OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

(12) (19) (CA) **Brevet-Patent**

(11) (21) (C) **2,202,936**

(22) 1997/04/17
(43) 1997/10/20
(45) 2001/06/12

(72) HEINDL, Detlef, DE
(72) ERDRICH, Albert, DE
(73) HERAEUS KULZER GMBH & CO. KG, DE

(51) Int.Cl.^{6} C08K 9/06, C08F 2/50
(30) 1996/04/20 (196 15 763.3) DE

(54) CHARGE A BASE DE DIOXYDE DE SILICIUM, PROCEDE DE FABRICATION ET UTILISATION

(54) FILLER ON SILICON DIOXIDE BASE, PROCESS FOR ITS MANUFACTURE AND USE

(57) Porous silicon dioxide glass with a particle size of 0.5-50 µm, a pore size of 20-120 nm, a pore volume of 200-1000 mm_3/g and a BET surface of 10-100 m_2/g is suggested as an inorganic filler for polymerizable materials. Polymeric products containing this filler are characterized by very good abrasion resistance.

Abstract

Porous silicon dioxide glass with a particle size of 0.5-50 μm, a pore size of 20-120 nm, a pore volume of 200-1000 mm^3/g and a BET surface of 10-100 m^2/g is suggested as an inorganic filler for polymerizable materials. Polymeric products containing this filler are characterized by very good abrasion resistance.

FILLER ON SILICON DIOXIDE BASE, PROCESS FOR ITS MANUFACTURE AND USE

The invention pertains to a finely grained filler on silicon dioxide base, its manufacturing process and its use in polymerizable materials. In particular, the invention pertains to a finely grained filler on silicon dioxide base for dental materials hardening through polymerization, preferably to such materials used in making dental fillings.

In the realm of dental filling materials, it was considered a giant step forward when Rafael L. Bowen introduced long-chained monomeric dimethacrylates (reaction products of bisphenol A and its derivatives with glycidyl methacrylate, especially the so-called bis-GMA) to replace the methyl methacrylate used up to that time, and also fine quartz glass powder to reinforce the plastic matrix (US 3 066 112 A).

Another example of a dental material containing organic monomers, as well as a finely divided inorganic filler, is described in US 3 539 533 A. In this description, the polymerizable binding agent is a mixture of bis-GMA, bisphenol A-dimethacrylate, a diluting monomer, especially triethylene glycol dimethacrylate, and in some cases, small quantities of methacrylic acid; it is used together with approximately 65-75% by weight of the inorganic filler, such as silicon dioxide, glass, aluminum oxide or quartz. The inorganic filler can have a particle size of about 2-85 μm; and to improve the bond between plastic and filler, it is pretreated with a silane such as 3-methacryloyloxypropyltrimethoxysilane.

A material for dental purposes is known from DE 24 03 211 C3 (filling materials for cavities, materials for luting cements, sealing and protective coatings, crown and bridge materials, prosthetic materials, materials for making artificial teeth), which, in addition to polymerizable acrylate or methacrylate as an inorganic filler contains microfine (highly dispersed) silicon dioxide, with a particle size of approximately 0.01-0.4 μm and a BET surface of approximately less than 200 m^2/g. The polymerizable monomer consists of bis-GMA or another derivative of bisphenol A or a reaction product of hydroxyalkylmethacrylates and diisocyanates, occasionally combined with monomeric short-chained methacrylates and/or diacrylates or dimethacrylates. The dental fillings and similar constructions fashioned from material containing microfine filler are characterized by their ability to be highly polished and by a transparency resembling that of natural teeth.

Another step in the development of dental materials on resin base are the so-called hybrid materials which contain microfine fillers as well as conventional fillers (macrofillers). One such dental material is, for example, known from DE 24 05 578 C3. It contains 30-80% by weight of a mixture of amorphous silicic acid (pyrogenic silicon dioxide) with a maximum particle size of 0.07 μm made by flame hydrolysis and finely divided glass, preferably borosilicate glass, glass containing barium or lanthanoxide, or lithium aluminum silicate glass, with a particle size of up to 5 μm.

