

Review

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# **Inorganic Fillers for Dental Resin Composites - Present and Future**

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# Abstract:

Dental resins represent an important family of biomaterials that have been evolving in response to the needs in biocompatibility and mechanical properties. They are composite materials consisting of mostly inorganic fillers and additives bound together with a polymer matrix. A large number of fillers in a variety of forms (spheroidal, fibrous, porous, etc.) along with other additives have been studied to enhance the performance of the composites. Silane derivatives are attached as coupling agents to the fillers to improve their interfacial properties. A review of the literature on dental composite fillers seems to suggest that each of the fillers tested presents its own strengths and weaknesses, and often combinations of these yield resin composites with the desired balance of properties. Additives such as nanotubes, whiskers, fibers, and nanoclusters have been shown to enhance the properties of these hybrid materials, and their use in small fractions may enhance the overall performance of the dental resin materials.

**Keywords**: composite fillers, fibers, mechanical properties, organic hybrid, silane, whisker, nanotubes

# Introduction

Dental resin-based composites (RBCs) for both direct and indirect dental restorations have been in use for the last 50 years. Their advantageous aesthetic and biocompatibility properties have allowed them to gain prevalence, and gradually replace the mercury-containing dental amalgams that had previously been the standard of care for this type of restoration. While the toxicity of amalgam is still a topic of debate,<sup>1-5</sup> many countries are reducing the use of mercury or even banning mercury-containing products outright,<sup>6-7</sup> and so dental RBCs remain the main focus of current dental material research.

Dental RBCs are a mix of two major components: the resin matrix, which contains the monomers, photopolymerization initiators, accelerators, inhibitors, and tint compounds; and the inorganic filler particles that confer most of the mechanical properties observed in the final material in addition to the optical and radiopacity properties required for the composite. To enhance the binding of the filler particles, silane derivatives are covalently attached onto the inorganic fillers as coupling agents.

The monomers that have been used most frequently for this type of dental restorative have been bisphenol A glycerolate dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA). Many derivatives of these monomers have been developed to improve upon specific properties.<sup>8-9</sup> Several new classes of monomers are being explored to replace the bisphenol A-containing BisGMA, among which are oxiranes,<sup>10-12</sup> bile acid derivatives,<sup>13-14</sup> dendrimers,<sup>15-16</sup> isosorbides,<sup>17-18</sup> and more.<sup>19-21</sup> In addition to these methacrylate monomers, alternate polymerization chemistries have been proposed, and in some cases commercialized.<sup>22-23</sup> More thorough reviews concerning the resin monomers can be found in the literature.<sup>24-26</sup>

While the commercially-used monomers have remained largely unchanged, the most significant changes in dental RBCs have been in the type, size, and distribution of the inorganic fillers. The effects of size, shape, and size distribution of different fillers have been investigated quite thoroughly, such that spherical particles in multimodal size distributions generally showed superior mechanical properties. <sup>27-38</sup> This review will instead focus on the chemical composition of fillers in dental RBCs and how they affect the final RBC material. Many articles have covered

 the clinical performance of these composite restoratives;<sup>39-40</sup> this review focuses mainly on their material properties which are essential to determine their performance over time.

This review first describes the main filler types as classified by their chemical composition, followed by a section on filler additives, which are used in small fractions, including the surface silanization agents.

# **Filler Types**

## Silica

The first filler to be used for dental RBCs was silicon dioxide (**Table 1**), termed silica, or quartz when in its crystalline state. It can be considered the basis for many of the other types of fillers as the glass fillers are also silicates, but also include other elements. This material has been studied extensively including its syntheses and modifications, and is widely available at low cost.<sup>41-51</sup>

Table 1 - Filler types and their elemental compositions

Filler Type	Examples	Chemical Composition
Oxides	Silica, alumina, titania, zirconia	M <sub>x</sub> O <sub>y</sub>
Alkaline silicate glass	Barium glass, Strontium glass	$M_xO_ySiO_2$
Biomimetic filler	Hydroxyapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH
Organic-inorganic hybrids	ORMOCERs	SiO <sub>2</sub> -polymer

M = metal or metalloid, x = 1-2, y = 2-3.

