

## Recent Development in Composite Resins

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### Abstract

The esthetic quality of a restoration may be as important to the mental health of the patient as the biological and technical qualities of the restoration are to his/her physical or dental health, thus stressing the importance of esthetics. The research in the field of esthetic and restorative dentistry led to the achievement of the long sought dream of virtually bonding any type of material to the tooth surface. The advances in the restorative materials and bonding techniques have changed the concept of dentistry. These composite materials promise to be the most interesting development of the near future.

**Key words:** Composite, Bonding, Matrix, Polymerization, Filler, Esthetics

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Of all the innovative esthetic materials available today composite restorative materials have assumed a thrust in restorative dentistry. Properly placed composite restorations provide an excellent alternative to traditional metallic posterior restorations.<sup>1</sup> The search for an ideal esthetic material for restoring teeth has resulted in significant improvements in both esthetic materials and techniques for using them.

### I. Packable Composites

The packable composites have similar properties to posterior composites.

Fracture toughness of a composite has been correlated with its filler volume fraction. As filler volume increases, fracture toughness increases. So as filler volume of packables is in same range as that of Z100 and Heliomolar (Posterior Composites). It is filled with glass fibers, glass fibers have a significant toughening effect probably by enhancing crack blunting or by providing sites for energy dissipation during crack propagation through delamination. SEM shows rough fracture surface with signs of matrix – filler debonding and crack deflection from its primary path. Other composites have relatively smoother fracture surfaces.

Alert : 1.6 – 1.8 MPa m<sup>1/2</sup>  
Surefil : 1.25 – 1.45 MPa m<sup>1/2</sup>  
Solitaire : 0.65 – 0.75 MPa m<sup>1/2</sup>

Packable composites have flexure strength similar to Heliomolar (the microfill) composite, than to Z-100 (the minifill). Solitaire having the lowest value (50-70 MPa).

Packable composites have flexure modulus similar to the nonpackable posterior composites with Solitaire having lowest value.

The hardness values for the packable composites are also within the range of the nonpackable materials. Solitaire has lowest hardness value. In case of Solitaire, low hardness and modulus may be because of the matrix resin, multifunctional methacrylate ester instead of traditional dimethacrylates. Cross-linked network produced from this monomer likely includes many unreacted pendant methacrylates that serve as plasticizers and reduces the properties or it may be because of porous fillers.

**ALERT** exhibited the highest flexural modulus and fracture toughness, but the lowest wear resistance. **Solitaire** presented the highest wear resistance but lower mechanical properties than all other materials. **Surefil** revealed a significantly higher flexural modulus and wear resistance than Tetric Ceram and Ariston pHc. **Definite** has mechanical properties similar to Tetric Ceram and Ariston pHc but less wear.

Alert and Solitaire exhibited highest wears as a result of high filler load levels. Although Solitaire contains high filler fraction volume of 50% (66wt%) it is comprised of porous SiO<sub>2</sub> filler (30%) with a particle size of 3-22 μm, Ba- Al-B-F-Si glass (26%), Al-F-Si glass (5 wt%) and Sr-F (5 wt%). So may be due to air porosities included in the composite material.

Filler load level and filler matrix interactions have a greater influence on fracture parameter than the structure of the organic matrix.

Composites with smaller filler particles and high filler fraction volumes are suggested to wear less. Surefil is based on an interlocking filler technology (82wt%) bonded to an urethane modified Bis-GMA resin matrix which can strongly resist exfoliation dislodgment through abrasion.

The matrix of the Ormocer Definite is characterized by an interpenetrating network of inorganic organic copolymers.

Solitaire contains 30wt% of a porous SiO<sub>2</sub> filler which integrates part of the resin matrix within the porosities of the bodies of the filler particles resulting in firm bond of the filler particles to the matrix resisting wear better.

ALERT contains micro-filamentous glass fiber particles, which are 60-80 μm in length and 6 μm in diameter.

Large sized rod shaped particles most likely is responsible for the high abrasion wear.

**Ariston** has high wear rates than **Tetric Ceram** because of larger average filler size and contains a relatively hydrophilic monomer in its organic matrix. Interactions between the matrix and the ion releasing alkaline glass filler are probably different from Tetric Ceram.

