POROUS FILLERS IN POLYMERIZABLE COMPOSITIONS

The present invention relates to the use of porous inorganic particles defined in more detail below, in particular of SiO_2 or silicates, as fillers for polymerizable compositions, preferably dental compositions. The compositions according to the invention can be used, for example, for dental restoration and repair work, as crown and bridge materials and for the production of false teeth.

Hardenable filler-containing dental compositions based on ethylenically unsaturated polymerizable monomers (in particular mono-, di- and poly-functional esters of acrylic and methacrylic acid) are known, for example, from U.S. Pat. Nos. 3,066,112, 3,926,906 and British Patent Specification No. 1,544,776. The (inorganic) fillers must be added to the polymerizable compositions to reduce their polymerization shrinkage, to lower the coefficient of thermal expansion and to increase the hardness of the polymers obtained.

The amount of inert inorganic fillers in such dental materials can be up to over 80% of the total composition. Examples of fillers used are quartz, quartz glass or silicate glasses, such as lithium aluminum silicate or barium silicate glass, as fine powders. The particle sizes of these fillers are in the range from 1 to about 100 μm, the average particle diameter in general being of the order of about 10 μm.

The disadvantage in using these known fillers is that the dental materials produced therefrom are not yet satisfactorily abrasion-resistant and have a surface roughness when used as dental fillings. As a result of their poor abrasion properties, it has not been possible to use the dental filling materials containing such fillers in the region of posterior teeth, so that at present the amalgam fillings still prevail there.

However, the surface roughness of the materials mentioned also leads to problems when these are used in the region of anterior teeth, since deposition of dental plaque is promoted here and both discoloration and marginal secondary caries can thereby be caused.

In order to eliminate the disadvantages of surface roughness, German Patent Specification No. 2,403,211 proposes the use, as a filler, of highly disperse silicon dioxide obtained by flame pyrolysis, the particle size of which should be in the range from 10 to 400 nm; the BET surface area should be less than 200 m^2/g; the unsuitability of precipitated silicic acids is expressly referred to.

A combination of macrofiller and microfiller composites is described in European Patent Application No. 0,060,911. According to European Patent Application No. 0,040,232, granulation of pyrogenic or precipitated silicon dioxide with waterglass or boric acid gives stable agglomerates which allow higher degrees of filling and can be polished. The use of microporous fillers is also known per se. Porous glasses are described, for example, in U.S. Pat. Nos. 2,106,744, 3,549,524 and 4,306,913. Porous fillers can also be obtained by sintering glass fibers, as described in European Patent Application No. 0,048,681. These conventional microporous fillers have a specific surface area of not more than about 20 m^2/g.

A decisive weak point of the macrofillers hitherto known is the poor bonding between the filler surface and polymer matrix, which can be only partly improved by surface treatment. Although the bonding can be increased by increasing the surface area or the number of pores, fractographs obtained by scanning electron microscopy then also show, as is the case with the agglomerates, inadequate bonding between the filler surface and polymer matrix. A summary of the advantages and disadvantages of the individual systems in respect of their clinical properties is given by Lutz, Phillips, Roulet and Imfeld in Schweiz. Mschr. Zahnheilkunde 93, 914-929 (1983).

It has now been found, surprisingly, that synthetic amorphous highly porous particles which are known per se, in particular silicic acids, such as are described as matting agents in, for example, DE-OS (German Published Specification) No. 2,145,090 (U.S. Pat. No. 3,959,174), DE-OS (German Published Specification) Nos. 2,124,223 and 2,853,647, exhibit outstanding properties as fillers.

The invention relates to the use of microporous inorganic fillers in polymerizable compositions, characterized in that the fillers have (a) an average particle size of 0.5–50 μ, preferably 1–20 μ; (b) a BET surface area of at least 200 m^2/g, preferably 300–600 m^2/g; (c) a pore volume of 0.7–5 ml/g, preferably 1–3 ml/g; and (d) a pore diameter of 10–50 nm, preferably about 20 nm.

The invention furthermore relates to polymerizable compositions, in particular dental compositions, containing 20 to 65% by weight, preferably 30 to 60% by weight, of a polymerizable monomer and 10 to 60%, preferably 30 to 50% by weight, of an inorganic filler and, if appropriate, additives which are known per se, characterized in that the filler fulfils the abovementioned criteria.

Finally, the invention also relates to a process for the production of shaped articles, in particular dental shaped articles, characterized in that a composition according to the invention is polymerized, while being shaped.

Although the microporous fillers to be used according to the invention have a relatively large average particle diameter, the shaped articles produced according to the invention (in particular dental fillings) are outstandingly easy to polish. Pictures of fracture surfaces obtained by scanning electron microscopy show a smooth surface such as is otherwise only known of materials which are built up homogeneously.

Surprisingly, the shaped articles produced according to the invention are also substantially transparent, although the refractive indices of, for example, amorphous silicic acid (1.46) and conventional, polymerized methacrylic acid esters, such as bis-GMA/triethylene glycol dimethacrylate (1.55) differ noticeably. In contrast to the prejudice expressed in DE-OS (German Published Specification) No. 2,403,211, precisely those fillers with a BET surface area greater than 200 m^2/g (preferably 300–600 m^2/g) show the best properties.

The microporous fillers to be used according to the invention are commercially available (for example Syloid ® grades from W. R. Grace & Co., New York). They can be prepared, for example, by the processes described in DE-OS (German Published Specification) Nos. 2,145,090 and 2,853,647. Possible starting materials here are in principle all the gel-forming inorganic oxides and salts, in particular SiO_2, Al_2O_3 and silicates (preferably Ca silicates).

If appropriate, before being used according to the invention, the fillers can be surface-treated in a manner which is known per se. Organosilicon compounds in an amount of 5–40% by weight, based on the filler, are