Title: A DENTAL COMPOSITE MATERIAL AND USES THEREOF

Abstract: The present invention relates to a method of dental treatment comprising using a dental composite material comprising Portland cement and a viscosity enhancing substance. The present invention also provides the use of a Portland cement and a viscosity enhancing substance for the preparation of a dental composite material. The dental composite material may further comprise a radiopaque substance.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
A dental composite material and uses thereof

Field of the invention

The present invention relates to a dental composite material which can be used for various dental applications.

Background of the invention

The decay of teeth results in cavity formation. Depending on the degree of the decay, it may affect the various parts of the tooth, the principal components being the enamel, the dentin, the pulp, and the cementum. Dental decay is most likely to affect the enamel, dentin and/or pulp. Once a cavity is found in the enamel, the typical therapy is to remove it in order to prevent further penetration of the decay into the tooth. Such penetration could spread infection throughout the mouth and body, and possibly result in the loss of the tooth. Such therapy for cavities formed by decay is typically referred to as a "filling". A dentist or other authorised practitioner drills out the cavity formed by the decaying material and may also form undercuts in order to secure the filling material. The dentist then fills the cavity with a filling material which replaces the portion of the tooth lost to the decay.

When filling tooth cavities, it is important to keep the fluid and bacteria present in the mouth from re-entering the cavity and causing further decay. Thus, the chosen filling material must adequately seal the cavity to prevent the migration of the fluid and bacteria into the cavity. This sealing property is particularly important when the decay has caused access to the pulp of the tooth.

When the pulp of a tooth becomes infected due to the spread of the decay, a root canal treatment may be carried out in order to clean the root canals and avoid extraction of the infected tooth. However, if a root canal treatment fails
and there is persistent infection, an apicoectomy and root-end filling may be carried out. Apicoectomy is a surgical procedure where the root tip of a tooth is removed. A cavity is then prepared at the root end and a root-end filling is then placed to prevent the egress of bacteria from the root canal of the tooth into the periradicular tissues.

Also, the purpose of root-end filling is to establish, as well as possible, a hermetic lasting seal of all apical avenues in the tooth from the oral environment to the periradicular tissues (Gutmann JL et al., 1991). Ideally, the material used in root-end filling should be biocompatible with the periradicular tissues, non-resorbable, impervious to dissolution or breakdown by the tissue fluids, capable of adapting as closely as possible to the dentinal walls of the root-end preparation and possess good handling characteristics.

The materials that have been previously tried include amalgam, Cavit, composite resin, glass ionomer cement, gold foil, gutta-percha, Mineral Trioxide Aggregate (MTA), polycarboxylate cement, polyvinyl cement, and various zinc oxide and eugenol-based cements. Most of these materials exhibit significant shortcomings in one or more of the following areas: solubility, leakage, biocompatibility, handling properties and moisture incompatibility (Johnson BR, 1999).

An example of filling material commercially available is the ProRoot™ MTA which was developed for use in endodontics. There are two varieties available: ProRoot MTA, a grey coloured formula (GMTA), and ProRoot MTA (Tooth Coloured Formula) (WMTA) (Dentsply Tulsa Dental, Tulsa, OK). MTA has been shown to have less leakage than amalgam or zinc oxide-eugenol materials in leakage tests (Torabinejad M et al., 1994; Torabinejad M et al., 1995, J Endod, 21:109-112). Other properties that have been investigated include its in vitro cytotoxicity (Torabinejad M et al., 1995, J Endod, 21:489-492) and biocompatibility when embedded in bone and subcutaneous
connective tissue (Torabinejad M et al., 1995, J Endod, 21:569-571; Yaltirik et al., 2004). The use of MTA as root-end filling material in dogs and monkeys resulted in less periradicular inflammation when compared with amalgam. It was noted that new cementum was produced over the root-end filling of the long-term specimens (Torabinejad M et al., 1995, J Endod, 21:603-608; Torabinajed M et al., 1997). MTA has also been used as a pulp-capping material (Aeinehchi M et al., 2003), in repair of root perforation (Pitt Ford TR et al., 1995; Hardy I et al., 2004) and as an apical barrier in the management of immature teeth with open apices (Witherspoon DE et al., 2001; Hayashi M et al., 2004). Researchers have also assessed the use of MTA as a root canal filling material (Vizgirda PJ et al., 2004). A recent long-term study in human subjects has demonstrated that MTA provided an effective seal of root perforations with radiographically normal tissue architecture adjacent to the repair site at the recall visit conducted a year or more post treatment (Main C et al., 2004). ProRoot MTA, the grey coloured material, has been approved by the U.S. Food and Drug Administration for use in pulpal therapy (Schwartz RS et al., 1999). Besides pulpal therapy, ProRoot MTA has also been used for root-end filling and root repair with excellent experimental and clinical results (Schwartz RS et al., 1999; Aeinehchi M et al., 2003; Torabinejad M et al., 1997; Economides N et al., 2003; Arens DE et al., 1996).

Although the MTA has superior biocompatibility when compared to the traditional materials used in root-end filling and root repair, it has poor handling characteristics and is a costly material.

MTA is difficult to use in certain surgical situations because of the location of the surgical site and the small size of the root-end preparation. These include areas such as maxillary and mandibular molars and palatal roots of maxillary premolars which has poor surgical access. In contrast, traditional root-end filling materials such as Super EBA (ethoxy benzoic acid) and IRM
(Intermediate Restorative Material) have very good handling characteristic and do not require special delivery systems for placement of the material.

As a result, despite numerous carrier instruments that have been introduced in the market for the delivery of ProRoot MTA to help its surgical placement (Lee ES, 2000), dentists are still using materials such as Super EBA when carrying out root-end filling and root repair in areas with poor surgical access. Some researchers have compared the use of ultrasonic condensation technique with hand condensation during placement of MTA and found that hand condensation resulted in better adaptation and less voids (Aminoshariae A et al., 2003). However, the sealing ability of MTA was less than optimal when hand condensation using the intracanal delivery technique was employed in an apexification model (Hachmeister DR et al., 2002).

Studies have compared MTA with Portland cement (PC) and the findings suggest that the major ingredients of PC are similar to MTA (Torabinejad M et al., 1995, 21:349-353; Funteas UR et al., 2003; Estrela C et al., 2000). These include calcium phosphate, calcium oxide and silica. MTA also contains bismuth oxide, which increases its radiopacity and this is absent in PC. Researchers have also compared the biocompatibility of MTA and PC and found that the two materials have similar biocompatibility (Saidon J et al., 2003; Abdullah D et al., 2002). The results suggest that PC has the potential to be used as a less expensive root-end filling material. However, PC has similar handling characteristics as MTA.

There is therefore a need in the art for a filling material and/or a root repair material which combines the superior biocompatibility of ProRoot™ MTA with handling characteristics similar to materials such as Super EBA.
Summary of the invention

The present invention addresses the problems above, and in particular provides a new dental composite material.

According to one aspect, the present invention provides a dental composite material comprising Portland cement and a viscosity enhancing substance.

According to another aspect, the present invention provides a dental composite material comprising a Portland cement, a radiopaque substance and a viscosity enhancing substance.

In particular, the viscosity enhancing substance may be poly(vinyl alcohol), cellulose, cellulose derivatives, polyethylene oxide, natural gums and/or aqueous clay dispersion.

The Portland cement may be any suitable Portland cement known in the art, for example white Portland cement.

According to another aspect, the present invention provides a dental composite material comprising white Portland cement, a radiopaque substance and a viscosity enhancing substance. As a viscosity enhancing substance, poly(vinyl alcohol) may be used.

The radiopaque substance may be an oxide or halogen salt of a heavy metal. In particular, the radiopaque substance is bismuth oxide.

The poly(vinyl alcohol) may have an average molecular weight of between 13000 to 23000 Daltons.

The Portland cement may have a Blaine number between 4000 and 5500 cm²/g, and in particular, it may have a Blaine number between 4600 and 5500 cm²/g.
According to another aspect, the Portland cement makes up the powder (solid) component and the viscosity enhancing material makes up the liquid component.

According to a further aspect, the Portland cement and the radiopaque substance make up the powder (solid) component of the composite material and the viscosity enhancing material makes up the liquid component.

Accordingly, the radiopaque substance may be present at from 10 to 25% by weight of a solid component of the composite material, while the viscosity enhancing substance may be present at from 1 to 3 % of the weight of the solid component of the composite material. In particular, the amount of radiopaque substance is about 15% the weight of the solid component and the amount of viscosity enhancing substance is about 1.5% the weight of the solid component.

According to another aspect, a composition comprising the dental composite which is within the scope of the present invention is provided.

According to another aspect, the invention provides the use of Portland cement and a viscosity enhancing substance in the preparation of a composite material for dental treatment. The composite material may further comprise a radiopaque substance.

Another aspect of the invention is a use of a dental composite material comprising a Portland cement and a viscosity enhancing substance for the preparation of a medicament for dental treatment. The dental treatment comprises pulp capping, root perforation repair, root-end filling, apical barrier, management of root fracture, barrier cement for intracoronal bleaching and/or temporary or permanent filling.

According to a further aspect, the dental composite material may comprise a radiopaque substance. The radiopaque substance is as described above.
Accordingly, a method for pulp capping, root perforation repair, root-end filling, apical barrier, management of root fracture, root canal filling, barrier cement for intracoronal bleaching, temporary and/or permanent filling is provided, wherein the method comprises the use of the dental composite material comprising a Portland cement and a viscosity enhancing substance. The method of the invention may also comprise the use of a dental composite material which comprises a Portland cement, a radiopaque substance, and a viscosity enhancing substance.

Yet another aspect of the invention is a method of preparing a dental composite material of the present invention, wherein the method comprises the steps of:

- providing Portland cement which forms the powder (solid) component of the composite material;
- providing a viscosity enhancing substance;
- dissolving the viscosity enhancing substance in water to form a liquid component; and
- mixing the powder component with the liquid component.

According to another aspect, the method of the invention comprises the steps of:

- providing Portland cement and a radiopaque substance forming a powder (solid) component of the composite material;
- providing a viscosity enhancing substance;
- dissolving the viscosity enhancing substance in water to form a liquid component; and
- mixing the powder component with the liquid component.

In particular, the weight of the radiopaque substance is between 10-25 % of the weight of the powder component, more in particular, the weight is 15% of the weight of the powder component. The weight of the viscosity enhancing substance is between 1 to 3% of the weight of the powder component. In particular, the weight of the viscosity enhancing substance is 1.5% of the weight of the powder component.

According to another aspect, the present invention also provides a method of filling a tooth cavity using a dental composite material comprising a Portland cement and a viscosity enhancing substance, comprising the steps of:

- identifying the cavity of the tooth to be filled; and

- introducing the composite material into the tooth cavity whereby the path of communication between a inner portion of the cavity and the outer surface of the tooth is sealed.

According to a further aspect, the dental composite used for the above method may further comprise a radiopaque substance.

Another aspect of the invention is a method of treating tooth decay using the dental composite material comprising a Portland cement and a viscosity enhancing substance, comprising the steps of:

- identifying the decay;

- removing the decay to create a cavity to be filled; and

- introducing the composite material into the cavity whereby the path of communication between a inner portion of the cavity and the outer surface of the tooth is sealed.
According to a further aspect, the dental composite material used for the above method may further comprise a radiopaque substance.

According to another aspect, the invention provides a method of performing root canal therapy on a tooth using the dental composite material comprising a Portland cement and a viscosity enhancing substance, comprising the steps of:

- removing a portion of the tooth to expose the root canal;

- preparing the root canal to be filled; and

- introducing the composite material into the root canal whereby the path of communication between the root canal and the outer surface of the tooth is sealed.

According to a further aspect, the dental composite material used for the above method may further comprise a radiopaque substance.

Another aspect of the present invention is the use of the dental composite material comprising a Portland cement and a viscosity enhancing substance, for cosmetic purposes. According to a further aspect, the composite material may further comprise a radiopaque substance.

Accordingly, an aspect of the present invention provides a method of cosmetic treatment, wherein the method uses the composite material of any aspect of the invention.

Another aspect of the present invention provides a method for end-filling or repairing a tooth root comprising filling the pulp cavity of a tooth with a dental composite according to any aspect of the present invention.
Brief description of the figures

Figure 1 shows the ProRoot™ MTA material. Figure 1A shows the mixing of the material and Figure 1B shows the material ready for use.

Figure 2 shows the composite material of the present invention. Figure 2A shows the material being mixed; Figure 2B shows the material ready to be formed; and Figure 2C shows the material ready for clinical placement.

Figure 3 shows the pH of various materials over time. The materials are the composite material of the present invention (DM), Portland cement (Port), Grey ProRoot™ MTA (GMTA) and White ProRoot™ MTA (WMTA).

Figure 4 shows the setting time of the composite material of the present invention (DM) compared to various other materials such as Grey ProRoot™ MTA (GMTA) and White ProRoot™ MTA (WMTA), White Portland cement and Grey Portland cement.

Figure 5 shows the comparison of yield points of various materials. Dev Material is the composite material of the invention, White Port is a white Portland cement product, White Port 10 is the white Portland cement product at 10 minutes, Grey Port is grey Portland cement product, and Grey Port 10 is Grey Portland cement product at 10 minutes.

Figure 6 shows comparison of viscosity of various materials. Dev Material is the composite material of the present invention, White Port is a white Portland cement product, White Port 10 is white Portland cement product at 10 minutes, Grey Port is a grey Portland cement product, and Grey Port 10 is a grey Portland cement product at ten minutes.

Figure 7 shows a plot of shear rates versus strain with viscosity being the slope of the curves.
Figure 8 describes the results of the cytotoxicity tests of the composite material of the invention and of comparable materials. Figure 8A: unstained with composite contact, PE negative control; Figure 8B: zone of inhibition after NR stain, PE negative control; Figure 8C: unstained with composite contact, white MTA; Figure 8D: zone of inhibition after NR stain, white MTA; Figure 8E: unstained with composite contact, grey MTA; Figure 8F: zone of inhibition after NR stain, grey MTA; Figure 8G: unstained with composite contact, PVA; Figure 8H: zone of inhibition after NR stain, PVA. Figures 8A, C, E and G are under 4x magnification, while Figures 8B, D, F and H, are under 0.67x magnification. The cell line used is L-929.

Figure 9 shows the pH of Viscosity enhanced root repair material (VERRM), WMTA and GMTA at various time intervals.

