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(54) Title: COMPOSITE MATERIALS AND ADHESION PROMOTERS FOR DENTAL APPLICATIONS		
(57) Abstract <p>Composite materials particularly suitable in the dental art as a tooth filling material including a polymer matrix, a metal, metal alloy, metal oxide particulate, or combinations thereof, in the presence or absence of colloidal silica, and a coupling agent to adhere the particulate to the polymer matrix. Adhesion can also be facilitated by cleaning and/or coating the particulates prior to incorporation into the polymer matrix. One or two paste systems of the composition with suitable initiators, accelerators, etc. can be formulated.</p>		

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COMPOSITE MATERIALS AND ADHESION PROMOTERS FOR DENTAL APPLICATIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a composition of a composite material consisting of a resin matrix, a filler, a coupling agent and an initiator system. The composite can be used as a filling material in teeth, although it can be used in other applications requiring high-strength composites. The hardening of the composite can be initiated by chemical methods, by laser or visible light sources, or by microwave energy. Depending on the method of curing, the composite is provided as a one-paste system, or it can be divided into two pastes. In the latter case, whereby the composite hardening is chemically initiated, one paste contains the composite and chemical initiators while the second paste contains the composite and accelerators. For single paste systems, all components are present in the single paste.

This invention also relates to the use of new coupling agents used in the composition for bonding filler particles to the polymer matrix.

This invention particularly relates to the use of a metal, or a metal-alloy particulate, or metal-oxide particulate, or other ceramic particulate, alone or, in combination, which are especially of interest as filler materials in the construction of composites.

This invention also relates to a method of depositing a thiol monolayer on the surface of the metal or metal alloy, and building up a molecule having a functionality capable of reacting with a polymer used as a matrix for a composite. It also relates to the construction of thiol-containing molecules having additional functionalities which can react with polymers, and which can be deposited on the surface of the metal, or metal alloy particulate, thus forming metal-sulfur bonds.

This invention also relates to a method of constructing and depositing a phosphate compound on the metal, metal alloy or metal oxide particulate which has the capability of reacting with a polymer used as a matrix for a composite.

2. Description of the Related Art

Dental amalgam, commonly used as a filling material for teeth, consists of a powdered alloy. The alloy primarily contains silver, tin, and copper. Other metals are present at relatively low concentration. The alloy is mixed with mercury to produce dental amalgam. The wetting of metal alloy particles by mercury produces a plastic mass that can easily be inserted into a cavity preparation and shaped, after which time it hardens. Mercury is used for dental amalgam as it is the only metal that exists in a liquid state at room temperature. It is thus capable of wetting the alloy powder, a process which initiates the hardening reaction. The presence of mercury in dental amalgam is controversial, as numerous studies have demonstrated that mercury is released during in-service use. This release has generated much interest in developing new, safe and functional alternatives to dental amalgam.

A class of materials known as composite resins are commonly used as alternatives to dental amalgam. Composite resins generally contain a polymer phase (a matrix) reinforced by inert fillers, these generally consisting of various forms of amorphous silica (SiO_2), or polymorphs of silica. The fillers are bound to the matrix via silane couplers, with γ -methoxypropylene silane (γ -MPS) being the most commonly used silane. Siloxane linkages are formed to the particulate on the one end, and the methacrylate moiety at the other end co-polymerizes with the matrix. Modern composites additionally contain photoinitiators, accelerators, colorants and additives for maintaining chemical stability.

The longevity of different materials in dental restorations is of obvious importance in assessing their effectiveness. Several cross-sectional studies have shown that the median age for composite restorations is 5 to 8 years, while that for amalgam is 8-14 years. In a prospective study of up to five years in duration, failure rates for composites were approximately twice that of amalgam.

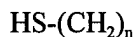
These survival relationships were similarly observed in children, where the median survival time for amalgam was 5 years while that for composites was 32 months. These data would clearly suggest that metal based restorations are superior to conventional composite resins with respect to survival.

Confirmation of the superiority of metal-based direct restoratives can be additionally gleaned from two initiatives in developing amalgam alternatives. Both involve the use of silver, one being a pure silver powder which is cold-welded into a solid mass by hand pressure. The other involves the mixing of a silver alloy with gallium, a metal in liquid phase at near-room temperature. The silver powder project appears to have some promise; however, the technique of placement may be time consuming, and would limit the widespread utility of the material. The gallium-containing amalgam has been shown to be sensitive to water at its early stage of set, and requires coating with a varnish to avoid water contact for the first 24 hours. Both initiatives have inherent limitations.

Development of new, or improved materials which harden when placed directly in the tooth is, therefore, a priority. Some of the ways of improving the properties of composites involve increasing its inherent strength through the use of metal particulates, or metal alloy particulates, or metal oxide particulates. Although polymers filled with silanated metal particulates are substantially reinforced, silane adhesion promoters are subject to hydrolysis. Since the composites are used in a water environment which promotes hydrolysis, further improvement in the durability of the metal reinforced polymer with sometimes more robust couplers would further be advantageous.

This invention finds utility in formulating new composites containing metal particulates dispersed in a matrix phase. Although the inventors consider conventional silanes for coupling the particulate to the matrix, the use of new and more robust adhesion promoters for this purpose are of particular interest. These new adhesion promoters are based on classes of materials referred to as alkylthiols, in the one case, and phosphate esters, in the other case.

Alkylthiols are materials that form chemically bound, self-assembling monolayers (SAM's) on transition metal surfaces by the interaction of sulfur with metal (S-metal). The formula for an alkane is given by:



where the value of n is from 2 to 100, and can be controlled to change the properties of the alkane chain. In addition, polar groups having a specific functionality for interaction with other compounds can be added to the terminal CH_2 group.

Alkylthiols are capable of coupling different metals with polymers. For example, a pendant thiol has been used to couple steel surfaces to various polymer matrices. Additionally, glycolic thioesters have been shown to form an S-metal bond, leaving self-assembled alkane chains that promote the adhesion of acrylate and epoxy adhesives. Besides participating directly in binding to the surface, a thiol group is also capable of an addition reaction across a vinyl group. Thiol-ene polymerizations based on this radical mechanism are known. For example, a two component coupling-agent layer used to bond copper with epoxy and polyimide resins is more resistant to corrosion, and provides higher adhesive strength than either component alone, even at high temperatures.

With respect to phosphates, the surface treatment of metal by phosphate is well-known as phosphating. A solution containing the free phosphoric acid, a primary metallic phosphate, and an accelerator are used in phosphating procedures. The surface physical, or physico-chemical properties of metal, such as aluminum and its alloys, are modified by this procedure. This procedure indicates the possibility that the deposition of phosphate compounds on the surface of metal or metal oxides.

SUMMARY OF THE INVENTION

The following are objects of this invention:

- i. The invention provides a composition, which, when hardened, is particularly suitable for application as a filling material in the dental arts.

- ii. The invention provides a composition, which contains a metal, or a metal alloy, or a metal oxide, or combinations of the preceding, with or without surface modification, which include cleaning methods to remove oxide layers, and/or the deposition of thin silver or gold films on alloy particles, these being comprised as fillers in a polymerizable composite. The composition has excellent physical and mechanical properties on hardening.
- iii. The invention provides new coupling agents, which form chemical bonds between the metal, or metal alloy, or metal oxide and resin matrix.
- iv. The invention provides a method of constructing adhesion promoters having thiol functionalities which, on one end, are reacted with the metal, or metal alloy, and on the other end, are capable of reacting with a polymer matrix.
- v. The invention provides a method of constructing adhesion promoters having phosphate functionalities which, on one end, are reacted with metal alloys, or metal oxides, and on the other, are capable of reacting with a polymer matrix.

Briefly, the invention provides a composition, which consists of a resin matrix, a filler, a coupling agent and an initiator system. The composition is particularly suitable as a filling material for teeth, having a preferable use in load-bearing surfaces of teeth. The composite has superior performance by use of metal, or metal alloy, or metal oxide particulates, or a combination of the preceding, with or without surface modification, as a filler, or as fillers dispersed in a polymer, in combination with different types of adhesion promoters. Surface modifications include the removal of surface oxides using various cleaning procedures, such as the treatment of the particles with acids. Surface modification also can involve the deposition of a thin silver or gold film on alloy particles. The adhesion promoters can be a form of a silane, but preferably, are thiol-containing or phosphate-containing compounds which act as coupling agents that bond both metal, or metal alloy particulates, or particulates consisting of oxides of metals to the polymer matrix. The metal oxide, if used in the composite, is bonded to the matrix via a

silane coupling agent. For curing by a laser or visible light source, or by microwave, the composition is provided in a single paste system, and contains sensitizers with reducers to harden the paste. For chemical initiation, the composition is divided into two pastes, with one paste containing the composite and initiators while the second paste contains the composite and accelerators. The curing or hardening will be carried out by mixing the two pastes together, or by heating or UV light depending on the initiator and accelerator used in these two pastes.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a scanning electron micrograph of particles of silver alloy.

Fig. 2 is a spectral representation of PA-FTIR spectra of a γ -MPS solution, a silver alloy in "as received" state, ethanol-washed alloy treated with γ -MPS, and ethanol and acid (HBF_4) treated silver as spectra (a), (b), (c) and (d) respectively.

Fig. 3 is a spectral representation of γ -MPS solution, titanium dioxide (TiO_2) in an "as received" state, and titanium dioxide after exposure to γ -MPS as spectra (a), (b) and (c), respectively.

Fig. 4 is a spectral representation of a silver alloy, a 2% solution of 3-mercaptopropyl trimethoxysilane (MMPS), and the silver alloy after treatment with MMPS as spectra (a), (b) and (c) respectively.

Fig. 5 is a spectral representation of the silver alloy, and cleaned (acid treated) silver alloy after treatment with an alkenethiol, shown respectively as spectra (a) and (b).

Detailed Description of the Preferred Embodiments

In accordance with the present invention, the composition consists of a polymer matrix, a filler comprised of a metal particulate, or a metal alloy particulate, or a metal oxide particulate, the preceding fillers being used alone or in combination, a coupling agent, being a silane, or a thiol compound, or a phosphate compound, and an initiator system.

The polymer matrix, according to the present invention, is formed from monomers of acrylates and methacrylates having at least one unsaturated carbon-carbon double bond in an amount comprising 5 to 50 weight percent of the total composition. Suitable monomers include 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BisGMA), ethyleneglycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA), 1,6-hexamethylene glycol dimethacrylate (HGDMA), trimethylolpropane trimethacrylate (TMP-TMA), pentaerythritol triacrylate, pentaerythritol triallyl ether, pentaerythritol tetraacrylate, eutectic monomers, hydrophobic monomers, urethane dimethacrylate, and spiro orthocarbonates, 2-hydroxyethyl methacrylate, and 2-hydroxymethylmethacrylate.

