

It has now been found that dental restorative composite compositions employing small percentages of polytetrafluoroethylene or other similar low friction coefficient non-toxic polyfluorocarbon resins or polychlorofluorocarbon resins, with other conventional fillers, impart to the cured composite greatly increased wear or abrasion resistance, without degrading the other desirable characteristics of the composite, such as coefficient of thermal expansion, translucency, thermal conductivity and compressive strength.

The other components of the improved dental restorative composite compositions of this invention, such as polymerizable organic binder matrix, catalysts, accelerators, coupling agents, UV-absorbers, stabilizers, pigments and the like, can be selected from any of the type conventionally used in dental restorative composite compositions.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

Any of the non-toxic polyfluorocarbon resins or polyfluorochlorocarbon resins which are solid at room temperature and which exhibit the low coefficient of friction which characterize this class of fluorinated hydrocarbon polymers in general and polytetrafluoroethylene in particular can be used in this invention. Examples of the polyfluorocarbon resins include polytetrafluoroethylene, fluorinated ethylenepropylene copolymer (copolymer of tetrafluoroethylene and hexafluoropropylene), polyhexafluoropropylene, polyvinylidene fluoride ($-\text{CH}_2\text{CF}_2-$)_n, etc. Copolymers of tetrafluoroethylene and perfluoroalkyl vinyl ethers, such as DuPont's Teflon PFA, can also be used. Examples of the polyfluorochlorocarbon resins include, for example, polychlorotrifluoroethylene, etc. Generally, any of the resins obtained by polymerizing monomers of the lower alkenes such as ethylene, propylene, butene, and 4-methylpentene-1, in which all of the hydrogen atoms are replaced with fluorine and/or chlorine atoms, providing at least two-thirds of the halogens are fluorine, can be used as the wear resistance imparting additive in this invention. Fluorinated graphite, (CF)_n can also be used. Polytetrafluoroethylene is the preferred additive.

The polyfluorocarbon or polyfluorochlorocarbon resin filler additive constitutes from about 1 to 10%, preferably about 1 to 5%, more preferably about 1.5 to 3%, of the total amount of filler. Generally, the total filler, including the additive, constitutes from at least about 50 parts by weight and up to about 90 parts by weight of the total filler and binder, and preferably, from about 65 parts by weight to about 85 parts by weight per 100 parts by weight of the total filler and binder and correspondingly, from 10 to 50 parts by weight, preferably 15 to 35 parts by weight of the polymerizable binder, per 100 parts by weight of the filler and binder.

Any of the conventional fillers can constitute the major proportion of the total weight of filler. Representative of such suitable filler materials include, for example, silica, glass beads, aluminum oxide, fused silica, fused or crystalline quartz, lithium aluminum silicate, barium glass, and the like.

The particle sizes of filler materials, including the conventional filler and the polyhalocarbon additive, generally range from submicron to about 125 microns, with the average particles having an average mean diameter in the range of from submicron to about 30 microns and preferably, from about 2 to 5 microns for

the conventional filler and from submicron to about 30 microns for the polyhalocarbon additive, most preferably about 0.1 to 5 microns.

A preferred filler contains about 95 to 99 parts by weight of the amorphous silica and about 1 to 5 parts by weight of polytetrafluoroethylene per 100 parts by weight of filler particles.

The dental restorative composite composition of this invention therefor includes, per 100 parts by weight, about 50 to 90 parts by weight, preferably 65 to 85 parts by weight of finely divided inert inorganic filler particles (including conventional siliceous filler plus polyhalocarbon additive), about 10 to 50 parts by weight, preferably about 15 to 35 parts by weight of liquid polymerizable organic resin binder (including polymerizable monomers and other reactive monomers or diluents), about 0.1 to 2% by weight based on the weight of the binder of catalysts, about 0.1 to 2% by weight based on the weight of binder of accelerators, and about 0 to 5% by weight based on the weight of the binder, preferably about 1 to 5% by weight of organosilane coupling agent.

The polymerizable organic resin binder can generally be any acrylic resin, such as, for example, methylmethacrylate, methylacrylate, ethylmethacrylate, etc., although dimethacrylates such as those derived from aliphatic glycols or those having structures known in the art as vinyl esters, are more suitable. The preferred polymerizable monomers are those based upon BIS-GMA and other di-, tri- and tetra-methacrylates, such as disclosed by Bowen in the aforementioned U.S. Pat. No. 3,066,112. Other suitable polymerizable monomer systems which can be used in this invention are disclosed, for example, in U.S. Pat. Nos. 3,179,623; 3,539,533; 3,730,947; 3,766,132; 3,774,305; 3,835,090; 3,839,065; 3,854,009; 3,860,556; 3,862,920; 3,882,600; 3,911,581; 3,923,280; and 3,991,008. Each of these patents teach suitable polymerizable monomers, reactive diluents, catalysts, accelerators and other conventionally used adjuvants and additives in dental restorative composite compositions for such applications as dental fillings, dental cements and the like. Accordingly, the disclosures of these references should therefor be considered to be incorporated herein by reference. For example, the polymerization catalyst is generally a peroxide such as benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, 4-chlorobenzoyl peroxide, etc. Suitable activators or accelerators which cause decomposition of the catalyst to provide free radicals for promoting the polymerization reaction include such preferred compounds as N,N-dialkylanilines and N,N-dialkyltoluidines. A particularly desirable class of catalysts, based on their greater shelf stability, are hydroperoxides which are used in conjunction with substituted thioureas as accelerators, as disclosed in U.S. Pat. No. 3,991,008. Other suitable activators include, for example, paratoluenesulfonic acid, para-tolyldiethanol amine and other tertiary amines. The binder system can also include various well known stabilizers or UV-absorbers to increase the shelf life of the unpolymerized composite resin compositions.

It is also preferred to include coupling agents for enhancing the adhesion between the polymerizable resin binder and the filler. Examples of suitable coupling agents, include, for example, vinyltrichlorosilane, tris(2-methoxyethoxy) silane, tris(acetoxy) vinylsilane, 1-N-(vinylbenzylaminoethyl)aminopropyltrimethoxy silane-3, 3-methacryloxypropyltrimethoxy silane, etc. Gener-