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FILLER MATERIALS FOR GLASS IONOMER CEMENTS

The present invention relates to filler materials and, more particularly, to a novel filler system for reinforcing dental restorative materials such as resin-modified and/or conventional glass ionomer cements.

Amalgam alloys remain the most widely used materials in the restoration of posterior teeth. Despite its excellent clinical record, however, the use of amalgam is becoming less and less desirable (Roulet JF, *J.Dent.* 25:459, 1997), and dental amalgam usage is expected to decrease because of (a) increased aesthetic demands by patients, (b) increased emphasis on alternative materials due to mercury controversy, and (c) environmental concerns causing changes in government regulations.

As an alternative to amalgam, the dental industry has previously focused on the development of new composite systems, which can be packed into a tooth cavity, like amalgam. Such systems include composite resins and so-called "condensable composites". Both types of system, however, have the disadvantages of (a) polymerisation shrinkage, (b) no chemical bonding to tooth tissue (bonding systems are required), (c) minimal to no fluoride release, (d) no dark-cure reaction and (e) greater co-efficient of thermal expansion than tooth tissue. In addition, the high viscosity of condensable composites has resulted in adaptation problems, which can lead to post-operative sensitivity.

Another group of dental restorative materials that have been developed are glass ionomer cements (GIC). Their properties include (a) chemical bonding to tooth tissue, (b) high fluoride release, and (c) similar co-efficient of thermal expansion to tooth tissues. They do not, however, have adequate strength and wear resistance for use in posterior teeth, and are initially moisture sensitive.

In order to enhance the physical properties of chemical-cure or traditional glass ionomer cements, addition of a dispersed phase, such as corundum, has been evaluated. The flexural strength was found to double, but little improvement in wear resistance was obtained (Prosser HJ, Powid DR., Wilson AD, *J.Dent.Res.* 65:146, 1986). The incorporation of alumina and metal fibres, and metal powders, was also found to increase the flexural strength of glass ionomer cements, but resulted in decreased wear resistance (GB-A-2028855). The low wear resistance was probably due to a lack of bonding between the metal fillers and the glass ionomer matrix, leading to dislodgement of the fillers during the wear process.

Currently, there are two methods of improving physico-mechanical properties of traditional glass ionomers. The first involves the addition of amalgam alloy to form an admixed restorative material (Simmons JJ, *Tex.Dent.J.* 100:6, 1983). Products include Miracle Mix (GC), Opus Silver (Schottlanders) and Hi-Dense (Shofu). The second involves sintering of silver ions to the glass powder to form a cermet material (US-A-4,527,979). However, the lack of bonding between the fillers and glass matrix in these types of metal-reinforced glass ionomers (cermets or admixes) can, again, lead to increased wear of the cement material, and the compressive and/or tensile strength of such metal-reinforced glass ionomer cements is still inadequate for high-stress tooth areas, such as in the restoration of posterior teeth.

Resin-modified glass ionomer cements were developed to overcome some of the perceived inadequacies of traditional glass ionomers. They contain the same components as traditional glass ionomer cements, but have resin materials added to them to provide strengthening, as well as the capability of "command-cure", with light-initiated curing of the resin component. Resin-modified glass ionomer cements have better physical and mechanical properties than traditional glass ionomers, and provide more resistance to fracture and breakage when large occlusal forces are present (Burgess JO, Barghi N, Chan DCN, *Am.J.Dent.* 6:137,1993, Kitamura M., Aoyama M., Miyazaki T., *J.Dent.Res.* 72:309, 1993, Berg JH, *Pediatr.Dent.* 20:93, 1998). They also have better handling properties, decreased initial moisture sensitivity, the capability of dual-cure mechanisms and higher bond strength to tooth *in vitro*. However, they still have the potential of some polymerisation shrinkage due to the resin added (Hinoura K., Miyazaki M., Onose H., *J.Dent.Res.* 70:1542, 1991, Sidhu SK., Watson TF., *Am. J.Dent.* 8:59, 1995) and still do not possess the physical and mechanical properties required for usage in posterior teeth. Although GC Corporation (Japan) introduced an improved version of resin modified glass ionomer cement, which featured smaller glass particles, in late 1997, this too was not recommended for use in posterior teeth.

Composite resins are another alternative to amalgam, but they have several limitations as mentioned earlier.

There, therefore, exists a need in the art for an improved glass ionomer restorative, which is economical, hard, strong, fracture resistant, wear resistant and aesthetically acceptable, and which is suitable for use in posterior teeth dentition.

It is an aim of the present invention to overcome or ameliorate any one or more of the above-mentioned disadvantages associated with prior art dental compositions, and/or improve the physico-mechanical properties of prior art resin-modified (light and chemical-cure) and/or conventional (chemical-cure) glass ionomer cements.

According to the present invention there is provided an ionic polymer matrix which comprises a filler material having one or more ionic polymers grafted thereto.

The one or more ionic polymers allows the filler material to bond to the ionic polymer matrix, thereby significantly and surprisingly improving the physico-mechanical properties of the ionic polymer matrix, and any material comprising the ionic polymer matrix as a whole. The grafted polymer also improves the rheology of the composition, so that high levels of filler content may be achieved, without compromising workability.