In its first iterations, silica fillers were made through a top-down approach by milling quartz, that resulted in coarse, irregularly-shaped particles (Figure 1A).<sup>52</sup> While this process produced good strength and modulus values, the size and shape of the particles caused problems of high roughness and low wear resistance in the final materials.<sup>53</sup> Today, top-down synthesis has largely been replaced with bottom-up solution particle synthesis and pyrogenic particle synthesis (Figure 1B). The most commonly used solution synthesis method called the "Stöber process" produces monodisperse solid particles of well-defined size and spherical shape.<sup>54-55</sup> This method can produce particles from 5 nm up to several microns. The spherical particle shape also has lower surface roughness when compared to milled quartz, while retaining a high strength. Alternately, silica pyrogenesis involves superheating of silicon tetrachloride or quartz sand to generate nano-

sized particles and particle aggregates. Pyrogenic or fumed silica gives easier access to very small-sized particles than solution synthesis, in the 5-50 nm range, but also leads to particle agglomeration, which may be considered as an inconvenience or an advantage (see section **3.2 Particle Clusters**). In terms of optical properties, silica has a refractive index of 1.46,<sup>56</sup> which puts it slightly below that of the traditional BisGMA-TEGDMA resin mix, making it slightly more opaque than some of the other fillers described below in such a resin system. Regardless of the synthesis method, due its advantageous properties and ease of use, silica has been widely used in dental composites and is still the subject of much research in composites for many applications.



**Figure 1**.SEM of (a) Irregular inorganic filler particles in microhybrid composite Esthet X, and (b) spherical filler in Estelite $\Sigma$ . Figure adapted from ref <sup>57</sup>

## **Alkaline glasses**

 Alkaline glasses are used in many of the currently available commercial composites including many of the leading products such as Tetric EvoCeram (Ivoclar Vivadent, Liechtenstein), Grandio (Voco, Germany), Esthet-X (Dentsply Caulk, USA), and Herculite XRV (Kerr, USA) (see **Table 2** for more examples). This class of fillers encompasses many different filler compositions. The material is composed primarily of silicon dioxide, but also includes a fraction of alkaline oxides such as barium oxide (BaO) and strontium oxide (SrO), which integrate into the silica network, disrupting the structure (**Table 1**). The resulting hardness of the material will be lower than that of pure silica, having a hardness of 5 on the Mohs scale, rather than 7 for silica.<sup>58</sup> Due to this reduction in hardness, tests have shown that while the wear rate for

this material is comparable to that of silica, for large particle sizes, it produces less wear on antagonist surfaces.<sup>58-59</sup> In addition to the reduction in hardness, research has shown that over time, glass particles leach ions in aqueous solutions, losing their dopant salts in addition to the constituent silicic acid itself whose loss also occurs for silica.<sup>59-61</sup> The main advantage of this material, however, is that due to the integration of heavier elements into the filler, the X-Ray radiopacity of the material is greatly increased, eliminating the need to add a separate radiopacity agent such as ytterbium or yttrium fluoride.<sup>62</sup> Many types of alkaline glasses have been used including barium borosilicates, barium aluminosilicates, barium aluminum borosilicates, and strontium silicates. The refractive index of these materials can vary greatly due to the variation of dopant types and concentrations, but these glasses generally have higher refractive indices than silica, coming much closer to that of traditional resin matrix mixes, resulting in more transparent composites. Thus, while the particle hardness is lower and small amounts of the material may leech into aqueous solutions, the mechanical properties for wear, strength, and modulus are comparable to that of silica, and the optical properties are superior in most cases, as reflected by its widespread use in commercial materials.

## **Other glasses**

Other glasses have also been tested in dental materials, often integrating other oxides such as calcium, sodium, or phosphorus oxides. Some of the specific formulations attempted are termed bioactive glass. These were originally designed for bone replacement, but were also tested as fillers for RBCs. In bone repair, these are used to provide a temporary structure which adheres strongly to bone, and then dissolves, which in turn stimulates the re-growth of bone tissue.<sup>63</sup> In the context of dental materials, their mechanical properties appear equal or worse than other types of fillers,<sup>64-65</sup> though most papers about them focus on bioactivity and cytotoxicity rather than mechanical performance. Beyond bioactive glass, the composition of glasses is extremely variable, and it is therefore possible to tune them for more advantageous properties, but due to the inclusion of ionic species into the matrix, the water-sorption and solubility of the resulting composites generally suffer when compared to ordinary silica, often leading to inferior mechanical properties. Such fillers may otherwise be of further use to regenerate the natural tooth structures rather than simply replacing damaged structures.

