Smart materials in dentistry

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Abstract

Most dental materials are designed to have a relatively 'neutral' existence in the mouth. It is considered that if they are 'passive' and do not react with the oral environment they will be more stable and have a greater durability. At the same time, it is hoped that our materials will be well accepted and will cause neither harm nor injury. This is an entirely negative approach to material tolerance and biocompatibility and hides the possibility that some positive gains can be achieved by using materials which behave in a more dynamic fashion in the environment in which they are placed.

An example of materials which have potential for 'dynamic' behaviour exists with structures which are partly water-based or have phases or zones with significant water content and for which the water within the material can react to changes in the ambient conditions. Such materials may even be said to have the potential for 'smart' behaviour, i.e. they can react to changes in the environment to bring about advantageous changes in properties, either within the material itself or in the material-tooth complex. The controlled movement of water or aqueous media through the material may cause changes in dimensions, may be the carrier for various dissolved species, and may influence the potential for the formation of biofilms at the surface. Some of these issues may be closely interrelated.

Clearly, materials which do not have the capacity for water transport or storage do not have the potential for this sort of behaviour.

Some materials which are normally resistant to the healthy oral environment can undergo controlled degradation at low pH in order to release ions which may prove beneficial or protective. It is doubtful whether such behaviour should be classified as 'smart' because the material cannot readily return to its original condition when the stimulus is removed.

Other materials, such as certain alloys, having no means of transporting water through their structure, can display smart behaviour by undergoing predictable changes in structure in response to applied mechanical or thermal stimuli. It has been difficult to harness such behaviour to the benefit of patients but progress in this area is slowly being made.
Abbreviations and acronyms

GIC
  glass-ionomer cement
HEMA
  hydroxyethylmethacrylate
PAA
  polyacrylic acid
PAN
  polyacrylonitrile
PVA
  polyvinylalcohol
QLF
  quantitative light-induced fluorescence
RMGIC
  resin modified glass-ionomer cement
SMA
  shape memory alloys

Introduction

Traditionally, materials designed for long-term use in the body or more specifically in the mouth are thought to survive longer if they are ‘passive’ and have no interaction with their environment. Materials such as amalgams, composites and cements are often judged on their ability to survive without interacting with the oral environment. Perhaps the first inclination that an ‘active’ rather than ‘passive’ material could be attractive was the realization of the benefit of fluoride release from materials.

The nature of smart materials

By definition and general agreement, smart materials are materials that have properties which may be altered in a controlled fashion by stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields. A key feature of smart behaviour includes an ability to return to the original state after the stimulus has been removed. Existing smart materials include piezoelectric materials which produce a voltage when stress is applied or vice versa. Structures made from these products can be made to change shape or dimensions when a voltage is applied. Likewise, a change in shape can be used to generate a voltage which can be used for the purpose of monitoring. Thermo-responsive materials, such as shape memory alloys or shape memory polymers adopt different shapes at different temperatures due to remarkable and controlled changes in structure. Magnetic shape memory alloys can change their shape in response to a change in magnetic field.
pH-sensitive polymers are materials which swell/collapse when the pH of the surrounding media changes. Other materials change colour in response to changes in pH, light or applied voltage. One common example of this sort of technology is the light-sensitive sunglasses which darken when exposed to bright sunlight.

Polymer gels offer a potential for smart behaviour. They consist of cross-linked polymer networks which may be inflated with a solvent such as water. The labile nature of the solvent enables a rapid and reversible swelling or shrinkage in response to a small change in their environment (e.g. temperature). The most common gel forming polymers are polyvinylalcohol (PVA), polyacrylicacid (PAA) and polyacrylonitrile (PAN). Microsized gel fibres may contract in milliseconds, while thick polymer layers may require much longer to react. It has been suggested that these gels can potentially deliver a stress equivalent to that of a human muscle of about equivalent size.

**Smart materials by chance or design**

The future use of smart materials will involve a degree of ‘smart behaviour’ by design. However, smart behaviour was first noted in some materials by chance and the significance of the special nature may not be recognized as being of any practical use until some time later. This was certainly the case for thermo-responsive materials, either shape memory alloys or shape memory polymers. Shape memory alloys based upon NiTi alloys have been used in orthodontics for many years and their remarkable properties have been commented upon without any insight into how the properties could be harnessed for a practical purpose. Likewise the potential thermo-responsive smart behaviour of some glass-ionomer cements was first suggested by Davidson and was then demonstrated as a result of attempting to measure the coefficient of thermal expansion. Heating or cooling of these materials may result in minimal dimensional change as the expected expansions (heating) or contractions (cooling) appear to be offset by a compensating reaction related to the movement of water in or out of the structure.

