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Review

Smart materials in dentistry – future prospects

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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 realisation 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(1).

Existing smart materials include piezoelectric materials which produce a voltage when stress is applied or vice versa(2). 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(3) or shape memory polymers(4) 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(5). Other materials change colour in response to changes in pH, light or applied voltage. One common example of this sort of technology are the light sensitive sunglasses which darken when exposed to bright sunlight.

Polymer gels offer a potential for smart behaviour(1, 6). 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 (eg temperature). The most common gel forming polymers are polyvinylalcohol, polyacrylicacid and polyacrylonitrile. Microsized gel fibres may contract in milliseconds, while thick polymers 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 recognised as being of any practical use until some time later. This was certainly the case for thermoresponsive materials, either shape memory alloys or shape memory polymers. Shape memory alloys(3) based upon nickel-titanium 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 thermoresponsive smart behaviour of some glass ionomer cements was first suggested by Davidson(7) and was then demonstrated as a result of attempting to measure the coefficient of thermal expansion(8-10). 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.

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[11].

SMART THERMAL BEHAVIOUR

The vast majority of materials respond to a temperature change in a predictable manner. This involves a dimensional change characterised 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. Whether testing was done dry or wet made little or no difference[8]. For glass ionomers little or no change in dimension was observed when heating and cooling between 20°C and 50°C (Fig. 1) in wet conditions[9, 10]. 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[11]. 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.

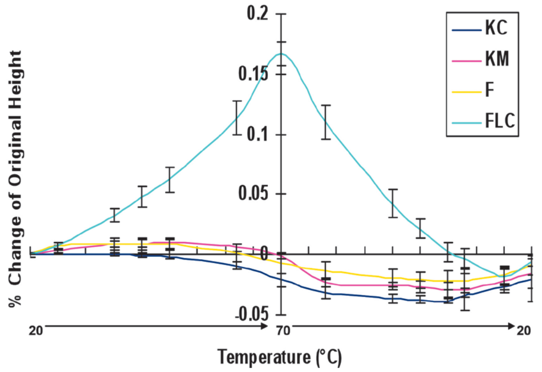

Fig. 1 Dimensional change plotted against temperature for three glass ionomers (KC, KM, F) and one resin modified glass ionomer (FLC).

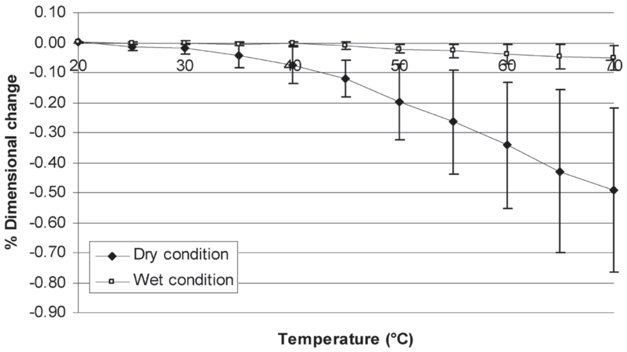

Fig. 2 Dimensional change of human dentine when heated under wet or dry conditions.

