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Review Paper

Restorative and Endodontic Materials Working Smarter Than Harder: A Contemporary Approach

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ABSTRACT

Currently, there is no perfect dental material that fits all criteria for excellence. As the search for the "ideal restorative material" continues, newer materials are being introduced. Several biocompatible materials have been developed and widely used in a variety of dental treatments.
As the demand for dental materials that mimic the properties of natural tooth structure increases, smart materials have emerged as a solution. These materials respond to environmental stimuli in a practical, reproducible, and reversible manner. They can undergo controlled transformations when exposed to factors such as stress, temperature, humidity, and pH. A key characteristic of smart materials is their ability to return to their original state once the stimulus is removed. Some examples of smart materials in dentistry include resin-modified glass ionomers, amorphous calcium phosphate-releasing pit and fissure sealants, smart composites, ceramics, orthodontic shape-memory alloys, smart impression materials, smart sutures, burs, and endodontic tools. This review highlights the current understanding of smart materials, their transformative role in dentistry, and the beginning of a new era in biosmart dentistry, while also providing an overview of various dental materials with smart behaviors.

Keywords: Biomimetic, Responsive materials, Smart materials, Stimulus.

INTRODUCTION

The term 'smart' and 'intelligent' were coined in the 1980s in the United States to characterize materials and systems. These smart materials were created by government entities working on military and aerospace programs, but they have recently been adopted in the civil sector for a variety of purposes. The first smart material application began with magnetostrictive technology, which used nickel as a sonar source to identify German U-boats by Allied forces during World War I.[1]
Dental materials are generally characterized as bioinert, bioactive, or bioresponsive.[2] Initially the thought was dental materials that are passive and not affected by their surroundings are more stable and lasting, in hope that the things would be well-received and not cause any harm.[1] This strategy for material tolerance and biocompatibility was wholly unfavorable.
Materials used in dentistry today are improvised by introduction of smart/ responsive materials.[3] Hence, McCabe Zrinyi defined smart materials as "Materials that are able to be altered by stimuli and transform back into the original state after removing the stimuli".[4] The stimuli can be in form of temperature, pH, moisture, stress, electricity, chemical or biomedical agents and magnetic fields.[5] These materials are

also known as responsive materials as they can easily sense the changes in the oral cavity and respond positively to these changes, resulting in a material with improved qualities and treatment outcomes for both the operator and the patient.[6] Additionally, Takagi in 1990, described them as intelligent materials.

Criteria for a smart material include:

- An asymmetrical nature
- The ability to receive and respond to stimuli
- Incorporation of at least one material with a smart structure [7]

Mechanism of smart material

Bio-smart materials use two processes to promote tissue repair and regeneration.

- Cells and tissues respond to external and internal stimuli such as pH, temperature, magnetic, and ionic strength, resulting in inductive and instructive effects.
- Individual properties and functions have been intelligently adjusted to actively engage in tissue regeneration.[7]

Ideal Properties of Smart Material

According to Williams, "smart" materials respond to external stimuli in predictable and regulated ways. The failure of traditional filling materials is often due to the formation of secondary cavities, restorative problems, tooth fractures, marginal damage, inconsistencies, or wear. By incorporating additives into new materials, their durability is enhanced, leading to a reduction in failure rates. Ideal properties of Smart Material are as follow:[8]

- Prevention of secondary caries
- Prevention of restoration fractures
- Prevention of tooth fractures
- Ensuring good marginal integrity
- Reducing wear
- Prevention of marginal discrepancies
- Minimizing wear

Classification of Smart Dental Material.

Smart materials are of two types, passive and active materials.[9]

Passive Smart Materials: These are materials that sense external change and react to it without external control. Example: Composites, GIC, Resin-modified GIC and Compomers.

Active Smart Materials: These are materials that sense change in the environment and respond to them. Example: Smart GIC, Smart composites, Smart Prep Burs. (Table 1& 2) [10,11]

Table 1: Types of smart materials used in dentistry

Speciality	Examples
Restorative dentistry	Smart composites, smart glass ionomer cement
Endodontics	Ni-Ti rotatory instruments
Prosthetic dentistry	Smart ceramics
Pediatric dentistry	Amorphous calcium phosphate (ACP) is released from pits and fissure sealants
Oral surgery	Smart sutures
Laser dentistry	Hollow-core photonic fibers

Table 2: General properties of Smart Material

Piezoelectric	When a mechanical stress is applied, an electric current is generated.
Shape memory	After deformation these materials can remember their original shape and return to it when heated.
Thermochromic	These materials change color in response to changes in temperature.
Photo chromic	These materials change color in response to changes in light conditions.
Magneto rheological	These fluid materials become solid when placed in a magnetic field.
pH sensitive	Materials which swell/collapse when the pH of the surrounding media changes.
Bio film formation	Presence of bio film on the surface of material alters the interaction of the surface with the environment.
Ion release and recharging	Salt phases of GIC offers some long-term solutions by the sustained re-release of fluoride after initial recharging.

