Dental Composites:
A Comprehensive Review

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Objectives

- Describe the basic physical properties of composites.
- Describe acid-etch bonding.
- Name the basic components of silicate cements.
- Name two fluxes and describe their uses.
- Describe the advantages and disadvantages of micro and macro-fillers.
- Explain thermal expansion coefficient.
- Explain depth of cure.
- Explain radiopacity.

Introduction

Dental Composites is a course that provides information about constituents in composite matrix, fillers, and restorations. The course describes physical properties of composites and various matrix and filler compositions and their uses. Bonding, etching, and various cement formulas are discussed as well. The course explains fluxes, resin-modified, and nano-filled and micro-filled composites. The advantages and disadvantages of various matrix and filler formulas are also explained paying attention to ease of use, appropriate applications, and wear resistance. Thermal expansion coefficients and mechanical properties of composites are described as well as their radiopacity and depth of cure specifications. Tables which provide dental professionals technical specifications of various composites are included in the course.

Martin S. Spiller, DMD

Martin Spiller graduated in 1978 from Tufts School of Dental Medicine. He is licensed in the state of Massachusetts and has been practicing general dentistry in Townsend, MA since 1984. Upon graduation from dental school, Dr. Spiller spent four years as an U.S. Army officer. During this time, he attended a dental general practice residency in which he received training in numerous dental specialties including oral surgery, endodontics, pedodontics, and orofacial surgical techniques and facial trauma. In 2000, he began work on a general dentistry website (www.doctorspiller.com). The intention at first was to educate the general public about dental procedures and the concepts behind them. Eventually, the website became popular with professional dental students. The content of the web pages began to reflect this readership. Dr. Spiller was asked to write this course based on academic study, hard won experience in the practice of dentistry, and his proven ability to write clear and concise content.
Dental Composites

A composite is any material that is composed of hard, pebble-like filler particles, similar to sand, surrounded by a hard matrix of a second material which binds the filler particles together. Filler particles can be of any coarseness varying from large rocks to microscopically fine powder and are made of particles of virtually any shape from spherical through fibers to flakes. The matrix material generally starts out as a paste, powder, or liquid and begins to harden when it is activated either by adding a catalyst, water, or other solvent. Before it hardens, the matrix can be pressed into a mold or stuffed into a hole.

The most commonly understood composite material is concrete, or "Portland cement". It is composed of sand, sometimes mixed with pebbles, and bound together by a matrix of lime, alumina, and iron. This material can be formed into bricks, poured into molds, or used to cement iron rods into the ground. Composites are an increasingly important part of everyday life from wooden particle board to Corian® countertops.

The images above show the microscopic structure of a typical composite material. The filler particles are the dark, irregular granules. The matrix is the lighter material that surrounds them. The composite in the picture on the left is not highly filled which means there is a lower density of filler particles compared to the amount of matrix material.

Compare that with the image on the right. This picture shows another composite material with differently shaped filler particles which are much more closely packed together. This is a highly filled composite. Because the characteristics and relative volumes of both the matrix materials and the various filler particles can be manipulated by the manufacturer of the composite, it is obvious that these materials show an almost infinite range of physical properties.

Physical Properties

The most common composite is made of an acrylic matrix called BIS-GMA mixed with a finely ground glass or quartz particle filler. The acrylic hardens with the addition of a catalyst similar to the way fiberglass hardens. In the case of light cured composites, the
catalyst is already mixed into the paste but does not become active until illuminated with strong light. To ensure bonding between the filler and matrix, the filler particles are coated with a silane coupling agent that contains a methacrylic group able to copolymerize with the matrix.

DEFINITION

Composite: made up of various parts or elements.
synonyms: compound, complex; combined, blended, mixed "a composite structure"

Dental amalgam is, by definition, a composite. It is made up of finely ground silver/tin metal powder mixed with mercury. The mercury dissolves the outside layers of the metal powder particles and forms a matrix of silver-tin-mercury. This mixture hardens around the unreacted metal powder particles and forms the finished amalgam composite.

Dental cements are all composite materials made from different powders mixed with different liquids. The liquid partially dissolves the powder particles and forms a matrix which becomes hard enough to act as glue. This matrix is used to cement crowns and posts. All nonmetallic, composite filling materials are more highly filled versions of their respective cements.

Porcelain is not generally thought of as a composite material. Porcelain is composed of a glass matrix filled with crystalline particles. Although ceramics are an extremely important part of dentistry, very few dental professionals really understand their chemical structure. For this reason, Dr. Spiller has written a Beginners Course in Dental Ceramics.

Bonding

The discussion of bonding below assumes that you understand the difference between enamel and dentin. These are marked on the illustration below. Restorations that are bonded stick to the tooth without the aid of undercuts or "lock and key" cementation. The four types of bonding used in dentistry today are discussed below.
Acid-Etch Enamel Conditioning

Acid-etch enamel conditioning was the first form of bonding used in dentistry. In this technique, a 10% solution of phosphoric acid is placed on the tooth enamel and left for 15 seconds. When it is washed off, the formerly shiny enamel surface now looks chalky or frosted. Under a microscope, the surface looks like a ragged landscape of jagged mountains and valleys (see micrograph below). These microscopic irregularities are filled with liquid acrylic plastic which hardens in place. Since the filling material is composed of the same plastic mixed with glass particles, it will bond onto the plastic.

Dentinal Bonding

The micrograph below shows what dentin looks like when it is sliced perpendicularly to the dentinal tubules. Tubule openings are clearly visible, but the hard material between them is still smooth and will not bond to liquid plastic as plastic bonds to etched enamel. Etching the dentin with 10% phosphoric acid does not create the same type of roughness in dentin that it does when etching enamel. Instead, the acid completely dissolves a small amount of the hard dentin material around the tubules. This allows the strands of collagen within the dentin to project beyond the cut surface and also partially opens up the tubules.
The first step to adhere a layer of resin to etched dentin requires placing a primer composed of 2-hydroxyethyl methacrylate (HEMA) on the tooth. HEMA is a hydrophilic polymer dissolved in acetone. Repeated applications of solvent evaporate water in the dentin and replace it with HEMA. Primer flows into the tubules and between exposed collagen fibers and acts as a bridge between hydrophilic collagen fibers and the layer of hydrophobic resin. The final layer of resin thoroughly fills the spaces in between the collagen fibers and tubules. Once the resin hardens, it serves as the basis for dentinal bonding.

Note that bonding composite to enamel and dentin always involves three steps.

1. Conditioning with acid.
2. Priming the dentin with HEMA.
3. Applying acrylic resin to the etched enamel and primed dentin.

A system that utilizes a separate conditioning step etching both dentin and enamel with phosphoric acid is called a total etch system.

Next generation bonding agents use a separate phosphoric acid conditioning step but combine HEMA and resin in a dilute mixture cut with acetone. Acetone is soluble in both water and hydrophobic materials such as plastic resin. The newest iteration of bonding agents combines all three steps: conditioning with acid, application of HEMA in solvent, and applying resin. These materials are called self-etching primer systems (SEPs).

**Chemical Adhesion**

Glass ionomer and polycarboxylate cements can be applied directly to unconditioned enamel and dentin without primer application. These cements are applied as a thick liquid or paste form. The liquid is fairly acidic. Metallic polyalkenoate salts combine with hydroxyapatite by replacing phosphate ions. The carboxylic groups in the polyalkenoic chains chelate with calcium in the hydroxyapatite and bond the cement to both dentin and enamel.
Amalgam Bonding

Bonding dental amalgam to a tooth involves any or all three steps described above. Enamel and dentin are conditioned with 10% phosphoric acid, HEMA is then applied to the dentin, and a layer of loosely filled resin is applied over the tooth structure. Dental amalgam is condensed into the tooth while the resin is still unset. Amalgam and filled resin intermingle at the interface, and when both materials set, they are mechanically locked together. The amalgam is locked to the resin, and the resin is bonded to the tooth.

How Fillings and Crowns Were Retained on Teeth Before Bonding

Prior to bonding technology, dental restorations had to be attached to teeth mechanically. Even though bonding technology is available, mechanical retention remains the most commonly used method to retain crowns and large fillings onto teeth. This is done by the use of undercuts placed inside the cavity. The filling material is condensed into the cavity preparation and flows into the undercuts. When hardened, the filling will not dislodge, because it is larger at the bottom of the hole than the top.