### **Other metal oxides**

While silicon dioxide is the most extensively explored filler, many other metal oxides have also been studied for use as fillers including aluminum oxide  $(Al_2O_3)$ ,<sup>66</sup> titanium dioxide  $(TiO_2)$ ,<sup>67-69</sup> zinc oxide (ZnO), and zirconium oxide (ZrO<sub>2</sub>). While alumina, titania, and zinc oxide have not seen very much use commercially (**Table 2**), many of the commercially available composites from 3M ESPE in particular contain significant amounts of zirconia filler and hybrid zirconia-silica fillers. There is little literature directly comparing zirconia with other filler types, but reports suggest that the high hardness of zirconia can lead to greater antagonist wear and fatigue wear.<sup>70-71</sup> The synthesis of these materials is analogous to that of silica, in that metal alkoxides are hydrolyzed slowly to generate solid particles. In addition to the increased radiopacity of both ZnO and ZrO<sub>2</sub> due to their higher atomic numbers, similarly to glasses, they also exhibit different optical properties from other fillers, due to their higher refractive indices (2.00 and 2.16, respectively).<sup>72-75</sup> Silicate particles with varying fractions of Al<sub>2</sub>O<sub>3</sub> or BaO have also been used to tune the refractive index of the particles from 1.46 to 1.55, to match that of the resin (n≈1.5) to obtain a more transparent composite.<sup>76-77</sup>

In addition to the use of other pure or binary metal oxide mixtures, several mineral crystals have been attempted as reinforcements to conventional fillers including mica,<sup>78-79</sup> feldspar, and leucite.<sup>80-81</sup> These minerals were generally used in crystalline form and were shown to have higher wear and strength properties than traditional silica fillers. Despite their apparent superiority, concerns have been raised that particles made from less habitual compositions should be tested more extensively to ensure similar results to the known silica fillers, particularly with regards to the brittle nature of these materials, a property that is not regulated by the ISO standards.<sup>82-83</sup> Thus particles of alternate compositions are still being explored for various reasons, but thorough testing must be performed before any can be adopted as a true replacement.

## Hydroxyapatite

Hydroxyapatite (HA, Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH), the main component of enamel and dentin, has also been explored as a dental filler. Its content in enamel is approximately 96% by weight,<sup>84</sup> and 70% by weight in dentin.<sup>85</sup> HA shows high bioactivity, which reduces the occurrence of secondary caries.<sup>86-87</sup> Spheroidal particulate HA was studied as dental filler in RBCs. The size of HA particles had a significant effect on the mechanical properties of composites. RBCs

containing only HA nanoparticles as filler were found to be unsuitable for practical application due to their extremely high solubility in water and poor mechanical properties.<sup>88</sup> However, when mixed with HA microparticles, these nanoparticles can increase the total filler loading to yield improved mechanical properties.<sup>88-90</sup> Other shapes of HA such as whiskers and nanofibers were of interest for composite development. The high aspect ratio filler reinforced dental RBCs showed better mechanical properties than those reinforced with spheroidal HA.<sup>91-95</sup> Recently, a novel urchin-like hydroxyapatite (UHA, Figure 1a) was prepared through microwave irradiation and was applied as a dental filler. UHA was embedded in resin matrix, and displayed strong interfacial adhesion. Compared with unfilled resin matrix, the addition of silanized UHA significantly improved the flexural strength, flexural modulus, compressive strength, and Vickers microhardness. Furthermore, when used in combination with silica nanoparticles, UHA increased the flexural strength, flexural modulus, and compressive strength by 50, 40, and 13%, respectively.<sup>96</sup> The main disadvantage of HA, however, remains its higher refractive index than resin matrix (n=1.65 versus 1.5 for the resin). The mismatch of refractive index could result in a decrease of monomer conversion and depth of cure.<sup>88, 97</sup> Despite this shortcoming, dental RBCs containing HA filler are promising bioactive restoration materials.