Figure 10 shows a radiograph showing a tooth specimen retrofilled with VERRM on the left and a tooth specimen retrofilled with GMTA on the right.

**Detailed description of the invention**

The objective of this invention was to develop a root repair material which has biocompatibility similar to ProRoot MTA and handling characteristics similar to materials such as Super EBA. This would facilitate clinical placement, even in areas with poor surgical access. The present invention involves the use of a viscosity enhancing substance to improve the handling characteristic of a root repair material which has a composition similar to ProRoot MTA.

Accordingly, one aspect of the present invention provides a dental composite material comprising Portland cement and a viscosity enhancing substance. The Portland cement makes up the powder component (solid component) of the composite material, while the viscosity enhancing substance when dissolved in water makes up the liquid component of the composite material.
According to another aspect, the present invention provides a dental composite material comprising Portland cement, a radiopaque substance and a viscosity enhancing substance. The radiopaque substance and Portland cement make up the powder component (solid component) of the composite material, while the viscosity enhancing substance when dissolved in water makes up the liquid component of the composite material.

References to developmental material (DM) or Viscosity Enhanced Root Repair Material (VERRM) refer to the composite material of the present invention.

The radiopaque substance may be an oxide or halogen salt of a heavy metal. Examples of heavy metals include gold, barium, silver or bismuth. However, it should be noted that any suitable heavy metal may be used. In particular, the radiopaque substance is bismuth oxide or bismuth trioxide. Other examples of radiopaque substances include ZrO₂ and BaO (Moszner et al., 2004). The bismuth oxide may also provide the colour to the composite material.

It is desired for the dental composite material to display radiopacity to enable visualisation and assessment in a radiograph and for the purposes of dental diagnostics. Depending on the degree of radiopaqueness desired, various ratios of a radiopaque substance may be added. For example, the radiopaque substance is present from 10 to 25% of the weight of the powder component of the composite material. In particular, the radiopaque substance makes up 15% of the weight of the powder component of the composite material.

The Portland cement used may be any suitable grade of Portland cement. In particular, the Portland cement used for the present invention has a Blaine number of between 4000 and 5500 cm²/g. Even more in particular, the Blaine number of the cement used is between 4600 and 5500 cm²/g. The fineness of a cement is indicated by the cement's Blaine number. The Blaine number
represents a ratio of the cement's particle surface area to its weight (cm² of surface per gram). The higher the Blaine number, the faster the cement sets.

The principal component of Portland cement by weight is calcium, usually in the form of calcium oxide (CaO) on an average of about 65% by weight. On the other hand, a cement mixture having calcium component present by weight in an amount of about 50-75% may be acceptable for use in the present invention.

The other important component by weight is silicon, usually present in the form of silicon dioxide (SiO₂), on an average of about 21 weight percent. However, a weight percent of about 15-25 may be acceptable. In addition, the combination of the calcium and silicon components may be present on an average of about 70-95% by weight, more in particular, 86% by weight.

The basic components of Portland cement are usually lime (CaO), silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃). These components are appropriately proportioned to produce the various types of Portland cement.

In general, there are five basic types of Portland cement. These are identified by the standard specifications promulgated by the American Society for Testing of Materials (ASTM).

Type I is called normal Portland cement and is a general purpose cement suitable for all uses when the special properties of the other types are not required. Type I Portland cement is more generally available than are the other types of cement. Type I Portland cement is typically used in assorted construction applications. In its normal applications, a Type I cement is used when the concrete is not subjected to special sulphite hazard or where the heat generated by the hydration of the cement will not cause an objectionable rise in temperature.
Such conditions are typical of the mouth, which would normally not necessitate the use of ASTM Types II through V. Therefore, the cement composition utilised in the present invention requires none of the special properties of Types II to V cements, and the preferred embodiment comprises an ASTM Type I Portland cement. However, the other types are within the scope of the present invention as being suitable for the purposes described herein.

A particular example of a Portland cement used for the present invention has the following approximate composition as shown (US 5,415,547 and US 5,769,638 herein incorporated by reference):

\[
\text{SiO}_2: 21\%, \text{Al}_2\text{O}_3: 4\%, \text{Fe}_2\text{O}_3: 5\%, \text{CaO}: 65\%, \text{MgO}: 2\%, \text{SO}_3: 2.5\%, \text{Alkalies (Na}_2\text{O, K}_2\text{O)}: 0.5\%.
\]

This Portland cement is commercially available as the Colton Fast-Set brand of the California Portland Cement Company. Further examples of suitable Portland cement are Aalborg Portland, PPC cement, SsangYong cement etc. However, it should be noted that any other type of Portland cement is within the scope of the present invention.

The viscosity enhancing substance may be poly(vinyl alcohol) (PVA), cellulose, cellulose derivatives (Ohama Yoshihiko, 1998). The viscosity enhancing substance may also be polyethylene oxide, natural gums and/or aqueous clay dispersion.

The PVA may have an average molecular weight of between 13000 and 23000 Dalton. The higher the molecular weight of the PVA, the less soluble in water it will be. The viscosity enhancing substance may be present in an amount from 1 to 3 % of the powder component of the composite material. It should be noted that any suitable viscosity enhancing material may be used for the present invention.
Cellulose derivatives include but are not limited to carboxymethylcellulose, hydroxypropylmethyelcellulose.

According to a second aspect, the present invention provides a method of preparation of the dental composite material according to any aspect of the present invention, wherein the method comprises the steps:

- providing the Portland which forms a powder component (solid component) of the composite material;

- providing the viscosity enhancing substance;

- dissolving the viscosity enhancing substance in water to form a liquid component of the composite material; and

- mixing the powder component with the liquid component.

According to another embodiment, the Portland cement is mixed with a radiopaque substance to form a powder component (solid component). The powder component is then mixed with the liquid component to obtain the dental composite material.

The weight of the radiopaque substance is between 10 and 25% of the weight of the powder component (solid component) of the composite material. In particular, the weight of the radiopaque substance is 15% of the powder component. As mentioned above, any suitable radiopaque substance may be used for the purposes of the present invention. A specific example would be bismuth oxide. The weight of the viscosity enhancing substance is between 1 and 3% of the weight of the powder component. In particular, the weight is 1.5% of the powder component of the composite material.

The viscosity enhancing substance is dissolved in a small quantity of water, typically about 5 to 15, more typically 10 to 12 times by weight of the amount
of viscosity enhancing substance, forming the liquid component of the composite material.

The powder component is then mixed with the liquid component. The mixing can be achieved by any known method. For example, any conventional means may be used such as using a spatula on a smooth, flat surface. Further, the mixing should be sufficient to hydrate the powder component. The liquid component according to the present invention can also be utilised to hydrate commercially available Portland cement based materials such as ProRoot MTA and MTA-Angelus.

Another aspect of the invention provides a dental composition comprising the dental composite material disclosed above.

Yet another aspect of the invention provides various uses of a composite material comprising a Portland cement and a viscosity enhancing substance. The composite material may further comprise a radiopaque substance.

In particular, the radiopaque substance may be an oxide or halogen salt of a heavy metal. The heavy metal may be chosen from any of the following but is not limited to gold, barium, silver and/or bismuth. Even more in particular, the radiopaque substance is bismuth oxide.