The dental filling material described in DE 34 03 040 A1 contains 60-90% by weight of a filler mixture consisting of 5-20% by weight of an X-ray opaque filler with a particle size distribution between 0.5 and 40 μm, 20-35% by weight of an X-ray opaque filler with a particle size distribution between 0.2

and 15 µm, and 45-75% by weight of a silicon dioxide microfiller with a particle size distribution between 5 and 150 nm.

Another example of a hybrid material is the dental composition described in EPO 382 033 A2, which, in addition to polymerizable acrylates or methacrylates and a catalyst for photo polymerization (photo activator), contains 5-80% by weight of a silanized glass or a silanized glass ceramic, with a mean particle size between 0.1 and 10 µm and 2-10% by weight of a surface-treated microfiller.

The inorganic fillers used to reinforce dental materials on resin base usually contain a surface treated with a silane, such as 3-methacryloyloxypropyltrimethoxysilane, which improves compatibility with organic components (DE 34 03 040 A1) and results in a chemical bond between the filler and the resin matrix. Further improvement of the filler/resin bond can be achieved if, in addition to the chemical bond, there is a possibility of a physical bond. For example, a physical bond can be accomplished according to a suggestion in US 4 215 033 A, i.e., using a semiporous filler obtained by etching a two-phase glass. The depth of the pores existing on the surface is 10-10,000 Angstrom units.

Dental materials containing porous fillers are also known from US 4 217 264 A, EP 0 048 681 B1 and EP 0 172 513 B1.

In addition to monomeric methacrylic acid esters and a catalyst for polymerization, the polymerizable dental material described in US 4 217 264 A also contains an internally microporous glassy filler, which is formed by calcining inorganic oxide sols, especially those of silicon dioxide, aluminum dioxide and at least one X-ray opaque oxide (zirconium, hafnium, tantalum and tin oxide). The filler can consist of 27-57% by weight of silicon dioxide.

EP 0 048 681 B1 relates to a method for manufacturing a composite material of organic resin and inorganic porous particles by impregnating the porous inorganic particles with resin that can partially harden, compressing so that the particles are in contact with one another and the pressure of the resin is equalized by the plastic flow of the excess resin through the pores of the inorganic particles, and gluing the particles together by hardening at least a portion of the resin material. This results in a resin structure with an adjacent inorganic phase.

The composite material is preferably suitable for use as a dental material, including filling and coating material, as a bonding agent, as material for crowns and bridges, and as material for dentures and artificial teeth.

EP 0172 513 B1 describes polymerizable dental compositions which, in addition to 20-65% by weight of polymerizable monomers, also contain 10-60% by weight of a microporous filler composed of silicon dioxide, aluminum oxide or calcium silicate. The microporous filler has a mean particle size of 0.5-50 μm, a BET surface of at least 200 m^2/g, a pore volume of 0.7-5 ml/g and a pore diameter of 10-50 nm, and it can be silanized. The dental compositions can be used, for example, for dental restoration and repair work, as crown and bridge material, and for making artificial teeth.

DE 195 24 362 A1 pertains to an inorganic composition and a dental composite material containing this composition for restorative purposes. The inorganic composition contains (A) 60-99% by weight of spherical oxide particles with an average particle diameter of over 0.1 μm, but not more than 1 μm, and (B) 1-40% by weight of fine oxide particles with an average particle diameter of not less than 0.1 μm, in which the volume of micropores, due to the densely aggregated particles with a pore diameter of no less than 0.08 μm, is not more than 0.1 cm^3 per gram of the inorganic composition. Amorphous silicon dioxide, silicon dioxide/zirconium oxide, silicon dioxide/titanium oxide, quartz, aluminum oxide, etc. are the preferred examples of the spherical oxide particles. The spherical oxide particles are generally produced through the hydrolysis of a metal oxide. After drying, they are often baked at 500°C to 1000°C to reduce the proportion of silanol groups on the surfaces. Pyrogenic silicon dioxide, pyrogenic aluminum oxide, pyrogenic zirconium oxide, amorphous silicon dioxide, quartz, aluminum oxide, etc. are examples of fine inorganic oxide particles.