The filler, according to this invention, consists of a metal, or a metal alloy, or a metal oxide particulate. The metal can be silver or gold, or a silver or gold alloy. The metal oxide can, for example, be an oxide of titanium. The silver alloy, for example, contains silver in the range of 40-85%, preferably in the range of 45-70%, and most preferably in the range of 50-65%; tin is in the range of 25-35%, most preferably in the range of 27-32%; copper is in the range of 5-35%, preferably in the range of 10-30%, and most preferably in the range of 12-20%. The silver alloy can additionally contain zinc in the range of 0.1 to 2%, or other metals, such as palladium or indium, having a concentration less than 1%. Gold alloys can contain gold in the range of 25-75%, preferably in the range of 45-70%, and most preferably in the range of 49-68%; silver is contained in the range of 5-55%, preferably in the range of 10-50%, and most preferably in the range 15 to 40%; copper is contained in the range of 5-25%, and most preferably in the range of 7-22%; palladium is contained in the range of 0.5-12%, most preferably in the range of 0.1-9%; other metals, such as zinc or indium, have concentrations less than 2%. Metal oxides can, for example, be oxides of titanium, aluminum, and calcium, but are not limited to these examples. In addition, the filler can contain colloidal silica. The overall weight percent of the filler particles, alone or in combination, is in the range of 20-98 weight % of the composition. The particles used are preferably spherical in shape, although they may be irregularly shaped. The size range for the filler particles is

preferably between 0.02 and 50 micrometers at the maximum diameter with a size range of 0.1 to 10 micrometers being most preferable, although particles of metal oxides or colloidal silica having a dimension of approximately 0.01-0.04 micrometers can be used in the most preferred range.

Metal alloy particles can have thin films of silver or gold deposited, to enhance the deposition of the thiol, although this may not be necessary.

The coupling agent, in accordance with this invention, can be a silane, in the case where there is a sufficient oxide layer on the surface of the particulate. Additionally, a phosphate ester can also be used with particulates having oxide layers. Preferably, the oxide layer is completely, or almost completely removed by a cleaning procedure, such as exposure to an acid, such as, but not limited to, nitric acid. When the oxide layer is removed, an alkenethiol can be used as a coupling agent. Examples of coupling agents are γ -methacryloxypropyl trimethoxysilane (γ -MPS), 3-mercaptopropyl trimethoxysilane (MMPS), 2-mercaptoethyl methacrylate, pentaerythritol triacrylate phosphoric acid ester.

For hardening in a tooth, the composition can be exposed to a laser light source, or a visible light source. In the case of the latter, the thickness of the composition should be minimal. The initiator system for laser or light curing consists of agents which are sensitive to the wavelength of the light source. Agents sensitive for this purpose include, but are not limited to, camphorquinone, benzoin ethyl ether, and benzoin methyl ether. Tertiary amines are generally used as reducing agents, and include but are not limited to such agents as *N, N* dimethyl-*p*-toluidine, dimethylaminoethyl methacrylate, 4-(*N, N*-dimethylamino) benzoate. The initiator system is present in the composition in an amount 0.1 to 5 percent by weight. For the two paste system, the initiator is generally mixed with one paste of composition and the accelerator, or reducing agent, is mixed with another paste. When ready to be placed in a tooth, the two pastes are mixed together on a mixing pad, and the composition is applied to the tooth where it hardens. The initiator and accelerator for this purpose include, but are not limited to, benzoyl

peroxide, and *N, N* dimethyl-p-toluidine. The composition can also be hardened by microwave energy, although hardening by this method has to be done outside the tooth, using a model of the tooth on which the filling is made.

The composition additionally contains polymerization inhibitors, such as hydroquinone, and may contain pigments, such as iron oxides, to change the coloration of the composition.

The combination of materials used in this composition provides a material which has high strength characteristics, and is suitable for use as a filling material under load-bearing conditions.

The invention will be understood by reference to the following examples.

Example 1

Measurement of size distribution of the particulate:

The size and shape of silver-alloy particles, which in this example, contain silver, tin, copper and palladium in the ratio of 49.5:30:20:0.5, are characterized by scanning electron microscopy (SEM) and image analysis software (SigmaScan Pro, Jandel Scientific, San Rafael, CA). Particle size distribution is determined by Sedigraph analysis. This method of analysis is based on Stoke's Law of fluid dynamics whereby particles are classified according to their rate of settling in a fluid, with sedimentation being dependent on the fluid viscosity and density. Particle size distribution is measured by an x-ray beam which passes through the fluid cell. X-ray intensity is measured and converted to percent of a given particle size.

The scanning electron micrograph (Fig. 1) generally confirms the near spherical nature of the particles while the image analysis indicates that the particle size ranged from approximately one to 12 μm in size. Roughly 85% of the particles were less than 10 μm , the preponderance being in the 4-7 μm range.

Example 2.

Coupling Agent Deposition:

The silver alloy is initially washed with ethanol (with ratio 1:10 by volume), and allowed to dry in a desiccator. To determine the ability to deposit a silane on the alloy, the particles were divided into two groups. The first consisted of the ethanol-washed particles, while the second was further treated with 10% fluoroboric acid (HBF_4) to remove surface contaminants. The acid-treated ("cleaned") particles were rinsed with distilled water, then with a final wash of ethanol and allowed to air dry. Each of the powders was immersed in a 10% (by volume) solution of γ -MPS and ethanol in a clean plastic beaker. The volume of the solution was determined by calculating the γ -MPS to be 2 weight % of the alloy particle. The supernatant was then filtered off, and the residual powder was washed extensively with propanol. The propanol was again filtered, and the residual powder collected in a clean plastic beaker, which was placed in an oven at 110 degrees Celsius for eight hours. In order to evaluate the result of deposition, the photoacoustic Fourier transform infra-red (PA-FTIR) spectra were recorded of the γ -MPS solution, the silver alloy as received, the ethanol-washed alloy treated with γ -MPS, and the acid-cleaned alloy treated with γ -MPS. These spectra are respectively seen in Fig. 2 below as (a), (b), (c) and (d).

Titanium dioxide (TiO_2) in an "as received" state was similarly exposed to γ -MPS, dried in an oven and washed as previously described. Spectra were recorded of the TiO_2 before and after silanation. These spectra are respectively seen in Fig. 3 below as (b) and (c). The spectrum of γ -MPS is shown again as (a) for reference.

The process was once again repeated for the silver alloy using a thiol-containing silane in an attempt to determine if a sulfur-metal bond could be established. A 2% solution of 3-mercaptopropyl trimethoxysilane (MMPS) was made. Cleaned silver alloy was immersed in the solution, and processed in a fashion similar to the γ -MPS. Spectra of MMPS, the silver alloy, and the treated silver were recorded and are seen in Fig. 4 below as (a), (b), and (c).