The viscosity enhancing substance may be any suitable substance known in the art, as described above. For example, poly(vinyl alcohol) may be used as the viscosity enhancing substance. The poly(vinyl alcohol) may have an average molecular weight of between 13000 and 23000 Dalton. Cellulose derivatives as mentioned above may also be used.

Further, the Portland cement used may be any suitable cement for the purposes of the present invention. For example, Colton Fast-Set brand of the California Portland Cement Company may be used.
The composite material comprising the Portland cement and the viscosity enhancing substance, and optionally comprising a radiopaque substance, may be used for several clinical dental procedures including, but not limited to, pulp capping, management of root fracture, root perforation repair, root-end filling, barrier cement for intracoronar bleaching and/or apical barrier/plug.

The composite material may also be used as a temporary filling material to be placed in the tooth until a permanent restoration can be placed. The composite material may also be used as a permanent filling material. The composite material may further be used as a protective cement barrier in internal bleaching. The composite material is placed above the root canal filling material to minimise the leakage of bleaching agents through the root. Yet another use of the composite material is as a management of root fracture, in which the composite material is used to root fill a tooth with root fracture.

According to a further aspect, the composite material comprising a Portland cement and a viscosity enhancing substance and optionally comprising a radiopaque substance, may be used in the preparation of a medicament for dental treatment.

When the composite material is used in pulp capping, it is used in the management of deep carious lesions, accidental mechanical pulp exposure and pulp exposure following traumatic accidents. The composite material is placed over the exposed pulp and a restorative filling is then placed over it.

In the case of root perforation repair, this is carried out via an intracanal approach or using a surgical approach. The intracanal approach involves placement of the composite material where the perforation is, in order to seal the perforation. The surgical approach is used to achieve the same after the intracanal approach fails or if the perforation is inaccessible through the access cavity of the tooth.
For root-end filling, it is a surgical procedure carried out to establish a seal at the root-end of the tooth. A cavity is prepared at the root end of the tooth and the composite material is placed in the prepared cavity.

Apical barrier/plug is carried out in non-vital, immature permanent teeth with an open root apex. The composite material is placed at the root end to create an apical plug which prevents the extrusion of root canal filling material.

Details of the procedures mentioned above may be found in any standard endodontics textbook (Pathways of the pulp. Eds Cohen S, Burns RC. 8th Ed. Mosby Inc. St. Louis). Further, it would be known to a person skilled in the art how to perform the procedures.

The composite material of the present invention is advantageous for use in various dental treatment and applications as its viscosity and handling characteristics are similar to that of IRM® (Intermediate Restorative Material). Further the setting time, pH, solubility, radiopacity and dimensional change upon setting are comparable to MTA. The in-vitro biocompatibility is also similar to that of MTA. This makes the composite material of the present invention suitable for use in place of MTA in all its existing clinical applications, as well as root-end filling and root repair in areas with poor surgical access.

Another aspect of the present invention is the use of the viscosity enhancing substance dissolved in water together with MTA. As noted above, MTA is difficult to use in certain surgical situations. When the viscosity enhancing substance of the present invention is added to MTA, forming a composition herein referred to as 'modified MTA', the increased viscosity would eliminate the need for special carrier devices as the material can be manipulated like Super EBA. This will mean that the modified MTA may be used even in such difficult surgical situations. In addition, it also makes manipulation of the modified MTA in all other clinical application such as pulp capping, non-
surgical root repair, apical plug etc. easier due to its superior handling characteristics.

According to another aspect, the present invention also provides a method of filling a tooth cavity using the dental composite material comprising Portland cement, a viscosity enhancing substance and optionally, a radiopaque substance, comprising the steps of:

- identifying the cavity of the tooth to be filled;
- providing the composite material; and
- introducing the composite material into the tooth cavity whereby the path of communication between a inner portion of the cavity and the outer surface of the tooth is sealed.

Another aspect of the invention is a method of treating tooth decay using the dental composite material comprising Portland cement and a viscosity enhancing substance and optionally, a radiopaque substance, comprising the steps of:

- identifying the decay;
- removing the decay to create a cavity to be filled;
- providing the composite material; and
- introducing the composite material into the cavity whereby the path of communication between a inner portion of the cavity and the outer surface of the tooth is sealed.

According to another aspect, the invention provides a method of performing root canal therapy on a tooth using the dental composite material comprising
a Portland cement and a viscosity enhancing material and optionally comprising a radiopaque substance, comprising the steps of:

- removing a portion of the tooth to expose the root canal;

- preparing the root canal to be filled; and

- introducing the composite material into the root canal whereby the path of communication between the root canal and the outer surface of the tooth is sealed.

Another aspect of the present invention is the use of the dental composite material comprising a Portland cement and a viscosity enhancing substance and optionally comprising a radiopaque substance, for cosmetic purposes. For example, the composite material may be used for sealing gaps between teeth, or external appearance of the tooth.

Accordingly, an aspect of the present invention provides a method of cosmetic treatment, wherein the method uses the composite material comprising a Portland cement and a viscosity enhancing substance and optionally containing a radiopaque substance.

Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting of the present invention.

**EXAMPLES**

**Example 1**

**Composition of the viscosity enhanced root repair material**
Powder (solid) component

White Portland cement 0.85g
Bismuth oxide 0.15g

(Bismuth oxide was obtained from Sigma-Aldrich Co. St. Louis, U.S.A.)

Liquid component

0.015 g of Poly(vinyl alcohol) (PVA) is dissolved in 0.35 ml of distilled water. The average molecular weight of the PVA is between 13000-23000 Dalton and is 98% hydrolysed. The PVA used for the present example is from Sigma-Aldrich Co. St. Louis, U.S.A.

The powder component is mixed with the liquid component for about 1 minute to ensure that all the powder particles are hydrated (Figures 1, 2A and 2B). The material is then ready for clinical placement (Figure 2C).

Example 2

Note that for all the examples that follow, reference to White MTA (WMTA) and Grey MTA (GMTA) refers to MTA manufactured by Dentsply Tulsa Dental, Tulsa, OK. Reference to Portland cement refers to Type I Portland cement. In particular, white Portland cement is Davco cement (Australia) and grey Portland cement refers to Asia cement, manufactured in Singapore.

Radiopacity of the composition

ISO specification 6876:2001(e) (Dental root canal sealing members) provides that the material when tested according to the ISO specifications should have a radiopacity equivalent to not less that 3 mm of aluminium.

Apparatus
1. A ring mould having an internal diameter of 10±1mm and a height of 1±0.01 mm together with a plastic cover which is radiolucent.

2. Single-phase Dental X-ray unit operating at 65 kV.

3. Dental X-ray occlusal film of speed D and suitable developing solution and fixer.

4. Radiopacity gauge consisting of an aluminium step wedge of at least 98% purity with a maximum copper content of 1% and 54 mm long and 20 mm wide having a thickness from 0.5 to 9.0 mm in equally placed steps of 0.5 mm.

5. Optical Densitometer (X-Rite Model 301, Grandville, Michigan, U.S.A.)

**Methodology**

The components of the materials (VERRM; WMTA; GMTA) were mixed according to the manufacturer’s instructions (VERRM was prepared by mixing the powder and liquid components together on a flat surface using a spatula). The materials were then individually packed into moulds and covered with impervious plastic sheets and microscopic glass slides to obtain specimens about 1 mm thick.