Restorative Materials

Smart composite, pit and fissure sealant and remineralizing agents

Skritic developed innovative biologically active restorative materials containing an amorphous calcium phosphate (ACP) filler within a polymer binder. These materials release calcium, fluoride, and hydroxyl ions when the intraoral pH falls below the critical threshold of 5.5, helping to counteract tooth demineralization and promote remineralization. Amorphous calcium phosphate, a physiologically relevant calcium phosphate, is the most soluble and converts quickly to crystalline hydroxyapatite in smart composites.

During a carious attack, amorphous calcium phosphate precipitates and replaces the missing hydroxyapatite (HAP) at low pH levels, below 5.5. Therefore, when pH in the mouth falls below 5.5, these Ions rapidly combine to form a gel. After two minutes, the gel forms amorphous crystals and releases calcium and phosphate ions and in this way, composites containing ACP responded intelligently to pH.[12]

It can be adequately cured in a bulk thickness of up to 4 mm and has reduced risk of polymerization shrinkage, which minimizes the risk of gaps or post-operative sensitivity.[12]

Example- Ariston pH control (Ivoclar Vivadent), Aegis® Pit and Fissure Sealant, Recaldent TM, Enamelon TM, Novamin TM.

Self-Healing Composites

Materials typically have a limited lifespan and degrade due to various physical, chemical, and/or biological factors. These include external static or dynamic forces, internal stress, corrosion, dissolution, erosion, or biodegradation, all of which gradually lead to the deterioration of the material's structure and eventual failure. Inspired by nature, scientists and researchers have developed materials that can repair themselves. Unlike traditional, rigid composites, these materials are capable of automatic recovery and adaptation to environmental changes in a dynamic manner.[13]

Self-healing composites can be categorised into three groups, on the bases of mechanism of action-

a) Capsule-based self-healing system

In capsule-based self-healing materials, tiny capsules containing a liquid capable of filling and sealing cracks are embedded beneath the material's surface. When the material is damaged and cracks form, some of these capsules rupture, releasing the liquid to close the gap. For example, capsules containing dicyclopentadiene (DCPD) and Grubbs' catalyst are dispersed within a polymer matrix during the material's formulation. Upon damage, when a crack occurs, the healing agent inside the capsules is released as the polyurea formaldehyde (PUF) capsule shell fractures. The healing agent then floods the crack and solidifies through the Ring-Opening Metathesis Polymerization (ROMP) of DCPD, catalyzed by the Grubbs catalyst. ROMP is a chain-growth polymerization process in which cyclic olefins are converted into polymeric materials by opening the strained rings of the monomers and linking them into long chains.[13]

b) Vascular self-healing system

While capsule-based self-healing composites replicate the natural healing process on a cellular level, vascular self-healing materials imitate the healing mechanisms of the vascular and circulatory systems in animals on a macro scale. With a tunnel-like circulation system, the healing agent can be replenished, enabling continuous delivery and flow control. When a crack forms and disrupts the vascular network, the healing agent within the network fills the gap.[13]

c) Intrinsic self-healing systems

Other than these in intrinsic self-healing systems, the polymeric network contains latent functional groups capable of reorganizing and re-forming bonds, which makes the organic matrix inherently after a damage, in the presence of external stimulus such UV light, heat, or chemicals.[13]

Smart GIC

Smart behavior of GIC was first suggested by Davidson as it mimics the behavior of human dentin, hence it is also known as man-made dentin.[5]

A common misconception is that glass ionomer cement (GIC) is considered a smart material because of its fluoride release, but this concept is not true. Dentin is made of dentinal tubules that contain fluid into it, whenever the temperature rises inside the oral cavity as a natural phenomenon, the dentin should expand, however by loosing its moisture it shrinks, compensating the expansion caused by heat. The opposite happens when oral cavity temperature drops down, dentine gains water compensating the shrinkage caused by decrease in temperature.[14]

For glass-ionomers, there is minimal or no dimensional change when heated and cooled between 20°C and 50°C under wet conditions. However, under dry conditions, the material exhibits significant contraction when heated above 50°C. The explanation for this behaviour is that GIC has both bonded and unbonded water. So, whenever a GIC restoration in the oral cavity is exposed to heat it loses its loosely bonded water thus compensating for its expansion. On contrary when cooled in wet surrounding, it absorbs water from the surrounding to compensate shrinkage occurred due to cooling.[1]

Along with this ability to replenish the lost mineral when surrounding environment has increased concentration of fluoride ion is also a smart property of this material.

