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Composites structure in dentistry and evolution of filler systems and their effects on properties of composites structure

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Abstract: The properties of composite material are dependent on the properties of the constituent phases forming the composite, their relative amounts, and the geometry of the dispersed phase .The concept of multiphase composites provided opportunities for designing a large variety of materials with different combinations of properties that cannot be achieved by using a single metal, alloy, ceramic, or polymeric material.

Keywords: Tribology, Hardness, Friction, and Tooth Wear.

Introduction

Composite material is a solid formed from two or more distinct phases (e.g., filler particles dispersed in a polymer matrix) that have been combined to produce properties superior to or intermediate to those of the individual constituents.(1)

The properties of composite material are dependent on the properties of the constituent phases forming the composite, their relative amounts, and the geometry of the dispersed phase (shape, size, distribution, and orientation) .

The concept of multiphase composites provided opportunities for designing a large variety of materials with different combinations of properties that cannot be achieved by using a single metal, alloy, ceramic, or polymeric material.

Composites structures occur in nature. As in bone which is a composite of soft collagen proteins and hard brittle mineral apatite. And wood consists of strong and flexible cellulose fibers surrounded and held together by a stiffer material called lignin.

Most composites have been created to improve the properties whether mechanical, thermal, electrical, magnetic or optical properties of different materials to suit the required application. (2, 3)

I. Classification of composite structures:

a. According to the matrix phase.
b. According to the dispersed phase.
c. According to the matrix filler interface.

II.a. Classification according to the matrix phase:

The matrix phase may be metal, polymer, or ceramic. In general, metals and polymers are used as matrix materials because some ductility is desirable.For ceramic-matrix composites the reinforcing component is added mainly to improve fracture toughness.

Functions of the matrix phase:

1. It binds the filler phase together and acts as the medium by which an externally applied force is transmitted and distributed to the fillers, only a very small proportion of the applied load is sustained by the matrix phase.
2. It protects the individual fillers to an extent from surface damage because of mechanical abrasion or chemical reactions with the environment. Such interactions may introduce surface flaws capable of forming cracks, which may lead to failure at low tensile stress levels.
3. It separates the fillers and prevents the propagation of brittle cracks from filler to filler which could result in catastrophic failure (the matrix phase serves as a barrier to crack propagation).
4. It maintains the orientation of the reinforcing phase for the high strength development.

- ### Polymeric matrix composites:

Polymeric matrix composites consist of a polymer resin as the matrix. These materials are used with great diversity in different applications.

Applications in dentistry

METHACRYLATE MONOMERS

The majority of monomers used for the matrix phase of resin composite are dimethacrylate compounds. Two monomers that have been commonly used are (Bis-GMA) and urethane dimethacrylate (UDMA). Both contain reactive carbon double bonds at each end that can undergo addition polymerization initiated by free-radical initiators.(4)

- Advantage: Bis-GMA has a higher molecular weight than methyl methacrylate (MMA), which helps to reduce the polymerization shrinkage. The polymerization shrinkage value for MMA resins is 22 vol. %, whereas for a Bis-GMA resin it is 7.5 vol%. (5)
- Disadvantage: The viscosity of the monomers, especially Bis-GMA, is rather high and diluents must be added, so a clinical consistency can be reached when the resin mixture is compounded with the filler.

Low- molecular-weight compounds with difunctional carbon double bonds, for example, triethylene glycol dimethacrylate (TEGDMA), or Bis-EMA are added by the manufacturer to reduce and control the viscosity of the compounded composite.these compound showed high polymerization shrinkage so it can’t be used with high concentrations.

LOW-SHRINK METHACRYLATE MONOMERS

A variety of other methacrylate monomers have been introduced since 2008 for controlling the volumetric shrinkage and polymerization stress of composites. The general approach relies on increasing the distance between the methacrylate groups resulting in lower cross-link density. This could be done using dimer acids, incorporation of cycloaliphatic units, and photocleavable units to relieve stress after polymerization. (4)

LOW-SHRINK SILORANE MONOMER

Silorane has been developed to reduce shrinkage and internal stress build-up resulting from polymerization. The name silorane was coined from its chemical building blocks siloxane and oxirane. The siloxane group provides hydrophobicity to the composite. The oxirane groups undergo ring-opening cross-linking via cationic polymerization. (4)

Bio HPP (High Performance Polymer)

- BioHPP (High Performance Polymer) is based on polyether-ether-ketone (PEEK) polymer.
- Microstructure: Thermoplastic polymer network based on PEEK containing ceramic fillers of 0.3-0.5 microns and occupy 20% of the total volume of BioHPP.
- Their strength is due to the special ceramic filler (with the grain size of 0.3 to 0.5 µm).
- Modulus of elasticity of around 4 GPa, BioHPP is close to modulus of elasticity of bone, which helps in reducing the stress shielding thereby makes it a very interesting material for the restoration of dental implants. (6)

• Metallic Matrix Composites

In metallic matrix composites the matrix is a ductile metal, and the reinforcement may improve stiffness, strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability. The reinforcement may be in the form of particulates, fibers, and whiskers. Concentrations normally range between 10 and 60 vol%.(2)

Advantages over polymer matrix composites:

1. Metallic matrices have high toughness, stiffness, strength, and modulus.
2. Metals have high melting points. It can withstand high temperatures and sustain their shape at high temperatures.
3. Lower coefficients of thermal expansion and contractions.
4. Higher electric and thermal conductivities
5. Better wear & fatigue resistances.

Disadvantages of metallic matrix composites:

- It has higher densities
- Need very high processing temperatures. (4)

- **Ceramic Matrix Composites**

It is composed of a ceramic matrix and embedded fillers of other material (dispersed phase; metal, ceramic, or polymer). Particulates, fibers, or whiskers have been embedded into a ceramic matrix. Different mechanical and optical properties have been improved significantly by this combinations. (2)

Advantages:

- Enhancement of the toughness while retaining the high temperature properties.
- High melting points and superior corrosion resistance.

Disadvantages:

- low tensile strength, impact resistance.

Applications in dentistry:

Zirconia-reinforced Lithium Silicate (ZLS)
(Vita Suprenity & Celtra Duo)

- The microstructure: The zirconia-reinforced lithium silicate (ZLS) is based on a lithium-metasilicate (Li_2SiO_3) glass ceramic, reinforced with 10% of zirconium dioxide (ZrO_2)
- The final crystallization process, leads to the formation of fine-grained microstructure (Li_2O-ZrO_2-SiO_2).
- ZLS combines the positive mechanical characteristics of the zirconia with the glass-ceramic aesthetic appearance. (7)

II.b. Classification according to the shape of the dispersed phase

Role of the dispersed phase in composite structures:

1) Enhance the mechanical properties of the final composite structure.
2) Reduce the amount of matrix material. Thus, decreasing the polymerization shrinkage in case of polymeric matrix and decreasing the cost.
3) Adjusting the rheological properties according to the application. Thus, improving its workability.
4) The use of heavy metals, such as barium and strontium provide radiopacity.

5) The fillers provide the ideal means of controlling various aesthetic features such as color, translucency, and fluorescence.

1.Particle reinforced composites:(2)

The dispersed phase for particle-reinforced composites is *equiaxed* (i.e., particle dimensions are approximately the same in all directions). Particle reinforced composites could be subdivided into **large-particle** and **dispersion-strengthened composites** the difference between both is the reinforcement or strengthening mechanism.

Large-particle composites	**Nano-particle composite (Dispersion-strengthened composites)**
The term large is used to indicate that particle–matrix interactions cannot be treated on the atomic or molecular level. The particulate phase is harder and stiffer than the matrix. These reinforcing particles tend to restrain movement of the matrix phase in the vicinity of each particle. The matrix transfers some of the applied stress to the particles, which bear a fraction of the load. The degree of reinforcement depends on mechanical properties of the particle & strong bonding at the matrix–particle interface.	Particles are normally much smaller (10 and 100 nm). Particle–matrix interactions that lead to strengthening occur on the atomic or molecular level. The mechanism of strengthening is similar to that for precipitation hardening. The small, dispersed particles hinder the plastic deformation. Thus, plastic deformation is restricted such that yield strength, tensile strength, and hardness are improved.