Preferably, the ionic polymer is an acid polymer, most preferably, polyacrylic acid.

Preferably, the filler material is an inorganic material, and more preferably, the filler material is a non-metallic material, a glass material, a ceramic material, a porcelain material, or a mixture of any two or more of these materials. Most preferably, the filler material is alumina, silica and/or zirconia.

Preferably, the ionic polymer is grafted to a surface modifying group on the filler material.

Preferably, the surface modifying group is an organic molecule comprising an unsaturated moiety. More preferably, the unsaturated moiety is methacrylate.

Preferably, the surface modifying group is a silane moiety. More preferably, the silane moiety is, or is derived from, 3-methacryloxypropyltrimethoxysilane

The surface modifying group not only allows the ionic polymer to be grafted or covalently bonded to the filler material, but depending on the functionality of the surface modifying group, also allows the filler material to bond to a resin polymer matrix, such as in resin-modified glass ionomer cement.

Thus, in preferred embodiments of the invention, silanised and polyacrylic acid grafted fillers are targeted at bonding to the resin and ionic matrix of resin-modified glass ionomer cements, respectively. This provides excellent bonding between the filler and matrix phases, and a consequential further improvement in the physico-mechanical properties of the resin-modified glass ionomer cement.

According to the present invention, there is also provided a glass ionomer cement which comprises a filler material having one or more acid polymers grafted thereto, and a resin-modified glass ionomer cement which comprises a filler material having a silanised surface and one or more acid polymers grafted to the silanised surface.

The glass ionomer and resin-modified glass ionomer cements according to the preferred embodiments of the present invention have sufficient strength, hardness, compressibility, wear resistance, fracture resistance and thermal expansion properties to enable them to be used as possible substitutes for

dental amalgam, thereby avoiding the disadvantages normally associated with dental amalgam and prior art composite resins.

According to the present invention, there is further provided a method of reinforcing a material which comprises an ionic polymer matrix, which method comprises the step of incorporating into the ionic polymer matrix a filler material having one or more ionic polymers grafted thereto.

Preferably, the method further comprises the steps of (a) organically modifying a surface of the filler material and (b) grafting one or more ionic polymers on to the organically modified surface before incorporating the filler material into the ionic polymer matrix.

Alternatively, the method further comprises the steps of (a) synthesising a filler material with an organically modified surface and (b) grafting one or more ionic polymers onto the organically modified surface before incorporating the filler material into the ionic polymer matrix.

In the alternative method, step (a) advantageously comprises simultaneously synthesising and organically modifying the filler material via a sol-gel route.

This alternative method of the present invention enables the simultaneous synthesis and silanisation of the filler material in a single step, thereby saving on both time and costs.

In both methods, the ionic polymer is preferably an acid polymer, preferably polyacrylic acid, the filler material is preferably alumina and the organic modification step preferably comprises silanisation of a surface of the filler material.

Also provided by the present invention are materials which comprise an ionic polymer matrix, prepared by the aforementioned methods.

According to a further aspect of the present invention, there is provided a material comprising an ionic polymer matrix according to the invention, which is preferably a glass ionomer cement. According to this aspect of the present invention, the material may further comprise a resin polymer matrix. Such a material is preferably a resin-modified glass ionomer cement.

The aforementioned materials of the present invention may be provided in combination with a pharmaceutically acceptable diluent or carrier.

According to a further aspect of the present invention, materials according to the invention are provided for use in therapy, in particular, for use in a dental procedure and, specifically, for use in the repair or restoration of teeth, including posterior teeth.

According to a further aspect of the present invention, there is also provided the use of a material according to the present invention for the manufacture of a composition for use in a dental procedure, and specifically for use in the repair or restoration of teeth, including posterior teeth.

The filler-modified compositions and polymeric materials of the present invention are particularly intended for use in situations where enhanced bonding to calcified tissue is required, and for filling gaps in bone. The greatly enhanced physico-mechanical properties of the composite materials and compositions of the present invention are such that they are suitable for possible use in high stress areas such as posterior teeth.

Also provided by the present invention are kits for preparing glass ionomer or resin-modified glass ionomer cements. These kits may comprise (a) a glass ionomer liquid or resin-modified glass ionomer liquid, (b) a glass ionomer powder and (c) a filler material having one or more acid polymers grafted thereto, with each of parts (a), (b) and (c) being separately packaged, or (a) a glass ionomer powder mixed with a filler material having one or more acid polymers grafted thereto and (b) a glass ionomer liquid or resin-modified glass ionomer liquid, with each of parts (a) and (b) being separately packaged.

The kits of the present invention are intended to be activated at the point of use, for example, by mixing the separately packaged components, and provide for ease of use by the dental practitioner.

Preferably, a kit is provided in the form of one or more capsules. The use of such capsules improves shelf life, improves mixing, decreases porosity and facilitates packaging.

According to a further aspect of the present invention, there is provided a glass ionomer powder which comprises an ion leachable glass and a filler material having one or more acid polymers grafted thereto.