The depth of cure of packable is similar to that of other posterior composites. The increments should not be more than 2 mm to ensure adequate conversion throughout the restoration, light cured for 40s with a source of 1080 mW/cm<sup>2</sup>.

Similar to or greater than that of non-packable material Solitaire shows highest value 3% of polymerization shrinkage.

All packable composites, except Solitaire have radiopacity exceeding 2 mm of aluminium, may be due to low volume of radiopaque filler and chemical composition of the fillers.

Inorganic filler content:

Two distinct and relatively narrow distribution volume.

Low group-- 48% (approximately) **Pyramid enamel, Solitaire**

High Group-- 60% **ALERT, Pyramid Dentin, Surefil.**

The major advantage of these new composites is their thicker consistency, which may be deemed helpful in achieving tight interproximal contacts.<sup>2</sup>

## II. Compomers

### (Polyacid-Modified Resin Composites)

Compomer is resin- ionomer hybrid restorative material marketed as multipurpose material, as resin that may release fluoride but have only limited glass ionomer properties. It contains the major ingredients of both composites (resin component) and glass ionomer cements (Polyalkenoate acid and glass fillers component) except for water. They have a limited dual setting mechanism, dominant setting reaction is the resinous photopolymerisation and no acid base reaction can occur until the material absorbs water.

The compomers presently available contain two different resins for the matrix and the glass particles as fillers common to composite resins and glass ionomers.

The resin component contains functional groups of polycarboxylic acid and methacrylate combined in one molecule. This provides methacrylic groups for cross linking (as in composite resins) and carboxyl groups to undergo an acid-base reaction in the presence of water and metal ions (as in glass ionomers).

Fluoride containing glasses, typical of glass ionomers comprise the principal fillers to which may be added glass particles similar to those in composite resins. There may also be other fillers providing additional fluoride release and radiopacity. Eg: DYRACT, DYRACT AP, COMPOGLASS, F-2000

Dyreact is characterized by a unique single component compomer restorative and a newly developed primer/adhesive liquid for enhanced adhesion to tooth tissues and improved seal of the cavity.

### INDIRECT COMPOSITE RESINS

In the early 1980s, **Mormann and Touati** and colleagues pioneered the use of Composite resins for the fabrication of indirect inlays and onlays.

In the mid 1980s, **Touati and Pissis** developed the concept of metal composite inlays and bridges after the silinating technique, which enabled a strong bond between polymer and metal because of a very thin (0.1 mm) aluminium oxide layer.

**INDICATIONS:**

- Metal free dentistry
- Esthetics
- Decreased wear of opposing dentition
- Conservative tooth preparation

**CONTRAINDICATIONS:**

- Bruxism
- Opposing porcelain
- Long span fixed partial dentures
- High caries rate
- Difficult moisture control adhesion

**CLASSIFICATION:**

1. First Generation Indirect Composites
2. Second Generation Indirect Composites
3. Intermediate Generation Indirect Composites

• **First Generation Indirect Composite Resins:**

(Low filler and high matrix load)

They are microfilled composite resins, with 66% resin content and 33% inorganic particles. Particle size of 0.04 – 0.4 µm. Inorganic fillers are round in shape and consist of colloidal silica. Eg., **VISIO-GEM** (ESPE), **DENTACOLOUR** (Kulzer), **CONCEPT** ( Ivoclar)

- Flexural strength : 60-80 MPa (low)
- Modulus of elasticity : 2000-3500 MPa (low)
- Low wear resistance (owing to a low percentage of inorganic filler particles and a high percentage of exposed resin).
- High polymerization is by light, heat and pressure or argon laser).
- First generation laboratory composites remain somewhat fragile and subject to chipping and color variation.

The lower the percentage of inorganic particles, the lower the mechanical properties of the composites resulting in failure of first generation laboratory composites.<sup>3</sup>

For inlays, onlays and laminates and implant supported prosthesis.

• **Second Generation Indirect Composite Resins:**

(High filler and low matrix loads)

**Advantages:**

- Decreased polymerization shrinkage
- High elastic moduli
- Better wear resistance

They are suitable alternatives to ceramics in some clinical situations.