When placing a cast restoration such as a crown or an inlay, there can be no undercuts or the casting won’t seat. The vertical walls of the preparation are made nearly parallel with a slight taper. The space between the restoration and tooth is filled with waterproof cement such as zinc phosphate which hardens and locks the restoration onto or into the tooth. The cement flows into tiny imperfections in the sides of both the preparation and the restoration and acts as a lock and key to keep the restoration from sliding out or off the tooth.
Dental Cements

All dental cements and tooth-colored filling materials are made of combinations of only two different powders and four different liquids. The chemical combination of various powders and liquids create a material which begins as a paste and sets as hard cement. Most these materials are water soluble during the setting phase but become waterproof after they solidify.

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Alumino-Fluoro-Silicate Glass (Powder)

Silicate cement was the first tooth-colored filling material. Silicon dioxide is the naturally occurring mineral known as quartz and the chief component in sand and most glass formulations. The melting temperature of quartz is very high. Pure quartz melts at °1713 C. Adding metallic oxides lower the melting temperature of quartz to °793 C. Stabilizers make glass strong and water resistant. Calcium carbonate acts as a stabilizer. Without a stabilizer, water and humidity attack and dissolve glass. Glass lacking a stabilizer is often called "water glass", since it can dissolve in water.
When lead is used as the stabilizer, the resulting glass has superior clarity and durability and will ring like a bell when tapped. Lead crystal has been used for years in the manufacture of fine tableware including drinking glasses and wine canisters (Reference Waterford Crystal). Lead is insoluble even in acidic solutions and has never been implicated in any case of lead toxicity in humans.

The U.S. Food and Drug Administration has recommended that lead-stabilized glass not be used to store liquids, as small amounts of lead have been known to leach out of the glass and into the liquid. Lead is not used to flux or stabilize any dental glass manufactured in North America or Europe.

Silicate cement is made by mixing a powder of alumino-fluoro-silicate glass with 37% solution of phosphoric acid. Phosphoric acid partially dissolves the glass and chemically combines with it. This creates a very hard, brittle matrix. A fluid mixture of silicate cement can serve the same purpose as zinc phosphate cement. Silicate cement is mainly used as a tooth-colored filling material.

Because the matrix is very hard, its brittleness and lack of wear resistance limits its use as a restorative in stress-bearing areas. Until the advent of resin composites, silicates were the only tooth-colored filling material available and the only alternative to silver amalgam as a simple, permanent filling material.

The use of silicates was limited to front teeth or areas of decay on non stress-bearing surfaces of back teeth. Its greatest advantage other than color is that the fluoride from the glass tends to prevent decay around the filling margin. This is true of glass ionomer restorations as well.

A major problem with silicate cements as a restorative material is its appearance. Glass particles dislodge from the filling surface which leaves it rough and prone to staining. The brittleness of the matrix is esthetically difficult, because it causes crazing and marginal chipping.

- Alumino-fluoro-silicate glass is used to produce silicate and glass ionomer cement. It is stabilized with alumina. This glass is ground into a very fine powder. Alumino-fluoro-silicate glass is formulated to remain partially soluble in high acidic solutions. It is not soluble in saliva, food, or liquids that are eaten. Using zirconium and other components, glass can be fabricated to match various colors and opacities of teeth.
- Alumino-fluoro-silicate glass partially dissolves and forms a hard, waterproof matrix when mixed with phosphoric or polyacrylic acid. When the powder-to-liquid ratio is correct, a stiff paste results. The paste is used to fill cavities and will form a hard and insoluble solid.
A major characteristic of cements made with Al-Fi-Si glass is that they are translucent. Their color characteristics can be controlled by varying the glass composition. The restoration's hardness, durability, and appearance are dependent on the chemistry of the matrix formed when the glass particles begin to dissolve in acidic solution.

Two cements made with Al-Fi-Si glass particles are silicate and glass ionomer cements. The advantages of restorations and cements made with alumino-fluoro-silicate glass are:

- Alumino-fluoro-silicate glass cements and restorations bond chemically with enamel, dentin, and most metallic dental alloys. They can be directly applied to clean teeth without etching, bonding, or even cutting retentive undercuts. These materials also bond to metallic substructures such as gold and base metal crowns and bridges. Alumino-fluoro-silicate glass cements can be used to anchor esthetic facings made of resin composite to these structures.
- Alumino-fluoro-silicate glass cements release fluoride into adjacent teeth, converting hydroxyapatite into fluoroapatite, strengthening teeth.

The disadvantages of restorations and cements made from unmodified alumino-fluoro-silicate glass are:

- Materials are water soluble during the setting phase. If they get wet during placement, they leach out which allows the final restoration to leak.
- They are not resistant to abrasion so are not suitable as restorations on occlusal or stress-bearing areas.

Note: Resin composite fillings and cements are filled with glass particles, but the glass in these composites do not chemically react with the surrounding matrix and do not need the same formulation as the alumino-fluoro-silicate glass described here.

**Glass Ionomer (Polyalkenoate Cement)**

Glass ionomer cements and restoratives are fairly new composites. The mixture of polyacrylic acid with alumino-fluoro-silicate glass causes glass particles to partially dissolve. Polyacrylic acid chemically combines with dissolved glass components and produces a hard matrix material similar to silicate cement. This is an acid base reaction which results in the formation of metallic polyalkenoate salts that precipitate out and begin to gel until the cement sets.

The characteristics of this matrix material are strikingly different than the characteristics of the matrix found in silicate cements. Unlike silicates, the matrix in glass ionomer
cements is translucent which allows the glass particle color to dominate the esthetics. Also, glass ionomer cement is less brittle than silicate cement and less prone to fracturing.

Since the filler is glass, its esthetics can be precisely controlled. Restoration margins and surfaces made with glass ionomers are less prone to chipping and crazing, and there is less staining than with silicates. As a restorative, glass ionomers can be used in all esthetically sensitive areas. Of all composite restoratives, glass ionomers are some of the most esthetic restorations available.

These restorations not only look good, but they bond well to teeth. Bonding between the cement and tooth is achieved through ionic exchange at the interface. Polyalkenoate chains enter the enamel’s molecular surface and dentin and replace phosphate ions. Calcium ions are displaced equally with phosphate ions and maintain electrical equilibrium. This leads to the development of an ion-enriched layer of cement that is firmly attached to the tooth.

Glass ionomer restorations leach fluoride into adjacent teeth and reduce the likelihood of recurrent decay around margins. Glass ionomers are biocompatible. They are especially useful as bases under composite resins. They are gaining popularity as pulp-capping agents and as permanent dressings placed over minor perforations during endodontic procedures.

Glass ionomer is a great luting agent for cementing crowns and bridges with metal and ceramic substructures. It bonds directly with metal substructures and teeth. Its biocompatibility produces less post-operative sensitivity.

Glass ionomer cements and restoratives exhibit less polymerization shrinkage than any other resin-glass composites. They make excellent bases for use under composite restorations and maintain excellent marginal seals. Glass ionomers are not likely to debond from the pulpal floor while polymerizing.

Thermal expansion of conventional glass ionomer cements and restoratives is close to the thermal expansion of dentin and enamel. Thus, glass ionomer bases are less likely than conventional composites to debond from the pulpal floor during service.

However, the matrix material in glass ionomer cements is not as hard as the matrix of silicate cement, so glass ionomer restorations wear faster than silicates. Glass ionomers lack fracture resistance and are more brittle than resin-glass composites. They are excellent fillings on buccal surfaces of anterior teeth but should not be used to rebuild incisal edges of anterior teeth.

Glass ionomers are sensitive to water contamination during placement. Poor technique
shortens the restoration’s lifespan. Many dentists use glass ionomer mixed with acrylic resin known as resin-modified glass ionomer for cementing cast metal and zirconium-based restorations.

The extra time needed to mix and apply a glass ionomer base and allow it to set can be a deterrent to its use by some dentists.

**Zinc Oxide Powder**

Zinc oxide powder is plain, powdered ZnO. It is opaque and white-colored and has antiseptic properties. It is familiar to most mothers as diaper rash ointment. (Desitin)

**Phosphoric Acid**

Pure, anhydrous phosphoric acid is a white solid that melts at 42.35°C and forms a colorless, viscous liquid. It is water soluble. Anhydrous phosphoric acid used with the powders presented here is $37\% \text{H}_2\text{PO}_4 = \text{H}_3\text{PO}_4(\text{s}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-$

**Polyacrylic Acid**

Polyacrylic acid is an acrylic acid polymer. It is composed of chains of acrylic acid strung together like beads. Acrylic acid’s formula is CH$_2$=CHCH$_3$. It is a clear liquid and has a thick, syrupy consistency.