**Figure 2**. SEM image of (a) urchin-like hydroxyapatite (UHA) particles, synthesized by microwave hydrothermal HA synthesis, and (b) hydroxyapatite whiskers.<sup>98</sup>

# **Organic-inorganic hybrids**

In order to improve overall composite properties, many research groups have tried attaching organic components to inorganic particles. One approach was using silane-modified polymers as seeds for the initial growth of silica particles. This type of filler was first developed and patented at Fraunhofer Silicate Research Institute and was later patented under the name ORMOCER<sup>™</sup>, for organically modified ceramics.<sup>99</sup> These materials were shown to have improved surface wetting properties and compressive strength compared with ordinary surface-modified silica.<sup>100</sup>

Their adhesion to dentin and enamel was also found to be superior.<sup>101</sup> In addition, materials containing these ORMOCERs were compared with a microhybrid composite and displayed increased surface roughness, but superior hardness.<sup>102</sup> Moszner *et al.* evaluated the flexural strength and modulus of these materials, and found that although these properties were equal to those of traditional fillers, their double bond conversion was lower.<sup>35, 103</sup> Finally, work by Muh *et al.*<sup>104</sup> made fillers using the same concept in combination with traditional BisGMA monomers. This composite mix yielded lower shrinkage (0.8-2.2%) than other commercially available composites (2-3%).

While traditional silane modification of particles only covers the surface, covalent core-shell type modifications have recently been made to increase the interfacial binding between the particles and the resin. Liu *et al.*<sup>87</sup> used this approach to synthesize crosslinked brush-modified HA particles to examine its effect on mechanical properties, but saw no significant improvements.

# **Other fillers**

Over time many materials have been tested for use as fillers and it is beyond the scope of this review to cover them all. Most notably, in 2002, Jandt *et al.*<sup>105</sup> tried novel compositions of filler, adding titanium nanoparticles as well as Ag-Sn-Cu particles to assess their effect on mechanical properties as well as radiodensity, citing the routine use of these metals in posterior restorations. They found that the addition of these particles increased diametral tensile strength, fracture toughness, as well as radiopacity. Due to its advantageous mechanical properties, but adverse aesthetic properties, they suggested the possibility of its use in core materials as an alternative to the currently used materials.

### **Prepolymerized Composite Particles**

In order to minimize the overall shrinkage of the composites upon photopolymerization while maintaining the advantageous properties of both large and small particles, an alternate filler preconditioning method has also been used. This method involved the mixing and prepolymerization of resin and filler before integration into the final composite. This type of preparation has can be considered a sub-class of micro-filled composites. This treatment can be applied to any type of filler, making a method rather than a filler type as described. With this prepolymerization, the viscosity of the unpolymerized paste is lower than that of traditional microfilled composites, allowing higher filler loading and superior workability prior to

 polymerization. In terms of performance, this method has also been shown to reduce the tendency to stain,<sup>106</sup> increase the fracture toughness,<sup>107</sup> and reduce the shrinkage.<sup>108</sup> In addition, since the resin matrix can be different for the pre-polymers and the final composite, by varying the composition of the resin matrix of the prepolymer, the mechanical properties can be tuned to obtain a superior final material.<sup>109</sup> Despite the advantages of this technique, some of their properties remain inferior to some of the competing hybrid materials in terms of yield strength.<sup>110</sup> Regardless, this type of material is the subject of many patents,<sup>111-113</sup> and remains a very useful method in the arsenal of methods for reinforcing RBCs (**Table 2**).

# **Porous Fillers**

Fillers are most frequently used as solid particles, but porous particles have also been explored. These are meant to improve the bonding between the filler and the resin matrix through mechanical retention in the irregular pores of the filler. These fillers have been made from many of the previously mentioned types including silica,<sup>114-115</sup> glasses,<sup>81, 116</sup> alumina,<sup>117-118</sup> as well as other minerals.<sup>119</sup> Thus porous versions of many fillers are being explored for potential improvement of existing properties. While the work on this filler type is ongoing, literature has shown improvements in modulus,<sup>81, 114</sup> strength,<sup>81, 119</sup> and fracture toughness.<sup>115</sup> In addition to the mechanical improvements, the porous structures have been proposed as a method of producing bioactivity, releasing compounds from the pores over time.<sup>118</sup>