According to a further aspect of the present invention, there is provided a composition which comprises an ionically hardenable material and a filler material, wherein the filler material has one or more ionic polymers grafted thereto. The latter composition may further comprise a polymerisable resin monomer.

According to another aspect of the present invention, there are provided methods of preparing glass ionomer or resin modified glass ionomer cements, which methods comprise the steps of (a) mixing a glass ionomer powder with a filler material having one or more acid polymers grafted thereto and (b) mixing the glass ionomer powder containing the filler material with a glass ionomer liquid or resin-modified glass ionomer liquid to form the glass ionomer cement or resin-modified glass ionomer cement, respectively. Preferably, the filler material is mixed with the glass ionomer powder by means of a high-speed dispersion technique.

According to another aspect of the present invention, there is provided a method of preparing an organically modified filler material, which method comprises the simultaneous steps of synthesising and organically modifying the filler material via a sol-gel route, as well as a filler material produced by such a method.

The organic modification preferably comprises silanisation of a surface of the filler material. A preferred filler material is alumina, and a preferred ionic polymer is polyacrylic acid.

Again, this method of the present invention enables the simultaneous synthesis and organic modification of a filler material in a single step, thereby saving on time and costs. It will be clear to a person skilled in the art that such a process will be particularly useful in any field where an organically modified filler material is required.

According to a further aspect of the present invention, there is provided a method for repairing or restoring a tooth, which method comprises the step of applying to a tooth a material of the present invention in an amount sufficient to effect the desired repair or restoration.

The materials of the present invention may be applied, for example, as filling agents, sealing agents or luting agents.

Disclosed herein are methods of treatment of the human or animal body, by surgery or therapy, using the fillers, materials, kits and compositions of the present invention.

The ionic polymer matrixes, materials and compositions of the present invention have substantially improved physico-mechanical properties, and may also be designed to exhibit enhanced radio-opacity properties. Characteristics of the filler-reinforced glass ionomer cements of the present invention include:

- (a) Bio-compatibility to tooth-tissue, including dental pulp tissue
- (b) Fluoride release
- (c) Chemical bonding to tooth tissue
- (d) Dual-cure mechanism (resin polymerization and acid-base reaction)
- (e) Increased filler loading without compromising workability
- (f) Enhanced physico-mechanical properties
- (g) Improved radio-opacity properties
- (h) Aesthetic (tooth-coloured) properties

The ionic polymer matrixes, materials, kits and compositions of the present invention are useful in a number of applications, which include, but are not limited to, the preparation of dental and medical adhesives, bases, liners, luting agents, sealants, core build-up and direct filling materials for primary or permanent teeth, dental implants, inlays and onlays for restorative uses, endodontic and orthopaedic uses. The fillers of the present invention may be used in both conventional and resin-modified glass ionomer cements, as well as in other types of cements and dental restorative materials, including polycarboxylate cements, polyacid-modified composites and orthopaedic cements.

For a better understanding of the present invention, embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 shows a scheme for modification of an alumina filler material with polyacrylic acid; and

Figure 2 shows a scanning electron micrograph of Material 5 (6% grafted alumina) of Example 3 herein.

Glass ionomer cements generally consist of a liquid component, containing an acid binder, such as polyacrylic acid (e.g. aqueous polyacid solution), and a powder component containing an ion leachable glass, such as fluoroaluminosilicate glass. When the glass and binder are mixed or slurried, H^+ ions from the acid penetrate the surface layers of the glass particles. Briefly stated, metal ions, such as calcium and aluminium ions, are leached out from the glass surface such that the glass surface is degraded to an hydrated siliceous gel. The metal ions migrate into an aqueous phase of the cement paste, where

they form metallic salt-bridges between the long chains of charged polyacrylate ions in an acid-base reaction, thereby cross-linking the chains, and causing the aqueous phase to gel and the cement to set. The end result is a composite of glass particles embedded within a cross-linked polyacrylate matrix.

Other types of cements may similarly be formed from a poly-functional acid and an acid-reactive filler (e.g. metal oxide or glass) to form an ionic polymer matrix.

The acidity of the polymeric binder in glass ionomer cements is not essential, but is preferred, because of the acid leaching utilised to promote curing of the glass ionomer cements. Examples of polymeric binders that may be used in the glass ionomer cements of the present invention include, but are not limited to homo-polymers or co-polymers of itaconic acid, tartaric acid, acrylic acid, polyacrylic acid, maleic acid, polymaleic acid, and/or other polycarboxylic acids. Derivatives of these acids, such as halogenated derivatives, in particular fluorinated derivatives, are also suitable. The polymeric binders may be liquid, solid, semi-solid, or a paste at ambient conditions. When used as a solid, the polymeric material can be a dehydrated, freeze-dried, or spray-dried liquid material.

