold sputtered and observed in the SEM (Phillips XL 20, Eindhoven, and NL, 4000x magnification).

Results

According to the matrix composition of all the materials tested, a general scheme of four different matrix systems, which characterizes the material's level of hydrophobicity, can be proposed. The subsequent SEM filler analysis shows a more complex scheme based on filler size and construction (Figures 1a-l). As can be seen on the SEM micrographs, the medium filler size of a macro-filled composite is about 2–5 µm (Figure 1b).

Microfilled homogeneous composites (Figure 1c) contain microfillers only in the order of 0.04 µm. Microfilled inhomogeneous composites, besides microfillers, show big prepolymerized blocks of 5–30 µm (Figure 1d). These blocks are made out of resin, reinforced with microfilled particles of 0.4 µm size.

Between macro- and microfilled composites a multitude of resin based restorative materials is present on the market with filler size ranging from 0.4 to 2 µm. An average filler size around 1 to 2 µm can be seen in Figure 1e, which is characteristic for a coarse hybrid composite. A fine hybrid composite, characterized by a mean particle size of 0.6 to 1.0 µm is shown in Figure 1f. A similar mean filler size is also characteristic for ormocers (Figure 1g), siloranes (Figure 1k) and compomers (Figure 1a). In these types of resin based restorative materials the filler

size corresponds in fact to a fine hybrid composite, while the resinous matrix has a different chemical nature.

The largest family of resin based restorative materials is represented by micro hybrid composites. They can be homogeneous (Figure 1g) or inhomogeneous. Their mean filler size ranges from 0.4 to 0.6 µm. A branch of this family is presented in Figure 1h where a composite material with aggregated particles (Filtek Supreme) is shown.

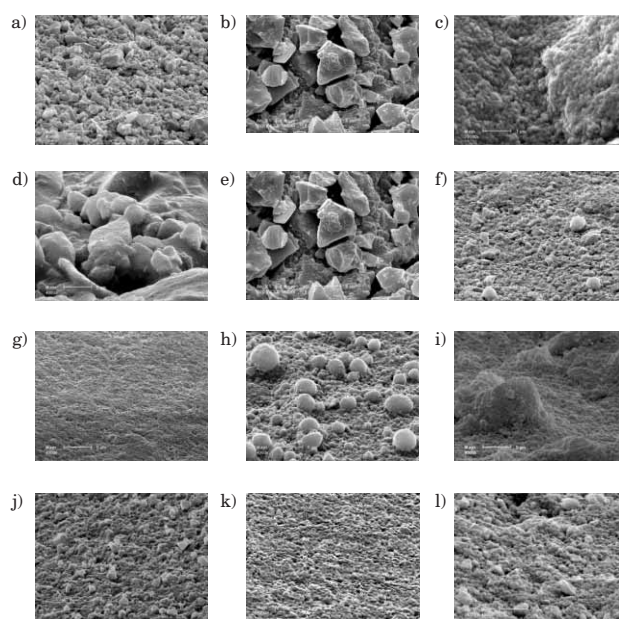


Fig. 1a) Compomer (Dyract), b) Macrofilled composite (Concise), c) Microfilled homogeneous composite (Isosit SR), d) Microfilled inhomogeneous composite (Durafill), e) Coarse hybrid composite (Clearfill PP), f) Hybrid fine composite (HFO), g) Micro hybrid homogeneous composite (Point 4), h) Micro hybrid inhomogeneous composite with aggregated particles (Filtek Supreme), i) Micro hybrid inhomogeneous composite with splinters (Tetric Evoceram), j) Ormocer (CeramX), k) Silorane (Filtek Silorane), l) Micro hybrid inhomogeneous composite with heterogeneous splinters (Gradia Direct).