Type of Filler *	Example Products Using Filler **
Silica	Voco Admira, Bisco micronew, Ivoclar Vivadent Artemis,
Alkaline Glass	Ivoclar Vivadent Artemis, Kuraray Noritake Dental Clearfil Majesty
Other Glasses	Voco Admira, Shofu Beautifil II, Dentsply Ceram X
Other Metal Oxides	Tokuyama Estelite $\Sigma$ , Shofu Beautifil II, 3M ESPE Filtek Supreme
Prepolymerized Filler	Kuraray Noritake Dental Clearfil Majesty, Kerr Premise

 Table 2 - Examples of Commercial Products Using Specified Filler Types<sup>38</sup>

\* Hydroxyapatite not included due to the lack of literature on its use in commercial composites \*\* Not an exhaustive list, and only representative examples are shown

## **Filler Additives**

#### Fibers, Nanotubes, and Whiskers

Due to the wide use of fiber-reinforced polymers to many other industry-specific composites, this class of materials has also been explored for use in dental composites. While the chemical composition of this type of filler has varied widely, they are primarily distinguished by the differences in their morphology and aspect ratio. Fibers have a very high aspect ratio (20 to 500)<sup>120</sup> and are often flexible; nanotubes also have a high aspect ratio but have a hollow center; and whiskers have the lowest aspect ratio of the three and are usually rigid. Addition of these higher aspect ratio fillers has been shown to improve the mechanical properties of the material. The mechanisms by which this occurs include whisker/fiber pinning and pullout, crack deflection, and bridging. Since more extensive reviews on the topic have been written recently,<sup>121-122</sup> we present here a general description and previously explored use of some of these materials.



**Figure 3**. Electron micrographs of different types of filler additives used to reinforce dental composites: (a) SEM of glass fiber-reinforced composite,<sup>123</sup> (b) SEM of silicon carbide whisker-reinforced composite,<sup>124</sup> and (c) TEM of single-walled carbon nanotube-reinforced composite.<sup>125</sup>

The most widely used fibers in dental composites have been glass fibers. The choice of glass was logical, given the nearly identical chemical composition and refractive index to the existing silica filler, as well as its extensive use for many other applications in addition to its low cost. While micron-sized fibers were shown to decrease the material properties, nano-sized electrospun fibers were generally found to improve composite properties when used in small fractions with spheroidal silica particulate filler. Flexural strength, modulus, and work of fracture were increased by as much as 77%, 29%, and 66%, respectively.<sup>123, 126</sup> An alternative to ordinary fibers was attempted by Ruddell,<sup>127</sup> where they used resin-filled impregnated fused-fiber filler

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blocks as dental restorative fillers. When blended with a traditional particulate composite, these composites showed improvements in mechanical properties, though it was difficult to completely wet the fused-fiber blocks with the resin, leading to voids and heterogeneity in the final material.

Polymeric fibers of many different types were also tried to improve the overall properties of the composites. These were often made by electrospinning, and include poly(vinyl acetate) fibers,<sup>128</sup> polyethylene and aramid fibers,<sup>129</sup> and nylon 6 fibers.<sup>130</sup> The addition of fibers was generally beneficial to the mechanical properties of the composites, as long as they were only added in small fractions (1-5 wt %) due to problems with aggregation and void creation upon the addition of larger amounts.

Several different kinds of nanotubes have also been explored as reinforcements of dental RBCs. The best known of these were carbon nanotubes. Zhang *et al.*<sup>125</sup> were able to oxidize single-walled carbon nanotubes, electrostatically bind silanized methacrylate groups onto their surface. When small fractions of these were blended into a commercial composite, the flexural strength was increased from 115 to 142 MPa, a 23% increase. There has also been work using random or aligned fibers made from electrospun nylon-6/multiwalled carbon nanotubes as reinforcement.<sup>131</sup> They found that incorporating 0.5wt % nanotubes into these nylon mats increased the strength performance of the composite. Finally, two-walled halloysite nanotubes were also used to reinforce unfilled and glass-filled dental composites. Chen *et al.*<sup>132</sup> found that the addition 1-2.5wt % of halloysite nanotubes yielded only a slightly higher flexural strength, but almost doubled the work of fracture of these composites. Therefore nanotubes yielded very similar results as fibers, where a small percentage was generally favorable to the mechanical properties.