**Eugenol**

Eugenol is a clear to pale yellow oily liquid extracted from certain essential oils such as clove, nutmeg, cinnamon, basil, and bay leaf. It is the main constituent in clove oil. In dentistry, eugenol has been used for centuries, because it has anesthetic and antiseptic qualities. Today, it’s used on strips of iodoform gauze to treat dry sockets. When mixed with zinc oxide powder, eugenol creates ZOE, a temporary filling that is used in decayed teeth to reduce toothache.

**Zinc Phosphate Cement**

Zinc phosphate cement has been used for two hundred years. Zinc phosphate is still used for cementing cast metal crowns and onlays. It is made by mixing a strong solution (37%) of phosphoric acid with zinc oxide powder. Zinc oxide powder partially dissolves in acid which creates zinc phosphate. When dry, zinc phosphate cement becomes a very hard, waterproof matrix which bonds unreacted zinc oxide particles together.

Mixing and cementing with this material is something of an art; it must be mixed slowly. Once set, zinc phosphate cement is the most reliable and durable cements for luting cast metal crowns and onlays. Zinc phosphate is also used to cement posts in teeth and
was used as a base under amalgam fillings. A base is a layer of material placed under a filling to protect the nerve from hot and cold. Some bases can also be used to desensitize nerves.

Phosphoric acid in zinc oxide etches tooth enamel and creates an irregular surface. Cement flows into tooth irregularities and creates a tight, mechanical seal. Cement also flows into irregularities in the casting structure and forms a lock and key bond between the tooth and casting. Because new cements are quicker and easier to work with, zinc phosphate is not used as much today.

Note that zinc oxide is an opaque white powder. It can be manufactured in any color, but the set material remains perfectly opaque. It lacks wear resistance and is not esthetic or tough enough to be used as a tooth-colored filling restorative.

**Polycarboxylate Cement**

Polycarboxylate cement is made of zinc oxide powder mixed with polyacrylic acid. If the powder is freeze dried, it is mixed with distilled water. Zinc oxide dissolves and creates a matrix which eventually becomes waterproof. Though not as strong a cement as zinc phosphate, zinc oxide is much easier to work with, sets quickly, and is less irritating to tooth nerves. Zinc oxide remains opaque. Its color is not easily controlled. It is rarely used as a restorative filling material. Zinc oxide cement is somewhat technique-sensitive in that it must be kept dry until completely set.

**Zinc Oxide and Eugenol (ZOE)**

Zinc oxide mixed with eugenol (ZOE) is used as both a cement and restorative material. It is most frequently used as temporary cement or to cement stainless steel crowns onto deciduous teeth. When used as cement, it is valued for its sedative properties and its ability to temporarily lute ill-fitting crowns.

Zinc oxide mixed with eugenol is used as a temporary filling either by itself or in conjunction with acrylic powder (IRM). Temporaries are the least expensive way to fill a tooth and can be done quickly. The patient is anesthetized, the decay removed, and the temporary filling mixed and inserted simply by pushing it into the cavity preparation with a gloved finger. The patient bites into it while it is still soft to adjust the bite. In a phrase, a temporary is fast and cheap.

Zoe fillings are sedative fillings, which mean they tend to soothe inflamed dental pulp. They can make the difference between extracting a tooth or performing a root canal or only having to fill the tooth. Sometimes a sedative filling is the best course to relieve pain.
Temporary fillings are made of two components.

1. Eugenol, a component of clove oil.
2. Zinc oxide, an excellent disinfectant.

Oil and oxide mix together to form a stiff paste that hardens into a waterproof substance. This substance soothes the pulp and kills germs while protecting the cavity like a hard Band-aid. (ZOE) is not very durable. It wears away after just a few weeks but works to relieve pain, calm the nerve, and protect the tooth.

During the Vietnam war, the U.S Army invented a more durable form of ZOE called Intermediate Restorative Material (IRM) which is fortified with plastic powder. IRM is commonly used in dental offices for temporary fillings. IRMs last three to six months and sometimes even longer.

**Fluxes**

Fluxes are alkaline metal oxides such as sodium, potassium, lithium, boron, and lead. They dissolve silica. Pure quartz melts at °1713 C. The addition of 25 % sodium oxide lowers the melting temperature of quartz to °793 C. The most common fluxes used in ceramics are sodium and potassium oxides, but there are others each one with its own set of characteristics and uses.

**Boron Oxide**

Boron oxide is a glass former. When added to silicon-based glass at a minimum of 5% by weight, glass becomes a borosilicate. Glass fortified this way is resistant to mechanical and thermal shock and is used to make baking pans (Pyrex), lab ware, and sealed-beam headlights.

**Alumina**

Alumina (aluminum oxide) is found combined with silicon in naturally-occurring glasses called feldspars. It is used as a stabilizer to toughen glass. Alumina acts as a sort of framework or skeleton. This framework stiffens glass during firing and makes it less likely to slump. The inclusion of crystalline structures transforms glass into porcelain which is much tougher and less prone to fracture than glass without such a matrix. Alumina is in clay and nearly all ceramic products such as dinnerware and china. It is added to dental porcelain in the form of aluminum oxide.

Trace metals give glass color. Cobalt imparts a blue color; gold imparts red, and copper, green. These metals are added as oxides. They have fluxing qualities, but they are not alkaline metals. Cobalt, gold, and copper are added in such small amounts that they are not considered fluxes for purposes of calculating glass formulas.
Zirconium and titanium oxides add opacity to glass. They form a crystalline structure within otherwise translucent glass. This structure diffuses light and creates a milky or pure white appearance depending on the amount of zirconium or titanium oxide used.

**Melting Temperature vs. Solidus**

When glass melts, it becomes liquid with the consistency of syrup on a cold day. Glass does not have a specific melting temperature and when cooled remains a super-cooled liquid. While glass does not have a specific melting temperature, it does have a definite solidus temperature. Solidus is the lowest temperature at which a non-crystalline material shows any characteristics of melting including a tendency to flow.

**Resin-Glass Composites (Filled Resins)**

The most widely-used filling materials are resin reinforced composites. These restoratives are composed of:

- A powdered filler material (in this case, glass or quartz particles).
- A hard, plastic resin matrix which binds the particles together. The most frequently used plastic resin is an acrylic known as bisphenol which is a glycidyl methacrylate commonly referred to as BIS-GMA. This material is a viscous liquid until it is cured by the addition of a peroxide catalyst or by applying a light source.

The glass particles are premixed with the acrylic liquid into a paste. When the dentist is ready to place the restoration, he or she mixes a catalyst into the paste. This hardens the acrylic around the particles. The material resembles a refined version of fiberglass.

Alternatively, the catalyst may be premixed into the paste by the manufacturer but it will not be activated until the dentist shines light on it causing it to harden. This procedure is known as light curing.

**The Plastic Resins**

The earliest plastics were actually invented in the 19th century. They included vulcanized rubber (1837), gutta-percha (1843), shellac (The history of shellac goes back 3000 years. It was mixed with slate dust to make phonograph records until vinyl was perfected in 1949.), polystyrene (1839–today, known mainly for its use as Styrofoam), rayon (1884), and cellophane (1908).

Acrylic was first invented in 1931 but was unsuitable for use as dental restorations. The monomer polymerization into solid plastic caused a volumetric shrinkage of 25%. Later improvements, including the use of large molecules and particles of prepolymerized plastic, reduced shrinkage to workable dimensions.
Acrylic resin has two characteristics which make it unsuitable for use as a restorative material if used without glass filler particles. Within a year or two of placement, unfilled resin restorations wear catastrophically. Unfilled resin shrinks as much as 3% while setting. Without glass filler particles, resin shrinks away from cavity walls. This creates large spaces between the filling and tooth, and the filling leaks. If bonding techniques are used, unfilled resin causes intolerable shrinkage which stresses the tooth and draws the edges of the cavity preparation together causing fractures. The addition of substantial amounts of rigid glass filler prevents most of the shrinkage associated with acrylic resin.

All resins used in composite materials are made with methacrylate monomers. Early formulations used simple methylmethacrylate. Now most resins use dimethacrylates, because dimethacrylates contract less during setting and have cross-linked, three dimensional structures.

Two resins commonly used to formulate dental composite matrixes are:

1. Bis-GMA.
2. Urethane dimethacrylate.

A third resin, triethylene glycol dimethacrylate (TEGDMA) is a co-monomer used to control viscosity of Bis-GMA.

Other matrix components include initiators such as benzoyl peroxide (for chemical activation), camphoroquinone (for visible light activation), co-initiators, polymerization inhibitors (to extend working time and storage stability), and various pigments.