Second Generation are microhybrid composite resin (sometimes called **ceramic polymers**) with a high density of ceramic filler particles. Eg., **ARTGLASS** (Kulzer), **BELLEGLASS HP** (Kerr), **TARGIS** (Ivoclar), **COLOMBUS** (Cendres), **SINFONY** (ESPE).

Consists of inorganic filler content of 66% by volume filler content differs from that of First generation in form (longer, whereas the first generation are round), size (bigger 1-5 µm) and composition (mainly silica and barium glasses and ceramics).

**Resin matrix:** 33%

- Flexural strength : 120 – 150 MPa
- Elastic modulus : 8000 – 12000 MPa
- Minimal polymerization shrinkage
- A bond to metal substructure of crowns and bridges, regardless of alloy used.
- Resistance to abrasion similar to that of enamel.

**Clinical applications:**

- Inlays and onlays
- Laminated veneers and jacket crowns

- Implant supported restorations (for progressive loading of implant supported prostheses).
- For easier repair directly in the mouth
- For modification and / or adjustment of proximal contacts.
- For reduction of occlusal stresses in bruxism cases (as composite resins, absorb some strains because of their elasticity)

This provides good esthetics, with a wide range of hue, chroma, and opacity, biocompatibility and tissue preservation.

Most second-generation composite resins require post-curing process.

- Heat and light (photothermic treatment) e.g., **Targis and Conquest**.
- Heat and nitrogen pressure e.g. **Belleglass HP**.

This procedure allows the optimal conversion rate to be reached within a few minutes (10 for Belleglass HP and 25 for Targis).

- **Intermediate Indirect Composite Resins:**

They are also microhybrid light cured composites. They cannot be classified as second-generation composites because they do not feature all the required characteristics like

- High mechanical properties
- High percentage in volume of inorganic microparticles
- Bond to metal

Used for inlays and laminate veneers

Metal – resin bonding can be mechanical or chemical.

- **Mechanical:** Macromechanical retention (beaded metal, metal mesh, pitted metal).  
Micro mechanical retention (sandblasting or etching)
- **Chemical:** Intermediate interface such as tin plating or ceramic coating is fused to the metal surface.

Eg. **Silicoating, Rocatec (ESPE), Adhesive silica**

## CEROMERS

The term ceromer stands for **Ceramic Optimized Polymer** and was introduced by Ivoclar to describe their composite Tetric Ceram. They are **microfilled hybrid resins or universal composite resins**. This material consists of a paste containing barium glass (< 1 µm), spheroidal mixed oxide, ytterbium trifluoride, and silicon dioxide (57 vol%) in dimethacrylate monomers (Bis-GMA and urethane dimethacrylate). They are set by a polymerization of C=C of the methacrylate. They must be bonded to the tooth structure. The properties of the ceromers are identical to those of composites and they exhibit fluoride release lower than conventional glass-ionomers or compomers. In 1996 a **CEROMER** (or Ceramic optimized polymer) was developed for indirect composite restoration **Targis** (Vivadent).

- It consists of 77% wt filler and 23% wt of organic resin.
- The filler is trimodal and consists of Ba glass with a mean particle size of 1 µm. Spheroidal silica filler – mean size 0.25 µm as well as colloidal silica filler – 0.015-0.050 µm
- The resin matrix consists of conventional monomer.
- Superior properties are claimed as a result of optimized chemical composition
- Ceromer can be used for veneers, inlay/onlay without a metal framework.
- Also can be used with Fiber Reinforced composite framework for inlays/onlay, crowns and bridges (3 unit) and for crown and bridges including implant restorations on a metal framework.
- Ivoclar in cooperation with several universities has developed advanced polymer systems and ceramic fillers from which high performance Ceromers (**ceramic optimized polymers**) have been produced. These Ceromers combine the advantages of ceramics with those of state-of-the-art composites.

Ceromers are composed of specially developed and conditioned fine particle ceramic fillers of submicron size (0.04 and 1.0 µm), which are closely packed (75 – 85 weight percent) and embedded in an advanced temperable organic polymer matrix.