More rigid whiskers were also attempted. These whiskers ranged from metal oxides to ceramics and carbides. Some of these are mentioned above (see sections **Other metal oxides**, and **Hydroxyapatite**). Other types of whiskers include zinc oxide,<sup>133</sup> zirconia/silica,<sup>134</sup> silicon nitride,<sup>135</sup> and silicon carbide.<sup>136</sup> A series of papers was published by Xu examining the influence of different parameters using either plain whiskers, or whiskers fused with silica nanoparticles,<sup>124, 135, 137-138</sup> These silica-fused whiskers showed 33% decrease in wear depth compared to the control. Furthermore, the evaluations of flexural strength also showed an almost two-fold improvement over the control composites. With the exception of hardness, these additives significantly improved the mechanical properties.

Many authors concluded that the optimal fraction of fiber loading is low (1-5 wt %), since at low concentrations, the number of fibers is sufficient to bridge cracks and prevent further damage, whereas at high concentrations, the difficulty in fully dispersing the additives and their agglomeration may cause defects in the materials.

### **Particle Clusters**

The size of the silica particles has always been a point of concern: larger sizes allowed higher filler loading, while smaller particles produced superior wear properties.<sup>139</sup> While the use of hybrids bridged this gap, an alternate strategy was developed to get the best of both worlds. With a similar object as porous fillers (**2.9 Porous Fillers**), with the aim of developing RBCs with excellent strength and esthetics, a novel filler called "nanocluster" was first introduced in Filtek<sup>TM</sup> Supreme Universal Restorative (3M ESPE, St. Paul, MN, USA) in 2003. Nanoclusters can be defined as an association of individually dispersed nanoparticles such as SiO<sub>2</sub> and ZrO<sub>2</sub> and their agglomerations, which are be fabricated by self-assembly methods,<sup>140</sup> spray-drying techniques,<sup>141</sup> aerosol-assisted technology,<sup>142</sup> calcination processes,<sup>143</sup> and coupling reactions.<sup>144-145</sup> Among all these synthetic routes, only the last two methods have been applied to dental RBCs, due to their ease and high yield of nanocluster fillers.<sup>143-145</sup> Contrary to prepolymerized fillers, these methods contain no resin to bind the particles together, but instead rely on direct

bonding between them, resulting in a large, porous, but convalently bonded particle assembly.

The manufacturers of Filtek<sup>TM</sup> Supreme Universal Restorative have suggested that the employed nanoclusters were fabricated by the calcination using a bottom-up approach. The obtained nanofilled RBCs exhibited superior esthetics and polish retention similar to those of microfilled composite, while maintaining a physical-mechanical performance comparable to hybrid RBCs, which could be applied for both anterior and posterior restorations.<sup>143</sup> Curtis *et al.* assessed mechanical properties of commercial microhybrid (Filtek Z250), microfill (Filtek Z100 and Heliomolar), nanohybrid (Grandio and Grandio Flow), and nanofilled (Filtek<sup>TM</sup> Supreme in Body and Translucent shades, FSB and FST) composites, and found that composites reinforced with the nanocluster system showed distinctly superior performance. For cyclic pre-loading of 20N, the Weibull modulus of both FSB and FST were increased by 42 and 182 %, respectively, over control samples without pre-cyclic load. This increase can be ascribed to the improved damage resistance due to the infiltration of silane coupling agents into the interstices of the nanoclusters, and subsequent reinforcement with the resin matrix.<sup>146-148</sup> Instead of using aqueous

 colloidal SiO<sub>2</sub> sols to synthesize SiO<sub>2</sub> nanoparticles,<sup>143</sup> Atai *et al.* used amorphous fumed SiO<sub>2</sub> (~12 nm, Aerosil® 200) to form porous clusters through the sintering process at 1300 °C. They prepared the corresponding composite named *Sintered nano*, and compared its mechanical properties and surface roughness with an experimental composite *Microfiller* reinforced with micron-sized glass fillers (average particle size:  $2-5 \mu m$ ) and commercial Filtek Supreme<sup>®</sup> Translucent (FST) mentioned above.<sup>149</sup> It was found that the flexural modulus and fracture toughness of *Sintered nano* were statistically higher than the other two composites (p<0.05, ANOVA and Tukey HSD tests), which could be ascribed to the mechanical interlocking formed between the resin matrix and the sintered fillers.<sup>114, 149</sup> The sintered nanocomposite and FST also exhibited a smoother surface finish after a toothbrush abrasion test compared to the microfilled composite, due to the introduction of nano-scale filler particles.