The setting contraction of Bis-GMA and urethane dimethacrylate is less than that of unfilled plain (methylmethacrylate) acrylic resins, because dimethacrylate monomer and co-monomer molecules are larger. Large monomer molecules affect three-dimensional polymer structures. Contraction values for Bis-GMA and urethane dimethacrylate are typically 1.5 to 3% compared to 6% for methylmethacrylate acrylic polymer resin. By itself, Bis-GMA has low shrinkage, but shrinkage is increased by the addition of TEGDMA diluents. Since urethane dimethacrylate resins do not require additional diluents, they have slightly lower shrinkage values than Bis-GMA formulations.

A third resin-system called silorane results from the reaction between oxirane and siloxane molecules. This resin-system shrinks less than Bis-GMA or urethane dimethacrylate systems. Silorane systems reduce shrinkage, because the oxirane ring opens during the polymerization process. Filtek™ LS (3M ESPE) is a silorane composite material. The disadvantage of silorane systems is that system specific bonding agents must be used to achieve the same bond strengths as are obtained
using standard systems.

**Glass Filler Particles**

The hard, plastic matrix in resin-glass composites do not depend on chemical reactions between acid and glass particles. The particles used in resin-based composites do not need to be soluble in acidic solutions. There is no inherent bond between glass particles and the surrounding matrix.

**Silane**

In order to increase filler particle retention in resin matrices, manufacturers coat them with a coupling agent. A common coupling agent is a silicone-containing molecule called methacrylopropyltrimethoxysilane. It has the following chemical formula:

\[
\text{CH}_2 = \text{CCH}_3\text{CO}_2(\text{CH}_2)_3\text{Si(OCH}_3)_3
\]

This molecule is part of a broad class of molecules called silanes. Silanes are double-sided molecules that have a silicone molecule in the center, one or more oxygen atoms on one side of the silicone, and an organic radical on the other side. The oxygenated silicone side adheres to glass particles, and the organic radical adheres to dimethacrylate resin, which strengthens the bond between glass and resin by creating a chemical and mechanical bond between them.

**Composition of Glass**

The fact that glass particles do not chemically react with matrix allows manufacturers much leeway when manufacturing glass powder. The manufacturer can flux and stabilize glass with materials that allow for better wear, workability, and esthetic qualities. Glass can be formulated to create unlimited variations in esthetics, and size and shape which define strength and wear characteristics.

However, because glass particles do not chemically react with matrix materials, fluoride cannot leach into nearby teeth. Resin composites do not bond to enamel unless the tooth is first acid-etched and layered with plastic bonding resin. Al-Fl-Si glass/acid mixtures chemically bond with teeth without the need for etching or special resin bonding agents.

Even without inherent bonding characteristics and fluoride release, the advantages of resin composites are great. By decoupling the chemical link between the glass filler particles and the surrounding matrix, the resulting flexibility creates developmental possibilities for manufacturers. The dental composite industry is currently working on a seventh generation of materials, and resin/glass composites have begun to replace silver amalgam as the inexpensive restoration of choice for back teeth.
Shape of Glass Particles

The trend in dentistry regarding dental composites is to achieve the greatest density of inorganic filler using the smallest particle size. The smallest particle sizes used in dental composites are .02-.04 microns (20 to 40 nanometers). They are fabricated in a furnace in which silicone tetrachloride is burned within an oxygen atmosphere. The particles are spherical.

Numerous manufacturers have fabricated different particle shape and size in order to reinforce composites but have not been successful. Studies that compared particle shape and size have shown composites containing small sized, spherical particles exhibit maximum mechanical strength and wear resistance. This is because spherical particles are easier to incorporate into resins and fill more space. These particles are difficult to dislodge from the restoration surface due to their small volume.

Manufacturers have tried many shapes, from spiny snowballs to long fibers, but none of have been successful for various reasons. Some shapes negatively impacted the working characteristics of the composite, some reduced the depth of cure, and none seemed to enhance the wear rate, polishability, or other surface characteristics of their respective composites.

Types of Resin Composites

Macro-filled composites were the first resin composites marketed in the 1960's to fill front teeth. Crystalline quartz was ground into a fine powder containing particles 1 to 50 microns (µM) in diameter. Particles larger than this are visible to the naked eye. Macro-filled composites contained no radiopaque materials which make it difficult to distinguish these composites from decay on x-rays.

Acrylic matrix shrinks on setting. Excessive shrinkage in a filling material is undesirable, because it leaves a gap between the tooth surface and material. If well bonded, cracks develop in the tooth when setting. Filling made from resin alone wears very rapidly. Inclusion of glass particles reduces these problems, because glass particles reduce acrylic volume and act as a skeletal structure within the composite. This helps maintain the filling's original volume when setting. Large numbers of particles can be incorporated into the paste without making it too stiff to manipulate. Macro-fills are 70% to 80% glass by weight and 60% to 65% by volume.

Due to large particle size, macro-fills are not very polishable. They feel rough and accumulate plaque and stain. Soft, acrylic polymer wears below glass particles, which come out of the tooth leaving holes in their place. This leads to a surface which microscopically looks like a series of craters interspersed with boulders. It is prone to staining. Wear is the major disadvantage of macro-filled composites. Loss of glass
particles exposes more and more of the soft plastic matrix to abrasive force, and the restoration wears away. However, large particles are able to be packed tightly into the resin matrix without the paste becoming too thick during handling. More glass in the mixture reduces shrinkage during setting.

A composite restoration wears exclusively, because glass particles dislodge from tooth surfaces leaving the matrix exposed. The less acrylic and more glass a composite contains the better. An ideal composite filling would contain only glass and no acrylic. This is impossible, since resin is needed to glue particles together. Resin also gives unpolymerized material handling characteristics that allow dentists to work with it. Because large glass particles dislodge from tooth surfaces, these restorations are unsuitable for posterior teeth. Occlusal surfaces of back teeth receive many abrasive challenges. A filling that wears excessively causes the bite to change.

**Hybrid Composites**

Hybrid composites contain various particle sizes, ranging from 1-3 microns (75%) to 0.02-0.04 microns (8%). Hybrid composites do not retain a high polish for long, because large particles pop out from tooth surfaces. However, hybrid composites are easy to work with and are resistant to wear. They include smaller and submicron-sized particles which are more difficult to dislodge than large particles.

Hybrid composites can be filled more densely with glass particles than composites containing only micro-sized particles. Large particles keep the paste consistency from becoming too stiff. Sub-micron sized particles take up space between large particles. The highest particle density attained with hybrids is 90% by weight. Because of high particle density, hybrids were the first composites promoted for posterior use, and they remain one of the most wear-resistant posterior composites on the market.

**Micro-Hybrids**

Micro-hybrids were the next step in hybrid evolution. They use up to three distinct particle sizes for more efficiency. They also include a small size range of large particles
(0.6 -0.7 microns). Micro-hybrids are more polishable but suffer from low particle density due to the small size of the largest particles in the mix. They also achieve superior color optics, because small filler particles fill in-between large particles and resin hardeners. This helps maintain a surface polish during prolonged use. Micro-hybrids have unique color-reflecting characteristics which give them a chameleon-like appearance. This makes them especially useful for anterior restorations. Micro-hybrids are not recommended for posterior fillings because of their low particle density. However, the micro-hybrid’s mechanical properties make them strong enough for rebuilding incisal edges on anterior teeth, and some are marketed for posterior use.

**Micro-filled and Nano-filled Composites**

Micro-fillers are particles smaller than 1 micron. Nano-fillers are particles smaller than 0.1 micron. Most older, micro-filled composites use particles that vary between .04 and .2 microns. Nano-filled composites are those that contain filler particles no larger than 0.1 micron. Nano-filled composites are a category of micro-filled composites. The smallest nano particles are formed by colloidal silica which is produced by burning silica compounds such as SiCl4 within an oxygen atmosphere forming spherical, macro-molecular structures.

**The Characteristics of Micro-Sized Particles**

A small particle has a greater surface area in relationship to its volume than a large particle. A cube has a surface area equal to the sum of the area of its six sides. If a cube is cut in half, the two pieces together have a total surface area equal to the original cube plus the area of the two new sides created when the original cube was cut. As you continue to cut it into smaller and smaller pieces, new surfaces are added to the original area of the cube. While the volume of the material you have is the same as the volume of the original cube, the surface area keeps expanding with each new segment created.