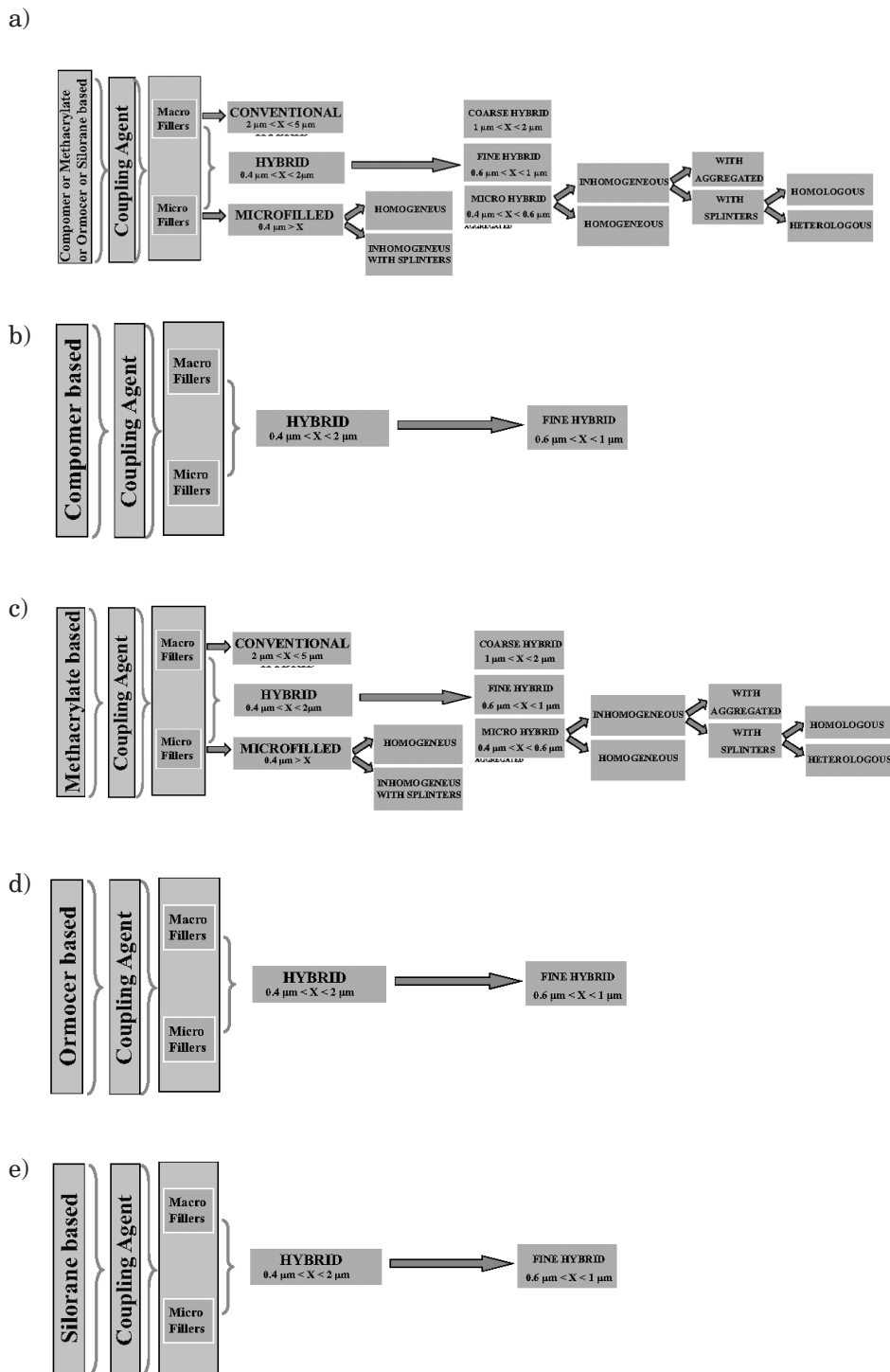


Fig. 2 a) Classification of resin-based aesthetic adhesive materials, b) Classification of compomer based materials, c) Classification of methacrylate based materials, d) Classification of ormocer based materials, e) Classification of silorane based materials.

The second ramification of this family is represented by the microhybrid inhomogeneous composite with splinters where two different subgroups can be described. The homologous one is filled with crunched down pre-polymerized particles made out of the same type of composite (micro hybrids) (Figure 1i) and the heterologous one

which is based on splinters made of another type of composite (a microfill) like Gradia Direct (Figure 1l).

A second level of classification, considering the matrix nature besides the filler morphology, leads to the situation represented in Figures 2a-e where all different combinations are illustrated in detail.

Discussion

Resin based restorative materials are made of two main parts, matrix and fillers, which are coupled by an organic silane. There are four matrices on the market today: methacrylate-based, compomer-based, ormocer-based, and silorane-based. Compomers consist of two main components: dimethacrylate monomer(s) with carboxylic groups and filler that is similar to the ion-leachable glass present in glass-ionomer cements⁶. Methacrylate resins are the most commonly used matrix in composites. A modification of this matrix is represented by ormocers, where the methacrylate-based resin is modified by the addition of small polysiloxane particles (2 to 3 nm). A completely different chemistry is represented by the silorane matrix. This matrix is based on molecules consisting of siloxanes and oxiranes, therefore called silorane, with a very hydrophobic characteristic. Another important point of this molecule is its intrinsic low shrinkage compared to resin composites and, in general, to all other resin based restorative materials. From the chemical point of view, the most important difference in respect to methacrylate-based chemistry is that methacrylates are cured by radical intermediates, siloranes on the other hand polymerize via cationic intermediates. During polymerization, the epoxy ring of the oxirane monomer is opened to form a linear chain, which reduces the volume loss during polymerization, thus reducing polymerization shrinkage⁷.