**Smart alloys – the first smart dental materials**

The term ‘smart material’ or ‘smart behaviour’ in the discipline which is now loosely defined as ‘dental materials science’, was probably first used in connection with nickel-titanium alloys, or shape memory alloys (SMAs), which are used as orthodontic wires. Frustratingly, although these materials were found to have fascinating characteristics in relation to the way their structure/properties changed in response to strain and temperature, it has never been clearly expounded how their characteristics could be used beneficially during patient treatment. The smart behaviour is essentially related to the ability of the alloy to initially undergo strain in response to stress in the normal way, but at the point identified as the yield stress there is a further increase in strain which in ‘normal’ alloys would be identified as irreversible yielding. In the SMA alloys, however, this ‘yielding’ is related to a reversible change in the crystal structure. The reverse process is temperature dependent and this lies at the heart of the difficulty in harnessing the characteristic for clinical benefit as the temperatures required can be very high. However, this knowledge has been used in the manufacture of wires of similar cross-section but markedly different stiffness. The phase changes involved in the crystal transitions involve a small exothermic/endothermic response which can be used to monitor or measure the extent of the change. However, the amount of energy involved is very small and very sensitive recording equipment is required (e.g. temperature modulated differential scanning calorimetry). In order to fully utilize the
super-elastic or shape memory characteristics, it would be essential to enable the phase transitions to occur in a controlled fashion at or near mouth temperature, and this is now claimed to be possible by some manufacturers. Wires exhibiting shape-memory behaviour at mouth temperature normally contain copper and/or chromium in addition to nickel and titanium.

**The role of water**

Many types of smart behaviour are related to the ability of a gel structure to absorb or release solvent rapidly in response to a stimulus such as temperature. In the oral environment, the key solvent is water and the structures may be gels or salts which contain water which may be bound either strongly or loosely and therefore may be absorbed or released at different rates. Some types of smart behaviour may also be defined by any species, such as fluoride ions dissolved in the water and which are capable of undergoing reversible interactions with the gel, salt or oral structures. Depending upon the nature of the water and how strongly it is bound, the observed changes may be dependent upon the dimensions of the structures.  

**Smart thermal behaviour**

The vast majority of materials responds to a temperature change in a predictable manner. This involves a dimensional change characterized by the coefficient of thermal expansion or expansivity. One problem with dental filling materials is their tendency to expand and contract to a greater extent than the natural tooth tissue when subjected to hot or cold stimuli. When samples of restorative materials were heated in order to determine their values of coefficient of thermal expansion, an interesting observation was made. For composite materials, expansion and contraction occurred in the expected way and a coefficient could readily be determined, and whether testing was done dry or wet made little or no difference. For glass-ionomers, little or no change in dimension was observed when heating and cooling between 20 °C and 50 °C in wet conditions (Fig 1). In dry conditions, the materials showed a marked contraction when heated above 50 °C. The explanation for this behaviour is that the expected expansion on heating is compensated by fluid flow to the surface of the material to cause a balancing of the dimensional changes. On cooling, the process was reversed. In dry conditions, the rapid loss of water on heating results in the observed contraction. This behaviour is akin to that of human dentine (Fig 2) where very little dimensional change is observed on heating in wet conditions and a marked contraction is noted in dry conditions. Both results can be explained by flow of fluids in the dentinal tubules. Hence, the glass-ionomer materials can be said to be mimicking the behaviour of human dentine through a type of smart behaviour.

*Figure 1.* Dimensional change plotted against temperature for three glass-ionomers (KC, KM, F) and one resin modified glass-ionomer (FLC).

*Figure 2.* Dimensional change of human dentine when heated under wet or dry conditions.
The role of porosity

The smart behaviour of glass-ionomers and related materials is closely linked to their water content and the way in which this can react to changes in the environment. Clearly, there are different ways in which water can be retained in and transported through the cement structure. One important feature which may provide a location for the formation of reservoirs within the material is porosity. The number and size of pores within a cement can be controlled by the method of mixing and is conveniently measured using micro-CT scanning. Figure 3 shows typical scans of a glass-ionomer cement mixed mechanically in capsules or handmixed. The volume of bubbles can readily be calculated and is shown in Table 1.

