

Dental Composites and Their Process

1. Introduction

If the enamel and dentin have been invaded by acid-producing bacteria or damaged for other reasons, the decayed hard tissue has to be removed. The resulting cavities must be filled in order to restore structural integrity and mechanical solidity of the tooth. Dental composites, which are placed in or onto a tooth, restore the dental function and shape when tooth structure has been lost due to decay or fracture (generally because of extensive caries which weaken the cusps or external trauma), or to improve the aesthetics of the tooth.

Presently, dental resin composite is a common type of filling material. It is a mixture of ceramic powder (fillers) and a resin (the polymer matrix) [1-3]. One of the advantages of resin composites is that their refractive index can match the appearance of the natural tooth, so they are commonly used to restore posterior teeth as well as anterior teeth. Moreover, the preparation of composite fillings requires less removal of tooth structure than amalgam to achieve adequate strength.

2. Constitutions of Composites

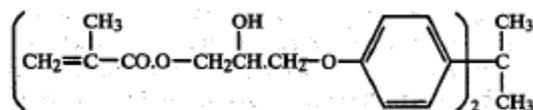
The dental compositions comprise of polymerizable materials and inorganic filler. Many polymerizable materials include polyurethanes, monomeric and polymeric acrylated and methacrylated, polyamides, epoxy-compounds, polystyrenes. They could be applied in fillings, crowns, denture base, coating, sealants and cements.

2.1 Polymerizable Materials

The preferred polymerizable materials used in dental filling compositions include the reaction product of bisphenol A and glycidyl methacrylate, sometimes called bis-GMA [4] and vinyl urethane prepolymer [5]. A preferred polymerizable material comprises of a mixture of vinyl urethane or glycidyl alkacrylate and 25 to 150% by weight of vinyl urethane or glycidyl alkacrylate of at least one polyfunctional monomer.

2.1.1 Product of Bisphenol and Glycidyl Methacrylate [6-11]

A preferred reaction production of a glycidyl alkacrylate and a bisphenol has the following formula:



Liquid ethylenically unsaturated monomers that are suitable as polymerizable materials include vinyl monomers, eg. vinyl esters such as n-hexyl, cyclohexyl and tetrahydrofurfuryl acrylates and methacrylates. The monomers should have low toxicity and volatility.

Polyfunctional monomers are also suitable as polymerizable materials vinyl monomers containing two or more vinyl groups. Suitable monomers include glycol, dimethacrylates, diallyl phthalate, and triallyl cyanurate. A preferred polymerizable material comprises a mixture of vinyl urethane or glycidyl alkacrylate and 25% to 150% by weight of vinyl urethane or glycidyl alkacrylate at least one polyfunctional monomer.

2.1.2 Vinyl Urethane Prepolymer

Preferred vinyl urethanes are the reaction product of a urethane prepolymer and an ester of acrylic or methacrylic acid with a hydroxy alkanol of at least 2 carbon atoms, the urethane prepolymer being the reaction product of a diisocyanate of the structure $\text{OCN-R}^1\text{-NCO}$ and a diol of the structure $\text{NO-R}^2\text{-OH}$ wherein R_1 is divalent hydrocarbyl group and R_2 is the residue of a condensate of an alkylene oxide with an organic compound containing two phenolic or alcoholic groups. Other suitable vinyl urethanes include those made by the reaction of alkyl and aryl, preferably alkyl, diisocyanates with hydroxy alkyl acrylates and alkacrylates [8-9].

These ethylenically unsaturated materials are polymerized in situ using a conventional redox (e.g. amine-peroxide) catalyst system, ultra-violet, or preferably visible light catalyst system [10].