Factors influencing the effectiveness of reinforcement:

1) The particles should be small and evenly distributed throughout the matrix.
2) The volume fraction of the two phases influences the behavior; mechanical properties are enhanced by increasing particle content.

The **rule-of-mixtures** equations predict that the elastic modulus should fall between an upper limit repre-

$$E_c(u) = E_mV_m + E_pV_p$$

sented by

And a lower limit represented by

$$E_c(l) = \frac{E_m E_p}{V_m E_p + V_p E_m}$$

Where, E and *V* denote the elastic modulus and volume fraction, respectively, and the subscripts *c, m,* and *p* represent composite, matrix, and particulate phases, respectively.

Applications in dentistry:

a) Fillers in dental adhesives:

Lohbauer et al. incorporated Zirconia nanoparticles into the adhesive of a commercial adhesive system with different concentrations (5, 10, 15 and 20 wt.%). It was found that Zirconia nanoparticles incorporation **increased bond strength to dentin** by reinforcing the interface adhesive layer. Moreover, nanofiller incorporation into the adhesive showed a tendency to increase bond strength with increasing concentration. At high concentrations (20 wt.%) nano-filler incorporation was more efficient in increasing bond strength.(8)

b) Fillers in denture base:

Alhareb et al. mixed the powder particles of the PMMA with **nitrile butadiene rubber** (NBR) as impact modifier particles and **ceramic fillers** as reinforcement particles fixed at 5 wt% (Al_2O_3 and YSZ).

It was found that the **impact and fracture resistance** of heat polymerized PMMA denture resin was enhanced after reinforcement with NBR particles and treated ceramic fillers. These properties can be improved by using silane coupling agent which offers the potential to further improved properties. This fillers combination offered resin with high impact strength and fracture toughness.

Thus, PMMA denture base reinforced by NBR & ceramic fillers is a good choice in removable prosthodontics.(9)

c) Fillers in glass ionomer

When zirconia and alumina fillers were added to glass ionomer cement.

- Alumina fillers increased the compressive strength of the glass ionomer cement.
- Zirconia particles (agglomerates) above 50 µm in the microstructure of the glass ionomer cement had a negative impact on compressive strength of the glass ionomer cement. As it acts as stress concentration areas.
- Alumina and zirconia containing GICs are promising restorative materials only if the appropriate particle size distribution is used.(10)

2. Fiber reinforced composites: (11)

Fiber shaped fillers are axial particulates embedded in fitting matrices. The primary objective of these fillers is to obtain materials with high strength in conjunction with higher elastic modulus. However, the strength elevation is affected with the applied load transmitted from matrix to fibers, interfacial bonding between fiber-matrix, their relative alignment and nature of fiber scheming the overall material behaviors.

The alignment of fibers may however be continuous or random depending on the end applications. The choice of the fiber reinforcement and its fitting matrix also depends on application requirements. In recent years, the advent of composite technology has led to the development of different fiber reinforced composite systems via varying manufacturing methodologies to obtain advanced material behaviors.

3.Whiskers reinforced composites: (2)

Whiskers have the following properties:

1. It has very thin single crystals
2. It has extremely large length / diameter ratios
3. It has high degree of crystalline perfection. Thus, nearly flawless.
4. It is exceptionally strong

Whiskers are not used extensively as a reinforcement medium:

1) They are very costly
2) The process of incorporating them in matrix phase is tedious

Applications

Whisker reinforced dental resin composite (DRC)

- Xu et al. studied the influence of the amount of silicon nitride (β -Si_3N_4) whiskers on the mechanical properties of DRCs:
  The flexural strength and vickers hardness of the DRCs increased monotonically with the amount of added β -Si_3N_4 whiskers.
  The flexural strength of the whisker-filled DRCs were more than twice those of conventional SiO_2-filled DRCs (12)
- According to the type of the whiskers:
  Silicon nitride whiskers were helpful to improve the strength and toughness of the material
  Silicon carbide whiskers improved the modulus and hardness of the material (13)

4.Urchin reinforced composites:

This morphology was designed to address the problem of **aggregation of whiskers**. Urchin-like fillers were developed which combine features of a whisker and a globule. These fillers were easier to disperse than whiskers. The fillers could be inserted into the resin matrix tightly through their spikes and improve the interfacial interaction between the resin matrix and the fillers.(14)

5.Nanotubes reinforced composite:

Nanotubes are hollow fibrous fillers with a high aspect ratio. They have the same strengthening and toughening mechanisms as fibrous fillers. Nanotubes vary in chemical composition, with the most widely studied being carbon nanotubes.