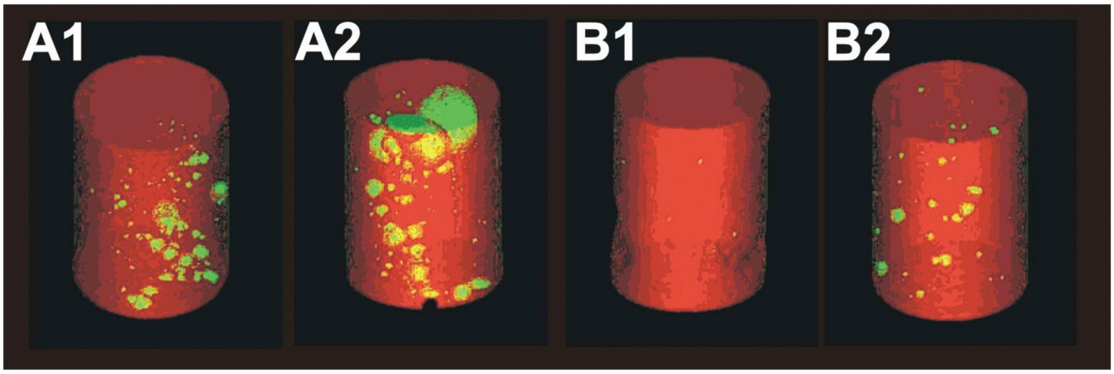

Fig. 3 Micro-CT scans of a glass ionomer cement mixed mechanically by shaking (A1, A2) or hand mixed (B1, B2). A1 and B1 are examples of low porosity and A2 and B2 examples of high porosity specimens within each group.

Table 1 The volume of bubbles in a low viscosity glass ionomer (Ketac-Cem) and a high viscosity glass ionomer (Ketac-Molar) using different methods of mixing

		Mixing method		
Material		CapMix	RotoMix	Hand
Ketac-Cem	Aplicap	2.8 (1.6)	1.8 (1.8)	−
	Maxicap	2.7 (2.6)	2.1 (2.1)	0.2 (0.2)
	Hand	−	−	0.1 (0.1)
Ketac-Molar	Aplicap	0.2 (0.2)	0.1 (0.1)	−
	Hand	−	−	0.1 (0.1)

Table 2 Porosity and water absorption of KetacCem glass ionomer cement

Mixing method	Porosity (%)	24h water absorption (%)
CapMix	2.7 (2.6)	1.32 (0.25)
Hand	0.2 (0.2)	0.84 (0.11)

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[12]. Fig. 3 shows typical scans of a glass ionomer cement mixed mechanically in capsules or hand mixed.

The volume of bubbles can readily be calculated and is shown in table 1. These results indicate that both the method of mixing and the viscosity of the cement have an effect on porosity. In the low viscosity material, hand mixing 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[11,13] as shown in table 2. Hence, this aspect of the smart behaviour of dental cements can be controlled by the operator.

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 hydroxyethyl-methacrylate (HEMA). However, the large and rapid water absorption of polymers containing HEMA can cause problems. Not only does the absorption result

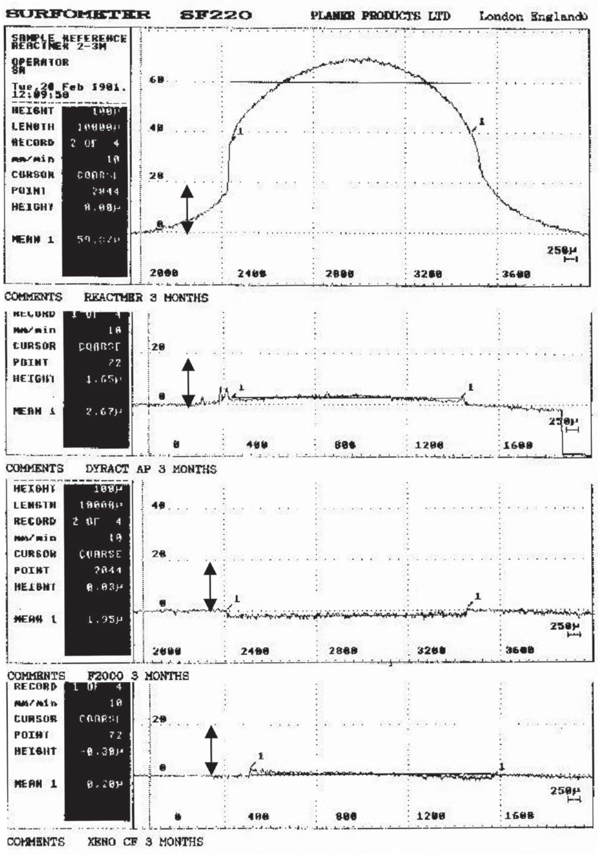

Fig. 4 Surface profiles across surfaces of cavities containing four different materials after 3 months of water storage. Top profile is a HEMA containing GIOMER material showing the material swelling from the cavity. Lower three profiles are for non-HEMA containing composites or compomers. The scale is indicated using the arrows which indicate a height of 20 microns.