2.1.3 Ketone

The dental compositions are cured by irradiating the composition with visible radiation, usually having a wavelength in the range 400 mμ to 500 mμ. The compositions contain at least one ketone selected from fluorenone and α-diketone and their derivatives as well as at least one organic peroxide. The derivative are in admixture with a similar amount of organic amine, which is capable of reducing that ketone when the latter is in an excited state, but in the absence of organic peroxide, which catalyzes cure of an ethylenically unsaturated material. The ketone has a cure time of less than 15 minutes at a radiation level of 1000 w/m² as measured at 470 mμ, bandwidth ±8 mμ.

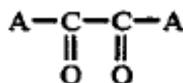
Evidence of cure can be detected by examining the change in viscosity of a mixture of the ethylenically unsaturated material containing the ketone and organic amine each at 1% by weight based on ethylenically unsaturated material using an oscillating rheometer, sample thickness 2 mm., whilst the mixture is being irradiated with light having wavelength in the range 400 to 500 mμ [11 in paragraph 6.4 provided that provision is made to allow visible light to be directed onto the mixture].

The ketone may be present in the composition in the concentration in the range 0.01% to 2% by weight of the polymerizable material in the composition. The more preferable measurement is 0.5% to 1% by weight of the ethylenically unsaturated materials in composition.

2.1.3.1 Diketones

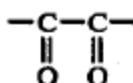
In general, α-diketones are capable of being excited by radiation in the visible region of the spectrum having a wavelength range 400 mμ to 500 mμ.

Diketones have this formula:

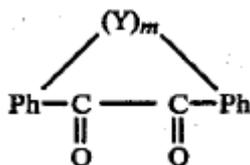


Here, the groups are hydrocarbyl or substituted hydrocarbyl groups and the group A may be further linked together by a divalent link or by a divalent hydrocarbyl or substituted hydrocarbyl group, or in which the group A together may form a fused aromatic ring system. The group A could be aliphatic or aromatic. Aliphatic include cycloaliphatic groups and aliphatic groups carrying aromatic substituent (i.e. aralkyl groups). Aromatic groups include groups carrying alkyl substituents (i.e. alkaryl groups and heterocyclic groups). The aromatic groups could also be a benzenoid aromatic group, e.g. the phenyl group, or a non-benzenoid cyclic group.

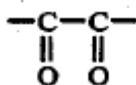
The group A, especially when aromatic, may carry substituent groups other than hydrocarbyl, e.g. halogen or alkoxy. The group A may be further linked together by a direct link, or by a divalent group, e.g. a divalent hydrocarbyl group; that is, in addition to the link through the group.



The group A may be further linked so as to form a cyclic ring system. For example, where the groups A are aromatic the α -diketone may have the structure



in which Ph is a phenylene group, Y is $>\text{CH}_2$, or a derivative wherein one or both of the hydrogen atoms are replaced by a hydrocarbyl group, and m is 0, 1 or 2. Preferably the group Y is linked to the aromatic groups in positions ortho to the group.



The group A together may form a fused aromatic ring system.

Suitable α -diketones include benzyl in which both groups A are phenyl, α -diketones in which both of groups A are fused aromatic, e.g. α -naphthyl and β -naphthyl, and α -diketones in which the groups A are alkaryl groups, e.g. p-tolyl. Example of α -diketone in which the groups A are non-benzenoid aromatic e.g. 2:2'-furyl. Derivatives of the α -diketone in which the groups A carry non-hydrocarbyl groups for example p,p'-dialkoxy benzyl, p,p'-dimethoxy benzyl, p,p'-dihalobenzil, p,p'-dichlorobenzil or p-nitrobenzil.

2.1.3.2 Fluorenone

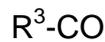
Fluorenone and its derivative could be alkyl (Cl-6), halo, nitro, carboxylic acid and esters, particularly in the 2- and 4- positions.

2.1.4 Organic Peroxide

Organic peroxides have this formula:



in which the group R which may be the same or different, are hydrogen, alkyl, aryl, or acyl groups, no more than one of the groups R being hydrogen. Acryl means groups having the formula of:



in which R^3 is an alkyl, aryl, alkyloxy or aryloxy group. Organic peroxide in the composition include diacetyl peroxide, dibenzoyl peroxide, ditertiary butyl peroxide, dilauroyl peroxide, tertiary butyl perbenzoate, ditertiary butyl cyclohexyl perdicarbonate.