On the basis of their composition and structure, Ceromers combine the advantages of ceramics and composites like:

- Durable esthetics
- High abrasion resistance
- High stability
- Ease of final adjustment
- Excellent polishability
- Effective bond with luting composite
- Low degree of brittleness

- Conservation of tooth structure

### FIBER REINFORCED COMPOSITE RESIN SYSTEMS

The mechanical properties of these materials allow them to withstand high stress, they lack critical requirements like esthetics as many are black (carbon fibers) or are somewhat opaque glass and resin fibers and ease of fabrication into numerous nonstandard shapes. The fibers used are composed of Kevlar, polyethylene and glass fibers.<sup>4</sup>

Revolution came into dental market with the introduction of **Targis-vectris system**. Others are **Sculpture/fibrekor, Belleglass/Connect, Belleglass/Vectris, etc.**

They are also called CEROMER (Ceramic optimized polymer), polyglass and polymer ceramic, as manufacturers try to convince dentists that these materials somehow were closer to ceramics than to composite resins. As ceramics are seen as stable materials whereas composites often have been viewed as high wear, color unstable materials. Fiber reinforced materials may be good esthetic options in cases where there are virgin teeth adjoining a pontic space where no metal is desired in low stress areas and for implant supported prostheses.

Conventional composite resins consist of micron and submicron glass or ceramic articles “floating” in a resin matrix. They are discrete particles not connected to each other. In fiber reinforced materials long continuous fibers about 10  $\mu$  in diameter are used to provide the bulk of the mechanical properties to the resin material. It resists stress better in multiple directions while maintaining flexibility, so does not become brittle like ceramics.

The type of fiber reinforcement is also important. It may be parallel fibers, fiber weaves or braided fibers. If the fibers are unidirectional, then their resistance to load is different in different direction. Whereas braided fibers are designed to better resist stresses placed on the material in multiple directions. Fiber reinforced composite resins can be classified broadly as resin preimpregnated or unimpregnated and may be primarily laboratory or chair side based.

### FIBER-REINFORCEMENT MATERIALS:

- CONNECT (polyethylene)
- DVA (polyethylene)
- FIBERFLEX (Kevlar)
- FIBREKOR (glass)
- FIBER-SPINT (glass)
- GLASSPAN (glass)
- RIBBOND (polyethylene woven)
- SPLINT-IT (glass)
- VECTRIS (glass)

### Clinical Applications:

- Splinting
- Restoration of endodontically treated teeth
- 3 unit bridge work
- Metal free crowns

### FRC SUBSTRUCTURE:

The nature of overlying composite (providing shape and anatomic contour), its wear resistance and its esthetic qualities are the factors influencing the effectiveness of FRC system in restorative dentistry.<sup>5</sup>

The fiber-reinforced composite (FRC) frame work replaces the classic metal framework of a porcelain fused to metal prostheses, while a particulate composite applied over this FRC substructure corresponds to the porcelain applied in a traditional restoration.

This 2 phase polymer prosthesis combines the best characteristics of the FRC (i.e., strength and rigidity) with those of the particulate composite (i.e., wear resistance and esthetics).

### Fiber –Reinforced systems:

1. Pre- impregnated e.g., TARGIS / VECTRIS  
SCULPTURE/ FIBERKOR
2. Non – impregnated e.g., BELLE GLASS HP/CONNECT  
RIBBOND, GLASS PAN

### COMPOSITE INSERTS

Preformed shapes and sizes of glass ceramic whose surfaces have been silane treated. They are available in different shapes L, T, round, conical, cylindrical size 0.5-2mm (mega fillers).

Application: Used to minimize the marginal contraction gaps in composite fillings.

Properties:

- Low coefficient of thermal expansion
- Wear resistant
- Their presence reduces polymerization shrinkage by upto 75% and increases the stiffness of the filling.
- Radiopaque

Manipulation: These inserts are pressed into a cavity preparation that is already filled with unpolymerized composite. The composite which is extruded during the insertion is removed and that which remains is cured. The restoration is then contoured using diamond rotary instruments and polished.

Cavity is prepared → Thin layer of composite is placed → above this glass fillers are placed → rest of the cavity is filled with composite resin →contouring done → cured→ finishing and polishing

### FLOWABLE COMPOSITES

Flowable composites were introduced in late 1996. They are broadly similar to resin cements and pit and fissure sealants, with filler loading and particles size less than hybrid composites resulting in a material of low viscosity.<sup>68</sup>

Filler content is generally less than 50% by volume, so polymerization shrinkage will be greater than for more heavily filled materials. The modulus of elasticity will also be lower than for conventional resin composite materials. This may allow the material to flex and flow under the conditions thought to occur in Class V cavities and the flow of the material may also be useful in absorbing stresses caused by polymerization shrinkage.