Figure 3. Micro-CT scans of a glass-ionomer cement (Ketac-Cem) mixed mechanically by shaking (CapMix) or rotating (RotoMix). L, M and H refer to low, medium and high examples of porosity within each group.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mixing method</th>
<th>CapMix</th>
<th>RotoMix</th>
<th>Hand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ketac-Cem</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aplicap</td>
<td></td>
<td>2.8 (1.6)</td>
<td>1.8 (1.8)</td>
<td>–</td>
</tr>
<tr>
<td>Maxicap</td>
<td></td>
<td>2.7 (2.6)</td>
<td>2.1 (2.1)</td>
<td>0.2 (0.2)</td>
</tr>
<tr>
<td>Hand</td>
<td></td>
<td>–</td>
<td>–</td>
<td>0.1 (0.1)</td>
</tr>
<tr>
<td>Ketac-Molar</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aplicap</td>
<td></td>
<td>0.2 (0.2)</td>
<td>0.1 (0.1)</td>
<td>–</td>
</tr>
<tr>
<td>Hand</td>
<td></td>
<td>–</td>
<td>–</td>
<td>0.1 (0.1)</td>
</tr>
</tbody>
</table>

The results given in Table 1 indicate that both the method of mixing and the viscosity of the cement have an effect on porosity. In the low viscosity material, handmixing reduces the porosity significantly compared to mechanical mixing, either by shaking or rotation. For the viscous material the levels of porosity are low and not significantly affected by
mixing. These differences in porosity are reflected in differences in water absorption (Table 2). Hence, this aspect of the smart behaviour of dental cements can be controlled by the operator.

<table>
<thead>
<tr>
<th>Mixing method</th>
<th>Porosity (%)</th>
<th>24 h water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CapMix</td>
<td>2.7 (2.6)</td>
<td>1.32 (0.25)</td>
</tr>
<tr>
<td>Hand</td>
<td>0.2 (0.2)</td>
<td>0.84 (0.11)</td>
</tr>
</tbody>
</table>

Table 2. Porosity and water absorption of Ketac-Cem glass-ionomer cement

Expansion and radial pressure

Smart materials which combine a special interactive characteristic with an acceptable durability or longevity are likely to combine some salt or gel characteristic with a resin component imparting some stability. The manufacturing of such materials presents a problem of compatibility. Traditionally, such problems are solved by also incorporating species with both hydrophilic and hydrophobic groups which have the function of bridging or coupling the two distinctly different ingredients. The most commonly used of these compounds is hydroxyethylmethacrylate (HEMA). However, the large and rapid water absorption of polymers containing HEMA can cause problems; not only does the absorption result in swelling but a considerable radial pressure can also be linked to the process. Profiles of cavities containing a blend of GIC and resin phases with HEMA constrained within a cavity show the ‘growth’ of the material out of the cavity and this is combined with a considerable radial pressure measured as around 26 MPa compared with <3 MPa caused by the water absorption of a typical resin matrix composite.

Ion release and recharging

The beneficial effect of fluoride release of dental materials has been the subject of much research over many years. There is some doubt about the efficacy of fluoride release in caries prevention since even products with high initial fluoride release tend to rapidly lose the ability to release fluoride in significant amounts. Even in the case of GICs, the fluoride release rate can become negligible within a week. However, the smart behaviour of materials containing GIC salt phases offers some long-term solutions to this problem. There is evidence that the fluoride released from salt phases can be replaced when the material is bathed in a high concentration of fluoride as may occur in a toothpaste or mouthrinse. In the long term, the fluoride re-released after recharging may be much more important than the initial ‘burst’ which is sustained only for a short time.

Figure 4 shows data for one material in which fluoride release over 24-hour periods into water is seen to decline sharply over just a few days. As the material becomes depleted of its inherent fluoride it is interesting that the ‘spikes’ of fluoride in the 24-hour period after recharging appear to increase slightly with age. This implies that the more inherent fluoride lost, the greater capacity for uptake through recharging. The levels of fluoride release maintained can be increased by beginning the recharging process as soon as possible after setting. Other work has shown that the rates of fluoride release and recharging are temperature sensitive. Hence, a more rapid recharging could be accomplished by using warm fluoride containing solutions and this can generate a more sustained release at mouth temperature.
Figure 4. Twenty-four hour fluoride release for a resin matrix system containing some GIC salt matrix zones as a function of time of storage in water. At days 8, 17, 23 and 30 the specimens were subjected to a soak in 250 ppm NaF solution for 1 hour. The two lines are for different methods of measuring fluoride concentration.

Another area where ‘smart’ fluoride interactions can have a significant benefit is in the prevention of demineralization around orthodontic brackets (Fig 5). Using fluoride releasing cements can help to prevent demineralization. This has been studied using quantitative light-induced fluorescence (QLF) (Fig 6).

Figure 5. White lesions corresponding to areas of demineralized enamel remaining in the areas surrounding the site where orthodontic brackets were bonded.

Figure 6. QLF device used to study demineralization in teeth and the positive effects of fluoride release and recharging. Taken from Inspektor™ Pro Manual.

