Filler characteristics of modern dental resin composites and their influence on physico-mechanical properties

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ABSTRACT

Objective. The mechanical properties of dental resin-based composites (RBCs) are highly dependent on filler characteristics (size, content, geometry, composition). Most current commercial materials are marketed as "nanohybrids" (i.e. filler size <1 μm). In the present study, filler characteristics of a selection of RBCs were described, aiming at identifying correlations with physico-mechanical properties and testing the relevance of the current classification. *Methods.* Micron/sub-micron particles (> or <500 nm) were isolated from 17 commercial RBCs and analyzed by laser diffractometry and/or electron microscopy. Filler and silane content were evaluated by thermogravimetric analysis and a sedimentation technique. The flexural modulus (E_{flex}) and strength (σ_{flex}) and micro-hardness were determined by three-point bending or with a Vickers indenter, respectively. Sorption was also determined. All experiments were carried out after one week of incubation in water or 75/25 ethanol/water. *Results.* Average size for micron-sized fillers was almost always higher than 1 μm. Ranges for mechanical properties were: $3.7 < E_{flex}^{water} < 16.3$ GPa, $86 < \sigma_{flex}^{water} < 161$ MPa and $23.7 < hardness^{water} < 108.3$ HV0.2/30. Values generally decreased after storage in ethanol/water ($\Delta max = 86\%$). High inorganic filler contents (>75 wt%) were associated with the highest mechanical properties (E_{flex} and $\sigma_{flex} > 12$ GPa and 130 MPa, respectively) and lowest solvent sorption (~0.3%). *Significance.* Mechanical properties and filler characteristics significantly vary among modern RBCs and the current classification does not accurately illustrate either. Further, the chemical stability of RBCs differed, highlighting differences in resin and silane composition. Since E_{flex} and sorption were well correlated to the filler content, a simple and unambiguous classification based on such characteristic is suggested, with three levels (ultra-low fill, low-fill and compact resin composites).

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1. Introduction

The popularity of dental resin composites is driven by their versatility, aesthetic quality and reasonable clinical performance. The development of resin composite materials are relentlessly researched and tested by academia and industry in an attempt to enhance clinical longevity by reducing their perceived shortcomings such as polymerization stress [1,2], residual monomer content [3,4], inadequate depth of cure [5], handling [6] and aesthetic characteristics [7]. Most often, these issues are not entirely addressed and new concepts aggressively marketed as "low-shrink" or "bulk-fill" and such. The resin composite market is highly competitive between manufacturers, and the incredibly rapid and iterative product cycle leaves the general practitioner with a vast choice from an array of similar materials types. As a consequence, and particularly for resin composites, the usefulness of classification systems as a means for practitioners to compare material properties is limited.

An area of substantial development since the inception of resin composite materials relates to filler type, processing and morphology, and probably much more so than advancements in resin chemistry. Continuous material developments among researchers and manufacturers have led to the use of refined filler technologies and design choices. Following the evolution of processing techniques, the size of filler particles, typically ground glasses, have decreased from tens of micron to about 1 µm [8]. With advancements such as jet-milling, sub-micron dimensions can be achieved with narrow distributions and microparticles averaging 0.5–1.0 µm are now used in some commercial composites. Pre-polymerized fillers (PPF) are also common and processed using ground cured composite, containing a variety of sub-micron particles. Such particles were introduced in part as a solution to reduce the stress resulting from polymerization and provide improved polishability compared with earlier hybrid types [9,10]. Nanoparticles, originally introduced in an effort to improve aesthetic quality are used today in some modern materials in the form of nano-sized aggregates, aimed at improving mechanical properties,

in particular strength [11]. Discrete nano-sized fillers, smaller than the wavelength of visible light, represent an additional asset in light-curing materials, since refraction and scattering are reduced, which may offer significantly improved depth of cure [12].

The classification of dental composite has evolved over the years, but in general has mostly focused on filler-size distribution, filler content or composition. From "microfills" or "nanofills", containing only micro or nanoparticles, respectively, most modern resin composites belong to a so-called "hybrid" category, and presently are commonly marketed as "nanohybrids". This terminology refers to materials containing a fraction of nanoparticles (<100 nm) and of sub-micron particles (≤1 µm, typically averaging 0.5–1.0 µm) [8] (Fig. 1). Compared to "microhybrids", nanohybrids can be expected to contain a greater fraction of nanoparticles. However, a classification based on filler-size distribution does not reflect filler composition, morphology or filler specificities (e.g. the use of PPF). It is therefore doubtful for example that all nanohybrids would display the same properties and many commercial resin-based composites (RBCs) claiming to be "nanohybrids" will have a significant proportion of larger size (>1 µm) fillers [13,14].

There is in fact a vast bank of data documenting various mechanical and physical property comparisons. These properties vary greatly from one material, or test-center, to another. For example, the flexural modulus measured in-vitro ranging from 3 to 15 GPa [15–17] or flexural strength, hardness or fracture toughness also varying, between 50–150 MPa [13,15,17,18], 19–80 HV0.5/20 [17] and 1–2.5 MPa $\sqrt{m}$ [17,18] respectively. These properties are interrelated and dependent on filler characteristics (geometry, composition, surface coating, size distribution) and filler content (filler mass and volume content). Excellent studies have covered the topic and general rules are that both the modulus and surface hardness increase with increasing filler content with a concomitant decrease in volumetric shrinkage [17,19]. At a given filler content, size and geometry, strength is influenced by the chemistry of the resin phase [20–22]. A biomimetic approach
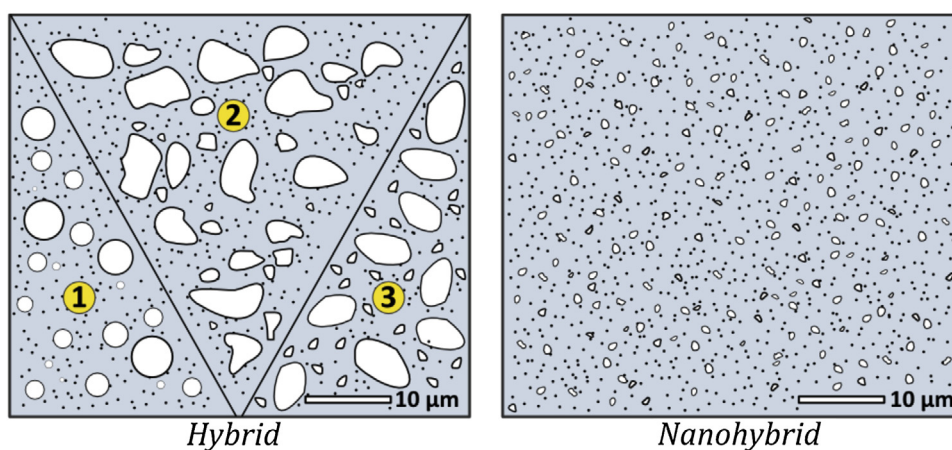

Fig. 1 – Schematic description of filler distribution according to current classification. Hybrid resin composites include a combination of micro and nanoparticles (left figure). Numbers denote continuous distributions (1 and 2) with spherical (1) or irregular particles (2) and a bimodal distribution (3) of micro particles. A nanohybrid resin composite contains nanoparticles (<100 nm) and sub-micron "microparticles" (≤1 µm) (right figure).