in swelling but a considerable radial pressure can also be linked to the process[14]. Fig. 4 shows profiles of a material based upon a blend of glass ionomer cement (GIC) and resin phases with HEMA constrained within a cavity. The 'growth' of the material out of the cavity is evident 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[15].

FLUORIDE RELEASE AND RECHARGING

The potential beneficial effects of fluoride release of materials has been the subject of a lot of 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

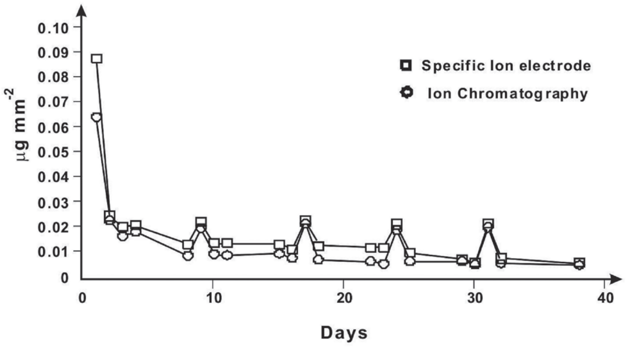

Fig. 5 Twenty four hour fluoride release for a resin matrix system containing some GIC salt matrix zones as a function of time of storage in water. At days 8, 17, 23 and 30 the specimens were subjected to a soak in 250 ppm NaF solution for 1h. The two lines are for different methods of measuring fluoride concentration.

