

These exchange reactions can be conducted in solvents, including diluent monomers, either with or without the presence of catalysts. Choice of the resin/silyl composition and reaction conditions can be used to design resins with controlled reactivity, hydrophobicity, and polymerization shrinkage.

The silylated resins combine the properties of both acrylic resins and coupling agents, thereby simplifying the preparation of glass or ceramic filled composites. For example, unsilylated glass fillers can be used directly in the formulation of sealants and composites. These resins can also be used with presilylated fillers to supplement and enhance interfacial bonding. Such resins and composites can be used directly as repair materials for composites, porcelain, sealants, and in a number of other adhesive applications.

Viscosity and shrinkage of the resins can be controlled by selection of the silylating agents. For example, long chain organosilanes will reduce both viscosity, hydrophilicity, and polymerization shrinkage. Strength and toughness are other properties that can be controlled by this technology.

EXAMPLE

Transesterification exchange reactions of Bis-GMA with MPTMS were investigated. Transesterifications of Bis-GMA (available from Esstech) and MPTMS (available from Aldrich Chemical) mixtures with mole proportions of 2:1, 1.5:1, 1:1, and 1:2 were conducted neat at 65° C. in open vials (or flasks equipped for removal of byproducts) for a duration of from 1 hour to 120 hours. All of the reagents were commercially available and were used without further purification. Some of the analogs of Bis-GMA were synthesized.

Commercially available silanes (Gelest, Inc.) which may be employed in the synthesis include, for example: include: acetoxymethyltriethoxysilane allyltrimethoxysilane; benzyltriethoxysilane; benzoyloxypropyltrimethoxysilane; (N,N-diethyl-3-aminopropyl)trimethoxysilane; ethyltriacetoxysilane; ethyltriethoxysilane; (heptadecafluoro-1,1,2,2-tetrahydrodecyl)triethoxysilane; methyltriethoxysilane; n-methylaminopropyltrimethoxysilane; methacryloxymethyltriethoxysilane; methacryloxypropyltrimethoxysilane; methacryloxypropyltriethoxysilane; vinyltrimethoxysilane; styryltrimethoxysilane; acetoxypyltrimethoxysilane; 3-(n-allylamino)propyltrimethoxysilane; cyclohexyltrimethoxysilane; 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane; (3-glycidoxypropyl) trimethoxysilane; 3-(2-imidazolin-1-yl) propyltriethoxysilane; isobutyltrimethoxysilane; isooctyltrimethoxysilane; n-octyltriethoxysilane; n-octadecyltrimethoxysilane; n-propyltriethoxysilane; n-phenylaminopropyltrimethoxysilane; phenyltriacetoxysilane; tris(dimethylamino)phenylsilane; phenyltrimethoxysilane; p-tolyltrimethoxysilane; pentafluorophenylpropyltrimethoxysilane; (3,3,3-trifluoropropyl)trimethoxysilane; (tridecafluoro-1,1,2,2-tetrahydrooctyl)triethoxysilane; tetraethoxysilane; tetrakis(dimethylamino)silane; (3-acryloxypropyl)trimethoxysilane; 3-cyanopropyltriethoxysilane; 5,6-epoxyhexyltriethoxysilane; hexyltrimethoxysilane; diethylphosphatoethyltriethoxysilane; 5-(bicycloheptenyl) triethoxysilane; and norbornenyltriethoxysilane.

The extent of reaction was determined by characterization of the reaction products by both FTIR (Nicolet Magna 550 Spectrometer) and ¹H NMR (JEOL-GSX270 Spectrometer) spectroscopies.

As depicted in FIG. 1, the relative OH content of the Bis-GMA product versus the mole proportion of the MPTMS/Bis-GMA charge indicates that considerable conversion of the hydroxyl groups of Bis-GMA to the silyl ether products (see, e.g., FIG. 2) occurs and is dependent on the composition of the reactants.

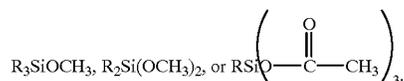
As depicted in FIG. 2, analysis by FTIR indicated significant decreases in intensities of the band at 2842 cm⁻¹, CH₃ stretch of CH₃OSi groups of MPTMS, and the presence of the broad band from about 3600 to 3100 cm⁻¹ due to OH groups of Bis-GMA (the band intensity changes were normalized to the Bis-GMA aromatic bands at 1608 cm⁻¹, 1582 cm⁻¹, and 1510 cm⁻¹). Analysis by ¹H NMR confirmed the FTIR results.

The residual SiOCH₃ and OH contents of the silylated resin were determined to be primarily a function of the initial composition of the Bis-GMA and MPTMS charge, as well as a function of both the temperature and duration of the reaction.

The various silyl derivatives of Bis-GMA were photoactivated for visible light polymerization with camphorquinone and 4-ethyl dimethylaminobenzoate. Irradiations of thin films of some of these resins between crossed glass slides resulted in polymers that adhered tenaciously to glass and resisted debonding under tensile or shear mechanical stress.

As expected, chemical activation, e.g., benzoyl peroxide plus a polymerization accelerator, can also be used to effect polymerization.

The present invention, therefore, permits the facile synthesis of a wide variety of silylated polymerizable resins having a wide spectrum of properties. Reaction conditions can be modified so that these resins can have pendant, readily converted silyl ether groups, such as, for example,



This flexibility in methodology allows viscosity and adhesive properties to be controlled. The synthesis of these novel resins typically involves only one step and employs readily available reactants. Many of the self-adhesive resins can be utilized both as coupling agents for siliceous and other fillers, and as the organic matrices of thermoset composites. These novel resins also can be designed to have minimal polymerization shrinkage, lower stress development, low water sorption, and improved affinity for glass and similar substrates. Their unique structural characteristics lend themselves to the preparation of condensable dental composites that are stronger, tougher, and more durable than currently available composites.

These novel resins, because of their silyl ether or silyl ester structure, also have the potential to provide a self-healing mechanism if hydrolytic degradation occurs: