Smart materials in dentistry – A review

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Abstract: There is no single material in dentistry that is ideal in nature and fulfills all the requirements of an ideal material. As the quest for an “ideal restorative material” continues, a newer generation of materials was introduced. These are termed as “smart” as these materials support the remaining tooth structure to the extent that more conservative cavity preparation can be carried out. Materials designed for long term use in body or oral cavity are perceived to be “passive” in nature and are designed so that there is no interaction with the internal environment. These materials may be altered in a controlled fashion by stimulus such as stress, temperature, moisture, pH, electric or magnetic field. Some of these are “biomimetic” in nature as their properties mimic natural tooth substance such as enamel or dentin. Some of these materials used are resin modified glass ionomers, amorphous calcium phosphate releasing pit and fissure sealants, smart composites, smart ceramics, compomers, orthodontic shape-memory alloys, smart impression materials, smart sutures, smart burs, smart endodontic files etc. This class of multi-functional materials will possess the capability to select and execute specific functions intelligently in order to respond to changes in the local environment. These materials could have the ability to anticipate challenges based on the ability to recognize, analyze, and discriminate. An important aspect of smart materials used in various areas of dentistry is their excellent biocompatibilities which have marked the beginning of an era of Bio-Smart Dentistry. As we progress towards innovation and to improve technology, we should utilize all the materials which have smartness by chance and also design existing materials to incorporate smartness in them.

Keywords: Ideal restorative material, biomimetic, compomers, smart endodontic files, Bio-Smart dentistry.

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 compared on their ability to survive without interacting with the oral environment. Perhaps the first inclination that the use of an ‘active’ rather than ‘passive’ material could be attractive was the realization of the benefit of fluoride release from materials.(1) Smart materials can be defined as materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, and electric or magnetic fields.(2) SMART materials are generally programmed by material composition, special processing, introduction of defects, or by modifying the microstructure. The “IQ” of smart materials is measured in terms of their “responsiveness” to environmental stimuli and their “agility.” The first criterion requires a large amplitude change, whereas the second assigns faster response materials with higher “IQ.” The Smartness of a material describes its self-adaptability, self-sensing, memory, and multiple functionalities.(3) Smart behavior occurs when a material can sense some stimulus from its environment and react to it in a useful, reliable, reproducible, and usually reversible manner. A really smart material will use its reaction to the external stimulus to initiate or actuate an active response. Smart materials can happen by chance or they can be designed to incorporate smartness in them.(4) The most important characteristic feature of a smart material includes an ability to return to the original state after the stimulus has been removed. It is a system or material which has built in or intrinsic sensor, activator and control mechanism whereby it is capable of sensing a stimulus, responding to it in a predetermined manner and extent, in a short appropriate time and reverting to its original state as soon as the stimulus is removed.(5)
The application of smart materials in various fields of dentistry has thrown light into a new era of materials which actively respond to oral stimuli. As oral cavity is frequently subjected to various types of diseases, the materials used inside the oral cavity in the cure of these diseases should be inert and in neutral zone. It should not harm the tooth structure and should remain inert. Currently, innumerable materials are available based on biocompatibility and strength. The newly emerging materials which have the ability not only to restore the lost tooth structure but are active, they respond to the stimuli of the oral environment, and release fluoride, calcium phosphate etc. The different types of smart materials used in the field of dentistry are piezoelectric materials, shape memory alloys or shape memory polymers, pH sensitive polymers, polymer gels, and others that have shown their own smart behavior. This group of multifunctional materials can possess the capability to select and execute specific functions intelligently in order to respond to changes in the local environment. With the advent and innovation in the fields of nanotechnology and biomedicine, new and promising frontiers are being introduced regularly, these aim for improved efficiency and reliability by inculcating the use of smart materials and structures in dentistry. These innovations in material science have already marked the beginning of the smart future of dentistry. This review provides a selective summary of smart materials in dentistry.