Flowable composites are available in a range of shades; some versions even include pink for use in masking areas of gingival recession (Pink revolution). A number of formulations contain fluoride, although the clinical benefit of this is not quantified.

Advantages of flowable materials are that they are fast and easy, that excellent access and placement can be achieved using the syringe tips in which they are supplied. Flowables should not be used in situation involving high stresses or associated with wear.

Wear resistance depends on

- Inter particle spacing, called the protection hypothesis
- Extent of the filler particle density

e.g., **AELITEFLO** 17.2 + 13.2  $\mu\text{m}$ , **FLOW RESTORE** 5.3 + 3.5  $\mu\text{m}$

	Vol %	Filler/Size	Compressive Strength (MPa)	Diametric (MPa) Tensile St.
<b>Aeliteflo</b>	43	Ba glass, Colloidal silica 0.7 $\mu\text{m}$	201	34
<b>Flow Restore</b>	48	Silica barium glass, Ba fluorosilicate 0.7 $\mu\text{m}$	209	35
<b>Revolution</b>	41	Ba Glass, synthetic silica, 1 $\mu\text{m}$	196	33
<b>Ultraseal XT Plus</b>	37	Glass Ionomer Glasses 1-1.5 $\mu\text{m}$	161	16

Flowable materials were developed principally to provide their own particular handling characteristics rather than with any particular physical or clinical performance property in mind and as a result, there is little known about their performance. In one study flowables are compared with hybrid composites with respect to physical properties.

1. Can be used as filling material in low stress applications but not in Class I and II in premolars and molars.
2. Resurfacing composite or GI restorations or for rebuilding worn composite contact areas.
3. In areas of difficult access or areas that require greater penetration, amalgam, composite or crown margin repairs, pit and fissure sealant or preventive resin restoration.
4. As liner or base in Class II proximal box.
5. For veneers or for cementing porcelain veneers.
6. Restoration of air abrasion preparation, Class V lesions, porcelain repairs, enamel defects, incisal edge repair in anteriors, Class III lesions.<sup>69</sup>

## SMART COMPOSITES

Smart Composites are active dental polymers that contain bioactive amorphous calcium phosphate (ACP) filler capable of responding to environmental pH changes by releasing calcium and phosphate ions and thus become adaptable to the surroundings. These are also called as **Intelligent composites**.

This class of composite was introduced as the product **Ariston pHc** in 1998. Ariston is an ion releasing composite material. It releases functional ions like fluoride, hydroxyl, and calcium ions as the pH drops in the area immediately adjacent to the restorative materials, as a result of active plaque.

- The composite material releases fluoride, hydroxyl and calcium ions in dependence on the pH value immediately adjacent to the restorative material.
- With a decreasing pH value due to active plaque the release rate of the functional ions increases and vice-versa.

This phenomenon is based on a newly developed alkaline glass filler and is expected to reduce the formation of secondary caries at the margins of the restorations due to an inhibition of bacterial growth, a reduced demineralization and a buffering of acids produced by cariogenic micro-organisms.

Smart composites work is based on the newly developed alkaline glass. The paste contains Ba, Al, and F silicate glass filler (1 $\mu$ m) with Ytterbium trifluoride, silicon dioxide and alkaline glass (1.6  $\mu$ m) in dimethacrylate monomers.

Filler Content: 80% by weight and 60% by volume. Dentin should be sealed to reduce sensitivity. It reduces secondary caries formation at the margin of a restoration by inhibiting bacterial growth. This results in reduced demineralization and buffering of the acid produced by caries forming microorganisms.

Fluoride released is lower than glass ionomers but more than that of compomers.

Flexural strength :	118 MPa
Flexural modulus :	7.3 GPa
Fracture toughness :	1.9 MNm <sup>-3/2</sup>
Mean wear rate :	7194 $\mu$ m

## ORMOCERS

Recently a new material was made available for dental restoration therapy the **ORMOCER**. **Dr. Herbert Wolters** from Fraunhofer Institute for Silicate Research introduced this class of material in 1994.