After the composite material had set in the mould, it was positioned in the centre of the X-ray film. The aluminium step wedge was placed adjacent to the material. A similar glass slide was placed under the aluminium wedge. Similarly, a sample of White MTA (WMTA) and Grey MTA (GMTA) was also prepared to be tested.

The specimen was irradiated at 65 kV at a target film distance of 300 mm and with an exposure time of 0.18s.
After developing, fixing and drying the exposed film, the density of the image of the specimen was compared with that of the aluminium step wedge using the optical densitometer. The radiopacity equivalent of the specimen was expressed in millimeters of aluminium.

The densitometer readings of the aluminium wedge are summarised in Table 1, while the results of the composite material, White MTA (WMTA) and Grey MTA (GMTA) are shown in Table 2.

<table>
<thead>
<tr>
<th>Thickness of Aluminium (mm)</th>
<th>Densitometer reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.84</td>
</tr>
<tr>
<td>1.0</td>
<td>0.78</td>
</tr>
<tr>
<td>1.5</td>
<td>0.73</td>
</tr>
<tr>
<td>2.0</td>
<td>0.72</td>
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<td>4.5</td>
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<tr>
<td>6.0</td>
<td>0.51</td>
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<td>0.39</td>
</tr>
<tr>
<td>9.0</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 1: Results showing the densitometer reading of the aluminium wedge
<table>
<thead>
<tr>
<th>Specimen</th>
<th>Densitometer reading</th>
<th>Equivalent Aluminium thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite material of Example 1</td>
<td>0.57</td>
<td>4.5</td>
</tr>
<tr>
<td>White MTA (WMTA)</td>
<td>0.47</td>
<td>6.5</td>
</tr>
<tr>
<td>Grey MTA (GMTA)</td>
<td>0.47</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 2: Equivalent aluminium thickness of composite material, White MTA and Grey MTA

From the results above, it can be seen that the specimen of the composite of Example 1 has a radiopacity equivalent to 4.5 mm of aluminium and conforms to the ISO specifications. However, the radiopacity of the composite material of the invention is a little lower than that of White MTA and Grey MTA.

**Example 3**

**Measurement of other properties of the viscosity enhanced root repair material**

Presently, root-end fillings are explicitly excluded from the scope of the ISO technical standards for root-canal-filling materials and they have not yet been subjected to standardisation (Hauman CH et al., 2003). As such, the following tests were conducted using the protocol used in a similar study (Torabinejad M et al., 1995, J Endod, 21(7):349-353), together with other appropriate ISO tests.

**pH measurement**

The pH of the composite material of Example 1 (herein referred to as developmental material, DM) was compared to that of Portland cement (Port),
Grey MTA (GMTA) and White MTA (WMTA). The pH was measured at short intervals from time 0 to 60 minutes. The results are shown in Table 3, while a plot of pH with respect to time is shown in Figure 3.

<table>
<thead>
<tr>
<th>Time</th>
<th>DM</th>
<th>Port</th>
<th>GMTA</th>
<th>WMTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>11.42</td>
<td>11.94</td>
<td>11.33</td>
<td>11.42</td>
</tr>
<tr>
<td>2</td>
<td>11.82</td>
<td>12.24</td>
<td>11.88</td>
<td>11.90</td>
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<tr>
<td>4</td>
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<td>12.92</td>
<td>12.21</td>
<td>12.21</td>
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<td>5</td>
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<td>12.24</td>
<td>12.35</td>
</tr>
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<td>6</td>
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<td>13.15</td>
<td>12.26</td>
<td>12.41</td>
</tr>
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<td>8</td>
<td>12.32</td>
<td>13.06</td>
<td>12.29</td>
<td>12.48</td>
</tr>
<tr>
<td>10</td>
<td>12.34</td>
<td>13.07</td>
<td>12.41</td>
<td>12.47</td>
</tr>
<tr>
<td>12</td>
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<td>13.07</td>
<td>12.84</td>
<td>12.80</td>
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<td>12.84</td>
<td>12.81</td>
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<td>12.78</td>
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<td>34</td>
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<td>12.83</td>
<td>12.81</td>
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<td>12.68</td>
<td>13.08</td>
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<td>12.69</td>
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<td>12.81</td>
<td>12.88</td>
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<td>46</td>
<td>12.67</td>
<td>13.13</td>
<td>12.82</td>
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<td>48</td>
<td>12.67</td>
<td>13.07</td>
<td>12.81</td>
<td>12.98</td>
</tr>
<tr>
<td>50</td>
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<td>56</td>
<td>12.68</td>
<td>13.07</td>
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<td>13.02</td>
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<td>13.08</td>
<td>12.84</td>
<td>13.01</td>
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<tr>
<td>60</td>
<td>12.69</td>
<td>13.07</td>
<td>12.84</td>
<td>13.02</td>
</tr>
</tbody>
</table>

Table 3: pH readings of the developmental material (DM), Portland cement (Port), Grey MTA (GMTA) and White MTA (WMTA)
From the results shown in Table 3, it can be seen that the pH of all 4 materials tested was about the same.

Another test to compare the pH of VERRM, GMTA and WMTA was carried out. The pH of VERRM, GMTA and WMTA during setting was measured with a pH meter, the Orion PerHect Log R Meter Model 370 (Orion Research Inc., Boston MA), using a temperature-compensated electrode. The electrode was inserted into the freshly mixed material and readings were taken at 2 minute intervals for 60 minutes at a temperature of 24 °C. This was repeated 3 times for each material. The mean pH was then plotted against time, as shown in Figure 9. Statistical analyses were carried out at 3 time points, namely, when freshly mixed, at 30 minutes and 60 minutes, using ANOVA and Fisher's LSD at 0.05 level of significance.

There was no significant difference in the pH of the three materials when freshly mixed and at 30 minutes. At 60 minutes, WMTA had significantly higher pH than both VERRM (p = 0.003) and GMTA (p = 0.040). There was no significant difference in the pH of VERRM and GMTA at 60 minutes.

Setting time measurement

The initial setting time was measured in accordance with the methods prescribed by the International Organization for Standardization for dental root canal sealing materials (ISO 6876:2001, 7.4). ISO 6876:2001 requirements state that for materials having a setting time greater than 30 minutes, and up to 72 hours, for which the manufacturer quotes a time range, the setting time measured shall be within the range stated by the manufacturer. The method for determining setting time as described in ISO 6876:2001 is identical to the method for determining initial setting time as described in ASTM C266-03 (American Society for Testing and Materials). In this test, the measurements
of both the initial and final setting times were carried out by using initial and final Gillmore needles respectively. The initial setting time of DM was compared to that of White MTA, Grey MTA, White Portland cement and Grey Portland cement. The setting times were measured four times. The results are shown in Figure 4 and Table 4. The results showed that the initial and final setting time respectively of all 5 materials tested were similar. The final setting time of GMTA was significantly higher than DM and WMTA. However, there was no significant difference in final setting time between DM and WMTA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Initial setting time (min)</th>
<th>Final setting time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>White MTA (WMTA)</td>
<td>45</td>
<td>140</td>
</tr>
<tr>
<td>Grey MTA (GMTA)</td>
<td>70</td>
<td>175</td>
</tr>
<tr>
<td>White Portland cement</td>
<td>40</td>
<td>135</td>
</tr>
<tr>
<td>Grey Portland cement</td>
<td>70</td>
<td>170</td>
</tr>
<tr>
<td>DM</td>
<td>40</td>
<td>140</td>
</tr>
</tbody>
</table>

Table 4: Results of initial and final setting times of White MTA, Grey MTA, White Portland cement, Grey Portland cement and developmental material (DM)

**Solubility measurement**

The solubility was measured in accordance with the methods prescribed by the ISO for Dental root canal sealing materials (ISO 6876:2001, 7.7). ISO 6876:2001 requirements state that the solubility of the set material shall not exceed 3% mass fraction. The solubility of DM at 24 hours was compared to the solubility of White Portland cement, Grey Portland cement, White MTA and Grey MTA. In addition, the solubility of DM at 7 days was determined. The results showed that the solubility of DM at 24 hours (dm1) was higher than the other 4 materials tested but still complied with the requirements.
stated in ISO 6876:2001. At 7 days, the solubility of DM (dm7) was lower than that observed at 24 hours. The results are shown in Table 5.