The reactivity of a peroxide is often measured in terms of a ten hour half life temperature, i.e. within ten hours at that temperature half of the oxygen has been made available. The peroxide should have ten hour half life temperatures of less than 100 C.

2.2 Inorganic Filler

Filler materials are generally ceramic powder including quartz, barium glass, and colloidal silica. Table 1 shows the regular commercial filler products and their properties. Fused silica (Aerosil-OX50, Degussa Co., Mobile, AL) is used as a control subject because most of current dental resin composites are reinforced with silica particles for facilitating the silanization and optical properties. Alumina (NanoTek® Aluminum Oxide, Nanophase Technologies Corporation, Romeoville, IL) is used as the primary filler material. The manufacturer's specification sheet indicates an equi-axed powder with an average particle diameter of 47 nm and a density of 3.6 g/cc. Three-micron alumina polishing powder (Buehler Ltd., Lake Bluff, IL) is used as a micro-sized filler material. Metal bond diamond powder (Advanced Abrasives Corporation, Pennsauken, NJ) is used to reinforce resin composites as well. Diamond is used because of its high stiffness. The diamond particles are of irregular shapes.

Table 1. List of filler materials (commercial products) and their properties [12]

Materials	Average particle size (nm)	Morphology	SSA (m ² /g)	Density (g/cc)	E (GPa)
Silicon oxide (Aerosil [®] OX 50)	40	Equi-axed	50	2.18	68~70
Alumina oxide (NanoTek [®])	47	Equi-axed	35	3.60	370~400
Buehler Alumina (Micropolish II)	3000	Irregular	N/a	3.96	370~400
Diamond (Advanced Abrasives)	375	irregular	7.47	3.2 ~ 3.5	800 ~ 924

The inert inorganic filler in the composition may contain up to about 90% by weight [13-20]

The particle size of the filler should not be not greater than 100 micron. In order for a hard dental filling to be produced by curing of the composition, it is desirable that the particles of filler have a Knoop hardness of at least 500.

Suitable fillers include apatite, soda glass, quartz, silica gel, borosilicate glass, synthetic sapphire (alumina) and radio opaque fillers, e.g. barium and strontium oxide glasses.

3. Materials Process

It is important when a tooth is being filled that the visible light cure filling material should cure (i.e. harden rapidly under exposure to visible light), and that the cure should be essentially homogenous throughout the entire volume of the filling. The dentist is then assured that the filling is satisfactory, and the patient can immediately use the teeth without waiting for the filling to cure post-treatment.

The compositions are fluid (that is, paste-like and not powdery or crumbly) at ambient temperature so that in the uncured state they may be shaped in a coherent mass and maintain that shape without substantial flow. Therefore, the composition can be inserted into a cavity in or mold on a tooth in the upper jaw without deformation before cure.

One of the difficult technical problems is how to compound this high-viscosity paste. The viscosity increases dramatically as filler is added, due to the increasing friction between particles and between particles and monomer. It is a particular problem with the addition of large volumes of filler. Since the nano-sized filler has higher specific surface area than

conventional micro-sized filler, the viscosity of nanofiller-reinforced composites is even higher than the micro-sized counterpart at the same filler loading.

The most suitable process of these paste-like materials is through three roll mill. In a three roll mill, particle sizes are reduced and agglomerates are dispersed by the combined crushing force of the rollers and the extremely high shearing force resulting from different roller speeds. Since the entire product is fed into the gap between the rollers, the result is a precise controllable and narrow particle size distribution. By setting the gap width, particle size can be controlled easily and accurately down to micron level. With other types of systems, this is much more difficult. Three roll mills enable a medium or high viscosity product to be dispersed with minimal liquid. Since liquid materials do not have to be dispersed, they can be added later.

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