The other variable of resin based restorative material structure regards filler size, shape, and distribution. Fillers can be divided depending on their size as macro fillers ($5\ \mu\text{m} < X < 20\ \mu\text{m}$) and micro fillers ($X < 0.4\ \mu\text{m}$). The microfilled group is composed of two subgroups, depending on the filler's homogeneity. While the homogeneous filler is rarely available on the market due to its poor mechanical properties⁸, the inhomogeneous filler is still in use and proposed as veneering material in anterior restorations⁹. Whenever the filler's mean size is more than $2\ \mu\text{m}$, the material is defined as a macrofilled. If a mixture of macro- and microfillers is present in the matrix, the material is defined as a hybrid. Within the large family of the hybrid group different categories can be found depending on their filler size. The coarse hybrid is a family of materials where the mean filler size is between $1\ \mu\text{m}$ and $2\ \mu\text{m}$, the fine hybrid between $0.6\ \mu\text{m}$ and $1\ \mu\text{m}$, and the micro hybrid between $0.4\ \mu\text{m}$ and $0.6\ \mu\text{m}$. This last group can be split into two sub-categories depending on the presence or absence of large particles that are composed of smaller units, i.e. aggregates of microfillers or prepolymerized splinters. While the homogeneous micro hybrids do not contain these particles, the inhomogeneous has them. Micro hybrids with aggregates may be at first sight confused with macro fillers, but the large particles are made of the aggregation of primary SiO_2 or $\text{SiO}_2/\text{ZrO}_2$ particles of about $40\ \mu\text{m}$. On the other hand, in the micro hybrid composites with splinters, the large fillers are obtained not by aggregation of

nano elements but by crunching down large prepolymerized hybrid or microfilled composites.

The classification based on fillers and on the matrix can be useful for practical reasons; in fact some general characteristics can be presumed once matrix nature and filler charge and morphology are known. The more the matrix is hydrophobic, the least the material should be subjected to hydrolysis¹⁰ and discolouration¹¹. For this reason, for example, compomers should be less indicated than silorane as definitive restorative materials due to their higher water sorption. The second fundamental component in adhesive material is represented by fillers. Generally large fillers (macro fillers) tend to increase the wear rate of the material¹². Exposure of filler particles because of resin matrix wears results in a higher surface roughness and in a dull aspect². As a consequence, this kind of material cannot be proposed as a restorative material for anterior restorations nor for posterior ones. On the other hand, due to the fact that generally macro-charged materials are highly filled⁵, they can be used as a base under other restorations or as core under prosthetic restorations. Higher filler load, in fact, results in increased stiffness, hardness, and compressive strength^{13,14}.

Micro-fillers give to materials a high and durable surface gloss, because they are smaller than the wavelength of visible light, thus being invisible to the human eye¹⁵. They may be used as veneering materials in anterior restorations, but are not indicated for large class four cavities or posterior reconstructions⁹. Micro-filled resin composites have a low filler load, thus a low Young's modulus and fracture strength, and, consequently, are prone to chipping and fracture¹⁶.

A good compromise between the high mechanical properties of macro filled materials and the good esthetic properties of micro filled materials can be found in hybrid materials. They couple the necessity of being resistant to support masticatory stresses with the esthetic requirements of modern dentistry. These characteristics confer to this family of materials a large indication both in anterior and posterior areas. That is why they are currently the most commonly used and produced multi-purpose restorative materials.

Conclusion

A new classification for resin based restorative materials is proposed in this article and illustrated with SEM micrographs. This kind of systematic categorization, which takes in consideration not only filler's size but also resin matrix nature, allows a better understanding of the clinical properties of resin composites as well as compomers, ormocers, and siloranes.

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NOVA KLASIFIKACIJA ESTETSKIH ADHEZIVNIH MATERIJALA BAZIRANIH NA SMOLI

SAŽETAK

Cilj ovog članka je prikazati novu klasifikaciju estetskih materijala baziranih na smoli, s obzirom na karakteristike njihovog matriksa i morfologije. Pripremljena su četiri uzorka po materijalu za SEM evaluaciju. Svaki uzorak je tretiran kloroformom kako bi se matriks razgradio i otkrila morfologija. Stvorena je općenita shema četiri različita sustava matriksa koji karakteriziraju stupanj hidrofobnosti materijala. Daljnjim analizama su stvorene kompleksnije sheme i predložena je nova klasifikacija bazirana na prirodi matriksa i morfologiji. S obzirom na ovaj koncept moguće je donijeti određene zaključke o mehaničkim i estetskim karakteristikama materijala.