Glass materials which are suitable for use in the glass ionomer cements of the present invention include silica, silicate glass, fluorosilicate glass, fluoroborosilicate glass, calcium silicate glass, calcium aluminosilicate glass, aluminosilicate glass, calcium aluminium, fluorosilicate glass, fluoroaluminosilicate glass and the like, or mixtures thereof, or any other ion-leachable glass, ceramic material, or porcelain material. The glass can be provided in the form of ground particles or powder, and may be amorphous, crystalline or spheroidal in shape.

Glass ionomer cements are noted for their inherent adhesiveness to teeth (both to dentine and enamel), their ability to release fluoride ions, which is useful in the prevention of dental caries, and the fact that they are tooth coloured when hardened. The inferior mechanical properties of glass ionomers, in particular, their extreme brittleness and low strength has, however, severely limited their use.

In the case of resin-modified glass ionomer cements, compatible resins, such as 2-hydroxyethyl methacrylate (HEMA) are used in combination with the acid polymer binder. These resins are generally chemically or photo-chemically curable, and chemical curing of the resin may be by standard methods in the art, for example, by means of cure enhancers, cure accelerators, catalysts, curing agents, cross-linking agents and the like. The resin in the resin-modified glass ionomer cement forms a matrix which interpenetrates with the ionic polymer matrix, and the ionic polymer matrix may, sometimes, even bond to the resin polymer matrix. The resulting resin-modified glass ionomer cement, thus, has two inter-penetrating matrixes when set, namely, an ionic matrix from the acid-base reaction and a polymerisation (resin) matrix from the free radical curing reaction. Resin-modified cements generally consist of approximately 95% glass ionomer matrix and approximately 5% resin.

According to the present invention, the physico-mechanical properties of glass ionomer cements is greatly enhanced by the use of a filler material which is specifically designed to bond to the ionic matrix of glass ionomer cement. In particular, the filler material of the present invention is specifically designed for ionic bonding to an ionic polymer matrix. This has been found to provide a surprisingly excellent degree of bonding between the filler and matrix phases,

with a similar degree of improvement in the physico-mechanical properties of the glass ionomer cement.

Specifically, bonding of the solid filler particles of the present invention to the ionic matrix of glass ionomer cement is achieved by means of one or more ionic (polyelectrolyte) polymers, e.g. polyacrylic acid. The one or more ionic polymers, which are preferably organic acid polymers or polyacids, are grafted or covalently bonded to the surface of the filler material, and are able to bond ionically to the ionic polymer matrix of the parent material. (Ionic polymers are polymers having ionic groups available for ionic bonding and acid polymers are polymers having acidic groups available for ionic bonding). It is believed that the ionic polymer grafted on to the filler material is able to crosslink to the polyacid in the ionic polymer matrix by means of metal ions leached out from the glass, i.e. by an ionic crosslinking reaction. Bonding between the grafted ionic polymer (e.g. polyacrylic acid) and polyacids present in the cement matrix may also take place by hydrogen bonding between the carboxylic acid groups of the polymer chains and/or formation of covalent bonds between these carboxylic acid groups via a condensation reaction.

In the case of resin-modified glass ionomer cements, bonding of the filler of the present invention to the resin polymer matrix may also be conveniently achieved by organic modification, e.g. silanisation of the surface of the filler material. The result is a tooth-coloured restorative material, which has all the benefits of glass ionomers, but with greatly improved physico-mechanical properties. The new material has the potential to serve as an amalgam substitute in the restoration of posterior teeth, and may revolutionise the practice of dentistry in countries where amalgam alloys are currently being phased out. It will be clear to a person skilled in the art that the fillers and

compositions of the present invention will also have far reaching uses in other areas involving cement and adhesive technology.

Polymer grafting of the filler surface according to the methods of the present invention also improves the rheology of the mixture. In this regard, previous work has shown that the flexural strength of glass ionomer cements increases with an increase in the powder:liquid ratio, which reflects the fraction of glass filler particles reinforcing the polymer matrix. (Prosser H J., Powid D R., Wilson A D., *J. Dent. Res.* 65:146, 1986). Maximum reinforcement is achieved at a glass:polyacid ratio of 1 gram to 0.14 grams. However, as the powder:liquid ratio is increased above this ideal ratio, the strength of the cement decreases dramatically, due to an inadequate amount of polyacids to form enough salt to bind the glass particles. The present invention, thus, has the additional advantage, that it enables fillers to be introduced into glass ionomer cements at levels above the optimal powder:liquid ratio, without compromising workability.

Examples of acid polymers that may be grafted onto the filler materials of the present invention include polyacrylic acid, maleic acid and the like. It will be clear to a person skilled in the art that the type of ionic polymer used may be varied according to the ionic components of the parent material. For example, in the case of glass ionomer cements, it will be clear to a person skilled in the art that the type of acid polymer used may be varied according to the acids used in the parent glass ionomer material. In other types of material, basic polymers, such as polyamines, could alternatively be used.

The filler particles of the present invention are, preferably, designed to bond chemically to a polymer which is common to the liquid component of the parent material.

Ionic polymers, such as acid polymers, can be grafted or covalently bonded to a filler material as long as a molecule is present on the filler surface with an appropriate functional group. In the case of an inorganic filler material, this can be any suitable organic molecule, e.g. a silane moiety, coupled or incorporated into the inorganic filler material. An inorganic/ceramic filler can even be directly functionalized with bridging groups for polymer grafting, by surface modification processes.