Disadvantages:

⇒ Severe CNT agglomeration
⇒ Poor interfacial interaction with the matrix. (non-reactive surface of the nanotubes)

- **Single-walled carbon nanotube (SWCNT)**
  It has excellent mechanical properties. To improve interfacial compatibility with the resin matrix,

Zhang et al. firstly coated SWCNT with a layer of nano-SiO_2, followed by modification using allyltriethoxysilane. The addition of modified SWCNT improved the mechanical properties of DRC, but it also had an adverse influence on the aesthetics of the material due to its dark color. (14, 15)

6. Halloysite nanotube (HNT)

⇒ It is a nanomaterial with characteristics of hollow tubular structure with high aspect ratio. The elastic modulus of HNT ranges between 230 ~ 340 Gpa. (16)

⇒ Chen et al. added silanized HNT to DRCs and found that small amounts (1 or 2.5% mass fraction) of HNT could be dispersed evenly in the matrix and improved the mechanical properties, while excessive HNT tended to form aggregates.

⇒ The impregnation of HNTs into dental resins/composites could result in **two opposite effects:** the reinforcing effect due to the highly separated and uniformly distributed HNTs, and the weakening effect due to the formation of HNT agglomerates/particles.(17)

⇒ Moreover, Utilizing the hollow structure of HNT, Liu et al. **loaded silver nanoparticles** into HNT and obtained DRC with excellent antibacterial activity and mechanical properties. The flexural strength of the DRC was increased by 25% when 3 wt% Ag-HNT was added.(16)

7.Porous fillers

- Porous fillers were introduced to solve the problem of **silane coupling agent degradation** by time which weakens the interfacial bonding between the fillers and the matrix. The porous fillers can form a stable physical interlocking with resin matrix through the pore structure.(18)
- The filler loading of DRC only reached 40 ~ 50 wt%, due to the high specific area of the porous fillers. This was increased by combining nonporous SiO_2 and mesoporous SiO_2. (18)
- Wang et al. synthesized wrinkled mesoporous (WMS) SiO_2 nanoparticles with a size of ~ 500 nm (controlled filler pore size and uniformity). Compared with non-porous SiO_2 nanoparticles similar in size, the wrinkled mesoporous SiO_2 nanoparticles were more conducive to the improvement of flexural

strength of DRC. WMS are beneficial for creating **strong micromechanical interlocking** between the filler and the resin matrix during the photo polymerization process and enhance the **interfacial retention**. Consequently, the stress may be more efficiently transferred between the resin matrix and WMS, increasing the fracture resistance and other mechanical properties (19)

8.Glass flakes

Glass flakes are generally modified c glass fillers with high aspect ratio. The geometrical structure and the inherent properties of the glass flakes stands for:

- Improvement in the overall mechanical properties of the composite structure as compressive strength and hardness.
- Improvement in the aesthetic properties (better translucency when compared with other irregularly shaped particle reinforced composite) attributed to:
    - Flat surface of the glass flake which suppress light scattering.(18, 19)

Applications in dentistry

Mohseni et al. studied that addition of silanized glassy flakes (GF) in spherical nanosilica particle containing dental composites.

The evenly distributed flakes among the spherical filler particles of the dental composites significantly improved the fracture toughness of the composite as it caused deviation of crack direction, which increased the energy required for fracture of the composites. The highest mechanical properties were observed for a dental composite sample with 15 vol % of GF. Further increase in the GF content resulted in a drop in the mechanical properties of the dental composite due to the stacking of the flakes on each other. (20)

9.Microcapsules

A microcapsule is a spherical particle with a polymer or glass shell that contains a healing liquid. Microcapsules are embedded into the matrix, upon exposure to forces induced by the propagating crack, it ruptures are releases the healing liquid that flows into the crack and meets the catalysts incorporated within the matrix leading to its polymerization, thus healing the crack.