A thiol having the formula $\text{HS}-(\text{CH}_2)_n$, where n can equal 2 to 100, preferably 12, was dissolved

in ethanol so that the proportion of the thiol would be 6 weight % of the silver particles. Cleaned silver-tin-copper-palladium alloy particles were immersed in the thiol solution (volume), which was then filtered off. The particles were recovered, extensively washed with ethanol (volume) and dried in a desiccator. Spectra of the powder before and after treatment were recorded, and are respectively shown as (a) and (b) in Fig. 5 below.

In Figs. 2d, 3c and 4c, the absorption of either the γ -MPS or MMPS is demonstrated on both the silver alloy and titanium dioxide by the presence of strong bands attributed to the particular silane being used to treat the metal. Of equal importance, Fig. 2c indicates the relatively weak absorption of a silane when the metal is not cleaned, which emphasizes the importance of developing cleaning techniques for the successful deposition of adhesion promoters. The deposition of alkenethiol on the silver alloy is further demonstrated in Fig. 5b, thus indicating that a thiol can, in fact, be deposited on a silver alloy. From this body of work, we conclude that under the appropriate conditions, adhesion promoters can be deposited on candidate metals to be used in the construction of a composite.

Example II

Preparation of thiolated gold colloid capped with methacrylate:

One method of building up a thiol monolayer with chemical bonding at both ends is by subsequent chemical reactions on top of the solid substrate. We have done this using commonly available chemicals in a 2-step, layer-by-layer synthesis on gold, rather than isolating and purifying the difunctional species separately.

Step 1 - Preparation of thiolated gold colloid:

In a 500 mL round-bottomed flask, 100 mL of 2×10^{-3} M AuCl_4 (aq) was added to 300 mL of 1×10^{-3} M ice-cold NaBH_4 (aq). The mixture was stirred for 10 minutes, 0.05 mL of $\text{HS}(\text{CH}_2)_2\text{OH}$ was added and stirring was continued for 6 hours. The precipitate was isolated by centrifuging. The product was washed with toluene and vacuum-dried.

Step 2 - Esterification of methacrylic acid onto the above OH-terminated Au colloid:

(1) the previous product (not soluble), (2) 0.05 mL of methacrylic acid, $\text{CH}_2\text{CH}(\text{CH}_3)\text{COOH}$, (3) 0.1 mL DCC (dicyclohexylcarbodiimide), $(\text{C}_6\text{H}_{11}\text{N})_2\text{C}$ and (4) 6 mg of DMAP (4-dimethylamino pyridine) were added to 10 mL ether. The mixture was stirred overnight at room temperature. The supernatant liquid was decanted, leaving a gray solid which dried. The reaction byproducts were removed by washing with EtOH and centrifugation. Four rinses with 30 mL portions of EtOH were used to wash the product, after which the product was dried under vacuum. The FTIR spectrum showed intense C=O and C=C bonds (1716 and 1650 cm^{-1}), indicating the successful addition of chemically bonded, polymerizable vinyl groups to the metallic core particles.

Example 3.

Preparation of a phosphate ester

A solution of pentaerythritol triallyl ether (9.9g) and triethylamine (3.8g) in dry ether (60ml) is slowly added into a solution of phosphorus oxychloride (15.3g) in dry ether (60ml) at 0 with stirring. After addition of the solution the mixture of two solution is stirring for 16 hours at room temperature. The precipitation of the triethylamine hydrochloride is filtered off and the solution is hydrolyzed by addition of the ether solution into ice water (100ml) with stirring. The mixture is separated and the ether layer is basified with sodium carbonate solution until pH =10 then acidified with hydrochloride acid until pH = 4. The ether layer is extracted and dried by magnesium sulphate. The ether is extracted by under reduced pressure to give the title compounds as a clear colorless liquid. The H^1 NMR spectrum of this compound shows peaks around 6.2-5.8, 5.6-5.1, 4.5-4.1, 4.0-3.8, 3.6-3.4, 2.2-2.0 1.5-1.2, 1.0-0.8 ppm.

Example 4

Effect of thio-methacrylate compound on resin adhesion to silver

For each of six replicates, flat surfaces perpendicular to the long axis of pure silver rods were prepared by abrading with 600 grit aluminum oxide paper. The surface was the treated with nitric acid (HNO_3). An unfilled resin was then placed on this surface, and a composite button was bonded to place. Using the same conditions of preparation for another six replicates, a 6 percent solution of an allyl mercaptan was placed on the nitric acid-treated silver surface. A composite button was then similarly

bonded to place. Each of the samples was then subjected to a load at the resin-metal interface one hour after preparation, using an Instron electromechanical testing device. The results of these tests are shown in table 1 below. The resin bonded by the allyl mercaptan showed a significant increase in strength compared to the group where no thiol-based adhesion promoter was used.

Table 1

# of samples	acid	primer	peak stress MPA, (SD)
6	HNO ₃	none	12.0, (1.7)
6	HNO ₃	allyl mercaptan	17.2, (3.6)

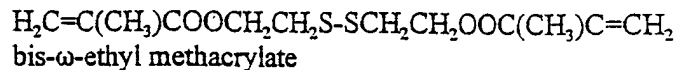
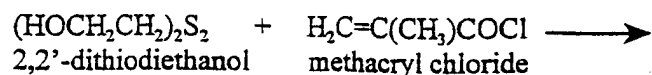
Example 5.*Effect of Metal Reinforcement:*

Standard bars (n=4) measuring 25 x 2 x 2 mm were made of a 50:50 Bis-GMA/TEGDMA mixture, and the same mixture (n=5) filled with silanated silver alloy particles and titanium dioxide (in a weight ratio of 4:1). The filler volume was 70 %. The composite was chemically hardened by a peroxide/amine system. After 24 hours, the bars were submitted to a three-point bend test in an Instron electromechanical testing instrument. Flexural strength was calculated from failure loads, and mean values and (standard deviations) were respectively 17.8 (4.2) and 36.3 (8.7) Mpa. Based on this data, we conclude that the dental polymers are reinforced by predominantly metal particulates.