<table>
<thead>
<tr>
<th>Material</th>
<th>Residue</th>
<th>Specimen</th>
<th>Solubility</th>
</tr>
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<tbody>
<tr>
<td>WP</td>
<td>0.0225</td>
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<tr>
<td>WP</td>
<td>0.0213</td>
<td>2.0611</td>
<td>1.03</td>
</tr>
<tr>
<td>WP</td>
<td>0.0221</td>
<td>2.0845</td>
<td>1.06</td>
</tr>
<tr>
<td>WP</td>
<td>0.0219</td>
<td>2.0755</td>
<td>1.06</td>
</tr>
<tr>
<td>GP</td>
<td>0.0205</td>
<td>2.0635</td>
<td>0.99</td>
</tr>
<tr>
<td>GP</td>
<td>0.0250</td>
<td>2.1510</td>
<td>1.16</td>
</tr>
<tr>
<td>GP</td>
<td>0.0228</td>
<td>2.0950</td>
<td>1.09</td>
</tr>
<tr>
<td>GP</td>
<td>0.0211</td>
<td>2.0450</td>
<td>1.03</td>
</tr>
<tr>
<td>WMTA</td>
<td>0.0258</td>
<td>2.0407</td>
<td>1.26</td>
</tr>
<tr>
<td>WMTA</td>
<td>0.0274</td>
<td>2.0845</td>
<td>1.31</td>
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<tr>
<td>WMTA</td>
<td>0.0261</td>
<td>2.0665</td>
<td>1.26</td>
</tr>
<tr>
<td>WMTA</td>
<td>0.0269</td>
<td>2.0852</td>
<td>1.29</td>
</tr>
<tr>
<td>GMTA</td>
<td>0.0202</td>
<td>2.0956</td>
<td>0.96</td>
</tr>
<tr>
<td>GMTA</td>
<td>0.0198</td>
<td>2.1024</td>
<td>0.94</td>
</tr>
<tr>
<td>GMTA</td>
<td>0.0211</td>
<td>2.1218</td>
<td>0.99</td>
</tr>
<tr>
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<td>0.0208</td>
<td>2.1046</td>
<td>0.98</td>
</tr>
<tr>
<td>dm1</td>
<td>0.0423</td>
<td>2.0763</td>
<td>2.04</td>
</tr>
<tr>
<td>dm1</td>
<td>0.0430</td>
<td>2.0613</td>
<td>2.09</td>
</tr>
<tr>
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<td>0.0480</td>
<td>2.0844</td>
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<td>2.08</td>
</tr>
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<td>dm7</td>
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</tr>
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</tr>
<tr>
<td>dm7</td>
<td>0.0148</td>
<td>2.1634</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Table 5: Solubility measurement of White Portland cement (WP), Grey Portland cement (GP), White MTA (WMTA), Grey MTA (GMTA) and developmental material (dm)

In Table 5, the term 'residue' is the amount of solid that has dissolved in water. Also, solubility is measured as a %, a measure of residue/original mass x 100%.

Viscosity measurement
The viscosity of a fluid is its resistance to shear or flow. Rheology tests are used to evaluate flow properties of a cement mix and treat fresh mix as a liquid. In the case of a rotational rheometer, the viscosity of a substance is calculated in accordance with the Newtonian conditional equation for viscosity:

\[
\text{Viscosity}(\eta) = \frac{\text{Shear Stress}(\tau)}{\text{Shear Rate}(\gamma)}
\]

The flow curve represents the shear stress as a function of shear rate while the viscosity curve shows the viscosity as a function of the shear rate. The experiment is conducted in the CR mode whereby the strain is controlled.

Newtonian fluids have a linear relationship whereas the pseudoplastic materials have a yield point, which is the minimum force required to initiate flow. Fresh cement paste having pseudoplastic properties is a Bingham material and a Bingham model is used to calculate the viscosity and yield point from the data obtained.

Materials and methods:

A Roto Visco 1 Rheometer (Haake karlsruhe, Germany) was used to measure the viscosity and RheoWin Pro software was used to evaluate the data. A Z DIN sensor system (Z20 DIN Ti) was used which comprises one rotor and one beaker each in accordance with the standard DIN 53019/ISO3219.

The shear rate is gradually increased from 1.00 per second to 100 per second over 30 seconds and 100 data points were collected. This phase is known as the 'up ramp' and then the shear rate is decreased from 100 to 1.00 and this is known as 'down ramp', and another 100 data points are collected. The temperature is maintained at 37°C to simulate oral conditions.
The RheoWin software is then used to calculate the viscosity and the yield point from the curves obtained using the Bingham model. The developmental material (DM), white Portland cement and grey Portland cement were used in this experiment.

20 g of each material was mixed in accordance with the manufacturer's instructions and the test was conducted immediately after mixing and 10 minutes after the mixing. To avoid discrepancy, the sensor was filled with the test materials to a fixed weight of 350 g to ensure equal amounts of each material was used.

Results:

The results are shown in Figures 5 to 7, and Table 6 below. The developmental material had a viscosity of about thrice that of Portland cement when freshly mixed, and 1.5 times that of Portland cement after 10 minutes.

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield Point (Pa)</th>
<th>Viscosity (Pa.s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM</td>
<td>38.53</td>
<td>0.76</td>
</tr>
<tr>
<td>DM, 10 min</td>
<td>70.36</td>
<td>1.17</td>
</tr>
<tr>
<td>White Portland cement</td>
<td>9.8</td>
<td>0.23</td>
</tr>
<tr>
<td>White Portland cement, 10min</td>
<td>23.76</td>
<td>0.77</td>
</tr>
<tr>
<td>Grey Portland cement</td>
<td>8.69</td>
<td>0.27</td>
</tr>
<tr>
<td>Grey Portland cement, 10min</td>
<td>8.55</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 6: Viscosity measured using RheoProWin software and Bingham model

Example 4

Biocompatibility of composite material

Biocompatibility of the composite material prepared in Example 1 was evaluated by the Direct Contact Test as described below.
Direct contact test

The test used is described in BS EN ISO 10993-5:1999, 4.3. Materials were evaluated using the direct contact test, in accordance with the methods prescribed by the ISO for Biological evaluation of medical devices – Part 5: Tests for in vitro cytotoxicity (ISO 10993-5:1999). Essentially, cells are cultured in the lab on a petri dish and the test material is placed in the middle of the cells. The cells are then observed for cell death or zone of inhibition. The length or area being measured refers to this zone where the cells are dead or do not grow (zone of inhibition). The greater the length or area around the specimen where the cells do not grow, the greater the toxicity of the material. The cell line used for the present example is the L-929 cell line.