In the case of the present invention, organic modification of a surface of the filler material by silanisation is the preferred means for achieving polymer grafting. This also has the advantage that the silane moieties, themselves, are able to bond to the resin matrix of a resin-modified glass ionomer cement, in addition to bonding of the grafted acid polymers to the ionic matrix. This enables bonding of the filler material to both the resin and ionic matrixes of resin-modified glass ionomer cements, leading to greatly enhanced physico-mechanical properties of these types of materials.

Examples of silanes that may be used in the present invention include (3-methacryloxypropyl) trimethoxysilane, (3-methacryloxypropyl) trichlorosilane and (3-amino propyl) triethoxysilane. In place of the silane, other organic molecules that contain a functional group capable of bonding to the filler material, and a second functional group that can be reacted with other organic molecules or macromolecules, may also be employed.

The silane moieties used are able to bond to the resin matrix because of the presence of a reactive double (unsaturated) bond. Indeed, any other unsaturated organic molecule coupled or incorporated into the filler material may be used to bond to the resin matrix in this way.

The organic modification process, e.g. silanisation, may be carried out directly on a suitable filler material by methods which are standard in the art, for example, by mixing with an unsaturated silane coupling agent such as 10-methacryloxydecyltrimethoxysilane (MDTMS) or 3-methacryloxypropyltrimethoxysilane (MPTMS), in an appropriate solvent. Alternatively, a sol-gel route may be employed to synthesise the organically modified filler material in a process which involves the simultaneous synthesis and organic modification of the filler material.

In recent years, the sol-gel process has demonstrated itself to be a potentially important route for ceramic processing (Brinker & Scherer, In *Sol-gel Science*, Academic Press, Boston, p1, 1990). Among the many advantages of the sol-gel process are new compositions, greater homogeneity, higher levels of purity, net-shaped casting of monoliths and control of powder size distribution. The low temperatures of sol-gel processing makes it possible to control surface chemistry of the resulting materials and allow simultaneous modification of ceramics with organic moieties that would otherwise degrade at the high temperatures of conventional ceramic processing. In the area of filler technology, sol-gel methods have been relatively less studied. It is, however, a potentially important route, because, as shown herein, the bonding of organic coupling agents to ceramic phases can improve physico-mechanical properties of dental restoratives. An advantage of the sol-gel method for the production of fillers is the ability to produce ceramic powders possessing high surface area and superior mechanical properties (Balakrishnan & Gonzales, *J. Catalysis*, 144:395, 1993). A high surface area and abundance of hydroxyl groups is expected to improve the efficiency of reaction of fillers with an organic coupling agent.

In the case of the present invention, the use of a sol-gel process allows for the simultaneous synthesis and organic modification of a filler material, in a single step. This is achieved by first hydrolysing a filler precursor in an appropriate solvent to obtain a sol. Hydrolysis may be catalysed by addition of acid or base. Where necessary, the hydrolysate is peptised to obtain the sol. The sol is subsequently combined with an organic component, e.g. silane, dissolved in an appropriate solvent. Gelation of the mixture is then effected by evaporation, solvent extraction, dialysis or other methods known to a person skilled in the art. A gel is allowed to form, which is dried and powdered to yield the filler material. In another variation of this method, gelation is not effected, and the sol-organic mixture is simply dried to obtain a particulate product. The resulting gel or particulate product is then powdered to obtain the organically modified filler powder. The powder may be used as such, as a filler material, or may be further subjected to modification with other organic residues for the purpose of improving the interaction of the filler material with, e.g., resin-modified glass ionomer cement. Following the second organic modification, the powder may be further ground to form finer particles, or re-dispersed, prior to incorporation into the cement.

Filler precursors that may be used in the sol-gel process include, but are not limited to, aluminium ethoxide, aluminium isopropylate, aluminium n-propylate, aluminium iso-butylate, aluminium n-butylate, zirconium propoxide, zirconium n-butylate, tetramethyl ortho silicate (TMOS) and tetraethyl ortho-silicate (TEOS).

For example, alumina fillers may be synthesised from aluminium ethoxide precursor and silanised with 3-trimethoxysilylpropylsilane, as described further below. Grafting of the polyacrylic acid onto silanised alumina filler may be achieved by free radical polymerisation of acrylic acid, employing, for

example, potassium persulphate as the free radical initiator. The resulting filler material may then be dispersed in glass ionomer powder via a high-speed dispersion technique.

While silica is by far the most common oxide for applications which require a surface amenable to chemical modification (Pesek JJ et al., *J. Chromotography*, 630:95, 1993), ceramics such as alumina and zirconia are superior in terms of their physical properties, such as strength and fracture toughness. Also, silica exhibits limited pH stability, generally in the range of 2 to 8. Alumina has advantages over silica in terms of both strength and inherent pH stability, which are properties relevant to its application as a filler material. Although alumina has been used in the following examples, the present invention covers the use of all potential filler materials, including silica and zirconia, and calcium phosphate-based materials such as hydroxyapatite.

A sol-gel process may also be used to prepare an alumina filler material with an abundance of hydroxyl groups on the surface thereof, as compared to alumina filler prepared by conventional methods. The hydroxyl groups can also provide a better filler - ionic matrix interaction in both glass ionomer and resin-modified glass ionomer cements.

The organically modified and polymer grafted filler materials of the present invention may be in the form of, for example, fibres, porous particles, regular particles, or irregular particles, and are preferably incorporated into glass ionomer powder via a high-speed dispersion technique. The weight fraction of filler material in the final product may range from 0 to 80%.

The illustrative methods and examples described herein are solely for the purposes of illustrating the present invention and are not intended to be construed as limiting.

EXAMPLE 1

Alumina fillers were synthesized and simultaneously silanised via a sol-gel route. 54ml of de-ionized water was heated on a hot-plate to a temperature of 70-80°C. 4.53g of aluminium ethoxide ($\text{Al}(\text{OEt})_3$) was slowly added to the hydrolyzed alkoxide solution and the suspension was allowed to stand for 24 hours at 95-100°C in a stoppered round bottom flask. 1.5ml of 3-(trimethoxysilyl) propyl methacrylate dissolved in 7.5ml of methanol (MeOH) was then added, and the suspension was magnetically stirred for 1 hour. The peptized alumina sol was then transferred to a beaker, which was allowed to stand in the fume cupboard. After several hours of solvent evaporation, a white opaque gel had formed. The gel was dried at 150°C for 2 hours to obtain a tooth-coloured (cream yellow) filler, which was ground to a fine powder. Thus, instead of applying a silanisation procedure directly onto ceramic fillers, the synthesis and silanisation of the filler is combined in a single step which translates to savings in both time and cost.

EXAMPLE 2

Grafting of polyacrylic acid (PAA) onto silanised alumina filler was achieved by free radical polymerization of acrylic acid, employing potassium persulphate as the free radical initiator, although it will be clear to a person skilled in the art that any suitable initiator may be used. The presence of methacrylate residues on the surface of the filler (due to the silane moieties) allows covalent bonding between the grafted polyacrylic acid and the alumina filler. The scheme for

chemical modification is shown in Figure 1. The grafting procedure was performed under a nitrogen atmosphere. 0.5g of silanized alumina filler was first dispersed into 18.4 ml of de-ionized water with a magnetic stirring. The suspension was then deaerated for 30 minutes while heating to a temperature of 80°C using a water bath. A solution of 0.0325g of potassium persulphate in 16ml of water was prepared and deaerated. 1.6ml of this initiator solution was introduced to the filler suspension with stirring, to give a final initiator concentration of 0.6ml . After 10 minutes, 2ml of acrylic acid was added. The reaction was allowed to proceed for 1 hour, during which the mixture became progressively viscous. The product mixture was poured into 120 ml of acetone, then centrifuged at 3000 rpm to isolate a white precipitate. This produce was washed with de-ionized water twice by re-suspending the sediment, followed by centrifugation. The supernatant was decanted and the precipitate was air-dried in a fume hood.

Silane absorption at 1720 and 1640 cm^{-1} , and polyacrylic acid absorption in the 1500-1600 cm^{-1} region with FT-IR confirmed successful silanisation and PAA grafting of the alumina fillers. The fillers were then introduced into resin-modified glass ionic cement powder by a high-speed dispersion technique. Organic modification with silane and polyacrylate groups is targeted at ensuring good bonding at the matrix-filler interface. In addition, organic modification with PAA also improves rheology. Filler loading could therefore be increased without compromise in workability.

EXAMPLE 3

A study was carried out to investigate the effects of filler reinforcement of resin-modified glass ionomer cement based on bonding to the resin matrix or the ionic matrix. Tests included micro-hardness, wear resistance and microstructure analysis. The materials evaluated included the following:

Group	Material
Material 1	Fuji II LC (Resin-modified Glass Ionomer Cement)
Material 2	Fuji IX (Glass Ionomer Cement)
Material 3	Fuji II LC + 2% wt Alumina
Material 4	Fuji II LC + 2% wt silanised Alumina
Material 5	Fuji II LC + 6% wt PAA grafted Alumina

LC = Light Cure

The mean particle sizes of the different fillers were analyzed with a laser scattering particle size distributor analyzer (HORIBA LA-910). The mean particle size was 2.57 (1.61) μm , 1.74 (0.93) μm and 2.67 (2.22) μm for pure alumina, silanised alumina and PAA grafted alumina respectively. Micro-hardness testing was done with a digital micro-hardness tester (Future Tech FM7) and wear testing was done with the BIOMAT RCS (reciprocal compression sliding) wear instrumentation. Micro-structural analysis was done using Scanning Electron Micro-graphy, SEM (Joel JSM-5800). Statistical analysis was done using one-way ANOVA and Scheffe's test at significance level 0.05. Results showed that the hardness of resin-modified glass ionomer cement was significantly improved with filler reinforcement, and wear resistance of Fuji II LC and experimental materials was significantly better than Fuji IX. Good bonding between the PAA grafted filler material and the ionic

matrix of the resin-modified glass ionomer cement was observed under SEM. Crack formation during SEM preparation runs through rather than around the fillers (see Figure 2).