Example 6.*Synthesis of bifunctional alkylthiols:*

There are three possible synthetic approaches in developing bifunctional thiol compounds. The first involves the synthesis of an ω -thioethyl methacrylate by esterification of 2-thioethanol with methacryl chloride. A second method uses the disulfide form of the thiol compounds throughout the synthesis, while a third method involves a solid state synthesis where the metal particles are first coated with ω -thio alcohol, and then reacted with methacryl chloride to add the methacryl group to the thiol. The latter two are described in more detail below.

The simplest synthesis of an ω -thioethyl methacrylate is from a mixture of 2-mercaptoethanol and methacryl chloride. Normally, thiols are applied using dilute ($< \approx 10^{-3}$ M) ethanol solutions to achieve full, well-ordered monolayer coverages. Generally, little difference is observed if the dilute thiol solution is replaced with a disulfide form. Here, a bis-(ω -ethyl methacrylate) disulfide compound is prepared in the presence of tetrahydrofluoran to form an omega terminated thiol compound according to the following reaction:



The third synthetic method protects the thiol group during the reaction of the alcohol with the methacryl chloride, this time by adsorbing the ω -thio alcohol onto a solid substrate. Adsorption takes place exclusively at the thiol group, leaving the outer surface of the particle rich in hydroxyl groups. The reaction proceeds as follows: AuCl_4 is added to NaBH_4 in water. 2-thioethanol is then added to cap the particles of colloidal gold and stop the reaction. After extensive washing with water, the colloid is separated by centrifugation. The silver is then re-suspended in water, and the outer -OH groups are reacted with excess methacryl chloride. Again, the particles are extensively washed, and centrifuged for collection.

What is claimed is:

1. A composition which is particularly suitable in the dental art as a tooth filling material, comprising a polymer matrix in an amount from 10 to 50 percent by weight of the composition; a filler being comprised of a metal particulate, or a metal alloy particulate, or in combination, in the presence or absence of metal oxides, in an amount from 20 to 98 percent by weight of the composition; and a coupling agent in an amount from 1 to 5 percent by weight.
2. The composition of claim 1, wherein the polymer matrix is formed from an acrylate or methacrylate monomer, or a phosphate of acrylate or methacrylate monomer, or a mixture of the preceding.
3. The composition of claim 2, wherein the monomers of acrylate or methacrylate include at least one selected from the group consisting of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane, ethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, 1,6-hexamethylene glycol dimethacrylate (HGDMA), and trimethylolpropane trimethacrylate, pentaerythritol triacrylate, pentaerythritol triallyl ether and pentaerythritol tetraacrylate.
4. The composition of claim 2, wherein the phosphate monomers of acrylate or methacrylate includes at least one selected from the group consisting of pentaerythritol triallyl ester monophosphate, pentaerythritol triacrylate monophosphate, dipentaerythritol pentaacrylate monophosphate and ethyl methacrylate monophosphate.
5. The composition of claim 1, wherein the filler includes metal, metal alloys and metal oxides, all in the form of particulates measuring from 0.2 to 50 microns.
6. The composition of claim 5, wherein the metal and metal alloys included are silver, gold, silver or gold alloys, or a mixture of these materials, in the presence or absence of a metal oxide.
7. The composition of claim 1, wherein the coupling agent is formed by a silane, an alkenethiol, or a phosphate ester having a vinyl functionality.
8. The composition of claim 7, wherein the silane is selected from the group consisting of γ -methacryloyloxypropyl trimethoxysilane, 3-mercaptopropyl trimethoxysilane and mixtures thereof.
9. The composition of claim 7, wherein the alkenethiol includes $\text{HS}-(\text{CH}_2)_n$, where n equals an integer of 2 to 100; and 2-mercaptoethyl methacrylate.
10. The composition of claim 7, wherein the phosphate ester has the formula:



where:

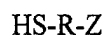
R_1 is a hydrogen atom, alkyl C_1-C_4 , or CN,

R is an aliphatic, cycloaliphatic or aryl radical containing from 1 to 10 carbon atoms and having a valence of $n+1$,

n is an integer from 1 to 5, preferably from 3 to 5.

11. The composite of claim 9 where n represents 12.

12. Omega-terminated thiols having organic functionalities capable of reacting with a polymer matrix having the formula:



where HS is the thiol, R is the linkage between the thiol and omega termination being comprised of $(CH_2)_n$, where $n=1$ to 100, and Z is the reactive omega termination having a reactive functionality comprised of, for example, a vinyl, or acyloxy, or a methacryloxy group.

13. Organic disulfides of the formula:



where S-S is the disulfide, R is the linkage being and Z is the terminal reactive group comprised of, for example, a vinyl, or acyloxy, or a methacryloxy group.

14. A method of constructing a thiol having the formula:



where M is a metal, or metal alloy, with or without a thin coating of silver or gold, R is the linkage between the thiol and omega termination being comprised of $(CH_2)_n$, where $n=1$ to 100, and Z is the reactive omega termination having a reactive functionality comprised of, for example, a vinyl, or acyloxy, or a methacryloxy group.