**ORMOCER**, the acronym of **Organically Modified Ceramic** is a brand-new material for all filling indications in the anterior and posterior area which serve as an optimum and upto date replacement for amalgam, composite and compomers.

This class of material represents a novel inorganic-organic copolymers in the formulation that allows for modification of its mechanical parameters.

Eg., **DEFINITE**

The inorganic-organic copolymer is synthesized from multi-functional urethanes and thioether (meth) acrylate alkoxy silanes as sol-gel precursors. Alkoxy silyl groups of the silane permit the formation of an inorganic Is-O-Is network by hydrolysis and poly-condensation reactions. The methacrylate groups are available for photochemical polymerization.

The filler particles are 1-1.5  $\mu$ m in size and the material contains 77% filler by weight and 61 % by volume.

The essential difference between ORMOCER and the previously available composites is found in the matrix. The matrix of conventional composites mainly consists of low molecular monomer components, mainly Bis – GMA. On light activation only 60-70% of the free monomers can be converted. Throughout the lifetime of the restoration they can be eluted.

Silicon oxide, a filler, serves as a basic substance for the ormocer. It is modified originally by adding polymerisable side chains in the form of methacrylate groups. Throughout bonding of the methacrylate molecules to the carrier medium, the methacrylate molecules can no longer be eluted during incomplete polymerization.

The matrix, consisting of ceramic polysiloxane (siliconoxygen-chains) presents a whole new approach. Instead of dimethacrylate monomer of traditional composites, ORMOCER has a biocompatible polysiloxane net with low shrinkage even prior to light curing. The inorganic network formation starts by hydrolysis and precedes polycondensation of Si (OR) 3 groups. Starting with silane, polysiloxanes with polymersiable groups are formed.

- **Definite** permanently releases fluoride, calcium and phosphate ions that protect the adjoining cavity margins.
- Biocompatible

•	Bending strength (3 point bending test)	:	100-160 MPa
•	Modulus of elasticity	:	10-17 GPa
•	Coefficient of thermal expansion	:	17- 25 x 10 <sup>-6</sup> K <sup>-1</sup>
•	Water uptake	:	< 1.2%
•	Solubility in water	:	Not detectable
•	Shrinkage	:	1.7 – 2.5 vol%

1. **Biocompatibility:** After the placement of the filling, ORMOCER will not release any detectable residual substances and is therefore biocompatible.

2. **Reduced polymerization shrinkage:** The material is found to have polymerization shrinkage of about 1.88%.

3. **High abrasion resistance:** Owing to its excellent abrasion resistance the material can be used in the posterior area that is exposed to masticatory load and ensure outstanding long-term stability of the filling in this area load bearing area.

4. **Lasting aesthetics:** Unlike amalgam, ORMOCER (**DEFINITE**) is a tooth coloured restorative material, which is available in twelve finely graduated shades.<sup>58</sup> Due to their chemical-physical characteristics, these materials have long-term protection against discolouration.

5. **Anticariogenic property:** It provides additional protection against dental decay. ORMOCER protects both the tooth structure itself by strengthening the tooth substance through permanent release of enamel hardening minerals like fluoride, calcium and phosphate ions that protect the adjoining cavity margins.

6. **Cost effective:** Excellent price to performance ratio.

7. **Fast and safe handling:** The innovative one-step bonding “Etch and Prime 3.0” with their water based bonding, the etching of the dental enamel with phosphoric acid gel otherwise required is not necessary, as well as the separate rinse and dry steps are redundant. With only one single liquid that contains the pyrophosphate, all steps of the procedure etching, priming and bonding can be carried out in one step and a safe and durable adhesive bond between tooth and filling material is created.

Due to minimum abrasion, reduced polymerization shrinkage, extreme material strength, natural appearance and fast handling, this material works well both in the posterior and anterior areas. Reducing the variety of materials in wide variety of clinical situation has convincing benefit to both the dentist and the patients, reduced allergy risks, easy storage as well as an overall reduction of imperfection, since we can cover all filling indications with only one material, that is, organically modified ceramics.

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