The improved wear resistance of Fuji II LC (Material 1) as compared to Fuji IX (Material 2) may be attributed to resin-modification and the smaller particle size of Fuji II LC. Fuji II LC, however, lacks the hardness and strength of Fuji IX. A significant improvement in hardness is obtained with the fillers of Materials 3, 4 and 5 (2% wt alumina, 2% wt silanised alumina and 6% wt PAA grafted alumina, respectively). In addition, a higher loading of filler material is achieved in the case of Material 5 than in the case of Materials 3 and 4.

The higher filler loading of Material 5 (6% wt PAA grafted alumina) as opposed to Materials 3 and 4 (2% wt alumina and 2% wt silanised alumina, respectively) is made possible by the polyacrylate coating in Material 5, which allows a larger filler loading without sacrificing workability, in this case, up to 6% wt filler. In contrast, for alumina and silanised alumina, a maximum of 2% wt can be incorporated, with higher filler loadings sacrificing the workability of the cement. Thus, an advantage of acid polymer grafting and subsequent bonding of the filler to the ionic matrix is the ability to achieve higher levels of filler loading without sacrificing the workability of the cement. Higher filler loadings lead to correspondingly enhanced material properties such as hardness, wear resistance or flexural strength, or at least one property is prevented from being diminished at the expense of another. This has been demonstrated by the present example, where hardness of Fuji II LC was increased by filler incorporation, without sacrificing its wear resistance or workability.

The glass ionomer or resin-modified glass ionomer cements of the present invention may, of course, contain other additives, such as colourings or pigments, adhesion promoters, oxidation inhibitors, surfactants, mineralising agents, antibiotics and the like.

The viscosity of filler-reinforced glass ionomer or resin-modified glass ionomer cements prepared according to the present invention may be modified for different uses. For example, a lower powder:liquid ratio is suitable for luting and lining applications, whereas a higher powder:liquid ratio is suitable for core build-up and direct filling applications. The workable consistency of the mixture prior to cure may similarly be varied, according to the specific requirements of the dental practitioner. In addition, the filler material of the present invention may be further optimised for its particular application or use (e.g. filling, lining, or cementing, etc.), by varying the particle size of the glass ionomer and filler material, amongst other considerations.

The filler-reinforced cements of the present invention may be packaged, for example, as capsules, with the filler, glass ionomer liquid or resin-modified glass ionomer liquid, and glass ionomer powder in separate compartments. The capsules may be activated and mixed at the point of use, with the filler material being dispersed into the glass ionomer powder before mixing with the glass ionomer liquid or resin-modified glass ionomer liquid. Alternatively, the filler materials may be incorporated into the glass ionomer powder at the point of manufacture, and then packaged, with the filler-reinforced glass ionomer powder and glass ionomer liquid or resin-modified glass ionomer liquid in separate compartments.

The way in which the various ingredients are packaged, activated and the order of mixing, may, of course, be varied according to specific requirements.

The exact conditions of the general procedures outlined above, including duration of reaction, sequence of reagent addition, period of reaction, temperature of reaction, volumes and concentrations of reagents, depend on the desired type and chemical composition of the filler material, and it is well within the scope of a person skilled in the art to vary the reaction conditions accordingly.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

In the present specification "comprise" means "includes or consists of" and "comprising" means "including or consisting of".

**CLAIMS**

1. An ionic polymer matrix which comprises a filler material having one or more ionic polymers grafted thereto.
2. An ionic polymer matrix according to Claim 1, wherein the ionic polymer is an acid polymer.
3. An ionic polymer matrix according to Claim 2, wherein the acid polymer is polyacrylic acid.
4. An ionic polymer matrix according to any one of the preceding claims, wherein the filler material is an inorganic material.
5. An ionic polymer matrix according to Claim 4, wherein the inorganic material is a non-metallic material, a glass material, a ceramic material, a porcelain material, or a mixture of any two or more of these materials.
6. An ionic polymer matrix according to Claim 4 or 5, wherein the inorganic material is alumina, silica and/or zirconia.
7. An ionic polymer matrix according to any one of the preceding claims, wherein the ionic polymer is grafted to a surface modifying group on the filler material.
8. An ionic polymer matrix according to Claim 7, wherein the surface modifying group is an organic molecule comprising an unsaturated moiety.



9. An ionic polymer matrix according to Claim 8, wherein the unsaturated moiety is methacrylate.
10. An ionic polymer matrix according to any one of Claims 7 to 9, wherein the surface modifying group is a silane moiety.
11. An ionic polymer matrix according to Claim 10, wherein the silane moiety is, or is derived from, 3-methacryloxypropyltrimethoxysilane.
12. A glass ionomer cement which comprises a filler material having one or more acid polymers grafted thereto.
13. A resin-modified glass ionomer cement which comprises a filler material having a silanised surface and one or more acid polymers grafted to the silanised surface.
14. A method of reinforcing a material which comprises an ionic polymer matrix, which method comprises the step of incorporating into the ionic polymer matrix a filler material having one or more ionic polymers grafted thereto.
15. A method according to Claim 14, further comprising the steps of (a) organically modifying a surface of the filler material and (b) grafting one or more ionic polymers onto the organically modified surface before incorporating the filler material into the ionic polymer matrix.