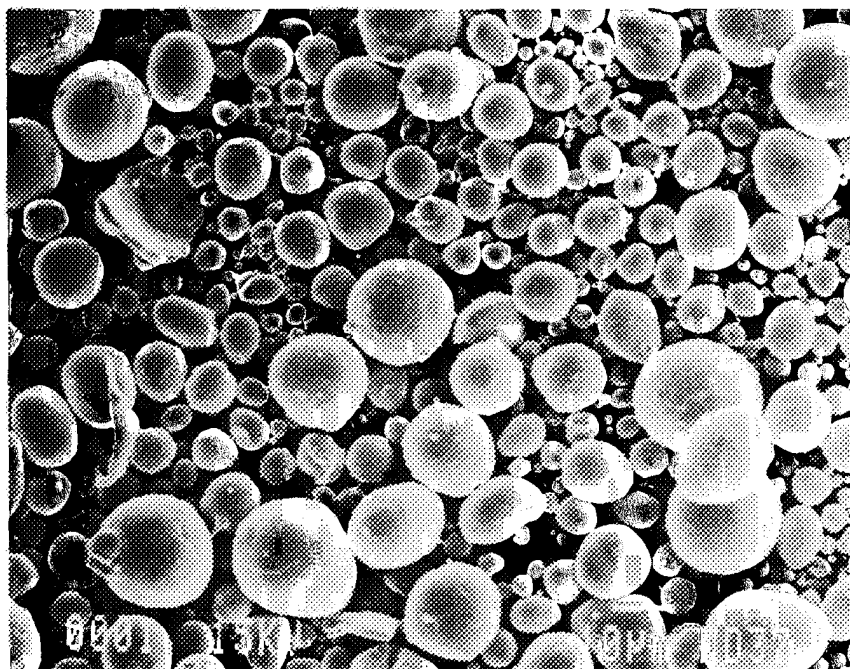
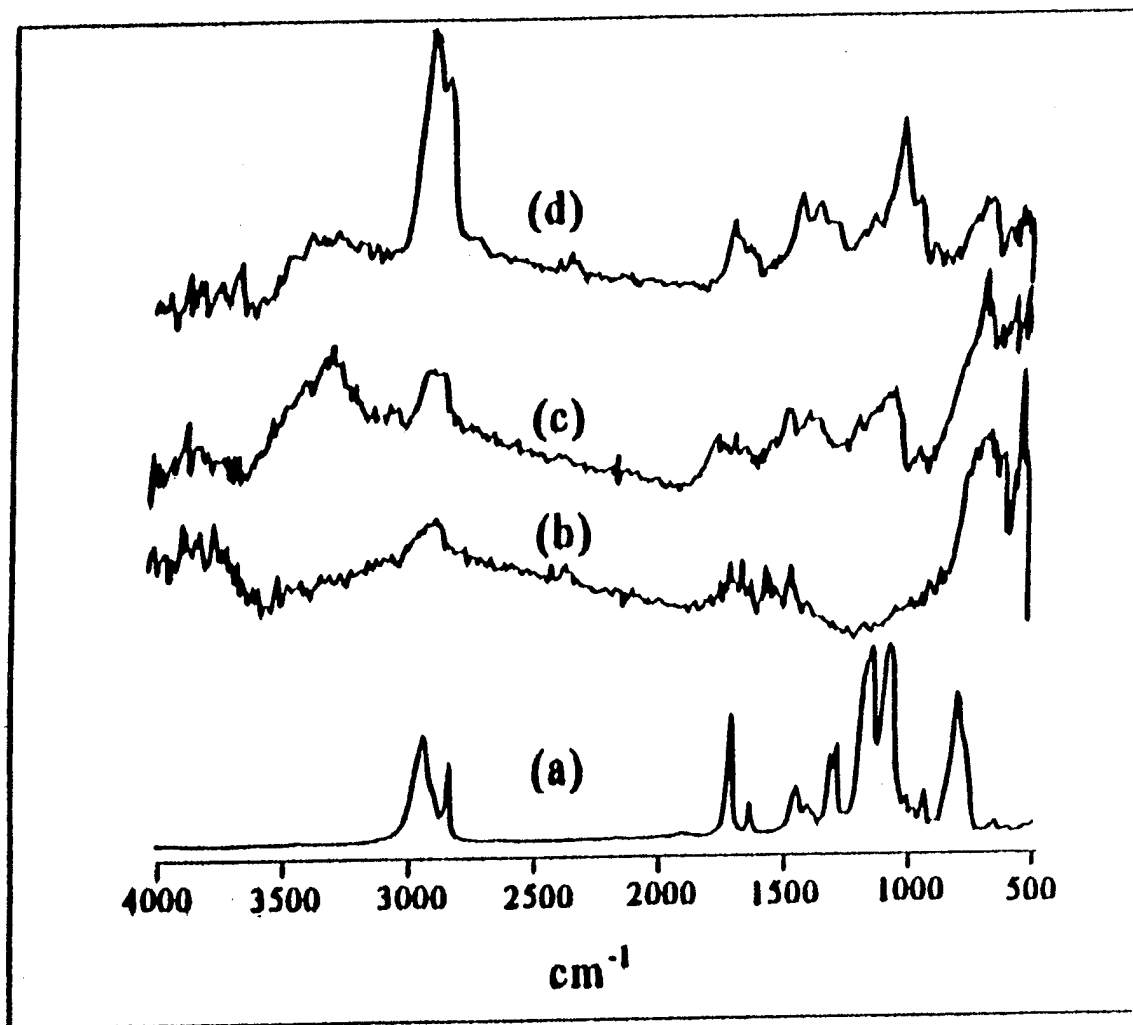