**Figure 4**. Silica nanoclusters synthesized of  $3-8 \mu m$  using chemical crosslinking reactions as in reference 1 with a primary particle size of approximately 70 nm.

Recently, Wang *et al.* introduced SiO<sub>2</sub> nanoclusters through a coupling reaction between amine and epoxide functionalized silica nanoparticles at room temperature, and constructed bimodal silica nanostructures comprising of SiO<sub>2</sub> nanoparticles and nanoclusters. Among all RBCs, the maximum filler loading of SiO<sub>2</sub> nanoclusters alone was only 60 wt%, due to its wide size distribution ( $0.07 \sim 2.70 \mu m$ ), but was increased to 70 wt% with the additional use of SiO<sub>2</sub> nanoparticles. When added at the optimal weight ratio at 70% loading, 20% of which were nanoclusters, the flexural strength, flexural modulus, compressive strength, and wear volume were improved by 28, 48, 42 and 38%, respectively, when compared to nanoclusters alone, which was mainly due to the increased filler packing density and the reduced inter-particle spacing.<sup>144-145</sup> Based on these results, it seems likely that the physical-mechanical properties of the optimized composite could be further increased by also utilizing smaller silica particles directly, or by including these as building blocks for nanoclusters. The introduction and further exploration of particle nanostructures might provide more insight into the design and fabrication of RBCs for clinical use.

#### POSS

 An interesting offshoot of silica that has emerged recently is polyhedral oligomeric silsesquioxanes (POSS). POSS is made from a minimally sized, caged silicon dioxide functionalized with organic groups on the corners (Figure 5). Being a liquid, POSS can be used as a replacement for resin matrix rather than the solid filler. Fong *et al.*<sup>150</sup> explored this use of POSS methacrylate as a partial or total replacement of the BisGMA monomer and showed that at the optimal ratio (10 wt % of the resin), it improved the flexural strength of the final composite by 20 %. Additional work with these compounds not only confirmed that a small fraction of POSS improved the mechanical properties, but also caused a significant decrease in polymerization shrinkage from 3.53 to 2.18%.<sup>151</sup> Therefore this work showed that such a monomer is promising<sup>73</sup>, but further studies are necessary to establish a more quantitative link between its inclusion and the improved material properties.



Figure 5. Structure of POSS-Methacrylate, used as a partial replacement for the resin matrix monomer.

# Silane coupling agents

The filler composition and morphology have a significant impact on the properties of the final composite, but the coupling agents determine the interfacial properties. A wide variety of silane coupling agents has been tested to enhance the interfacial interactions between the resin matrix

and the filler particles. The original paper citing the advent of dental RBCs used vinyltrimethoxysilane (Figure 6a).<sup>52</sup> After further studies,  $\gamma$ -methacryloxypropyl trimethoxysilane ( $\gamma$ -MPS, Figure 6b) was adopted as the industry standard coupling agent. Many more studies have examined other parameters of silane coupling agents such as fraction functionalization,<sup>152-153</sup> type of silanization agent,<sup>154-155</sup> and hyperbranched methacrylate surface functionalization (Figure 6c).<sup>16</sup> These papers mostly examined the influence of all these variables on the mechanical properties of the final materials, but also thoroughly evaluated the effects on water sorption, solubility, and swelling. While there is some conflicting information as to the true influence of the coupling agent on the final properties of the materials,<sup>156-157</sup>  $\gamma$ -MPS remains the most widely used. Wilson *et al.* showed that decreasing methacrylate density while maintaining surface hydrophobicity marginally increased the flexural strength of the material, and more importantly reduced the viscosity of the unpolymerized material.<sup>155</sup> In addition, Ye's work also showed that using a hyper-branched coupling agent significantly reduced the shrinkage stress,<sup>16</sup> suggesting that new modifications of this type could further improve dental materials' properties for clinical use.