PROPERTIES OF SMART MATERIALS:

Dentistry has been through an era which has seen widespread use of passive and inert materials. They were designed in such a way that they do not interact with body tissues and/or fluids. Materials such as amalgam are often judged on their ability to survive without reacting to the oral environment. This was followed by a period when some materials having caliber to act as “active” materials were noticed. The first active behavior noted in the field of dentistry was the release of “fluoride” from some dental materials. Based on their interactions with the environment, dental materials are currently broadly categorized as bioinert (passive), bioactive, and bioresponsive or smart materials. The first smart dental materials to be used in dentistry were the nickel-titanium alloys, or SMAs used as orthodontic wires. Likewise, the potential thermo-responsive smart behavior 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.

The idea behind smart materials is to produce non-biological structures that will mimic the biological systems with optimum functionality by virtue of their adaptive capabilities and integrated designs. Smart materials can detect the changes in the environment around them and respond in a predictable manner. These properties are:

1. Piezoelectric: when a mechanical stress is applied, an electric current is generated.
2. Shape memory: can change the shape whenever required and can return back to original shape once force / pressure applied is removed.
3. Thermochromic: these materials change color in response to changes in temperature.
4. Photochromic: these materials change color in response to changes in light conditions.
5. Magnetorheological: these are fluid materials, become solid when placed in a magnetic field.
6. pH sensitive: when pH of the surroundings gets altered they will change their shape.
7. Biofilm formation: presence of biofilm on the surface of material alters the interaction of the surface with the environment.

CLASSIFICATION OF SMART MATERIALS:

Smart materials are of two types namely passive and active materials.

Passive Smart Restorative Materials: They sense the external change and react to it without external control.

1. GIC.
2. Resin Modified GIC.
3. Compomer.
4. Dental Composites.

Active Smart Restorative Materials: Active materials sense change in the environment and respond to them. Utilize a feedback loop to enable them to function as a cognitive response through a controlled mechanism or system.

1. Restorative Dentistry:
   - Smart GIC.
   - Smart composites.
2. Prosthetic Dentistry:
   - Smart ceramics.
   - Smart impression materials.

3. Orthodontics:
   - Shape memory alloys.

4. Pediatric & Preventive Dentistry:
   - Fluoride releasing pit and fissure sealants.
   - ACP releasing pits and fissure sealants.

5. Endodontics:
   - Ni-Ti Rotary Instruments.

6. Smart Fibers for Laser Dentistry:
   - Hollow-core Photonic-Fibers.

7. Smart Sutures

Applications Of Smart Materials In Dentistry

Smart GIC: The smart behaviour of GIC was first suggested by Davidson. It is related to the ability of a gel structure to absorb or release solvent rapidly in response to a stimulus such as temperature, change in pH etc. The number and size of pores with the cement can be controlled by the method of mixing conveniently measuring using micro-computed tomography scanning.(14) One of the advantages of GIC (15), compared to other restorative materials, is that they can be placed in cavities without any need for bonding agents; they also have good biocompatibility. Although GI is usually used as cements in dentistry they have disadvantages too. The most important disadvantage of conventional GI is lack of sufficient strength and toughness. In order to increase the mechanical properties of conventional GIC, resin-modified glass-ionomers (RMGIs), compomers or giomers have been introduced, which contain hydrophilic monomers and polymers like HEMA. These smart ionomer mimic the behaviour of human dentin. In some recent studies, BAG has been incorporated into GI composition to improve bioactivity and tooth regeneration and reconstruction capacity and to control the prevalence of primary and recurrent caries.(16)

Smart Composite: Smart composites contain Amorphous Calcium Phosphate (ACP), one of the most soluble of the biologically important calcium phosphates. Generally, Boskey mentioned that Aaron S. Posner to have firstly described amorphous calcium phosphate (ACP) in the mid-1960s. It was attained as an amorphous precipitate by accident when mixing high concentrations (30mM) of calcium chloride with sodium acid phosphate (20mM) in buffer. ACP based materials have been developed for a number of applications like bases/liners, orthodontic adhesives, endodontic sealers, and as pit and fissure sealants. The basic building block of tooth enamel is hydroxyapatite; it is also an inorganic component of dentin. In case of carious attack, hydroxyapatite is removed from the tooth subsequently resulting in cavities or white spots. The carious attack is usually the result of exposure to low pH conditions (acid attack) either from bacteria, other biological organisms releasing acid, food (carbohydrate decomposition products) or acidic beverages. ACP has been estimated as a filler phase in bioactive polymeric composites. Skrtic has established exceptional biocompatible restorative materials containing ACP as filler encapsulated in a polymer binder, which may stimulate the repair of tooth structure because of releasing significant amounts of calcium and phosphate ions in a sustained manner. In addition to outstanding biocompatibility, the ACP containing composites release calcium and phosphate ions into saliva milieu, especially in the oral environment caused by bacterial plaque or acidic foods. This ion then gets deposited into tooth structures as apatitic mineral, which is similar to the hydroxyapatite (HAP) found naturally in teeth and bone. ACP at neutral or high pH remains as ACP. When pH values are low, which usually occurs during a carious attack, ACP converts into HAP and precipitates, thus substituting the HAP lost to the acid. So, when the pH level in the mouth drops below 5.8, these ions combine within seconds to form a gel. In less than 2 minutes, the gel converts into amorphous crystals, resulting in calcium and phosphate ions. This response of ACP containing composites to pH can be described as smart.(4) Ex: Ariston pH control - introduced by Ivoclar -Vivadent (Liechtenstein) Company.(7)

Self-healing composites: After a period of use, materials degrade due to different physical, chemical, and/or biological stimuli. This leads deterioration in the properties of the material finally leading to its failure. Self-healing has become one of the most desired properties in material development.
In the body, the best example of self-healing is the healing of a broken bone in the presence of nutrients and a source of blood supply. Continuous efforts are being made to replicate this biological model in material science. The first self-healing resin-based synthetic material has been developed by White et al. The material was an epoxy system which contained resin filled microcapsule dicyclopentadiene, a highly stable monomer with excellent shelf life, encapsulated in thin shell made of urea formaldehyde. In response to environmental stimuli, some of the microcapsules rupture and release resin, which further reacts with Grubbs catalyst in epoxy composite, causing a polymerization reaction to take place and repair the crack. The main concern is the potential toxicity of the resins in the microcapsules and from the catalyst. However, their amount is relatively small, and the concentration may well be below the toxicity threshold.(3)

**Smart Prep Burs:** These are polymer burs with shovel-like straight cutting edges. The polymer material has been designed to be harder than carious, softened dentin but softer than healthy dentin. It is claimed to remove carious dentin selectively; whereas, healthy dentin is not affected (minimally invasive excavation); the cutting edges wear down in contact with harder materials. Smart Prep burs are available in three ISO sizes 010, 014, and 018 and are meant for single-use only (self-limiting action). They should be used with light pressure and excavation should be done from the center to the periphery to avoid contact with the harder dentin.(3) Ex: SS White (145 Towbin Avenue, Lakewood, Newjersey,08701, USA) diamond and carbide preparation kit.(17)

**Smart Ceramics:** Smart Ceramics deliver outstanding aesthetics without reservations or compromise. These are metal-free and biocompatible. In 1995 the first ‘all ceramic teeth bridge’ was invented at ETH Zurich based on a process that enabled the direct machining of ceramic teeth and bridges. Since then the route and the materials were verified and introduced in the market as CERCON – Smart ceramics. The strength and technology of cercon allows bridges to be produced without stainless steel or metal. The Zirconia-based all ceramic material is not baked in layers on the metal. The overall product is metal-free biocompatible life like restoration with strength that helps resist crack formation. With Cercon unsightly dark margins and artificial grey shadows from the underlying metal are no longer a problem. Whether for “front” or “back” teeth. Cercon Smart Ceramics deliver outstanding aesthetics without reservations or compromise. Zirconium oxide is a highly stable ceramic oxide, typically used in industrial applications requiring high strength and stability, and has a history as a biomaterial dating back to the 1970s. It finds its applications in implants and other non-dental applications extensively, and is currently the material if choice for use in hip replacements. The Cercon system offers a comprehensive solution to these needs by taking advantage of the strength, toughness, reliability, and biocompatibility of Zirconium oxide. So the Cercon ceramics are said to be the smart material as they are bio responsive.(18, 19)

**Smart Impression Materials:** These materials exhibit more hydrophilic nature to get void free impression and shape memory during elastic recovery resists distortion for more accurate impression, toughness resists tearing. Its Snap set behaviour results in precise fit restorations without distortion with reduction of working and setting times by at least 33%. The viscosity of these materials is low with high flow.(8) Ex: Imprint™ 3 VPS, Impregim™, Aquasil ultra (3M ESPE Dental Products, USA).

**Shape Memory Alloys:** The shape memory effect was first observed in copper zinc and copper tin alloy by Greninger and Mooradian in 1938, but in early 1960 Buchler discovered and patented Nitinol (Nickel titanium naval ordnance laboratory) a nickel titanium alloy. Shape memory alloys, and in particular NiTi alloys, are characterized by two unique behaviors, thermally or mechanically activated: the shape memory effect and pseudo-elastic effect. These behaviors, due to the peculiar crystallographic structure of the alloys, assure the recovery of the original shape even after large deformations and the maintenance of a constant applied force in correspondence of significant displacements. These properties, joined with good corrosion and bending resistance, biological and magnetic resonance compatibility, explain the large diffusion, in the last 20 years, of SMA in the production of biomedical devices, in particular for mini-invasive techniques.(20) In dentistry the shape memory alloys are widespread because of their super elasticity, their shape memory, their good resistance to fatigue and wear and their excellent biocompatibility. All these properties led to their extensive use in orthodontics. The shape memory alloys apply continuous gentle forces within physiological ranges over longer periods of time.(9) Ex: Ni-Ti alloy.

**Fluoride Releasing Pit and Fissure Sealants:** Pit-and-fissure sealants can be used effectively as part of a comprehensive approach to caries prevention. While sealants have been used for primary caries prevention, current evidence indicates that sealants also are an effective secondary preventive approach when placed on early non-cavitated carious lesions. The two major types of pit-and-fissure sealant materials are available: resin-based sealants and glass ionomer cements. Available resin-based sealant materials can be polymerized by autopolymerization, photopolymerization using visible light or a combination of the two processes. Caries risk valuation is an important constituent in the decision-making process, and it is important to reevaluate a patient's caries risk status periodically. The recommendations address circumstances in which sealants should be placed to prevent caries, sealant placement over early (non-cavitated) lesions, conditions that favor the placement of resin-based versus glass ionomer cement, and techniques to improve sealants' retention and effectiveness in caries prevention.(20)

**ACP Releasing Pits and Fissure Sealants:** Amorphous Calcium Phosphate (ACP), thought to be a precursor in the formation of Hydroxyapatite, has also shown anti-cariogenic properties with remineralization potential. ACP containing bioactive materials stimulates mineral growth by increasing the Calcium and Phosphate concentrations within the lesion, especially in the acidic oral environment, to levels that exceed those existing in ambient oral fluids thereby shifting the solution thermodynamic driving forces toward the formation of apatite. ACP can sustain these super saturation conditions over extended periods of time. ACP and Fluoride have been incorporated in restorative composites, glass ionomer cements, orthodontic adhesives, crown and bridge adhesives, pit
and fissure sealants to arrest incipient white spot lesions in primary caries.(21) (under the name ReCaldent). It is marketed as GC tooth mousse plus®.(7)

**Ni-Ti Rotary Instruments:** In Endodontics, 55wt% Ni and 45wt% Ti are commonly used, referred to as —55NiTiNOL. Walia et al. in 1988 introduced Ni-Ti to Endodontics. Nitinol basically exists in two phases. The low -temperature phase is called the martensitic or daughter phase (a body - centered cubic lattice) , and the high -temperature phase is called the austenitic or parent phase (hexagonal lattice).This lattice organisation can be altered either by stress or temperature. The super-elasticity of NiTi rotary endodontic instruments provide improved access to curved root canals during the chemo mechanical preparation with a less lateral force exerted. It allows more centered canal preparations with less canal transportation and a decreased incidence of canal aberrations. Nitinol shows stress-induced thermoelastic transformation. Generally, it is in an austenitic crystalline phase that gets converted to a martensitic structure on stressing at a constant temperature. In this martensitic phase, only a light force is sufficient for bending. If the stress is released, the structure recovers to an austenitic phase and its original shape.(7)

**Smart Fibers for Laser Dentistry:** Laser means Light Amplification by Stimulated Emission of Radiation. Laser is a type of electromagnetic wave generator. The emitted laser has three characteristic features:

- **Monochromatic:** waves are of the same frequency and energy.
- **Coherent:** waves have certain phase and are relation to each other, in speed and time.
- **Collimated:** emitted waves are almost parallel and the beam divergence is very low.

Laser radiation of high-fluency can be delivered by Hollow-core Photonic-Fibers (PCFs) which can ablate tooth enamel been developed. These photonic fibers are known as Smart Fibres. Photonic Crystal Fibre are not only to transport the high power laser pulse to a tooth surface, but can be used for detection and optical diagnosis through transmit plasma emission. Care should be taken while using these fibers as laser light may escape and can harm healthy tissue.(7)

**Smart Sutures:** Smart sutures are made up of thermoplastic polymers that have both shape memory and biodegradable properties. They are applied loosely in its temporary shape and the ends of the suture were fixed. When the temperature is raised above the thermal transition temperature, the suture would shrink and tighten the knot, applying the optimum force. This thermal transition temperature is close to human body temperature and this is of clinical significance in tying a knot with proper stress in surgery. Smart sutures made of plastic or silk threads covered with temperature sensors and micro-heaters can detect infections. Ex: Novel MIT Polymer (Aachen, Germany)®.(17)

**Smart materials by design:**
Materials that contain a poly salt matrix can be designed to include and exhibit smart behavior by utilizing the following:

- **Function of water:**
  Smart behavior can be correlated to the ability of a structure to absorb or release solvent rapidly in response to a thermal stimulus. Depending on the nature of water and the strength of the bonds present, the dimensional stability of the structure may be enhanced or decreased.

- **Thermal behavior:**
  Mostly the thermal behavior of any material is mainly dependent on its coefficient of thermal expansion. The problem with most dental materials is the discrepancy in their coefficients of thermal expansion as compared to the tooth therefore the materials tend to expand and contract to a greater extent than the natural tooth.

- **Expansion and radial pressure:**
  By incorporating resins within the salt and gel matrix of the material the durability and longevity can be stabilized.

- **Biofilms and smart behavior:**
  The presence of biofilm on the surface of a material alters the interaction of the surface with the environment and may act as a lubricant which prevents abrasive wear. The formation of biofilms and how they change the interaction of the material with the environment can affect the property of a material to great extent. It seems that biofilms can protect the surface from abrasive forces, initiation of caries and also concentrate fluoride. If the above mentioned properties can be integrated into materials and smart materials can actually be designed care should be taken so as not to neglect the requirements and original properties of the materials. According to Friend 1996‘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 and the newly developing science of shape chemistry. Further need is to harvest this knowledge into designing a material which not only has a controlled design and structure but also fulfills the requirements of longevity and balanced smart interactions.(9)

**Conclusion:**
The potential future benefits of smart materials, structure and systems are amazing. The technology promises optimum responses to highly complex problems by providing enhancements to many products it could provide better control by minimizing distortion and increasing precision. It could also enhance preventive maintenance of systems and thus improve their performance. The numerous applications of smart materials have revolutionized many areas of dentistry and there is no doubt that “smart materials” hold a real good promise for the future. With the availability of these intelligent materials, which possess multifunctional capabilities, it will
be easy and comfortable to correlate with dental therapy and execute specific function smartly to respond to changes in the local environment.

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