The inorganic composition has a surface that has been treated with silane. The products obtained from the composite material after hardening are characterized by good mechanical properties, a smooth surface structure, and very low abrasion at the tooth antagonist.

The object of the invention is a finely grained filler on silicon dioxide base, characterized in that it consists of porous silicon dioxide glass, having a particle size of 0.5-50 μm, a pore size of 20-120 nm, a pore volume of 200-1000 mm^3/g and a BET surface of 10-100 m^2/g.

It is preferable that the porous silicon dioxide glass has a particle size of 0.5-20 μm, a pore size of 90-100 nm, a pore volume of 800-900 mm^3/g and a BET surface of 20-40 m^2/g.

The porous silicon dioxide glass can be produced by applying the method described in DD 250 310 A1, with subsequent grinding, such as in a ball mill with zirconium oxide grinding balls, and classifying in an air classifier, for example.

The porous silicon dioxide glass has proven to be especially successful when it is available in a silane-treated form; 3-methacryloyloxypropyltrimethoxysilane has proven to be a particularly suitable silane.

A particularly advantageous embodiment of the invention results when the porous silicon dioxide glass is provided with an impregnation containing one or more monomeric acrylic acid esters, methacrylic acid esters or a mixture thereof — hereinafter referred to as (meth)acrylic acid ester.

The impregnated silicon dioxide glass can be produced by treating the porous silicon dioxide glass with an impregnation agent containing a monomeric (meth)acrylic acid ester. To this end, the porous glass and impregnation agent are thoroughly mixed, preferably at a high temperature. The mixture is then subjected to treatment under reduced pressure, preferably also at a high temperature.

The quantity of the impregnation agent used in the treatment depends on the pore volume of the silicon dioxide glass, as well as on the intended purpose of the impregnated silicon dioxide glass; the quantity can be determined by experimentation.

If the impregnated silicon dioxide glass is to be further used in dry form and the pore volume of the silicon dioxide glass is, for example, 1000 mm^3/g, it is recommended that equal amounts of glass and impregnation agent be used.

The monomeric (meth)acrylic acid esters can be monomeric mono-, di- and poly(meth)acrylates. If the silicone dioxide glass is used as a filler in polymerizable dental materials, the (meth)acrylic acid esters are selected from among those (meth)acrylic acid esters which are known and have proven successful for such materials.

The following are the preferred monomers:

Hydroxyethylmethacrylate,
Hydroxypropylmethacrylate,
Triethylene glycol monoethylethermono(meth)acrylate,
Diurethane di(meth)acrylate from 2,2,4-trimethylhexamethylendiisocyanate and
2-hydroxyethyl(meth)acrylate,
Diurethane di(meth)acrylate from bis-(diisocyanatomethyl)-tricyclodecane and
2-hydroxyethyl(meth)acrylate,
Decanedioldi(meth)acrylate,
Dodecanedioldi(meth)acrylate,
Triethylene glycol di(meth)acrylate,
Bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl]-dimethylmethane,
Bis-[4-(2-hydroxy-3-acryloyloxypropoxy)-phenyl]-dimethylmethane,
Tri(meth)acryloyloxyethoxytrimethylolpropane,
Tetra(meth)acryloyloxyethoxypentaerythritol,
Tetra(meth)acryloyloxyisopropoxypentaerythritol and

Hexa(meth)acryloyloxyethoxydipentaerythritol.

It has proven to be particularly successful when impregnation is carried out with impregnation agents which, in addition to the monomeric (meth)acrylic acid esters of appropriate viscosity, also contain polymerization catalysts. The polymerization catalysts can be catalysts for hot polymerization, cold polymerization or photo polymerization. Organic peroxides such as dibenzoyl peroxide are examples of suitable catalysts for hot polymerization; redox systems are examples of suitable catalysts for cold polymerization, preferably those from organic peroxides and amines; and, ketone/amine systems such as those known from GB 1 408 265 B1, e.g. camphorquinone/amine are examples of suitable catalysts for photo polymerization.

Impregnations with a catalyst for photo polymerization are preferred, because they also allow for single-component formulation. In that case, the impregnation or the agents to produce it contains 0.1-0.5% by weight, preferably 0.1-0.3% by weight of a ketone/amine system, with N,N-dimethyl-p-toluidine, N,N-bis-(2-hydroxyethyl)-p-toluidine and esters of the 4-dimethylaminobenzoic acid, such as ethyl- and butoxyethylester, which have proven to be particularly successful as amines. Another photoactive component that may be present is benzilacetal, preferably in quantities of 0.02-0.1% by weight.

The impregnation should also preferably contain a silane, especially 3-methacryloyloxypropyltrimethoxysilane. A silane content of 1-8% by weight in the impregnation or in the impregnation agent has proven to be successful.

According to the invention, the silicon dioxide glass is extremely well-suited for use as a filler in polymerizable materials.

Surprisingly, the resins reinforced with the silicon dioxide glass are characterized by very good abrasion resistance (wear resistance). Shrinkage due to polymerization is low.

The following example describes in greater detail the production of a silicon dioxide glass according to the invention, which is impregnated with monomeric (meth)acrylic acid esters, a catalyst system for photo polymerization and a silane. Shrinkage of the impregnated silicon dioxide glass during polymerization, and the abrasion resistance of specimens obtained from the silicone dioxide glass impregnated with the monomeric (meth)acrylic acid esters, are determined and identified with the appropriate characteristics of a commercial composite (Charisma®, registered trademark of Heraeus Kulzer GmbH, Germany), or of specimens made thereof.

Example:

Impregnated silicon dioxide glass

Basic products:

A) porous silicon dioxide glass
pore size: 90-100 nm
mean particle size: 8 μm
pore volume: 880 mm^3/g
BET surface: 30 m^2/g

B) Impregnation liquid consisting of
41.24 g tetraacryloyloxyisopropoxypentaerythritol
31.08 g bis-[4-(2-hydroxy-3-acryloyloxypropoxy)phenyl]-dimethylmethane
7.77 g hydroxypropylmethacrylate
6.0 g triethylene glycol monoethylethermonomethacrylate
0.39 g benzildimethylacetal
0.16 g camphorquinone
0.23 g 4-dimethylaminomethylbenzoic acid-(2-butoxyethyl)-ester
5.5 g 3-methacryloyloxypropyltrimethoxysilane

Heat the impregnation agent to 70°C and add 90 g of the porous silicon dioxide glass. Stir the resulting mixture for 20 minutes, until the impregnation agent perfuses the glass evenly. Expose the mixture for 20 minutes to a reduced pressure (10^{-1} to 10^{-2} torr, $1.3332 \cdot 10^{-2}$ MPa to $1.3332 \cdot 10^{-3}$ MP) while maintaining the temperature at 70°C. After cooling to room temperature, impregnated silicon dioxide glass is attained in the form of a white, opaque substance.

To determine the shrinkage due to polymerization, produce samples from the impregnated silicon dioxide glass, measuring 15 mm in diameter and 1 mm in thickness. Focus a laser beam onto the surface of the samples while irradiating the opposite side of the samples with a light polymerization apparatus (Translux EC by Heraeus Kulzer GmbH, Germany). Due to the shrinkage that occurs with polymerization, the laser beam must be tracked to remain focussed. The difference in focusing is a measure of the linear shrinkage due to polymerization of the samples.