(C) SEM showing typical microcapsules

Huyang et al. developed a novel self-healing dental composite using silica microcapsules containing aqueous solutions of polyacrylic acids (silanated to the matrix) and a healing powder (strontiumfluoroaluminosilicate). Huyang et al. reported that the average healing efficiency reached up to 25% when 10 wt% microcapsules were added without affecting the mechanical properties.(21)

10. Laminar composites: (2)

- A **laminar composite** is composed of two-dimensional sheets or panels bonded to one another. Each sheet has a preferred high-strength direction.
- A multi-layered structure such as this is termed a laminate.
- Laminate properties depend on how the high-strength direction varies from layer to layer.
- There are four classes of laminar composites: unidirectional, cross-ply, angle-ply and multidirectional.

modulus of elasticity and strength of unidirectional laminates are highly anisotropic.

While, multidirectional can be fabricated to be most isotropic; degree of isotropy decreases with angle- and cross-ply materials.

Laminar composites

(a) Unidirectional laminates
(b) Cross-ply laminates
(c) Angle-ply laminates
(d) Multidirectional laminates

11.Sandwich Composites(2)

- It is constructed by sandwiching foam core between two skins of high strength laminates.
- Face sheets carry most of the loading and stresses. Core may be a honeycomb structure which has low density than the face sheets and resists perpendicular stresses and provides shear rigidity.
- A well-designed sandwich panel should be able to withstand both compressive, tensile and shear stresses without failure.

II. c. Classification according to the interface (23)

The interface is defined as the region where the filler and matrix are either chemically or physically attached to each other. Stronger interfacial interaction between the composite constituents can lead to a better isotropic stress distribution.

Types of interfacial interactions:

The properties of the composite materials are dependent on the interfacial characteristics of the fillers and matrices. The interactions between the filler and matrix are categorized as **covalent** and **non-covalent** interactions.

Non-covalent interaction:

(Van der Waals , electrostatic, and hydrogen bonding)

The noncovalent interaction between the matrix and fillers can be enhanced by employing:

- **Bridging:**It happens when a polymer chain interacts with two or more reinforcing fillers simultaneously. By increasing the filler content and using higher molecular weight polymer, the chance of bridging phenomenon will be higher.
- **Wrapping fillers by polymer chains**: It is useful for better dispersion of the fillers in the matrix
- **Crystallization of the semicrystalline polymer:** It improves the interfacial interactions. In this process, the fillers will act as a nuclei and the semi-crystalline host will crystallize at the interface.

Covalent interactions

Covalent interaction happens when polymer chains are chemically connected to the reinforcing fillers. For that purpose, proper chemical treatments are required to attach:

⇒ Functional group to filler surface to react with the matrix.
⇒ Polymer chains to the filler
⇒ Different functional groups to the same filler using plasma treatment

Role of functionalized fillers:

- ⇒ Enhance the interaction between fillers and matrix
- ⇒ Improve their dispersion
- ⇒ Improve the final properties of the composites compared to conventional fillers. This could be achieved by in situ polymerization, where the monomers react with each other and the fillers simultaneously.

Influence of interface on mechanical properties

The interface is important for the evaluation of the mechanical load transfer from polymer matrix to fillers. For instance, strength and toughness of the composites strongly depend on the interfacial adhesion.

Strength

The tensile strength of the composite depends on the efficiency of stress transfer between the constituents of the composite.

- By increasing the strength of interfacial bonding between the composite constituents. The applied load will be transfered to the fillers and the strength will be improved.
- The smaller particles have larger interface area at a constant volume fractions of fillers, leading to a large portion of stress transfer regions. Thus, increasing the final strength.

On the contrary, strength will be decreased in composites with poorly bonded fillers. This is due to the presence of discontinuity or de-bonding at the interface, which prevents the filler from carrying the applied load efficiently. This could be avoided by the introduction of chemical bonding to filler-matrix interfaces to effectively enhance the strength of composites.