Example- GC Fuji IX GP extra (Zahnfabrik bad sackingen, Germany).

Smart monochromatic composite

This composite is based on structural color concept which occurs when different wavelengths of light either amplified or weakened by the structure of a material itself, expressing colors other than what the material may actually be. In dentistry inspired by this smart monochromatic composite has been developed.

It is based on the principle that homogeneously sized spherical shaped filler particles adjust the light that is transmitted all along the red yellow area of the colour scale which is specific to match entirely 16 vita classical shade. Another shade is termed blocker, used during through and through restoration like in class 4 as it acts like opaque dentin, blocking the light to pass through it and giving the restoration a natural appearance. A blocking agent is applied as a 0.5 mm thin coat before the insertion of the smart monochromatic composite. It effectively camouflages the internal part of the crown, especially in cases of discoloration, and also minimizes shade-matching interference.[15]

Example- Omnichroma, Spherichrome, Vittra APS unique, One shade.

Smart burs

Carbide dental burs were originally designed to efficiently remove non-decalcified enamel and dentin. However, they do not help differentiate between carious and healthy dentin during cavity preparation. When this aggressive technique is combined with the dentist's aim to achieve a smooth, normal-feeling surface, there is a high risk of unintentionally removing sound dentin. This led to the discovery of the Smart Prep single use bur.

It is made of a medical-grade polymer with hardness of 50 KHN, less than that of healthy dentin as the knoop hardness value of caries-affected dentin is in the range between 0-30 while healthy dentin is within the range of 70-90.[16]

Polymer burs feature cutting elements designed to efficiently cut softer dentin but are ineffective at cutting normal dentin. When they come into contact with normal or partially decalcified dentin, the cutting blades deflect and deform, reducing cutting efficiency and altering the operator's tactile feedback. It is also known as dentin safe bur which works at speed of 500-800rpm.[16]

The bur blades are designed to primarily remove carious dentin through a plowing action, where the blades first locally

compress the carious dentin. The compressed, softened carious dentin is then pushed along the sound dentin surface, causing rupture at this boundary, and the loosened fragments are carried to the surface. In contrast, the removal of normal dentin occurs through chip formation via orthogonal cutting, where the blade penetrates the dentin in a wedge-like manner, leading to plastic deformation and shearing.
Example- SS white smart bur.

Smart ceramic

Aesthetics is a key consideration in dentistry. While ceramics have long been used to fabricate crowns, they were traditionally paired with a metal substructure in porcelain-fused-to-metal (PFM) crowns. However, the metal substructure compromises the aesthetic quality of the restoration. To address this, advanced ceramic zirconia is now available as an alternative. [17]

Zirconia exists in three phases, monoclinic at room temperature, tetragonal from 1170 to 2370 degree Celsius and cubic at more than 2370 degree Celsius. The volume of monoclinic crystal is 6% more than tetragonal. As on cooling from tetragonal to monoclinic the ceramic shows expansion and fracture, therefore yttrium is added to stabilize tetragonal crystal at room temperature without fracture but these tetragonal crystals are now under heavy stress and full of energy. So, when such zirconia is exposed to any crack formation the partially stabilized tetragonal crystal absorbs that stress and convert into monoclinic structure to attain equilibrium. As the crystal volume of monoclinic is 6% more than tetragonal, the larger crystal tends to close the gap formed due to crack formation. Additionally, the monoclinic crystal formed at the tip of crack inhibit crack propagation.[18]

Example- IPS e max ceram (Ivoclar), cercon (Dentsply Sirona).

Smart bonding agent

Microleakage is a major concern in adhesive dentistry, as it can lead to the breakdown of the bond and secondary caries formation. Recently, bonding agents containing nanoparticles of amorphous calcium phosphate (NACP) has been developed which is a bioactive smart material that can release calcium and phosphate ions, which are essential for remineralizing enamel and dentin, along with the development of new quaternary ammonium monomer, dimethylaminododecyl methacrylate, imparting a potent antibiofilm activity to bonding agent.

NACP containing bonding agents can help reduce microleakage by enhancing the bond between the tooth and the restoration while also promoting mineralization at the interface, making it more resistant to environmental factors like saliva or acids. When incorporated into bonding agents, NACP can help repair early stages of demineralization by replenishing lost minerals, leading to stronger and more resilient tooth structures. NACP particles in the bonding agent are extremely small, nano sized and are capable of interacting directly with the tooth structure. These particles release calcium and phosphate ions, which are the same minerals that make up tooth enamel. These ions can infiltrate the areas and promote the remineralization of the tooth surface, effectively reversing early signs of decay and strengthening the tooth's resistance to future demineralization. It rapidly neutralizes a pH 4 solution and increases the pH to a safe level of above 5.5.[19]

Endodontics

Smart Nickel-Titanium (NiTi) files

The term "smart" was initially associated with NiTi alloys or shape-memory alloys due to their unique properties of superelasticity and shape memory. These properties, along with changes in volume and density, contribute to the material's ability to change shape. Superelasticity refers to the ability to withstand stress and return to its original lattice shape without permanent deformation. When an austenitic material is deformed, it transforms into detwinned martensite but tends to revert to its original state (spring back), demonstrating superelasticity. Shape memory, on the other hand, describes the NiTi file's ability to return to its original shape without deformation. When detwinned martensite is heated, it transforms into austenite, and upon cooling, it becomes twinned martensite, thus returning to its initial shape. By applying stress or changing temperature, the lattice structure can be altered. Nitinol has two phases: the martensitic (daughter) phase, a low-temperature phase with a body-centered cubic lattice, and the austenitic (parent) phase, a high-temperature phase with a hexagonal lattice. During root canal treatment, NiTi files undergo stress, causing a transformation from the austenitic to the martensitic state at the speed of sound. The superelasticity of NiTi rotary instruments facilitates easier access to irregularly shaped root canals during biomechanical preparation, with less lateral force applied and a reduced risk of canal aberrations and transformations.[10]

Smart seal obturation system

Obturation refers to the three-dimensional filling of instrumented canals, accessory canals, and dead spaces. By properly obturating the canal, reinfection can be prevented, thus avoiding periapical infection. There are several canal-filling techniques used by dentists, but since gutta-percha is an impermeable material, leakage between the sealer and the dentin, as well as between the gutta-percha and the sealer, along with the presence of voids, can lead to treatment failure. This has led to an ongoing search for materials with better sealing properties, such as the smart seal system. The C-point system, also known as the smart seal system, is a newly introduced point-and-paste system that utilizes hydrophilic polymer-based technology. The smart seal system consists of two main components: hydrophilic obturation points and a sealer. The obturation points are made from polymorphs and come in various tip sizes and tapers. The hydrophilic nature of the smart obturating material allows it to absorb moisture and expand laterally, filling any voids. However, for proper sealing, a sealer should be used alongside these endodontic points. SmartSeal™ is available in different tip sizes and tapers. (Table 3) [11]

TABLE 3: SmartSeal™ in various tip sizes and taper

Taper	Tip sizes
6% taper	ISO tip sizes 25-45
4% taper	ISO tip sizes 25-45
ProTaper™	F1, F2, F3, F4, and F5
Sendoline™	S5 - S2, S3, and S4

Smartpaste bio

Another example of a resin-based sealant is Smartpaste Bio, which contains bioceramics. During the setting process, Smartpaste Bio produces calcium hydroxide and hydroxyapatite as byproducts, enhancing the material's biocompatibility and antibacterial properties. It has a delayed setting time of 4 to 10 hours and is hydrophilic, which encourages the obturation points to hydrate and expand, effectively filling all voids. The lateral forces generated by Smartpaste Bio are lower than the tensile strength of dentin and are also less than the forces created by traditional methods. The bioceramics in Smartpaste Bio provide dimensional stability to the sealer, ensuring it remains non-resorbable within the root canal.[20]

Smart suture

The most common issue associated with sutures were that a tight knot may cause the damage of healthy cells, leading to skin necrosis. Whereas a loosely sealed wound line would introduce foreign substances to infiltrate wound site.

To address these issues, smart sutures have been introduced in the field. The term "suture smartness" refers to the suture's ability to revert to its original shape after being altered. These sutures can be stretched below critical temperatures before being implanted. Initially, the suture is applied loosely to the wound site, and once the temperature increases—either due to body heat or external sources—the suture returns to its original shape. Some of the smart suture consists of two outer sheaths of braided fibers and a core comprising of silicone and salt, the salt particles within the silicone core elute out, leaving behind a micro porous structure within the silicone core. These small voids are consequently filled with fluid as the core hydrates, resulting in a suture tightening.[6]

Commercial name: Dynacord suture (Depuy synthes).

CONCLUSION

The development of these newer and better smart materials will completely revolutionize various treatment modalities in the fields of dentistry, making them more comfortable for the patient and convenient for the operator. The level of intelligence of smart materials is always increasing, and dentists investing in these materials will undoubtedly be a wise move.

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