The abrasion resistance is determined by measuring the wear with the "Kausimulator" described in Schweiz. Monatsschr. Zahnmed. Vol. 100 (1990), pp. 953-960. To measure the wear, use samples with a diameter of 10 mm and a thickness of 2 mm, produced by irradiating for 180 seconds with the light polymerization apparatus and polishing with silicon carbide sandpaper, using a ceramic stick as a counter punch.

Shrinkage due to polymerization and abrasion resistance are indicated in the Table.

Table

Sample	Shrinkage due to polymerization (μm)	Abrasion resistance (μm)
Example	7	25-40
Composite (comparison)	14	90-100

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. Finely divided filler on a silicon dioxide base comprising porous silicon dioxide glass having a particle size of 0.5 - 50 micrometers, a pore size of 20 - 120 nanometers, a pore volume of 200 - 1000 mm^3/g and a BET surface area of 10 - 100 m^2/g wherein the porous silicon dioxide glass is provided with an impregnant containing monomeric (meth)acrylic acid esters.

2. Filler according to claim 1, wherein the porous silicon dioxide glass has a particle size of 0.5 - 20 micrometers, a pore size of 90 - 100 nanometers, a pore volume of 800 - 900 mm^3/g and a BET surface area of 20 - 40 m^2/g.

3. Filler according to claim 1 or claim 2, wherein the impregnant additionally contains a catalyst for photo polymerization.

4. Filler according to claim 3, wherein the catalyst for photo polymerization is a camphorquinone/amine system.

5. Filler according to claim 1 or 2, wherein the impregnant additionally contains a silane.

6. Filler according to claim 5, wherein the silane is 3-methacryloyloxypropyltrimethoxysilane.

7. A method of preparing a finely divided filler on a silicon dioxide base comprising the step of treating a porous silicon dioxide glass having a

particle size of 0.5 - 50 micrometers, a pore size of 20 - 120 nanometers, a pore volume of 200 - 1000 mm^3/g and a BET surface area of 10 - 100 m^2/g with an impregnant agent containing monomeric(meth)acrylic acid esters.

8. Method according to claim 7, wherein the impregnant agent additionally contains a catalyst for photo polymerization.

9. Method according to claim 8, wherein the catalyst for photo polymerization is a camphorquinone/amine system.

10. Method according to claim 7, wherein the impregnant agent additionally contains a silane.

11. Method according to claim 10, wherein the silane is 3-methacryloylloxypropyltrimethoxy silane.

12. For use in a polymerizable material, a finely divided filler on a silicon dioxide base comprising porous silicon dioxide glass having a particle size of 0.5 - 50 micrometers, a pore size of 20 - 120 nanometers, a pore volume of 200 - 1000 mm^3/g and a BET surface area of 10 - 100 m^2/g.

13. A finely divided filler according to claim 12, wherein the porous silicon dioxide glass has a particle size of 0.5 - 20 micrometers, a pore size of 90 - 100 nanometers, a pore volume of 800 - 900 mm^3/g and a BET surface area of 20 - 40 m^2/g.

14. A finely divided filler according to claim 12 or 13, wherein the porous silicon dioxide glass is silanized.

JJ:mw

15. For use in a polymerizable material, a finely divided filler on a silicon dioxide base comprising porous silicon dioxide glass having a particle size of 0.5 - 50 micrometers, a pore size of 20 - 120 nanometers, a pore volume of 200 - 1000 mm^3/g and a BET surface area of 10 - 100 m^2/g, wherein the porous silicon dioxide glass is provided with an impregnant containing monomeric (meth)acrylic acid esters.

16. A finely divided filler according to claim 15, wherein the porous silicon dioxide glass has a particle size of 0.5 - 20 micrometers, a pore size of 90 - 100 nanometers, a pore volume of 800 - 900 mm^3/g and a BET surface area of 20 - 40 m^2/g.

JJ:mw