Because of added surface area, micro-sized particles are disadvantageous compared to macro-sized particles. Since friction is a function of involved surface area, increased surface area increases internal friction. More particles in the paste make the composite stiff. It becomes very difficult to manipulate. According to Phillips Science of Dental Materials, "Colloidal silica particles, because of their extremely small size, have extremely large surface areas ranging from 50 to 400 square meters per gram." Macro-filled composites are easier to handle than micros filled to the same density.

However, greater surface-to-volume ratios give micro-particles one advantage over macro-particles. Greater surface area, combined with smaller volume of micro-sized particles, makes micro-particles more difficult to dislodge from plastic matrix. Moreover, when a micro-sized particle does pop out, it leaves a smaller crater behind and is more resistant to wear.
Macro composites can be filled to a high degree without becoming too stiff to work with, have minimal shrinkage, have good mechanical properties, and are fine for anterior teeth, but they do not wear or polish well. They are unsuitable for posterior applications, because wear is a factor. However, micro-filled composites look great, resist shrinkage, and wear very well. Unfortunately, any composite that contains a high percentage of disbursed micro and nano-sized quartz particles is so stiff that it is impossible to handle.

Micro-filled composites are filled to a maximum of 38% by weight and 25% by volume. Even though the particles are tiny, low-density glass particles in the composite give them poor mechanical properties including poor flexural and yield and tensile strength. Low-fill density makes them wear almost as badly as the macros, so micro-filled composites are not suitable for posterior restorations. Even so, their superior esthetic qualities make them popular. They are used mostly to veneer over large particle-sized macro-filled or hybrid restorations in anterior teeth to make them more polishable.

Agglomerated Micro-filler (Prepolymerized Filler)

Manufacturers developed a solution to the low-particle density in micro-filled composite paste by prepolymerizing it before putting it into paste form. Prepolymerized composites can be fabricated to 80-90% by weight of nano-sized glass particles using industrial machines. After the compressed composite polymerizes, it can be milled into a powder with particle sizes between 10 and 20 microns. Composite powder, made of complex particles called agglomerated micro-filler, prepolymerized filler (PPF), or nano-clusters is mixed with resin to make composite paste. The final composite may contain between 70% to 80% glass particles by weight.

The composite is well-filled with nano-sized particles, yet is not difficult to place. The paste flows easily and has good wear characteristics due to the tiny size and high density of filler particles. The particle fill-density is 72%-77% which is about 61% to 64% by volume. Micro-fills (sometimes referred to as nano-fills) wear quite well and are suitable for restorations on occlusal surfaces of posterior teeth.

Even though agglomerated micro-fill particles are the same size as silica particles in older macro composites, they do not create the same handling characteristics found in traditional macro-fills. Each agglomerated particle is manufactured with the same plastic found in liquid resin. There is a great deal of resin between particles. This changes the flow characteristics of the paste which makes it more difficult to work with than macro-filled or micro-hybrid composites.

A major problem with micro-filled composites is that they tend to be sticky and slump. Their main advantage is their superior ability to resist wear and polish to a high shine. The viscosity of nano-composites can be adjusted by varying the size and density of the agglomerated nano-clusters. However, this does little to make the paste more viscous,
and adjusting the size and density of the particles only slows down the slumping. Micro-filled composites tend to be more opaque than other forms of resin-glass composites. They are less attractive for anterior buildups in spite of their inherent strength.

**Nano-hybrid Composites**

Nano-hybrid composites are the newest addition to the pantheon of composite filling materials. They are becoming popular, because they have superior esthetic and wear characteristics, high polishability, and superior handling characteristics. They are marketed as universal composites. Their handling and esthetic qualities make them suitable for anterior buildups, while their agglomerated nano-clusters interspersed with micro-sized particles give them acceptable wear characteristics.

The compressive and diametral strengths and fracture resistance of the nano-hybrid composites are equivalent to or higher than those of other composites such as hybrids, micro-hybrids, and micro-fills. Nano-hybrid composites are mechanically at least as good as universal hybrids and are suitable for posterior applications.

These composites have three types of filler particles.

1. Prepolymerized, finely milled, agglomerated nano-clusters.
2. Larger, submicron-sized glass or silica particles in the range of 0.4 micron.
3. Individual nano-sized particles, approximately .05 micron.

Large, agglomerated nano-clusters supply the composite with densely packed, nano-sized particles giving the composite a wear-resistant surface. They keep the composite paste fluid and easy to work with. Micro-sized particles fill in the spaces between large agglomerated particles. Plain, agglomerated nano-fills are sticky and tend to slump. Nano-hybrids use smaller, intervening particles which give the paste handling and esthetic characteristics making them acceptable for anterior and posterior restorations. These composites have the wear characteristics of tiny-sized particles in the agglomerated nano-clusters and the working characteristics and esthetics similar to micro-hybrids.

**Flowable Composites**

Flowable composite’s particle sizes range between 1 and 2 microns. Filler is reduced by 50% by weight, and unfilled resin matrix material is increased. New brands are dilute forms of nano-filled and nano-hybrid composites with varying filler densities to keep the mix flowable. Some brands contain Al-FI-Si glass particles and release fluoride into adjacent teeth. Flowable composites are delivered via syringe.

Flowable composites flow freely over the inside surfaces of cavity preparations. This material has made it possible to fill small cavities on occlusal surfaces without
anesthesia, since decay areas are often removable with little or no sensation in the tooth. Flowable composites will bond even if there are no undercuts in the cavity preparation and are often used to seal the dentin prior to placing filling material. Due to low levels of filler particles, flowable composites are prone to shrinkage and wear. They are not used to fill large cavities.

**Resin Composite Cements**

When formulated with a separate catalyst manually mixed into the base at time of use, filled resins make remarkably strong cements for crowns, veneers, onlays, posts, Maryland bridges, orthodontic brackets, and other bonded appliances. Since both porcelain and teeth can be etched with acids, resin can flow into microscopic irregularities in appliances to be cemented as well as irregularities etched into the tooth. The etched bond is strong, and filler particles add a second lock and key mechanism to cementing the appliance.

**Composite Characteristics**

**The Criteria Dentists Use to Evaluate Composites**

The ability to retain a high polish has become a selling point for modern composites. As more dentists switch from amalgam to posterior composites, they discover the ability to retain a high polish is far down the list of properties they desire in composites. Most dentists spend little time polishing composite restorations but prefer to finish them with a fine diamond or carbide bur. New composites are made with micron-sized glass particles. Dentists compare composite properties on the following characteristics.

- The ability to minimize polymerization volumetric contraction. The unfilled resin matrix of all composites shrinks as much as 3% during setting. The higher the volume of inorganic filler, the lower the shrinkage. Micro-hybrids and nano-hybrids have the highest percentage of inorganic filler particles and the lowest percentage of polymerization shrinkage. Values of contraction for Bis-GMA and urethane dimethacrylate are typically 1.5 to 3%. By itself, Bis-GMA has low shrinkage but shrinkage is increased by TEGDMA diluents. Since urethane dimethacrylate resins do not require the addition of diluents, they have slightly lower shrinkage values than Bis-GMA formulations.

The defects produced by polymerization contraction are the following:

- Open margins and white lines around margins.
- De-bonding and open margins.
- Enamel cracking, especially when using strong bonding agents and acid-etching techniques.
• Cuspal deflection, especially in well bonded restorations.
• Marginal staining.
• Secondary caries, especially in patients using a lot of sugar.

Note that micro leakage is less dependent on the degree of shrinkage than on the effectiveness of the bonding technique. Studies show that the degree of micro leakage varies from bonding agent to bonding agent but not because of the composite restorative used.

Post-Op Sensitivity

Post-op sensitivity is due both to cuspal deflection and the tendency of composites to shrink toward the light source. This results in the composite de-bonding from the pulpal floor and often leads to a small space through which water may enter by way of leakage or by drawing fluid from open dentinal tubules. This micro layer of water between the pulpal floor and the restoration accounts for much of the temperature and pressure sensitivity a patient experiences after a large cavity is bulk-filled with composite.

Glass ionomer is often used as a base under composite restorations. It is less prone to polymerization shrinkage than composite and bonds well to the floor and walls of a cavity preparation.

Note: Most resin-modified glass ionomers have nearly the same polymerization contraction as resin-glass composites and offer little benefit as bases under composite restorations.

Dentists may avoid post-op sensitivity without using a glass ionomer base by using this simple technique.

1. Etch all surfaces. Place and cure bonding agent(s).
2. Dry off any excess water with air.
3. Place sufficient flowable composite into prep and using a disposable brush, brush the unset flowable material over the enamel, dentinal surfaces, and preparation until a very thin layer covers all parts of the prep. Cure this layer.
4. Place additional thin puddles a fraction of a millimeter thick of flowable composite onto the pulpal floor, and especially into deeper areas of the prep. Cure this layer.
5. Fill the preparation in steps placing bulk composite against the vertical walls of the prep and then backfilling the central areas.

