HYDROPHILIC CROSSLINKING MONOMERS AND POLYMERS MADE THEREFROM

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1. Field of the Invention

Hydrated collagenous assemblages give strength to tendons, ligaments, bones and teeth. Hydrated polysaccharidic assemblages are important in both plant and animal structures. Also, synthetic industrial materials often have hydrophilic and hydrated surfaces. Most of the important structural biological polymers (collagen, cellulose, etc.) and many structural industrial substrates (oxidized or anodized metal alloys, hardened cement aggregates, etc.) are thus hydrophilic and hydrated when in typical environments.

However, the emphasis in recent research on adhesives for industrial and other applications has been on the development of hydrophobic monomers and polymers. In particular, most prior art dental resins, the derived "vinyl ester resins" used in industry, and most polyester resins, which polymerize by rapid free-radical mechanisms, do not adhere well to moist surfaces, or to hydrophilic substrates exposed to water. The success of dental adhesive composition bonding by current methodologies is limited due, at least in part, to a partitioning of the various components such as initiators, promoters, and monomers as they diffuse into the substrate material. This partitioning or separation effect, resulting from different solubility characteristics of the monomers, initiators, and other components, separates components that must work together for effective polymerization and consequential adhesive bonding.

The need for monomers that polymerize and crosslink very rapidly, indifferent to the presence of water, with substantial water-solubility and surface-activity characteristics, has not been adequately recognized.

2. Description of the Prior Art

U.S. Pat. Nos. 3,066,112 and 3,194,783 describe an insoluble filling material. The filling material includes a clear, colorless, fused silica filler, a keying agent, such as vinyl trichlorosilane which is used to impart hydrophobic properties to the filler, and a binder made up of a polymerizable resin.

U.S. Pat. No. 4,514,527 describes materials and methods for improving the adhesion of composite materials and resins to dentin, enamel and other substrates. The invention includes a three-step method wherein the first step comprises contacting the surface of the dentin with an aqueous solution comprising an acidic salt containing a cation which is capable of changing valence. The second step involves contacting the surface of the dentin with a solution comprising NTG-GMA in a volatile water-miscible solvent solution. Finally, the dentin surface is contacted with a solution of PMDM and/or BTDA-HEMA in the same or different volatile water-miscible solution.

U.S. Pat. Nos. 4,521,550; 4,588,756 and 4,659,751 are related patents which describe materials and methods for improving the adhesion of composite materials and resins to dentin, enamel and other substrates. The patents describe. inter alia, a method for preparing a dentin surface for adhesion of a composite resin comprising contacting the surface of the dentin with an aqueous solution comprising an acidic salt. Next, the surface is contacted with a solvent containing NPG, NTG-GMA, or NPG-GMA. The dentin surface is finally contacted with a solution consisting of addition reaction products of pyromellitic acid dianhydride and 2-hydroxyethyl methacrylate, or the addition reaction product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 2-hydroxyethyl methacrylate, or 4-methacryloxyethyltrimellitic anhydride.

SUMMARY OF THE INVENTION

Affinity and adhesive bonding frequently are associated with materials having similar physiochemical characteristics. Therefore, synthetic monomers, and their formulations that will have physiochemical characteristics similar to hydrated natural and artificial materials would be highly useful as adhesion promoters. Such synthetic monomers could infiltrate these materials on a molecular scale or manifest sufficient affinity for durable bonding to permeable hydrophilic surfaces.

In certain dental or medical applications, it is particularly important to match a monomer and its formulation with the physical characteristics of hydrated collagen such as slightly decalcified dentin or bone surfaces. Collagen, in either its natural or denatured state, may be penetrated, infiltrated, and impregnated by entropic migration of these monomers into the hydrated and/or expanded fibrils or polypeptide chains. These permeated monomer chains become part of the same collagen fibrils that are embedded within the hydroxyapatite of the underlying, unaltered tooth or bone. A strong and lasting bond can be obtained by the thorough polymerization of these monomers in situ. An essential feature of the present invention is the disclosure of novel crosslinking monomers and polymerization initiators, which, utilized together, will equally penetrate such hydrous or hydrophilic substrates, form strong crosslinked polymers, and copolymerize with less-hydrophilic structural resins applied thereupon.

It is therefore useful if the disparate classes of compounds or compositions used in the dental adhesive composition have uniform physical properties. The entire composition, made up of various components, constitutes a major aspect of the invention, in addition to the novelty of individual chemical compositions of matter.

This invention relates primarily to hydrophilic polymerizable adhesive compositions comprising hydrophilic polymerizable monomers; polymerization initiators, accelerators and stabilizers, which may be an integral part of the hydrophilic polymerizable monomer molecules (herein termed "hybrid hydrophilic monomers"), or separate therefrom; a dianhydride component, which when reacted with the hydrophilic monomers in the presence of a catalyst (optionally the same as the amine polymerization accelerator) gives rise to a polyfunctional monomer intermediate; and, preferably, water.

The preferred hydrophilic polymerizable monomers are dimethacrylates and/or diacrylates containing one or more (preferably two) carboxyl groups, with connective moieties that, together with the carboxyl groups, provide sufficient affinity with water to allow any desired amount of water and/or miscible fugitive solvents to be mixed homogeneously with these monomers and formulations containing them. The activity of water can thereby be made equal to that in biological tissues,