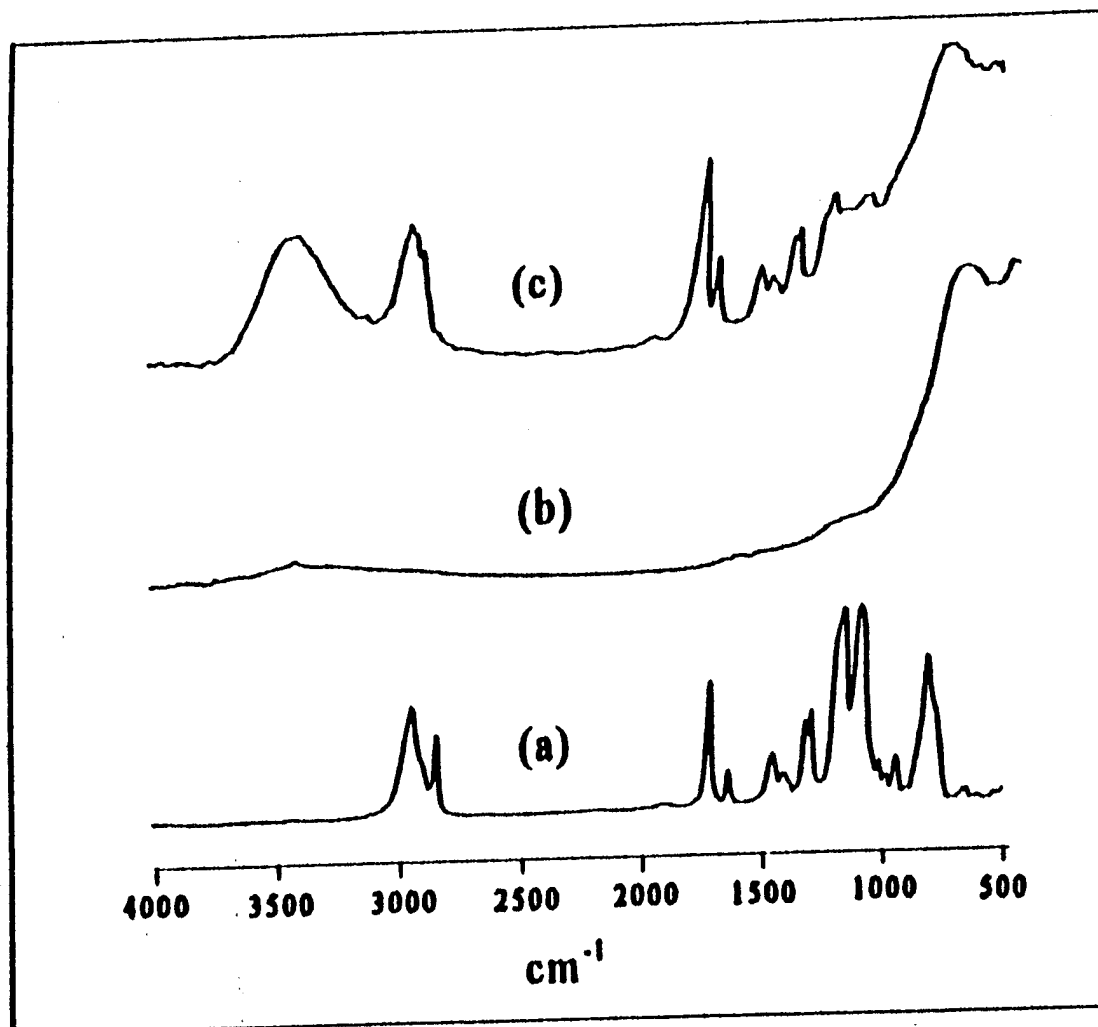
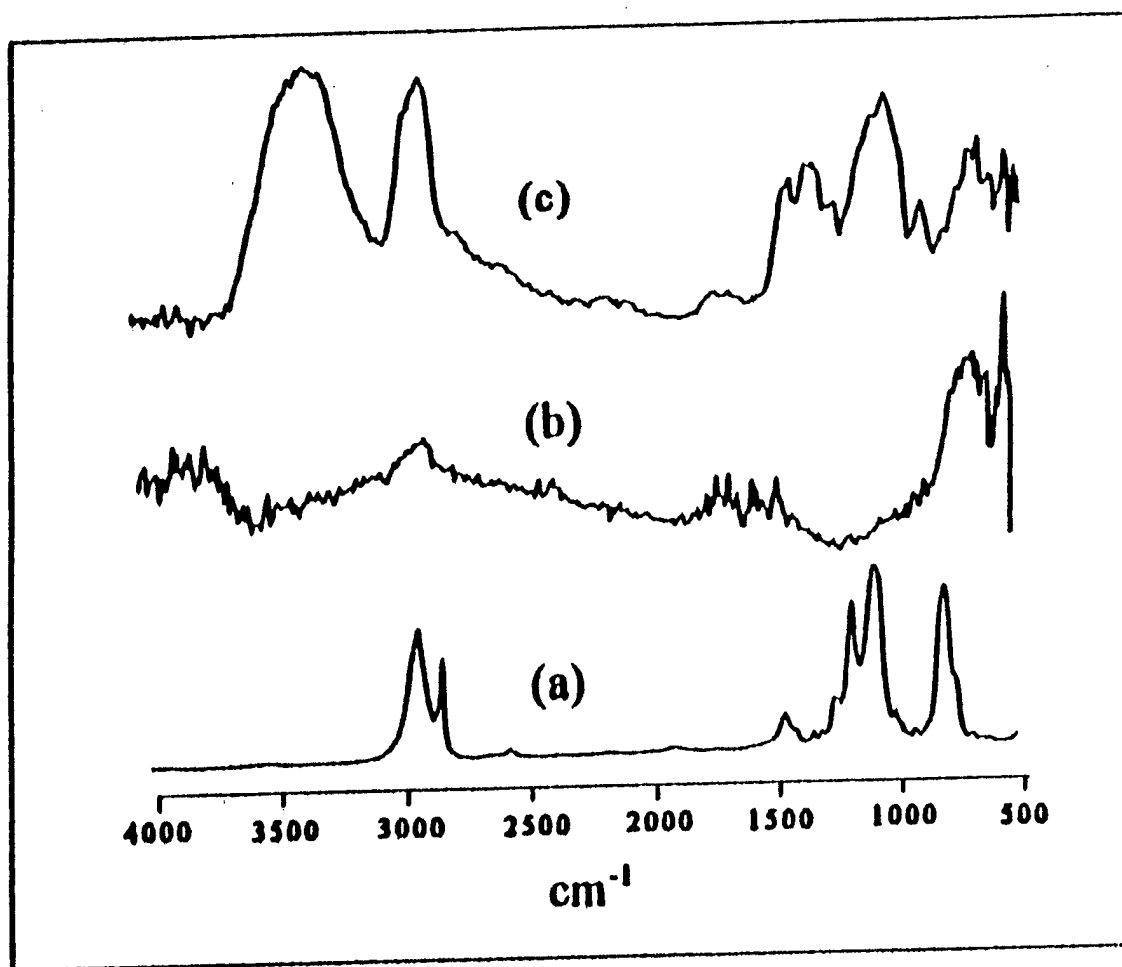


