

# Goethite Nanofibers as Bio-Fillers in Dental Composite Resin

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## Abstract

Composite resins represent an important member of biomaterials family that have been evolving due to the needs in biocompatibility and mechanical properties. Fillers in a variety of forms and types have been evaluated and the impact of fillers to improve the performance of the dental composites have been studied in vast. Various composite resin fillers tested had revealed its own strengths and weaknesses. Bio polymers when they are reinforced with biofillers can produce novel biocomposites. The biocomposites with the biofillers will replace and be a substitute for synthetic fibre-reinforced composites. In recent years, natural bio-fibres have gained attention as suitable reinforcements in polymeric matrices. These bio-fillers possess high specific strength and can be effectively used for dental composites resin. The most commonly occurring natural bio-fibres are the teeth of limpets. The teeth of limpets have a distinctive composite nanostructure which comprises of high-volume fractions of reinforcing goethite nanofibers to provide mechanical integrity. The limpet tooth is effective at resisting failure to abrasion. The goethite nanofibers are expected to be significant for novel dental biomaterials with extreme strength and hardness.

**Keywords:** Bio-filler, Nanoparticles, Nano-filler, Dental Composite resin.

## Introduction

Composite resin are tooth-colored restorative materials with synthetic polymers, reinforcing fillers and silane coupling agents. The silane coupling agents helps to bond the reinforcing fillers to the polymer matrix. Each component of the dental composite resin is important for the success of the final restoration. The developments in commercial dental composites have been a focused on the modifications to the filler component<sup>(1)</sup>.

Reinforcing fillers are particles added to any materials such as to plastics, concrete etc. They are added to bring out the better properties of the mixed material. Such materials can be in the form of solid, liquid or gas. Most of the materials used in dentistry contain fillers as a part of their composition. Fillers are aimed to improve the chemical and mechanical properties of the dental composite material<sup>(1),(2)</sup>. Combination of individually dispersed nano sized filler particles and nano clusters enhance the aesthetics<sup>(3)</sup>.

### TRADITIONAL FILLERS:

Initially, crystalline quartz and borosilicate or

lithium aluminosilicate glasses were used as fillers. The quartz was ground or milled into particles of sizes ranging 0.1nm to 100nm. Crystalline quartz has an excellent optical match to the polymer resin. However, quartz can be very abrasive to enamel. The glass filler particles and the crystalline quartz filler particles are large in diameter and very hard to the surrounding polymer matrix. The hardness and the larger diameter ensured that as the surface of the composite was abraded, the polymer would wear at a faster rate than the fillers, leaving them raised and exposed from the surface. This makes the surface of the restoration rough and less natural like. Thus, polishability and esthetics were compromised<sup>(1),(2)</sup>.

To improve the esthetics, the quartz filler particles where replaced with silica particles. These silicon dioxide particles have a diameter of approximately 0.04 $\mu$ m. The surface area of the silicon dioxide particles is more hence they require considerable amount of monomer to wet their surface. This characteristic of the silicon dioxide filler particle will limit the filler concentration to approximately 35 wt%, which in turn limits the mechanical properties of the material. The silica fillers though they have a good polishability but the

strength and stiffness values are considerably lower than other fillers incorporated composite resin.<sup>(1)</sup>

To improve the esthetic, optical and mechanical properties of composite resin, nano particles as filler has been added. Nano particles enhance wear resistance and reduce polymerization shrinkage. Fillers with nano sizes have an increased surface area which provides an increase in flexural strength.<sup>(2)(4)</sup>

In spite of developing materials to lower stress and improving the strength in the materials, researchers have also focused on developing materials with bioactive characteristics. The ideal restorative material of the future will not only be able to withstand occlusal loads and develop low polymerization stress but also will have an antibacterial, and remineralizing, properties in addition to being biocompatible<sup>(5)</sup>

Although modifications have been tried with the resin monomer, most significant modifications in dental composite resin is been with the fillers. The modifications have been in the type, size, and distribution of the inorganic fillers. The effects of size, shape, and size distribution of different fillers.<sup>(6)</sup>

As many articles have covered the review of fillers in composite resin; this review focuses mainly on the availability and performance of bio-filler's materials and focus on the goethite nanofibers as fillers.

#### BIO-FILLERS

A biomaterial by definition is a substance can be used to fix the defects, repair or replacement of defective organ in the body. These materials can be synthetic (synthetic - mineral or organic) or natural.<sup>(6)</sup>

The development of bio degradable and recyclable materials from renewable resources have drawn attention as they are found to be suitable replacements for synthetic materials. The plant fibers and cellulose based fibers are natural fibers and are the most commonly used bio-fibers. These bio fibers are used for reinforcing various types of polymer matrices<sup>(7)(8)</sup>.

Bio-fillers in dental composite resin act as a biomaterial and hence reduce the bacterial penetration into marginal gaps for composite restorations. With the advent of modern technology, various attempts are made

to modify these fillers to make them more beneficial for a better material. Strong scientific and collaborative foundations presently exist for further development and improvement of the filler system, which will certainly continue to hold a pivotal role in the dentistry.<sup>(3)</sup>

The bio-fillers because of their properties such as biodegradability, and high specific strength, have received extensive attention as a replacement for traditional synthetic fillers. Hence, the bio-fillers are used in the fabrication of hybrid composites and bio-composites<sup>(8)</sup>.

The mechanical and the physical properties of bio fillers filled composite resin varied considerably. The variations of the properties depends on the stiffness, physical and chemical composition of the material, type of particulates, and growth environment<sup>(9)</sup>

#### BIO-NANO-COMPOSITES

The inorganic fillers are added to the polymer matrix in dental composite resin is to improve the mechanical properties of the composite resin. With the aid of nanotechnology, the dental composite resin fillers have been manufactured in nano scale level. The intrinsic toughening of the composite resin with the bio nano filler prevents the micro crack formation and increases the material toughness.

The bio-fillers in nano scale has been introduced in the composite resin and these composites have been termed as bio-nano-composites. Interest in the use of bionanocomposites has been increased over the past 20 years. As a dental material, bionanocomposites has the ability in mimicking native tissue structure and properties. The bionanocomposites has the ability to endure high biting force and shows a good mechanical flexibility in harsh environment. Similar structure or properties to bionanocomposites are often found in dentin and enamel. Therefore, if the bionanocomposites replaces enamel or dentin, they are expected to act as single entity and stay for a longer period of time.<sup>(10)</sup>

#### GOETHITE NANOFIBRES AS BIO-FILLERS:

The inorganic phase of minerals in the biological system from highest animals to plants are made of bio minerals. Although bio minerals composed of calcium predominate, bio minerals of barium, strontium, iron,

and silica are also well known. Bio mineral generally occur as oxides, hydroxides, phosphates, and carbonates in the biological system<sup>(11)</sup>.

This reinforcing bio minerals in many organism approaches nano metre in length, at the orientation is always in one-dimension. Which has been proposed as promoting flaw insensitivity and in turn increases the tensile strength of the bio mineral<sup>(11)</sup>.

The aquatic snail (Limpet) teeth are an example of a biomineral produced biologically that is optimized for strength. Studies have shown that the teeth of limpets have the high aspect ratio mineral nanofibres of goethite with a reinforcing protein matrix<sup>(11)</sup>.

### LIMPET-THE AQUATIC SNAIL

The intertidal zones are mostly inhabited by primitive marine mollusks. These marine mollusks are Limpets (Mollusca, Gastropoda) and are characterized by their inverted cone-shaped shells. The limpet radula is a highly mineralized tooth structure. The radula contains more than 100 rows of teeth. The outermost rows of the teeth are actively used. During the growth and maturation of the radula, the radula advance in position to the scraping zone. The scraping zone of radula will be in contact with the substrate while feeding. Once the teeth start to function, they begin to wear down, at an average rate of one tooth row per day. At the same time, a new row of teeth emerges. The radular teeth has a membrane and it is manipulated by various muscles and cartilages which are used to graze or cut food. There exist seven basic types of radula morphology<sup>(12)</sup>.

### MINERALIZATION OF RADULA

According to the extent of mineralization the radulae of Limpets can be segmented into 4 stages. The First stage there is no mineralization formation. The organic framework of tooth from the odontoblast is initiated in this stage. In the second stage, mineralization formation occurs. The minerals are deposited at the cusp and the rows of teeth. In the third stage, the mineralization gets completed. The cusps of the radula are solid and firm with full mineral deposition. In the fourth and the final stage the fully grown mineralized teeth move and replace the worn-out teeth. The mineralization of tooth cusps begins in the posterior region of the radula. The

limpet teeth are organic structures composed of chitin and proteins rich in tyrosine<sup>(13)</sup>.

The mineralization of limpet teeth consists primarily of mineral nano fibres typically many micrometres in length but only a few tens of nanometers in diameter. These mineral nanofibers occupy a significant volume fraction of approximately 80% in mature teeth. The strength and hardness of the limpet tooth is critically dependent on the strength of the mineral nanofibres within the composite structure<sup>(11)</sup>.

Mineralization of the limpet teeth begins with the formation of elongated crystals of goethite (-FeOOH) crystals. The goethite crystals are closely associated with the organic matrix. Hydrated amorphous silica phase fills the space between the goethite crystals. The pre-formed matrix of limpet teeth consists of organized arrays of densely packed chitin fibers, with no apparent gaps or holes for crystal growth, other than the few nanometers between adjacent fibers. The organization of the goethite crystals along with the amorphous silica plays an important role in determining the fracture and wear characteristics of the functional tooth. The orientations of the goethite crystals are controlled by the chitin fibers in the organic matrix. The orientation of the goethite crystals results in teeth which are self-sharpening and resistant to fracture.

As the radula develops in the radular sac, the iron is secreted into the radula from the superior epithelium. Copper in the limpet radula are involved in the enzymic cross linking of the organic component. Zinc in the radula plays a role in the control of iron oxide crystallization. Calcium in the radula is incorporated in the crystalline phosphatic mineral hydroxyapatite<sup>(14)(15)</sup>.

The goethite nanofibers with other minerals are expected to dictate the flaw tolerance. This might be due to their diameters are being below a critical threshold value of the order of tens of nanometres. The tensile strength of limpet teeth can reach values higher than spider silk, considered currently to be the strongest biological material, and only comparable to the strongest commercial carbon fibres.

The radula of Limpet structure highlights the efficiency of biological control in assembling a composite structure of nano fibrous goethite for optimal

strength and hardness. This corresponding structural design features are expected to be significant for novel biomaterials with extreme strength and hardness, such as next-generation dental restorations <sup>(11)</sup>.

### Discussion

It is apparent from the previous studies that the current composites have significantly improved clinical performance compared with their predecessors, especially in posterior teeth with respect to strength and hardness to resist crack or fracture. However, Considerable effort are expended in the laboratory to ensure that the new materials handle and perform at and above the level of existing materials in respect to strength for the posterior teeth and superior polishability in the anterior region. Laboratory composite resin will identify the weaknesses, and further refinements in formulations will then take place to maximize performance. There are, further changes awaited in dental composite formulation in the areas of new fillers which produce particles in high yields. These newly developed particles will ideally be very fracture-resistant and only minimally abrasive. In addition, the refractive index of the modified filler has to accurately match to existing as well as newly developed polymers. The continued development of fillers containing biocompatible material will have an enhanced therapeutic effect. <sup>(1)</sup>

### Conclusion

The novel biomineral fillers such as goethite nanofiber present in the radula of the limpet with a nanofiber dimension with extreme strength and hardness present an alternative to the present fillers in the dental composite resin.

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**Source of Funding** – Nil

**Conflict of Interest** – Nil.

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