Results of laboratory studies show that the use of fluoride-releasing cements can minimize the demineralization, and that this effect is not simply dependent upon the extent of the initial fluoride release. Materials having various levels of fluoride release appear to be almost equally effective when compared with a material having negligible fluoride release, as shown in the QLF images (Fig 7). Another aspect of smart behaviour for this type of material involves the development of materials having mechanical properties adequate for the retention of brackets but which enable easy debonding of brackets at the end of treatment.
Some resin based materials have a potential to release fluoride and neutralize acids. Other resin based materials have been designed to release calcium, fluoride and hydroxyl ions at low pH and these materials are reported to have the potential to neutralize acids and to prevent, or even reverse, demineralization. However, clinical performance of such reactive products is often reported to be unsatisfactory. This highlights the potential problem which exists for many types of smart material: their smart behaviour depends upon a degree of reactivity which may not be compatible with longevity. Taking this a stage further, smart composite materials have been developed which contain amorphous calcium phosphate particles or whiskers which at low pH provide a source of calcium and phosphate ions which may act to prevent demineralization of tooth structure and reportedly maintain acceptable mechanical properties in the process.

**Biofilms and smart behaviour**

Biofilms formed on the surface of materials in the mouth may enhance the smart behaviour of materials containing fluoride releasing salt phases. Recent work with saliva, using live/dead staining techniques, has shown that fluoride release from materials does not prevent biofilm formation or growth. Figure 8 shows that the daily fluoride release in natural saliva is significantly lower than the release into distilled water or artificial saliva. However, when samples are stored in acidified (pH 4) saliva the rate of fluoride release is markedly increased (Fig 9). More interesting are the results which show that when the specimens are cycled through both acidic and neutral conditions, an increase in fluoride release is seen at day 1 and then also at day 2 after placing into acidic conditions. This offers some proof that fluoride becomes concentrated within the biofilm and is made available when the film is disturbed.

**Figure 8.** Fluoride release (24-hour values) from a GIC into different storage media. Release into natural saliva is slower than into water or artificial saliva.

**Figure 9.** Fluoride release into natural saliva in acidified, neutral or cycled (A &N or N&A) conditioned. Note the marked increase in fluoride release over both the first and second day of placement into acidic conditions.
The presence of a biofilm on the surface of a material alters the interaction of the surface with the environment and in the case of a restorative material, the biofilm may act as a lubricant which prevents abrasive wear (Fig 10). The formation of biofilms and the way in which this changes the interaction of the materials with the environment represents a clear example of smart behaviour for these materials. It seems that biofilms can protect surfaces from abrasive forces and at the same time concentrate fluoride which is liberated through a change in pH or mechanical debridment.

**Figure 10.** Surface profiles of a GIC at baseline and after brushing in acidified saliva (natural or artificial). This illustrates the protective effect of the biofilm formed in natural saliva.

**Design of smart materials**

Now that the ways in which materials containing a polysalt matrix can exhibit smart behaviour have been demonstrated, it is appropriate to consider whether future materials can have ‘smartness’ designed into them. If so, can the smart behaviour be accommodated without compromising the other key requirements, such as clinical function and longevity? Of the currently available dental materials, the products which most positively react with their environment in a manner which could be interpreted as smart are the glass-ionomer cements. However, these products are known to have limited durability and longevity due to their brittleness and solubility.

Materials demonstrating an optimum combination of smart interactions and longevity are likely to have some combination of stable resin matrix combined with a coexistent salt matrix or discrete gel phase. The rapid developments in nanotechnology suggest that such features can be manufactured into compounds by using building blocks at a molecular or even atomic level. However, in 1996 Friend stated, ‘The development of true smart materials at the atomic scale is still some way off, although the enabling technologies are under development. These require novel aspects of nanotechnology (technologies associated with materials and processes at the nanometre scale, \(10^{-9}\) m) and the newly developing science of shape chemistry’. This statement still holds true to an extent today. However, our understanding of the potential benefits of smart behaviour have enabled scientists to appreciate the potential benefits of ‘active’ as opposed to ‘passive’ materials and the development of materials exhibiting smart behaviour is now recognized to be possible outside the realms of nanotechnology with its rather artificial and
restricting boundaries and definitions. Hence, even with existing technologies we are able to consider building materials with controlled structure and properties.

Within the spectrum of materials which lie in the continuous scale between resin matrix composites and salt matrix glass-ionomers, we are already able to identify various materials described as resin modified GICs (RMGICs), polyacid-modified resin composites (compomers) or glass-ionomer composites (giomers). These have been shown to exhibit some smart characteristics, albeit more through chance than design. The next stage is to harvest the current knowledge into the design of materials with controlled and designed structure in which the requirements of longevity and smart interaction are balanced. For example, when resin matrix and salt matrix setting reactions are competing during the setting of an RMGIC material, it is possible to conceive of means of controlling the extent to which one or other of the processes dominates and hence to influence the structure and properties of the set material.

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