Even with greater polymerization shrinkage seen in flowable composites, thin layers used in this technique reduce stress on the pulpal floor to negligible levels.
According to Clinicians Report March 2019, Vol. 3, Issue 3, the measured shrinkage (measured after five minutes of light curing) of the twelve most popular nano-hybrid composite restoratives varies between 0.9% and 2.8%, while the shrinkage of the nine most popular flowable nanos varies between 3.0% and 6.0%.

The following two tables list actual shrinkage percentages of selected posterior composite restoratives and flowables. (Clinicians Report, March 2019, Vol. 3, Issue 3)

<table>
<thead>
<tr>
<th>Composite restorative</th>
<th>Type</th>
<th>Shrinkage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek LS</td>
<td>Nano-hybrid</td>
<td>0.9</td>
</tr>
<tr>
<td>Reflexions XLS</td>
<td>Nano-hybrid</td>
<td>1.5</td>
</tr>
<tr>
<td>Grandio</td>
<td>Nano-hybrid</td>
<td>1.6</td>
</tr>
<tr>
<td>Kalore</td>
<td>Nano-hybrid</td>
<td>1.8</td>
</tr>
<tr>
<td>Estelite Sigma Quick</td>
<td>Nano-hybrid</td>
<td>1.9</td>
</tr>
<tr>
<td>Heliotmolar</td>
<td>Micro-fill</td>
<td>1.9</td>
</tr>
<tr>
<td>Tetric EvoCream</td>
<td>Nano-hybrid</td>
<td>1.9</td>
</tr>
<tr>
<td>Venus Diamond</td>
<td>Nano-hybrid</td>
<td>2.1</td>
</tr>
<tr>
<td>Filtek Supreme Plus</td>
<td>Nano-hybrid</td>
<td>2.4</td>
</tr>
<tr>
<td>N’Durance</td>
<td>Nano-hybrid</td>
<td>2.4</td>
</tr>
<tr>
<td>Herculite Ultra</td>
<td>Nano-hybrid</td>
<td>2.8</td>
</tr>
<tr>
<td>Esthet X HD</td>
<td>Nano-hybrid</td>
<td>2.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flowable composite</th>
<th>Shrinkage %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surefil SDR Flow</td>
<td>3.0</td>
</tr>
<tr>
<td>Clearfill Magesty Flow</td>
<td>3.1</td>
</tr>
<tr>
<td>Grandio Flow</td>
<td>3.1</td>
</tr>
<tr>
<td>Filtek Supreme Plus Flow</td>
<td>3.8</td>
</tr>
<tr>
<td>N’Durance Dimer Flow</td>
<td>4.1</td>
</tr>
<tr>
<td>Tetric EvoFlo</td>
<td>4.3</td>
</tr>
<tr>
<td>Gradia Direct Flo</td>
<td>4.4</td>
</tr>
<tr>
<td>Aelitelflo LV</td>
<td>4.8</td>
</tr>
<tr>
<td>Fusio</td>
<td>6.0</td>
</tr>
</tbody>
</table>

The following table lists the Maximum Polymerization Shrinkage stress for eleven popular nano-hybrid and micro-fill composite restoratives. (All shade A3, stress values approximate. Lower values are better.)

<table>
<thead>
<tr>
<th>Restorative</th>
<th>Type</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aelite LS Posterior</td>
<td>Hybrid</td>
<td>1.7</td>
</tr>
<tr>
<td>Durafill VS</td>
<td>Micro-fill</td>
<td>1.2</td>
</tr>
<tr>
<td>Esthet-x</td>
<td>Nano-hybrid</td>
<td>2.6</td>
</tr>
<tr>
<td>Filtek Supreme Plus</td>
<td>Nano-hybrid</td>
<td>2.5</td>
</tr>
<tr>
<td>Gradia Direct Posterior</td>
<td>Micro-fill</td>
<td>1.5</td>
</tr>
<tr>
<td>Grandio</td>
<td>Nano-hybrid</td>
<td>2.4</td>
</tr>
<tr>
<td>Restorative</td>
<td>Type</td>
<td>Depth of cure (MM)</td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Aelite LS Posterior</td>
<td>Hybrid</td>
<td>1.5</td>
</tr>
<tr>
<td>Durafill VS</td>
<td>Micro-fill</td>
<td>2.5</td>
</tr>
<tr>
<td>Esthet-x</td>
<td>Nano-hybrid</td>
<td>2.4</td>
</tr>
<tr>
<td>Filtek Supreme Plus</td>
<td>Nano-hybrid</td>
<td>2.9</td>
</tr>
<tr>
<td>Gradia Direct Posterior</td>
<td>Micro-fill</td>
<td>2.5</td>
</tr>
<tr>
<td>Grandio</td>
<td>Nano-hybrid</td>
<td>3.1</td>
</tr>
<tr>
<td>Heliomolar</td>
<td>Micro-fill</td>
<td>1.9</td>
</tr>
<tr>
<td>Heliomolar HB</td>
<td>Micro-fill</td>
<td>1.7</td>
</tr>
<tr>
<td>Herculite XRV</td>
<td>Micro-hybrid</td>
<td>2.7</td>
</tr>
<tr>
<td>Heraeus Venus</td>
<td>Nano-hybrid</td>
<td>2.5</td>
</tr>
<tr>
<td>Z100</td>
<td>Hybrid</td>
<td>2.5</td>
</tr>
</tbody>
</table>

According to the Tables on this page were composed from the ADA Professional Product Review, Spring 2019, Vol. 5, Issue 2.

**Depth of Cure**

Depth of cure is extremely important, since it affects the length of time it takes to finish a large restoration. It also affects the restoration’s long-term properties, since all mechanical and thermal properties are degraded when composites fail to reach a minimum of 80% of ideal cure hardness.

The depth of cure depends on several factors:

- The opacity of filler particles.
- The density of filler particles.
- The shade of the composite, darker shades having less depth of cure than lighter shades.

According to Clinicians Report, March 2010, Vol. 3, Issue 3, the depth of cure of micro and nano composites varies widely, between 1.9 mm and 4 mm. The following table lists total depth of cure for eleven most popular nano-hybrid and micro-fill (nano-fill) composite restoratives. (All shade A3, depth of cure values approximate. Higher values are better.)
Workability

Dentists want a composite that is not too sticky. They want a composite that sticks to the tooth but not their instruments! If the composite is too sticky, it is difficult to be certain it will not pull away from the walls or floor of the cavity preparation when the packing instrument is removed. Dentists want a composite restorative that flows easily enough to form a shaped bulk that does not slump especially on anterior teeth.

Dentists also want a composite with the maximum depth of cure. Dentists that begin using composites based on other criteria may soon discover the length of time it takes to place some composites is too great because of the number of increments they need to use, especially for darker or more opaque shades. The best composites for these qualities are probably the macro-fills followed (in approximate order) by the hybrids, the micro-hybrids and the nano-hybrids. Nano-fills (also called micro-fills) tend to be too sticky and slump more than the others.

The Ability to Resist Wear

When it comes to wear resistance, the only thing that matters is the filler-particle density and the size of the particles. The more densely packed, the less the wear, and the smaller the particle size, the better. Hybrids do well in terms of density but not so with particle size. Recently developed hybrids resist wear well, because they are highly filled. Hybrids are some of the most wear-resistant composites sold.

Agglomerated nano-fills (micro-fills) do better with respect to particle size but less well with respect to particle density. They exhibit poor working characteristics and shallow depth of cure, but they have the best wear characteristics compared to any other composite category. Nano-fills are more prone to fracture than other types of composites. Nano-hybrids are 75% to 82% filled by weight and contain agglomerated nano-fill particles interspersed with micro and nano-sized individual particles. They have good working characteristics and wear resistance. Nano-hybrids also cure to a greater depth than the agglomerated nano-fills and are less prone to fracture in unsupported areas.

For occlusal restorations, amalgam beats all composites hands down. A well placed, posterior amalgam can last 20 or 30 years with minimal wear. Amalgam is not superior in other respects when compared to a properly placed posterior composite restoration. Amalgam’s superior wear characteristics mask its deficiencies such as marginal leakage and occult areas of recurrent caries.
Thermal Expansion Coefficients

Matching thermal expansion coefficients between restoration and tooth is a desirable quality. Teeth and restorations expand and contract at different rates when patients eat or drink hot and cold foods. The larger the mismatch between the thermal expansion coefficient, the greater the likelihood of fluid percolation down the margins. Leakage may result in marginal staining or caries.