Toughness

Toughness can be significantly enhanced by the enhancement of the interfacial adhesion between the thermoplastic matrix and filler.

- If the interaction between the matrix and fillers was weak. The crack will propagate through easily.
- If the interaction was strong. The crack pattern will be changed by crack deflection & debonding.

Liu et al.. studied the effect of silanization and BisGMA grafting on mechanical properties and polymerization shrinkage. The HA whiskers were firstly silanized, followed by the graft of poly(BisGMA) onto their surface. Compared with the HA whiskers without any treatment and with only silane treatment, the poly(BisGMA)-grafted HA whiskers showed better mechanical properties and lower polymerization shrinkage (24)

Evolution of fillers system in dental composite(22)

In an attempt to overcome the drawbacks of the silicate and acrylic resin materials, composite restorative materials came out in the early 1960s. Over the years. Fillers have been modified in three main trends: size of fillers, type of fillers and fabrication technique.

In the early 1960s, **macro-filled resin composite** was introduced using irregular quartz particles with size ranging between (5-25µ). Quartz fillers were hard that cannot be cut in smaller size. Filler content was approximately 75 to 80 wt%. It showed physical & mechanical properties better than unfilled. But, poor surface finish, low wear resistance & more prone to staining and wear resistance. Later, fine filled resin composite was introduced with quartz filler particles (0.5-3µ). It showed good mechanical properties with superior finish and polish than macro-filled.

In late 1970s, **Micro-filled resin composite** was introduced. With filler particle size ranging between (0.04-0.2µ) formed by hydrolysis and precipitation of fine silica fillers allowing better polishability. Filler content was approximately 35-50wt%. microfiller particles exerted extremely high surface area limiting the filler loading . Lower filler load resulted in inferior mechanical properties as low modulus of elasticity, low tensile strength, high water sorption, high coefficient of thermal expansion & contraction and high polymerization shrinkage.

One way to increase the filler content and mechanical properties, was the addition of microfiller-based complexes or prepolymerized resin fillers into the resin matrix of microfilled composites. These organic-inorganic fillers were produced by milling the prepolymerized microfilled composite into particles (1–200 µm) or by incorporating silica microfillers into prepolymerized spherical particles (20–30 µm). Prepolymers were able to increase the filler content in microfilled composites up to 60 wt%. However, prepolymers could not be covalently bonded to the resin matrix due to the lack of available C=C bonds at their surface resulting in low wear resistance in load-bearing areas.

Shortly after, in early 1980s, **hybrid composites** were introduced as a true combination of macrofilled and microfilled composites. They contained macrofiller quartz, glass, or (Ba/ Sr/Al/Zr)-silicate particles (1–50 μm) with amorphous silica microfiller particles (0.04 μm). Hybrid composites were considered an optimal combination for favorable mechanical and optical properties and improved wear resistance.

Quartz was being replaced with other types of fillers due to its high abrasiveness toward enamel and lack of radiopacity. Ba-glass and ytterbium/yttrium trifluoride fillers were added for radiopacity and potential fluoride release. However, it was shown that trifluoride-containing composite released significantly lower amounts of fluoride than a glass-ionomer cement excluding anticariogenic potential of such composites.

Around the year 2000, nanotechnology allowed further improvement of dental composites and the launch of nanofilled and nanohybrid composites. Nanofilled composites contain silica and/or zirconia particles (5–20 nm) in the form of non-agglomerated particle and agglomerated nanoclusters (avg. size = 0.6– 10 μm). Nanohybrid composites contain silica/ zirconia nanoparticles and larger 0.6–1 μm glass/ zirconia/silica particles. Nanohybrid composites also contain prepolymerized resin fillers and nanoclusters.

The new sol-gel technology used to create nano-sized filler particles allowed greater nanofiller content (more than 80 wt%) compared to the traditional microfilled composites. This led to excellent optical properties, high polishability, and gloss. While their mechanical properties, hardness, strength, and wear resistance did not exceed microhybrid composites.

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