

**DENTAL COMPOSITES COMPRISING
GROUND, DENSIFIED, EMBRITTLED
GLASS FIBER FILLER**

**CROSS-REFERENCE TO RELATED
APPLICATIONS**

This is a continuation of application Ser. No. 09/092,370 filed Jun. 5, 1998 entitled DENTAL COMPOSITES COMPRISING GROUND, DENSIFIED, EMBRITTLED GLASS FIBER FILLER, now abandoned, which is a continuation of application Ser. No. 08/951,414 filed Oct. 16, 1997 entitled DENTAL COMPOSITES COMPRISING GROUND, DENSIFIED, EMBRITTLED GLASS FIBER FILLER, now U.S. Pat. No. 6,013,694.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to dental composite materials and methods of manufacture thereof. In particular, this invention relates to improved glass fiber fillers for dental composite materials, wherein the glass fibers are densified and embrittled by heating the fibers.

2. Brief Discussion of the Related Art

Compositions useful for repairing damaged teeth in situ are known in the art as direct filling materials, and include alloys and resin composites. Dental amalgam alloys have widely been used as direct filling material, and provide excellent handling characteristics, and physical properties. The technique of mechanically packing and condensing a material into a tooth cavity is previously known to the dental profession in connection with the use of dental amalgams as a direct filling material. It has well known advantages in that it permits a close adaptation of the filling material to the cavity walls and also makes it possible to make firm contacts between the restored tooth and its neighbor. Further, it makes it possible to give the restoration its final anatomic form before hardening, thereby avoiding the time consuming and difficult finishing work with rotating instruments required with composite materials. These advantages are achieved by the densified, embrittled glass fiber composites on the present invention and the method of manufacture thereof. However, there are perceived health hazard concerns regarding the use of high amounts of mercury or gallium present in amalgam alloys.

Dental resins have accordingly been developed, which comprise polymeric matrices, for example polyamides, polyesters, acrylates, polyolefins, polyimides, polyarylates, polyurethanes, vinyl esters, or epoxy-based materials. Other polymeric matrices include styrenes, styrene acrylonitriles, acrylonitrile butadiene styrene polymers ("ABS polymers"), polysulfones, polyacetals, polycarbonates, polyphenylene sulfides, and the like. The most popular polymeric matrices are based on monomers having at least one ethylenically unsaturated group, in particular acrylate and methacrylate groups. One commonly used monomer of this class is the reaction product of bisphenol A with glycidyl methacrylate (hereinafter BIS-GMA). In addition, these resins have also been used to make artificial teeth and denture basis.

Unfilled (i.e., pure) curable acrylic and methacrylic resins generally suffer from polymerization shrinkage and poor durability. These drawbacks have been reduced in direct filling applications, in part, through the addition of inert fillers. See, for example, U.S. Pat. No. 3,066,112 which is herein incorporated by reference. The combination of binder plus filler is commonly referred to as a composite direct

filling material. Currently used fillers for curable dental resins generally are inert materials in the form of finely divided irregular particles, fibers or beads, present in an amount from about 35 to about 80 percent by weight of the total composite direct filling material.

Commonly used inorganic fillers include fumed silica, quartz, glass, various mineral silicates (e.g., β -eucryptite, lepidolite, petalite, spondumene, beryl, topaz and zircon), silicon carbide, alumina, and mixtures thereof. Commonly-assigned U.S. Pat. No. 4,544,359 to Waknine, for example, discloses a filler mixture comprising barium silicate, borosilicate glass, and colloidal silica. In general composite direct filling materials which are fully loaded with inorganic fillers (i.e. combined with the highest workable volume loading) having particles in the range of 0.01–1.2 microns are the most wear-resistant currently available composite direct filling materials. However, these composite direct filling materials containing finely divided inorganic fillers and acrylic binder resins may not polish as easily as unfilled dental resin.

Organic materials have also been used as fillers. For example, U.S. Pat. No. 3,923,740 discloses a direct filling material containing finely divided cured polymethyl methacrylate, alone or in conjunction with an inorganic filler. Composite direct filling materials which are wholly or partly filled with finely divided polymethyl methacrylate have better polishability (i.e. better surface finish after polishing with ordinary dental tools) than composite direct filling materials which are fully loaded with inorganic fillers, but generally have poorer durability (i.e. poorer wear resistance in vivo) than composite direct filling materials having inorganic fillers only.

Regarding fibrous fillers in particular, U.S. Pat. No. 2,477,268 to Saffir discloses short glass fibers randomly dispersed in dental resin materials, as does U.S. Pat. No. 2,514,076 to Kelly. Use of long, fully wetted fibers in structural components for dental restorations and the like are disclosed in U.S. Pat. No. 4,894,012 to Goldberg et al. However, none of these patents is discloses a composite having the feel of amalgam.

Fused-fibrous filler compositions in the dental arts are also known. Such fused fibrous fillers are of particular interest because they reportedly provide a feel similar to that of amalgam when used by the dentist, and may be applied using similar techniques. In U.S. Pat. No. 4,381,918 and U.S. Pat. No. 4,392,828 to Ehrnford there is disclosed a filler comprising porous inorganic particles which are completely or partially impregnated with a resin material. The porous inorganic particles are formed by heating inorganic fibers under pressure to fuse the fibers at their points of contact, thereby forming a rigid three-dimensional network of inorganic fibers. Fused-fibrous fillers compositions are also disclosed in U.S. Pat. No. 5,621,035 to Lyles et al. Such fillers comprise silica fibers together with either alumina or aluminosilicate fibers which are fused in the presence of a fusion source such as boron nitride. The presence of boron lowers the melting point of the fibers sufficiently to allow formation of a porous, interconnected network. The network is then ground to particles having a size of about 180 microns, and used as fillers in dental composites.

Unfortunately, use of the fused-fibrous filler compositions disclosed in the Ehrnford and Lyles patents requires multiple steps and extensive preparation time. Accordingly, there is a need in the dental arts to develop a dental resin composite which is similar to or approaching to dental amalgam alloys in handling characteristics, physical properties, and appli-