

SILYLATED RESINS AND THE SYNTHESIS THEREOF

The present application claims priority of U.S. Provisional Patent Application Ser. No. 60/068,535, filed Dec. 23, 1997, and incorporated herein by reference.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to silylated resins and methods for preparing and using the same. The invention relates more specifically to silylated resins which exhibit a strong affinity for glass substrates, and which on polymerization yield strong, tough materials, suitable, for example, as dental restorative composite compositions, and in industrial applications as structural composites, caulks, adhesives, sealants, and coatings.

2. Discussion of the Prior Art

Polymeric dental composites have found increasing use in restorative dentistry. Because of their limited strength, toughness, and durability, however, such dental composites have been used primarily for restoring defective tooth structure that is not subject to high levels of masticatory stresses, e.g., anterior teeth rather than the occlusal areas of posterior teeth. Although currently used composites are not inherently adhesive to tooth structure, they are capable of being bonded to tooth structure via the prior application of an adhesive system.

The base monomer compound 2,2-bis-[4-(2'-hydroxy-3'-methacryloxypropoxy)phenyl]propane ("Bis-GMA") is widely used in dental composites, sealants, and adhesives. A disadvantage of Bis-GMA, however, is its high viscosity due mainly to the presence of its two hydroxyl groups. The hydroxyl functionality also enhances the water absorptivity of the Bis-GMA polymer, which can promote plasticization of the polymeric matrix and also compromise the critical interfacial phase of dental composites. Because Bis-GMA and similar dental resins do not adhere strongly to the glass fillers used with conventional dental composites, silane coupling agents such as the polymerizable trialkoxyorganosilane, 3-methacryloxypropyltrimethoxysilane ("MPTMS"), are used as surface treatment agents so that the siliceous fillers can be bonded to the polymer matrix and, thereby, reinforce the weaker organic phase of the composite and provide a mechanism for stress transfer from the lower modulus matrix to the higher modulus filler phase.

In order to provide a dental restorative composite possessing improved mechanical properties, especially wear or abrasion resistance, the addition of a polyfluorocarbon or polychlorofluorocarbon resin to a conventional inert inorganic filler used in combination with conventional liquid polymerizable binder systems are disclosed in U.S. Pat. No. 4,197,234 to Temin, and in Venz and Antonucci, *J Dent. Res.* 65, 183 Abstract 191 (1986). The inclusion of coupling agents to enhance the adhesion between the polymerizable resin binder and the filler are also disclosed. These references indicate that the filler particles are either pretreated with a silane coupling agent prior to blending the filler and liquid polymerizable matrix, or that the agent can be added

to the polymerizable resin binder prior to addition of the inorganic particulate filler. In either method of silanization, however, the objective is to surface modify the filler phase, and not to modify the resin by silyl ether formation (by a silylation exchange reaction).

U.S. Pat. Nos. 5,071,933, 5,241,081, and 5,294,646 to Muller et al. all describe the development of adhesive resins for bonding to collagenous tissues, especially dentin. In U.S. Pat. No. 5,071,933, for example, the hydroxylated product is silylated to yield a trimethyl silyl derivative for mass spectrometric analysis. As in the aforementioned U.S. Pat. No. 3,860,556, however, the use of the monofunctional trimethylsilyl reagent is to enhance the volatility of the product, and thereby, facilitate its analysis. Trimethylsilylation is also used for analytical purposes in U.S. Pat. Nos. 5,241,081, and 5,294,646 in order to render certain reaction products sufficiently volatile for characterization by mass spectrometry.

The aforementioned silane-derived interfacial phase can be vulnerable to hydrolytic degradation, especially if the matrix and the interface allow significant absorption and transport of oral fluids. Therefore, there is a need to make the organic phases of the interface and the matrix of composites more resistant to the adverse effects of fluids in the oral environment.

The vinyl resin systems used in dental composites and related materials should ideally achieve on polymerization the contradictory goals of high conversion and minimal contraction. A high degree of conversion, with homogeneous network formation, is desirable because it maximizes the glass transition temperature of the matrix, thereby rendering it less susceptible to the softening effects of the oral environment, such as plasticization and degradation. Since polymerization shrinkage is directly correlated with conversion, a high degree of conversion can have undesirable consequences, such as the formation of gaps and stress sites in the composite and at the composite-tooth interface.

Base monomers such as Bis-GMA, with rigid molecular structures and high cohesive energy densities, require significant amounts of smaller, more flexible diluent monomers (e.g., triethylene glycol dimethacrylate) to yield resin systems with workable viscosities and matrices of relatively high degrees of conversion and glass transition temperatures. Another deficiency of conventional Bis-GMA resins is that they have a propensity to form matrices that are excessively brittle, i.e., they lack toughness.

A potential method of minimizing polymerization shrinkage while maximizing the degree of conversion is to use less viscous monomers of greater bulk and flexibility than Bis-GMA. An alternate method is to modify Bis-GMA by exchange reactions such as silylation so that the ensuing polymers have these desirable properties.

The use of silylated resins in dental composites such as those derived from Bis-GMA can have several advantages over Bis-GMA type composites, including: 1) conversion of the hydroxylated resin in virtually quantitative yields to more hydrophobic silyl ether derivatives; 2) increase in the molecular size of the resin without a concomitant increase in viscosity (with some silyl derivatives a viscosity decrease occurs); 3) control of the adhesivity and crosslinking potential of the resin through selection of the composition of the