**Figure 6**. Organic silanes to modify the inorganic particle surface: (a) the originally used trimethoxyvinyl silane, (b) the most commonly used  $\gamma$ -methacryloyl propyltrimethoxysilane ( $\gamma$ -MPS), and (c) a hyperbranched multimethacrylate ligand for reduced shrinkage stress.<sup>16</sup>

In addition to varying methacrylate surface density, using different types of alkenes, or even growing polymer brushes; the most promising recent trend has been the use of mixed polymerization chemistry, combining the traditional methacrylate free-radical polymerization with the so-called click chemistry using the radical-initiated thiol-ene reaction, though this approach has mostly been explored for the modification of monomers, rather than fillers.<sup>22-23</sup> While there is still much work to do with this method, its advantageous properties may lead to their wider exploration as a promising alternative method for dental composite polymerization.

# **Conclusions and Perspectives**

The main challenges for fillers in RBCs remain the same as those for the composites themselves. The primary cause of failure is the development secondary caries, thought to be indirectly caused by polymerization shrinkage,<sup>158</sup> and restoration breaks due to fracture; both of these remain the main issues to overcome.<sup>159</sup> While the monomer can be said to be directly responsible for the volumetric shrinkage of the materials, some filler technologies such as POSS addition have been shown to decrease the volumetric shrinkage, and therefore could be used to aid in minimizing this problem.

The greatest obstacle in composites that is directly caused by the fillers, however, is the overall opacity of the material. Aside from purely esthetic considerations, the difficulty in perfectly matching the refractive indices of the resin and the filler prevents the curing light from fully penetrating the restoration, thus multiple increments are needed for a full cure (in addition to shrinkage concerns). In recent years, "bulk fill" restoratives have made great strides in the use of non-incremental curing.<sup>160-163</sup> These composites allow non-incremental curing due to high transparency and low shrinkage. Therefore the main solution so far has been the reduction of filler particle size to reduce light scattering. Smaller particles, however, cause problems of their own. The most promising results for refractive index matching so far have been in the use of chemical hybrid fillers specifically designed for such a purpose (See **2.4 Other Metal Oxides**).

The mechanical properties of many of the commercially available composites are already far superior to those required by the ISO standards for mechanical properties,<sup>83</sup> but many of the additives discussed were shown to further improve these properties. Beyond the standards, many properties such as wear resistance and fracture toughness have a significant influence on the material performance that should be assigned a greater importance in order to produce materials that have better resistance and longer functional life spans.

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The aim of dental RBCs is to restore teeth to their original working shape. While the true regeneration of enamel under clinical conditions has not been achieved due to its highly complex structure, the ideal solution would be to simply rebuild it, or at least a framework that can be transformed into it. Some preliminary work by Fan<sup>164-165</sup> has shown promise for the eventual development of enamel regeneration. This may become an interesting research objective in this field, though still distant for now.

Despite a few key properties to improve upon, there is no clear unified direction of research for dental fillers.<sup>166</sup> New types of reinforcements are being explored; new types of surface modifications are being attempted. The only clear trend is the use of increasingly small particles to favor advantageous optical and polishing properties. In addition, fillers are currently being developed with more sophisticated functionality such as antibacterial compound release and bioactivity such as remineralization and fluoride release.<sup>167-168</sup> Composites with these functions will likely be commercialized in the near future.

A final consideration for dental RBCs is that due to the staggering number of possibilities for both filler and resin matrix, most investigations have focused on the effect of single components on these complex mixtures, assuming there was no change in the interaction between the two. The future of RBC fillers will likely continue as begun by ORMOCERs<sup>™</sup> where the line between monomer and filler is no longer so stark, and specific interactions between the resin matrix and the filler are optimized for superior overall RBC properties. The drive for innovation will bring about a new generation of dental fillers and composites that will respond to the rapid and growing need for new biomaterials that are safe, strong, and easy to use.

Since their advent, a great variety of different fillers have been developed and tested. The difficulty in using these materials remains that it is impossible to directly compare all the materials available simply due to the large number of possible compositions and combinations. Most of the fillers offer distinct advantages and inconveniences, and so can be used in specific applications that play to their strengths. Despite their current shortcomings, much of the research discussed above highlights ways in which one can improve the current commercially-used fillers. In concert with the development of more sophisticated monomers and resin systems, the lifespan of current dental products are expected to increase, and only by using optimized combination of all these available methods will one be able to achieve a truly great dental RBC.

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# Inorganic Fillers for Dental Resin Composites - Present and Future

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**TOC Figure** 1 - Fillers for dental resin composites come in all shapes, sizes, and chemical compositions. These largely determine the mechanical properties of the final composite.