16. A method according to Claim 14, further comprising the steps of (a) synthesising a filler material with an organically modified surface and (b) grafting one or more ionic polymers onto the organically modified surface before incorporating the filler material into the ionic polymer matrix.
17. A method according to Claim 16, wherein step (a) comprises simultaneously synthesising and organically modifying the filler material via a sol-gel route.
18. A method according to any one of Claims 15 to 17, wherein the organic modification step comprises silanisation of a surface of the filler material.
19. A method according to any one of Claims 15 to 18, wherein the filler material is alumina.
20. A method according to any one of Claims 15 to 19, wherein the ionic polymer is an acid polymer.
21. A method according to Claim 20, wherein the acid polymer is polyacrylic acid.
22. A material which comprises an ionic polymer matrix prepared according to the method of any one of Claims 14 to 21, or by a method equivalent thereto.
23. A material which comprises an ionic polymer matrix according to any one of Claims 1 to 11.
24. A material according to Claim 23, which is a glass ionomer cement.



25. A material which comprises an ionic polymer matrix according to any one of Claims 1 to 11, and a resin polymer matrix.
26. A material according to Claim 25, which is a resin-modified glass ionomer cement.
27. A material according to any one of Claims 22 to 26 in combination with a pharmaceutically acceptable diluent or carrier.
28. A material according to any one of Claims 22 to 26 for use in therapy.
29. A material according to any one of Claims 22 to 26 for use in a dental procedure.
30. A material according to any one of Claims 22 to 26 for use in the repair or restoration of teeth.
31. Use of a material according to any one of Claims 22 to 26 for the manufacture of a composition for use in a dental procedure.
32. A use according to Claim 31, wherein the dental procedure involves the repair or restoration of teeth.
33. A kit for preparing a glass ionomer cement, which kit comprises (a) a glass ionomer liquid, (b) a glass ionomer powder and (c) a filler material having one or more acid polymers grafted thereto, with each of parts (a), (b) and (c) being separately packaged.



34. A kit for preparing a resin-modified glass ionomer cement, which kit comprises (a) a resin-modified glass ionomer liquid, (b) a glass ionomer powder and (c) a filler material having one more acid polymers grafted thereto, with each of parts (a), (b) and (c) being separately packaged.
35. A kit for preparing a glass ionomer cement, which kit comprises (a) a glass ionomer powder mixed with a filler material having one or more acid polymers grafted thereto and (b) a glass ionomer liquid, with each of parts (a) and (b) being separately packaged.
36. A kit for preparing a resin-modified glass ionomer cement, which kit comprises (a) a glass ionomer powder mixed with a filler material having one or more acid polymers grafted thereto and (b) a resin-modified glass ionomer liquid, which each of parts (a) and (b) being separately packaged.
37. A kit according to any one of Claims 33 to 36, wherein the kit is provided in the form of one or more capsules.
38. A glass ionomer powder which comprises an ion leachable glass and a filler material having one or more acid polymers grafted thereto.
39. A composition which comprises an ionically hardenable material and a filler material, wherein the filler material has one or more ionic polymers grafted thereto.
40. A composition according to Claim 39, further comprising a polymerisable resin monomer.



41. A method of preparing a glass ionomer cement, which method comprises the steps of (a) mixing a glass ionomer powder with a filler material having one or more acid polymers grafted thereto and (b) mixing the glass ionomer powder containing the filler material with a glass ionomer liquid to form the glass ionomer cement.

42. A method of preparing a resin-modified glass ionomer cement, which method comprises the steps of (a) mixing a glass ionomer powder with a filler material having one or more acid polymers grafted thereto and (b) mixing the glass ionomer powder containing the filler material with a resin-modified glass ionomer liquid to form the resin-modified glass ionomer cement.

43. A method according to Claim 41 or 42, wherein the filler material is mixed with the glass ionomer powder by means of a high-speed dispersion technique.

44. A method of preparing an organically modified filler material, which method comprises the simultaneous steps of synthesising and organically modifying the filler material via a sol-gel route.

45. A method according to Claim 44, wherein the organic modification comprises silanisation of a surface of the filler material.

46. A filler material prepared according to the method of Claim 44 or 45, or by a method equivalent thereto.

47. A method for repairing or restoring a tooth, which method comprises the step of applying to a tooth a material according to any one of Claims 22 to 26 in an amount sufficient to effect the desired repair or restoration.



48. A method according to Claim 47, wherein the material is applied as a filling agent.

49. A method according to Claim 47, wherein the material is applied as a sealing agent.

50. A method according to Claim 47, wherein the material is applied as a luting agent.