If the bond between tooth and restoration is strong, the constant expansion and contraction of the restoration places stress on the tooth and will crack the enamel causing sensitivity to hot and cold. The only way to reduce a composite’s thermal expansion coefficient is to increase the filler particle density. The highest density of filler particle in the hybrids is 90% by weight.

No composite can match dentin’s coefficient of thermal expansion, since its coefficient of thermal expansion is 9 ppm/°C. The coefficient of the most highly filled nano-hybrid composites is approximately 30 ppm/°C. Agglomerated nano-fill’s coefficient of thermal expansion is 60 ppm/°C. Dental amalgam is rated at 25 ppm/°C, and unfilled acrylic rates at 90 ppm/°C.

Mechanical Properties of Dental Composites

Other mechanical properties of dental composites are related to filler particle density in the mix. The higher the density, the better the composite’s properties. The following table lists the flexural strength for eleven of the most popular nano-hybrid and micro-fill composite restoratives. (All shade A3, strength values approximate. Flexural strength measures the ability to resist fracture when subjected to bending. It predicts a restoration’s ability to resist occlusal load without cracking. Higher values are better.)

<table>
<thead>
<tr>
<th>Restorative</th>
<th>Type</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aelite LS Posterior</td>
<td>Hybrid</td>
<td>130</td>
</tr>
<tr>
<td>Durafill VS</td>
<td>Micro-fill</td>
<td>76</td>
</tr>
<tr>
<td>Esthet-x</td>
<td>Nano-hybrid</td>
<td>140</td>
</tr>
<tr>
<td>Filtek Supreme Plus</td>
<td>Nano-hybrid</td>
<td>120</td>
</tr>
<tr>
<td>Gradia Direct Posterior</td>
<td>Micro-fill</td>
<td>85</td>
</tr>
<tr>
<td>Grandio</td>
<td>Nano-hybrid</td>
<td>130</td>
</tr>
<tr>
<td>Heliomolar</td>
<td>Micro-fill</td>
<td>110</td>
</tr>
<tr>
<td>Heliomolar HB</td>
<td>Micro-fill</td>
<td>80</td>
</tr>
<tr>
<td>Herculite XRV</td>
<td>Micro-hybrid</td>
<td>140</td>
</tr>
<tr>
<td>Heraeus Venus</td>
<td>Nano-hybrid</td>
<td>125</td>
</tr>
<tr>
<td>Z100</td>
<td>Hybrid</td>
<td>195</td>
</tr>
</tbody>
</table>
The following table lists the fracture toughness for eleven of the most popular nano-hybrid and micro-filled composite restoratives. (All shade A3, toughness values approximate. Fracture toughness measures the ability to resist crack propagation. Higher values are better.)

<table>
<thead>
<tr>
<th>Restorative</th>
<th>Type</th>
<th>MPa-m0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aelite LS Posterior</td>
<td>Hybrid</td>
<td>1.1</td>
</tr>
<tr>
<td>Durafill VS</td>
<td>Micro-fill</td>
<td>0.7</td>
</tr>
<tr>
<td>Esthet-x</td>
<td>Nano-hybrid</td>
<td>1.1</td>
</tr>
<tr>
<td>Filtek Supreme Plus</td>
<td>Micro-fill</td>
<td>1.1</td>
</tr>
<tr>
<td>Gradia Direct Posterior</td>
<td>Micro-fill</td>
<td>.95</td>
</tr>
<tr>
<td>Grandio</td>
<td>Nano-hybrid</td>
<td>1.45</td>
</tr>
<tr>
<td>Heliomolar</td>
<td>Micro-fill</td>
<td>.85</td>
</tr>
<tr>
<td>Heliomolar HB</td>
<td>Micro-fill</td>
<td>.83</td>
</tr>
<tr>
<td>Herculite XRV</td>
<td>Micro-hybrid</td>
<td>.84</td>
</tr>
<tr>
<td>Heraeus Venus</td>
<td>Nano-hybrid</td>
<td>1.15</td>
</tr>
<tr>
<td>Z100</td>
<td>Hybrid</td>
<td>1.16</td>
</tr>
</tbody>
</table>

**Resin-Modified Glass Ionomers (Glass Ionomer Containing Restoratives)**

Resin-modified glass ionomers are glass ionomer cements and restoratives that contain 20% polymerizable resin component. These materials have most advantages of glass ionomer materials with the added advantage of water insolubility. Resin-modified glass ionomers are dispensed as two-component systems and begin hardening only when both components are mixed together. The resins included in some systems have dual-curing capability. They will cure chemically once the pastes are mixed, but curing can be accelerated by use of high intensity light. The ability to light-cure the excess material reduces chair time.

Resin modified glass ionomers appear to have advantages of both glass ionomers and resin-based composites.

- Command set on application of visible light. The resin sets immediately, but the glass ionomer component sets much more slowly. It may take as much as 40 hours to fully set.
- Good adaptation and adhesion.
- Acceptable fluoride release.
- Aesthetics similar to those of composites.
- Superior strength characteristics when compared with standard glass ionomer restoratives but inferior when compared with resin-glass restoratives.
- Chemically adhere to enamel and dentin without acid-etching or bonding agents.
• Chemically adhere to metal and tooth structure.
• Are biocompatible as glass ionomer and often work well as pulp-capping agents or sealants for minor root and furcation perforations during endodontics.

Resin modified glass ionomers have the following drawbacks.

• Their setting shrinkage is not much less than that of resin-glass restoratives which makes them inferior to regular glass ionomers when used as bases under composite or amalgam fillings.
• They have a limited depth of cure compared with resin-glass restoratives. They are manufactured as chemical-cure or dual-cure materials.
• They are not recommended for restoration in stress-bearing areas of adult teeth, since they wear much faster than resin-glass restorations.
• They are not recommended for cementing all porcelain crowns or veneers.

**Resin-Modified Glass Ionomer Cements**

Resin-modified glass ionomers have become the standard material used to cement metal and ceramic crowns and bridges onto prepared teeth. Some resin-modified glass ionomer cements have dual-cure capability meaning they will set chemically under a restoration, but setting can be accelerated by using a curing light.

Resin-modified glass ionomers have many of the advantages of glass ionomer cements. They adhere to tooth structure without bonding, are good esthetically, release fluoride, and they also have resin’s ability to rapidly harden using visible light. Resin-modified glass ionomer cements reduce post-operative sensitivity and utilize resin’s water resistance to reduce the likelihood of cement washout. Resin-modified glass ionomers bond to slightly wet teeth and chemically bond to the metal inside a PFM crown which makes them effective crown and bridge cements.

Resin-modified glass ionomers exhibit less shrinkage on setting than resin-based composites. They are also easy to use and simple to mix. Resin-modified glass ionomer cements are not indicated for cementing all porcelain crowns or veneers. Resin-only cements are used for this purpose. Resin-modified glass ionomer cements are not as strong as resin-only cements, but the bond is still more than sufficient to lute metal or zirconium crowns and bridges.

**Resin-Modified Glass Ionomer Restoratives**

Resin-modified glass ionomer restoratives do not resist occlusal wear well, but they have become the filling material of choice for deciduous teeth. Since they bond chemically to metal, resin-modified glass ionomers can be used to repair broken
porcelain over metal substructure. They can even be used to place tooth-colored veneers over gold crowns.

Resin-modified glass ionomers are more biocompatible than composites. They are becoming popular as pulp-capping agents and release fluoride. They are especially useful for filling cavities around the gum line. They leach fluoride into the tooth so reduce the likelihood of recurrent decay. Because of continual release of fluoride ions, resin-modified glass ionomers are also useful in geriatric dentistry as these patients are prone to recurrent caries due to xerostomia.

**The Compomers (Polyacid-Modified Resin Composites)**

A compomer is a modified composite resin. These materials have two main constituents.

1. A resin modified with dimethacrylate monomer(s) with two carboxylic groups present in their structure.
2. A filler that is similar to the alumino-fluoro-silicate present in glass ionomer cements. The filler particles are only partially silanated to help resin adhere to glass particles. They allow soluble fluoride in the glass to leach out into the tooth.