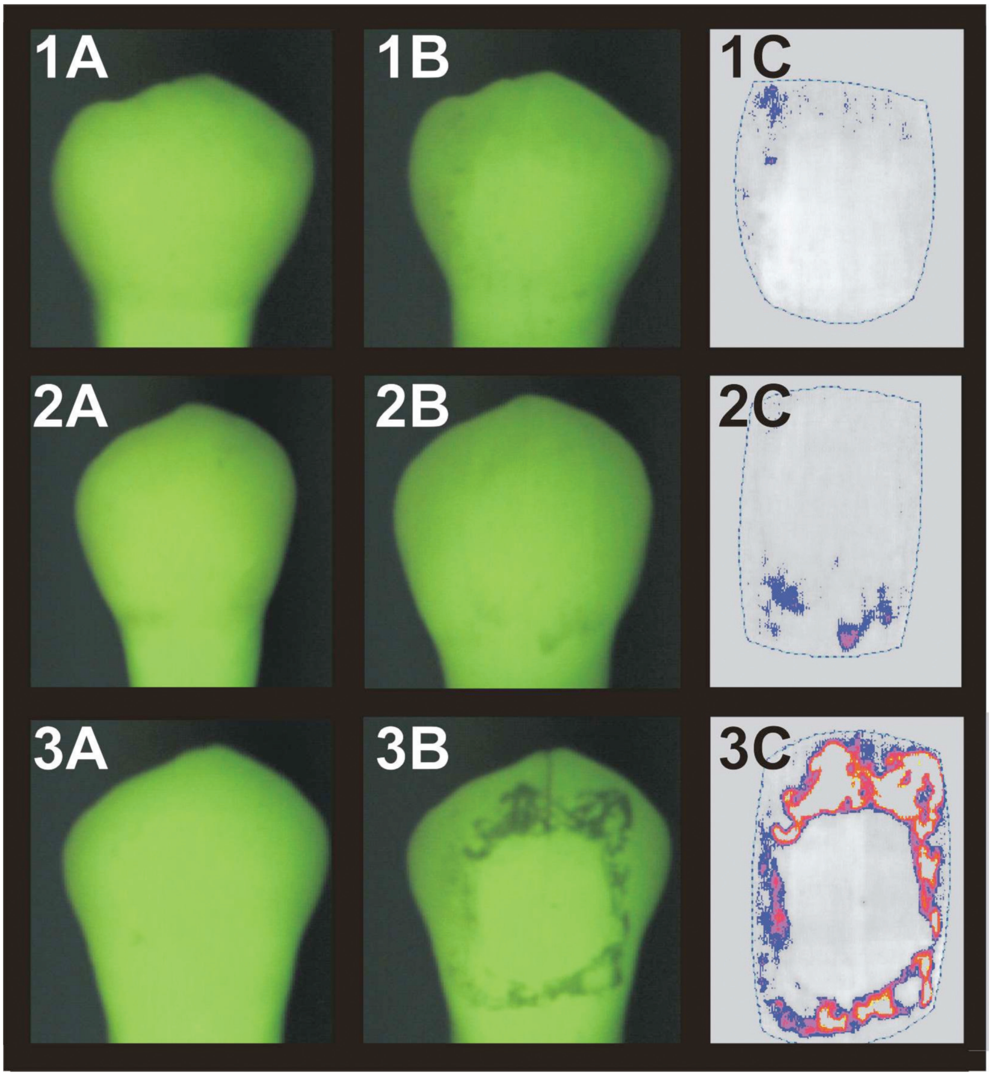

Fig. 6 Pre (A) and post (B) demineralisation QLF images around orthodontic brackets showing significant demineralisation around a non-fluoride releasing cement (material 3) and minimal demineralisation around cements with 'large' (material 1) or moderate (material 2) fluoride release or re-charging capacity.

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[16-19]. 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[13,16,20]. 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.

Fig. 5 shows data for one material in which fluoride release over 24h 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 24h period after recharging appear to increase slightly with age[21]. This implies that the more inherent fluoride lost the greater capacity for uptake through re-charging. 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[13]. 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.

Another area where 'smart' fluoride interactions can have a significant benefit is in the prevention of demineralisation around orthodontic brackets. Using fluoride releasing cements can help to prevent demineralisation. This has been studied using Quantitative Light-induced Fluorescence (QLF). Results of in-vitro studies[22] show that the use of fluoride releasing cements can minimise the demineralisation 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 given in Fig. 6. 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[23].

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[24,25]. Recent work with saliva, using live/dead staining techniques, has shown that fluoride release from materials does not prevent biofilm formation or growth[25]. Fig. 7 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 as shown in Fig. 8. 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[24]. This offers some proof that fluoride becomes concentrated within the biofilm and is made available when the film is disturbed.

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

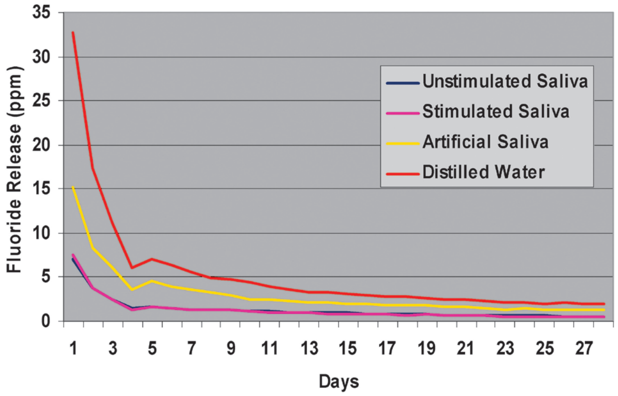

Fig. 7 Fluoride release (24h values) from a GIC into different storage media. Release into natural saliva is slower than into water or artificial saliva.