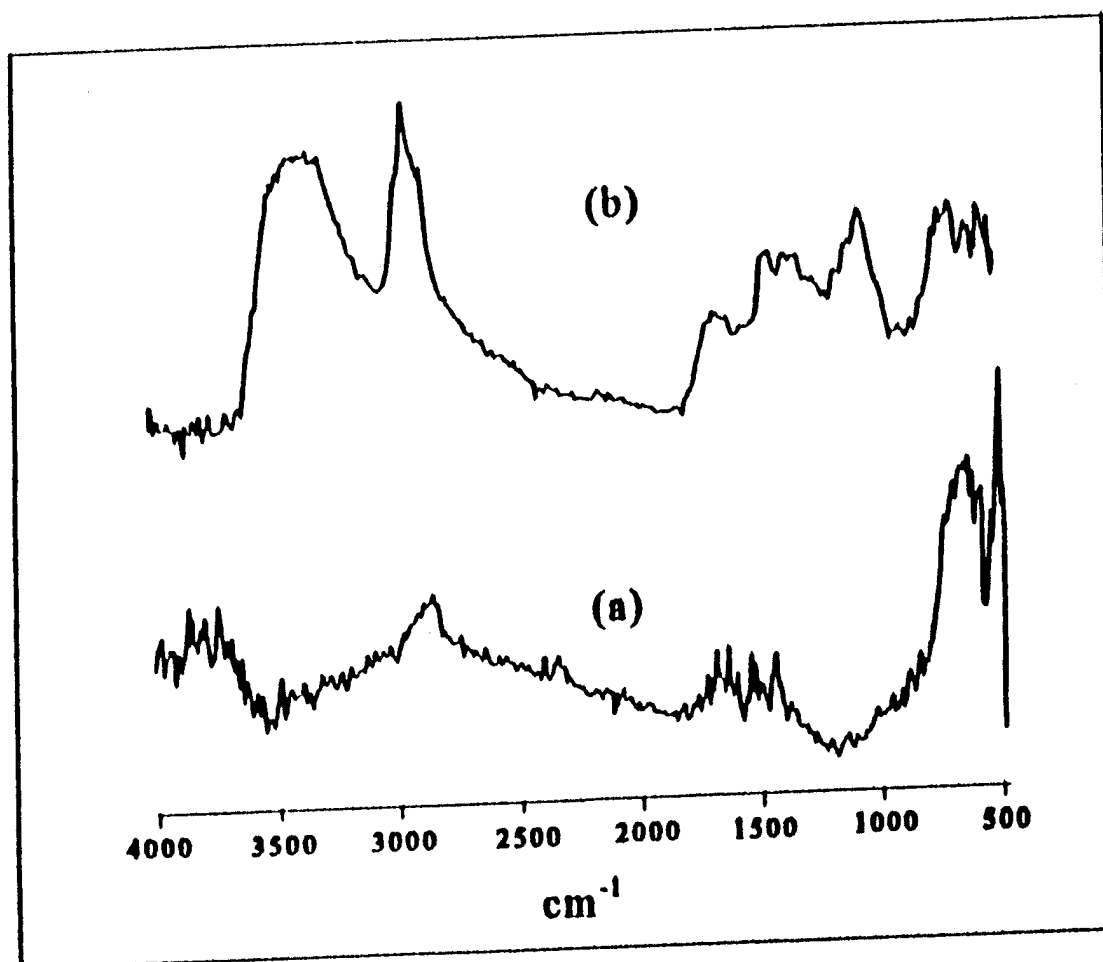
FIG. 1

2/5

**Figure 2**

**Figure 3**

**Figure 4**

**Figure 5**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/12715

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :A61K 6/04; C08K 3/10, 5/37

US CL :523/115, 116, 205; 524/392, 395, 440, 547; 526/286, 289

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 523/115, 116, 205; 524/392, 395, 440, 547; 526/286, 289

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,713,403 A (YOSHIDA et al.) 15 December 1987, abstract, column 2, lines 13-68, column 3, lines 1-11 and 20-25, and claims 1 and 13-14.	1-3, 5-8
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Y		1-10
Y,P	US 5,733,644 A (TANAKA et al.) 31 March 1998, abstract, column 9, lines 35-46, column 10, lines 23-27 and 41-69, and column 15, lines 25-65.	1-9, 12
Y	US 4,816,495 A (BLACKWELL et al.) 28 March 1989, abstract, column 1, lines 5-15, column 9, lines 1-15 and 33-55 and example 2.	4-5, 7, 10

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*g* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search	Date of mailing of the international search report
27 AUGUST 1998	02 OCT 1998

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/12715

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,064,495 A (OMURA et al.) 12 November 1991, abstract, column 1, lines 9-16, column 2, lines 40-69, columns 3-14, especially 9-14, and column 18, line 60 to column 19, line 16, and column 20, lines 55-67.	12-13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12715

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

search terms: gold, silver, alloy, thiol(s), mercaptan(s), disulfide, methacrylate, coupling agent, adhesion promoter, keying agent, phosphoric, methacrylate phosphate, dental, surgical, medical