When first marketed, it was claimed that carboxylic groups in resin would adhere to teeth without using the acid-etch bonding technique similar to glass ionomer cements. This turned out to be false. Even so, compomers are still popular for filling deciduous teeth, and due to their high degree of translucency are highly esthetic when used for the repair of cervical (gum line) caries. Compomers release fluoride into the tooth, although less than the fluoride released from glass ionomer and resin modified glass ionomer restoratives. Compomers prevent recurrent decay while allaying parents' concern about the presence of mercury in standard amalgam fillings.

Compomers do not have the surface durability of standard composite resins, but will wear quite well for the life of a deciduous tooth. Unlike glass ionomer and resin-modified glass ionomer restorations, they do not adhere to tooth structure without using an acid-etch bonding technique. They are esthetically pleasing and seem to resist recurrent decay for several months after placement when used to fill cavities near the gum line.

**Paste Compomer Restorative Filling Material**

Paste compomer restorative filling materials are excellent tooth-colored filling materials and can be used on front teeth in non stress-bearing areas such as at the gum line. They may be used in larger restorations if they are fully supported by natural tooth structures and do not involve incisal or occlusal surfaces. They are especially good on
the buccal or labial surfaces of teeth. They are often used to cover exposed, sensitive root structures on both anterior and posterior teeth.

Paste compomer restorative filling materials are less wear-resistant than regular composites. Some dentists use light-activated compomers to fill deciduous teeth because of their extended fluoride release and also to allay parents’ fears about the mercury in amalgam fillings. Deciduous teeth generally exfoliate before wear becomes a problem. Compomers are also useful in geriatric dentistry. The combination of poor oral hygiene and dry mouth causes rampant decay in geriatric patients, and fluoride release at the tooth/restorative junction can be helpful to prevent recurrent decay. They have a limited shelf life.

**Flowable Compomer**

Flowable comomers are like paste compomer restoratives, but they contain much more unfilled resin. They are used in the same fashion as flowable composites except are rarely used in stress-bearing areas such as occlusal surfaces of adult teeth.

**Radiopacity of Dental Materials**

X-rays are an essential part of dental diagnosis, and it is important that any material remaining implanted in any part of a patient’s body, including his teeth, be radiographically distinguishable from natural structures or disease processes. Materials such as amalgam, gold, and titanium are made of metal and are naturally radiopaque.

Restorative composites, porcelain, or various dental cements are not inherently radiopaque and without modification of their composition would not be visible on x-ray films. Tooth decay shows up as a dark area on x-rays. In the early days of composite technology before the addition of radiopacifiers, it was often difficult to distinguish between a composite filling and an area of decay. The addition of zirconium dioxide, barium oxide, or ytterbium oxide to any radiolucent material imparts radiopacity. These three oxides are chosen for their compatibility with composite chemistry.

The addition of radiopacifiers is important in the production of dental cements used to lute crowns and bridges. Even though the cement spends its lifetime under a crown, excess cement will be forced out from between the crown and the tooth during placement and often end up between the teeth or under the gums where it cannot be directly seen.

When this happens, cement can cause gum inflammation and tooth loss. X-rays will reveal presence of cement. As a clinician, it is important to remember bonding agents are not generally radiopaque, and thick layers especially at internal prep-line angles may yield dark lines around composites on x-rays. These dark lines can mimic decay,
and many perfectly adequate composite restorations have been replaced needlessly for this reason.

**Recent Study: 1 year clinical follow up in comparing 2 types of composite resins**

In the April 2014 Tanta Dental Journal, researchers R.M.Attia, W.M.Etman and T.M.Genaid, collaborated efforts to compare silorane-based composites to methacrylate-based composites, one year after placement. “Regarding the clinical performance of the tested materials there was no statistical significant difference among the different recall periods in all the tested criteria in both materials and no statistical significant difference between group I versus group II at all follow up periods (P > 0.05). In addition Kappa test revealed a statistical agreement between marginal discoloration as well as color match and both marginal integrity and surface roughness (P < 0.05).”

Concluding then, “1-The clinical performance of silorane based composite (Filtek P90) was deemed acceptable after one year; with no obvious advantage compared to methacrylate based composite. 2-The low shrinkage associated with (Filtek P90) may not be a determinant factor for its high clinical performance.” (Tanta Dental Journal, 2014)

**Conclusion**

Use of composites in dentistry is an example of the evolution of technology in the best sense. So much has been learned and applied in both the many differences of composition of various composites, as well as, in the advancing of the chemical make-up to produce more ideal composites, combining only the most desirable components. Composites are stronger and more durable than ever, while still being superior aesthetically! Dental professionals are now able to produce sophisticated restorations, bonding elements, and effective cementation based on patient needs. By understanding the chemical and physical nature of composites, the clinician can choose appropriate materials, manipulate them properly, and produce a high quality product for the patient’s dental needs.

**References**


Spiller, Martin: http://www.doctorspiller.com/Composites/dental_materials.htm
Retrieved September 2011 with permission from the author.
Course Test: Dental Composites: A Comprehensive Review

1. Composites are composed of fillers and matrix.
   a. True
   b. False

2. The most common composite is made of an acrylic matrix called:
   a. Glass ionomer.
   b. Resin modified glass ionomer.
   c. BIS-GMA.
   d. Silane.

3. The first form of bonding used in dentistry was:
   a. Dentinal bonding.
   b. Phosphoric acid conditioning.
   c. Acid-etch enamel conditioning.
   d. All of the above.

4. Glass ionomer and polycarboxylate cements may be applied directly to unconditioned enamel and dentin without conditioning or primer application.
   a. True
   b. False

5. Mechanical retention remains the most commonly used method to retain crowns and large fillings onto teeth. This is done by:
   a. Acid-etch enamel conditioning.
   b. Undercuts inside the cavity.
   c. Phosphoric acid conditioning.
   d. None of the above.

6. All dental cements and tooth-colored filling materials are made of combinations of only two different powders and four different liquids.
   a. True
   b. False
7. Stabilizers make glass strong and water resistant. One type of stabilizer is called:
   a. Eugenol.
   b. Phosphoric acid.
   c. Calcium carbonate.
   d. Polyacrylic acid.

8. Glass particles in silicate cements are prone to dislodge from filling surfaces.
   a. True
   b. False

9. Alumino-fluoro-silicate glass is stabilized with:
   a. Alumina.
   b. Boron oxide.
   c. Eugenol.
   d. ZOE.

10. Margins and surfaces made with glass ionomers are less prone to chipping and crazing than materials used in other restorations.
    a. True
    b. False

11. Glass ionomer bases are less likely to debond from the pulpal floor during service than conventional composites. This is because:
    a. Micro sized particles are advantageous compared to macro sized particles.
    b. Thermal expansion of glass ionomer cements is close to that of dentin and enamel.
    c. They are made with resin.
    d. None of the above.

12. Glass ionomers are very sensitive to water contamination during placement.
    a. True
    b. False

13. An example of a zinc oxide powder is:
    a. Glass ionomer cement.
    b. Resin composite cement.
    c. Silicate cement.
    d. ZOE.
14. Zirconium and titanium oxides add color to glass.
   a. True.
   b. False.

15. Trace metals add opacity to glass.
   a. True
   b. False

16. Acrylic resin has two characteristics which make it unsuitable as a restorative material if used by itself without glass filler particles.
   a. Gaps between the restoration and tooth.
   b. Difficulty of use.
   c. Premature wear.
   d. A and C.

17. Two resins most commonly used to formulate dental composite matrixes are BisGma and urethane dimethacrylate.
   a. True
   b. False

18. Fluxes are used to:
   a. Lower the melting temperature of quartz.
   b. Prevent crazing.
   c. Dissolve silica.
   d. A and C.

19. Large glass particles in cements:
   a. Make cements easier to work with.
   b. Reduce shrinkage in the filling while setting.
   c. Are not polishable.
   d. All of the above.

20. Hybrid composites can be filled more densely with glass particles than composites containing only micro sized particles.
   a. True
   b. False
21. Increased surface area of micro particles increases internal friction.
   a. True
   b. False

22. The depth of cure depends on several factors:
   a. The opacity of filler particles.
   b. The density of filler particles.
   c. The shade of the composite, darker shades having less depth of cure than lighter shades.
   d. All of the above.

23. Compomers have two main constituents. They are:
   a. A resin modified with dimethacrylate monomers with two carboxylic groups present in their structure and a filler that is similar to alumino-fluoro-silicate present in glass ionomer cements.
   b. A thermal expansion of 9 ppm/°C and glass ionomers.
   c. A and B.
   d. None of the above.

24. It is desirable for composites and cements to have similar thermal expansion coefficients as does enamel.
   a. True
   b. False

25. Restorative composites, porcelain, or various dental cements are not inherently radiopaque
   a. True
   b. False