The materials used for this experiment include: ‘Control PE’, a polyethylene material used as a negative control; ‘PVA’, a material that is a combination of poly(vinyl alcohol) and Portland cement; White MTA (ProRoot MTA (Tooth-Coloured Formula)); and Grey MTA (ProRoot MTA). The results of the test are shown in Figure 8. In the Figure, the term ‘unstained with composite contact’ illustrates the junction between the cells and the material tested and also shows the condition of the cells as well as whether there is an area around the material where the cells did not grow. ‘Zone of Inhibition after NR stain’ refers to the area around the specimen after staining with neutral red (NR), a dye that stains only living cells and therefore used to differentiate the living cells from dead cells. ‘Unstained with composite contact’ photos are at a higher magnification compared to ‘Zone of inhibition’.

All the pictures showed normal living cells growing right up to the edge of the specimen except. The results showed that the cytotoxicity of ‘PVA’, White MTA, and Grey MTA was similar, and all three materials were non-cytotoxic.

The data for the Direct Contact test is shown in Table 7 below:
<table>
<thead>
<tr>
<th>Variable</th>
<th>Area (mm²)</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7.692</td>
</tr>
<tr>
<td>1</td>
<td>58.81</td>
<td>8.421</td>
</tr>
<tr>
<td>1</td>
<td>43.677</td>
<td>7.917</td>
</tr>
<tr>
<td>2</td>
<td>57.109</td>
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</tr>
<tr>
<td>4</td>
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<tr>
<td>4</td>
<td>49.701</td>
<td>7.274</td>
</tr>
</tbody>
</table>

Table 7: Results of direct contact test, showing the area and length around which the cells were dead or did not grow. Variable 1 is White MTA (3 replicates), Variable 2 is Grey MTA (4 replicates), Variable 3 is PVA (3 replicates) and Variable 4 is negative control (5 replicates)

The variable 3 is the composite material of the present invention, without the radiopaque substance.

For area and length analyses, there was no significant statistical difference of the tested variables 1-3 compared to the negative control.

It should be noted that the area analysis with the measurement of true inhibition zone would be more accurate compared to the length (diameter). If the zone of inhibition (area of cell death) is not a true-to-type circle, then determining the diameter would not be precise. Therefore, measurement of this area, regardless of the shape of the zone, is the recommended mode of assessment.
Example 5

Apical Sealing Ability

Twenty-two single-rooted human premolars extracted for orthodontic reasons were used. The teeth were inspected under microscope to ensure that they were intact and had no cracks, fractures or caries and that the roots were relatively straight. The crowns were removed at the cemento-enamel junction. Root canal preparation was carried out with K-type files using step back technique (Principles and practice of endodontics. Editors Walton RE, Torabinejad M, W.B. Saunders Co. Philadelphia, U.S.A.) with 5.25 % sodium hypochlorite as irrigant. The master apical file size for each tooth was set at 3 sizes larger than the initial apical file size. The root canals were obturated with gutta-percha and Roth Root Canal Cement Type 801 sealer (Roth International Ltd., Chicago, IL), using lateral condensation technique (Principles and practice of endodontics. Editors Walton RE, Torabinejad M, W.B. Saunders Co. Philadelphia, U.S.A.). The access cavities were then sealed with Cavit-W (ESPE, Seefeld, Germany). Apical root resections were performed on all roots by removing 3 mm of the apex perpendicular to the long axis of the tooth using a high-speed handpiece. A 3 mm deep root-end cavity was prepared using a round bur and slow speed handpiece. The teeth were coated with 2 layers of nail varnish except at the tip where the retrofilling was to be placed. The teeth were randomly divided into 3 groups of 6 teeth each and retrofilled as follows: Group 1 - VERRM, Group 2 - GMTA, Group 3 - WMTA.

In addition, 2 teeth with retropreparation received no retrofilling and served as positive controls. Two teeth which were instrumented and obturated but without root-end resection were completely covered with nail varnish and these served as negative controls. All teeth were stored at 37 °C and 95 % humidity for 24 hours to allow the materials to set. They were then stored in
non-buffered 1% methylene blue solution for 72 hours. The teeth were rinsed
and the nail varnish removed. The specimens were sectioned longitudinally
using the Microslice 2 (Metals Research, Cambridge, England). The roots
were then examined under a stereomicroscope (Olympus SZ-40, Olympus,
Japan) at magnification of x10. The depth of dye penetration was measured
using a measurescope (Nikon MM-11, Yokohama, Japan) and this was
expressed as a percentage of the length of the retrofilling. Statistical analyses
were carried out using ANOVA and Fisher's LSD at 0.05 level of significance.
The results are shown in Table 8.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean depth of dye penetration</th>
</tr>
</thead>
<tbody>
<tr>
<td>VERRM</td>
<td>66.87 ± 6.00 %</td>
</tr>
<tr>
<td>GMTA</td>
<td>54.25 ± 6.96 %</td>
</tr>
<tr>
<td>WMTA</td>
<td>62.72 ± 6.08 %</td>
</tr>
</tbody>
</table>

Table 8: Results of apical sealing test with VERRM, GMTA and WMTA

The positive controls leaked throughout the length of the canals whereas the
negative controls had no dye penetration. VERRM and WMTA showed
significantly greater dye penetration than GMTA (p=0.004 and p=0.036
respectively). There was no significant difference in depth of dye penetration
between VERRM and WMTA. None of the specimens in the three test groups
showed leakage beyond retrofilling.

Discussion

The examples above showed that VERRM has similar pH as GMTA. The
mean initial setting time of VERRM is 40 minutes while that of WMTA is 45
minutes. The mean final setting time of the two materials was the same at 140
minutes. When used as a root-end filling material, this slight difference in
initial setting time is unlikely to be of clinical significance. The values for pH,
setting time, radiopacity and solubility of GMTA are comparable to that
reported by Torabinejad et al., J Endod, 1995, 21:349-353. The solubility of
VERRM is higher than that observed with GMTA and WMTA but still complied with the ISO 6876:2001 requirement, as it did not exceed 3% mass fraction.

An earlier study has reported that the degree of solubility and porosity increased as the water-to-powder ratio of MTA increased (Fridland M et al., 2003). However, in the case of VERRM, the increase in solubility may be due to the presence of the viscosity enhancer.

A root-end filling material should ideally be radiopaque to enable visualization and assessment on the radiograph. The radiopacity of VERRM was slightly lower than GMTA and WMTA but still complied with the ISO 6876:2001 requirement which states that the material should have a radiopacity of equivalent to not less than 3 mm of aluminium. Although slightly less radiopaque than GMTA and WMTA, VERRM was clearly visible on the radiograph (Fig.10).