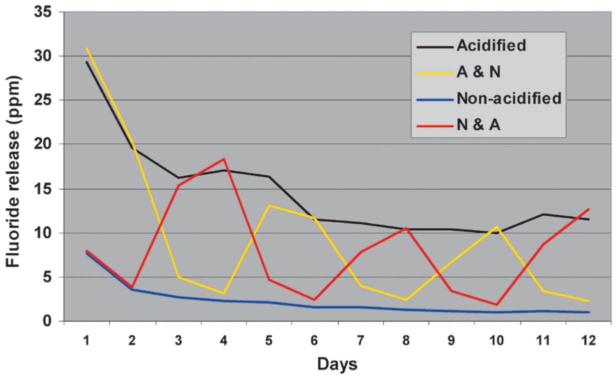

Fig. 8 Fluoride release into natural saliva in acidified, neutral or cycled (A&N or N&A) conditions. Note the marked increase in fluoride release over both the first and second day of placement into acidic conditions.

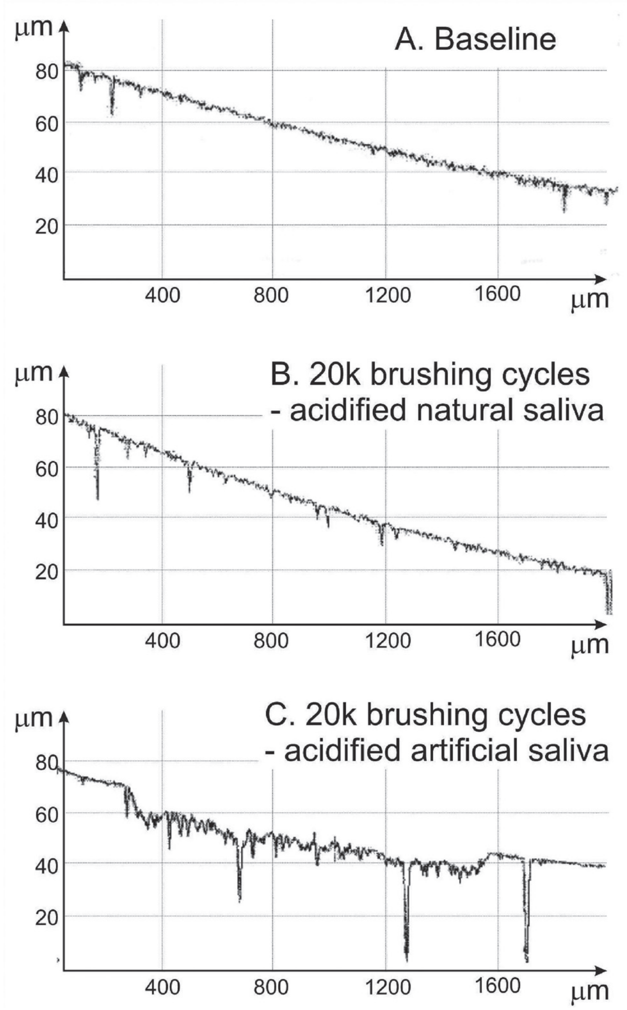

Fig. 9 Surface profiles of a GIC at baseline and after brushing in acidified saliva (natural or artificial). This illustrates the protective effect of the biofilm formed in natural saliva.

the biofilm may act as a lubricant which prevents abrasive wear[24] as shown in Fig. 9.

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 debridement.

DESIGN OF SMART MATERIALS

Now that we have demonstrated the ways in which materials containing a polysalt matrix can exhibit smart behaviour it is appropriate to consider whether future materials can have ‘smartness’ designed into them. If so, can the smart behaviour be accommodated without neglecting 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 very 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 co-existent salt matrix or discreet phase. The rapid developments in nanotechnology suggest that such features can be manufactured into compounds using building blocks at a molecular or even atomic level. However, in 1996 Friend[26] 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 recognised 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[27], we are already able to identify various materials described as Resin Modified GICs (RMGICs), Compomers or Giomers and these have been demonstrated as exhibiting 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 a 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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