All three materials, VERRM, GMTA and WMTA, showed slight expansion on setting which was not significantly different. This slight expansion is helpful in ensuring that an effective seal is present upon setting, reducing the likelihood of subsequent leakage. Many different methods have been employed to assess endodontic leakage (Wu et al., 1993). Often, these include the use of bacteria, dye or radioisotope as tracers, with or without the application of pressure or a vacuum system. There is a lack of evidence to suggest that the use of any particular method is superior to the others, although the linear measurement of tracer penetration along a root filling is the method most popularly employed (Wu et al., 1993). In the present study, linear measurement of methylene blue penetration was carried out and this had the advantage of providing quantitative data. The results showed that both GMTA and WMTA provided excellent apical sealing ability. This is consistent with earlier reports on the apical and furcation sealing ability of both GMTA and WMTA (Torabinejad et al, 1994; Aqrabawi et al, 2000; Ferris et al., 2004;
Tang et al., 2002; Weldon et al., 2002). Although the three materials, WMTA, GMTA and VERRM tested varied in the depth of dye penetration, all three materials effectively sealed the root canals as none of the specimens in the three test groups showed leakage beyond the retrofilling.
References


Torabinejad M, Hong CU, McDonald F, Pitt Ford TR, Physical and chemical properties of a new root-end filling material; J Endod, 1995(a); 21(7):349-53.


Claims

1. A dental composite material comprising Portland cement and a viscosity enhancing substance.

2. The dental composition of claim 1, further comprising a radiopaque substance.

3. The composite of claim 2, wherein the radiopaque substance is an oxide or halogen salt of a heavy metal.

4. The composite of claim 3, wherein the heavy metal is any one of gold, barium, silver and/or bismuth.

5. The composite of claims 2-4, wherein the radiopaque substance is bismuth oxide.

6. The composite of claims 1-5, wherein the viscosity enhancing substance is poly(vinyl alcohol), cellulose, cellulose derivatives, polyethylene oxide, natural gums and/or aqueous clay dispersion.

7. The composite of claim 6, wherein the poly(vinyl alcohol) has an average molecular weight of between 13000 and 23000 Dalton.

8. The composite of claims 1-7, wherein the Portland cement has a Blaine number in the range of 4000 to 5500 cm$^2$/g.

9. The composite of claim 8, wherein the Portland cement has a Blaine number in the range of 4600 to 5500 cm$^2$/g.

10. A dental composition comprising the dental composite material of claims 1-9.

11. A method of preparation of the dental composite material of claims 1-9, wherein the method comprises the steps of:
- providing the Portland cement which forms a powder component;
- dissolving the viscosity enhancing substance in water to form a liquid component; and
- mixing the powder component with the liquid component.

12. The method of claim 11, wherein the powder component is obtained by mixing the Portland cement and a radiopaque substance.

13. The method of claim 12, wherein the weight of the radiopaque substance is between 10-25% of the weight of the powder component.

14. The method of claim 13, wherein the weight of the radiopaque substance is 15% of the weight of the powder component.

15. The method of claims 11-14, wherein the weight of the viscosity enhancing substance is between 1-3% of the weight of the powder component.

16. The method of claim 15, wherein the weight of the viscosity enhancing substance is 1.5% the weight of the powder component.


18. The use of claim 17, wherein the composite material further comprises a radiopaque substance.

19. The use of claim 18, wherein the radiopaque substance is an oxide or halogen salt of a heavy metal.

20. The use of claim 19, wherein the heavy metal is any one of gold, barium, silver and/or bismuth.
21. The use of claims 18-20, wherein the radiopaque substance is bismuth oxide.

22. The use of claims 17-21, wherein the viscosity enhancing substance is poly(vinyl alcohol), cellulose, cellulose derivatives, polyethylene oxide, natural gums and/or aqueous clay dispersion.

23. The use of claim 22, wherein the poly(vinyl alcohol) has an average molecular weight of between 13000 and 23000 Dalton.

24. The use of claims 17-23, wherein the Portland cement has a Blaine number in the range of 4000 to 5500 cm²/g.

25. The use of claim 24, wherein the Portland cement has a Blaine number in the range of 4600 to 5500 cm²/g.


27. The use of claim 17-26, wherein the dental treatment is a cosmetic treatment.

28. A method for pulp capping, root perforation repair, root-end filling, apical barrier, management of root fracture, root canal filling, barrier cement for intracoronal bleaching and/or temporary filling, wherein the method comprises the use of a dental composite material comprising Portland cement and a viscosity enhancing substance.

29. The method of claim 28, wherein the dental composite material further comprises a radiopaque substance.

30. The method of claim 29, wherein the radiopaque substance is an oxide or halogen salt of a heavy metal.
31. The method of claim 30, wherein the heavy metal is any one of gold, barium, silver or bismuth.

32. The method of claims 29-31, wherein the radiopaque substance is bismuth oxide.

33. The method of claims 28-32, wherein the viscosity enhancing substance is poly(vinyl alcohol).

34. The method of claims 33, wherein the poly(vinyl alcohol) has an average molecular weight of between 13000 and 23000 Dalton.

35. The method of claims 28-34, wherein the Portland cement has a Blaine number in the range of 4000 to 5500 cm$^2$/g.

36. The method of claim 35, wherein the Portland cement has a Blaine number in the range of 4600 to 5500 cm$^2$/g.

37. The method of claims 28-36, comprising the steps of:

- identifying the cavity and/or fracture of the tooth to be filled, repaired and/or capped; and

- introducing the composite material into the tooth cavity and/or fracture whereby the path of communication between a inner portion of the cavity and/or fracture and the outer surface of the tooth is capped, temporarily sealed or permanently sealed.

38. The method of claims 28-36, wherein the method is for treatment of tooth decay comprising the steps of:

- identifying the decay;

- removing the decay to create a cavity and/or fracture to be filled; and
- introducing the composite material into the cavity and/or fracture whereby the path of communication between a inner portion of the cavity and/or fracture and the outer surface of the tooth is capped, temporary sealed or permanently sealed.

39. The method of claims 28-36, wherein the method is for performing root canal therapy on a tooth comprising the steps of:

- removing a portion of the tooth to expose the root canal;

- preparing the root canal to be filled; and

- introducing the composite material into the root canal whereby the path of communication between the root canal and the outer surface of the tooth is sealed.

40. The method of claims 28-36, wherein the method is for cosmetic dental treatment.

41. A kit comprising the dental composite material of claims 1-9.
FIGURE 3

Graph of pH vs time

- DM
- Port
- GMTA
- WMTA

Time (min)
FIGURE 6

![Viscosity Chart](image-url)
FIGURE 9

![Graph showing pH over time for different materials: VERRM, GMTA, WMTA. The graph indicates changes in pH levels from 11.0 to 13.6 over a period of 70 minutes.]
# INTERNATIONAL SEARCH REPORT

**PCT/SG2004/000350**

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.?: A61K 6/06

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)

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)

- DWPI, MEDLINE; keywords: MTA, mineral trioxide aggregate, Portland, Portland cement, dental, dentist, dentistry, tooth, teeth; IPC A61K, A61C

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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- Further documents are listed in the continuation of Box C  
- X See patent family annex

* Special categories of cited documents:
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Date of the actual completion of the international search

2 December 2004

Date of mailing of the international search report

9 DEC 2004

Name and mailing address of the ISA/AU

AUSTRALIAN PATENT OFFICE
PO BOX 200, WODEN ACT 2606, AUSTRALIA
E-mail address: pct@ipaustralia.gov.au
Facsimile No. (02) 6283 3929

Authorized officer

TERRY SUMMERS
Telephone No: (02) 6283 3126

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<tr>
<td>WO 9424955</td>
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<td>US 5769638</td>
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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX