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Smart materials

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Abstract: Smart materials technology enables us to adapt to environmental changes by activating its functions. Such materials have one or more properties can be significantly changed in a controlled manner in response to external stimuli. These properties have a beneficial application in various fields including dentistry which had revolutionary effect on it.

Keywords: Smart material; Shape memory alloy; Piezoelectric; Magnetorheological.

Smart materials are materials that have properties that may be altered in a controlled fashion by stimuli, such as stress, temperature, moisture, pH, and electric or magnetic fields. They are highly responsive and have the inherent capability to sense and react according to changes in the environment. ^{1,2} Smart behavior generally occurs when a material senses some stimulus from the environment and reacts to it in a useful, reliable, reproducible, and usually reversible manner. The most important key feature of smart behavior includes its ability to return to original state even after the stimulus has been removed. These properties have a beneficial application in various fields including dentistry. ³

Traditionally materials used in dentistry were designed to be passive and inert, to exhibit little or no interaction with body tissues and fluids. As there was no single material in dentistry that is ideal in nature and fulfills all the requirements of an ideal material, searching for an “ideal restorative material” continued and a newer generation of materials was introduced. These smart materials support the remaining tooth structure to the extent that more conservative cavity preparation can be carried out. Some of these can mimic natural tooth structures such as enamel or dentin. The use of these smart materials has revolutionized dentistry. ⁴

Classification of smart materials

Smart materials are classified into four categories either:

Passive

Passive smart materials can only sense environmental conditions or stimuli without external control. ⁵

Active

Active smart materials sense and react to the condition or stimuli. It has both actuators and sensors. The actuators act upon the detected signal either directly or from a central control unit. ^{2,5}

Very Smart

Very smart materials can sense, react and adapt themselves to environmental conditions or stimuli with sensors. It consists of a unit, which works like the brain, with cognition, reasoning and activating capacities.⁵

Intelligent

Intelligent materials are those capable of responding or being activated to perform a function in a programmed manner. Intelligent materials can sense, react and adapt themselves to environmental conditions or stimuli without sensors.⁵

Nature of smart materials

Smart materials sense changes in the environment around them and respond in a predictable manner. In general, these properties are:^{2,5}

➤ Piezoelectric

Piezoelectric materials 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.⁶

➤ Shape memory

After deformation, these materials can remember their original shape and return to it when heated. e.g.: Nickel titanium alloys.⁷

➤ Thermochromic

These materials change color in response to changes in temperature. E.g. Thermochromic brushes.²

➤ Photochromic

These materials change color in response to changes in light conditions. e.g.: photochromatic pits and fissure sealant (Clinpro™ Sealant (3M)).²

➤ Magnetorheological

These are fluid materials that become solid when placed in a magnetic field.²

➤ PH-sensitive

Materials which swell/collapse when the pH of the surrounding media changes. eg: - Smart composites containing amorphous calcium phosphate (ACP).²

➤ Biofilm formation

Presence of biofilm on the surface of material alters the interaction of the surface with the environment.²

➤ Ion release and recharging

The beneficial effect of fluoride release of dental materials has been the subject of much research over many years. As the products (even with high initial fluoride release) tend to rapidly lose their ability to release fluoride in significant amounts by time. However, the smart behavior of materials containing glass ionomer cement (GIC) salt phases offers some long-term solutions by the sustained re-release of fluoride after initial recharging which may be much more important than the initial burst.²

Smart materials in dentistry

I. Smart Memory Alloy (SMA)

The term “smart material” or “smart behavior” in the field of dentistry was probably first used in connection with Nickel Titanium (NiTi) alloys, or shape memory alloys (SMAs). Such alloys show unique properties such as super elasticity, shape memory, superior fatigue and wear resistance and relatively better biocompatibility. In 1970's, Ni-Ti was introduced in orthodontics for fabricating brackets. Wires revealing shape memory behavior at intra-oral temperature usually comprise of copper and or chromium in addition to nickel and titanium.^{2,8}

The shape memory effect (SME) was observed in the gold cadmium alloy in 1951, but this was of insignificant use. Ten years later in 1962, an equiatomic alloy of titanium and nickel was found to exhibit shape memory effect.

The SME describes the manner of a material changing shape or remembering a particular shape at a particular temperature (i.e. its transformation or memory temperature). Materials that can only demonstrate the shape change or memory effect once are known as **one-way SMAs**. However, some alloys can be skilled to show a **two-way effect** in which they remember two shapes, one below and one above the memory temperature. At the memory temperature, the alloy undergoes a solid-state phase transformation i.e. the crystal structure of the material changes resulting in a

volume or shape change and this change in structure is called a thermoelastic martensitic transformation. This occurs as the material has a martensitic microstructure below transformation temperature, which is characterized by a zig-zag arrangement of the atoms, known as twins. The martensitic structure is soft and is easily deformed by removing the twinned structure. The material has an austenitic structure above the memory temperature, which is stronger. To change from the martensitic to the austenitic shape the material is heated through the memory temperature. Cooling down reverts the alloy to the martensitic state.^{2,9} Fig.1,2

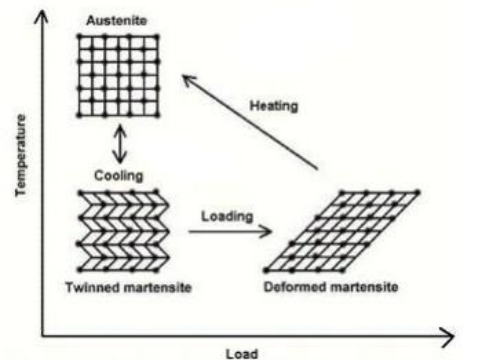


Fig. 1. Microscopic Diagram of the Shape Memory Effect.

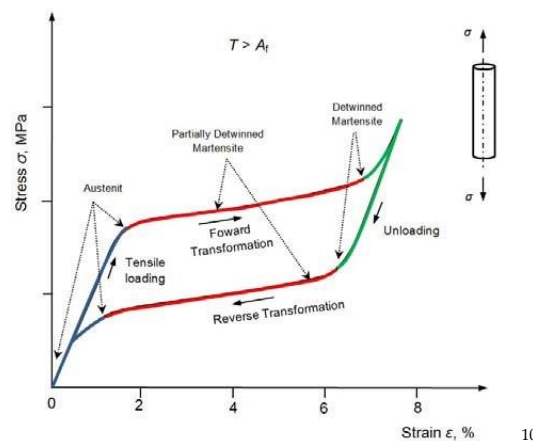


Fig.2 Diagram of the stress-strain curve for the superelasticity shape memory alloy NiTi in the tension loading Applications

In endodontic, NiTi endodontic files offer super flexibility, durability, and torque ability as compared to the stainless-steel files used. Another important application of NiTi is in the field of orthodontics. Superelasticity of these wires along with shape memory applies continuous, gentle forces that are within physiological range over a longer period with less discomfort. Wires that exhibit shape memory behavior at mouth temperature contain copper and or chromium in addition to nickel. Other SMA devices are also being used for healing fractured bone, staples of the shape memory materials are attached to each part of the bone and these staples then apply a constant force to pull the two pieces together, as the SMA is warmed by the body temperature it tries to return to its original configuration.²

II. Smart resin composites

It is a light activated alkaline, nano-filled glass restorative material, which releases calcium, fluoride and hydroxyl ions when intraoral pH values drop below the critical pH of 5.5 and counteract the demineralization of the tooth surface and help in remineralization. The material can be adequately cured in bulk thickness up to 4mm. It is recommended for the restoration of class I and class II lesions in both primary and permanent teeth. Ex: smart dental resin composites (**Ariston** pH control) introduced by Ivoclar- Vivadent Company.¹¹

Smart composites containing amorphous calcium phosphate are one of the most soluble calcium phosphate compounds of biological importance, exhibiting the most rapid conversion to crystalline hydroxyapatite (HAP). The ACP when integrated into specially designed and formulated resins to make a composite material, will have an extended time release nature to act as a source for calcium and phosphate which will be useful for preventing caries. The ACP has been evaluated as a filler phase in bioactive polymeric composites. Active restorative materials that contain ACP as

fillers may stimulate the repair of tooth structure because of releasing significant amounts of calcium and phosphate ions in a sustained manner. Then these ions can be deposited into tooth structures as apatitic mineral, which is similar to the hydroxyapatite (HAP) found naturally in teeth and bone. The ACP at neutral or high pH remains as ACP. When low pH values (at or below 5.8) occur during a carious attack, ACP converts into HAP and precipitates, thus replacing the HAP lost due to the acidic attack. So, when the pH level in the mouth drops below 5.8, these ions merge within seconds to form a gel. In less than 2 minutes, the gel becomes amorphous crystals, resulting in the release of calcium and phosphate ions. This response of ACP containing composites to pH can be described as smart.¹²

III. Self-healing composites

Materials usually have a limited life span and degrade due to different physical, chemical, and/or biological stimuli. These may include external static or dynamic forces, internal stress states, corrosion, dissolution, erosion or biodegradation. Therefore, the focus of current scientific research is the development of newer bio-inspired material systems. One of the first self-repairing or self-healing synthetic materials reported interestingly shows some similarities to resin-based dental materials. As this is an epoxy system that contains **resin filled microcapsules**, if a crack occurs in the epoxy composite material, some of the microcapsules disintegrate near the crack and they release the resin. The resin subsequently fills the crack and reacts with a catalyst that is dispersed in the matrix, resulting in a polymerization of the resin and a repair of the crack fig.3. The self-repairing mechanism based on microcapsules disintegration may have a promising future and composites repaired in that way may perform better than those repaired with macroscopic repair approaches.¹³

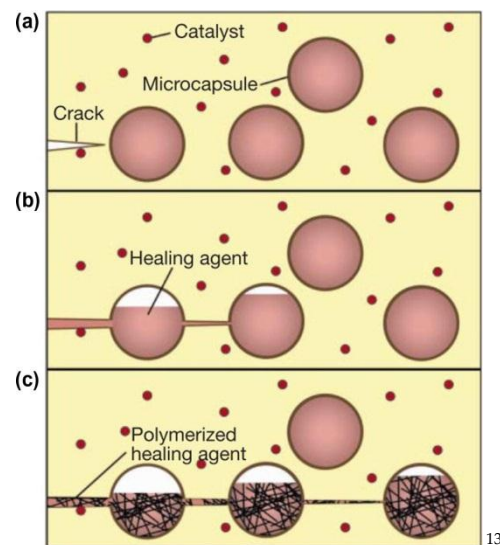


Fig.3: Mechanism of the microcapsule approach in Self-healing composite

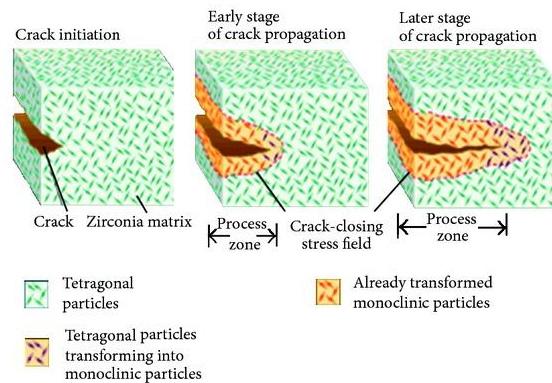
IV. Smart ceramics

Zirconia is polycrystalline ceramics that do not contain glass. Hence, polycrystalline ceramics generally are much tougher and stronger than glass-based ceramics. In addition, zirconia exhibits phase transformation toughening increasing its mechanical properties.^{1, 2}

The fracture toughness and flexural strength of zirconia are significantly higher than any other currently available ceramic. At firing temperature, zirconia is tetragonal and at room temperature monoclinic, with a unit cell of monoclinic occupying about 4.4% more volume than when tetragonal. Unchecked, this transformation was a bit unfortunate since it would lead to crumbling of the material on cooling. In the late 1980s, ceramic engineers learned to stabilize the tetragonal form at room temperature by adding small amounts (app. 3–8 mass%) of calcium and later yttrium or cerium. Although stabilized at room temperature, the tetragonal form is really only “metastable,” meaning that

trapped energy still exists within the material to drive it back to the monoclinic state. It turned out that the highly localized stress ahead of a propagating crack is sufficient to trigger grains of ceramic to transform in the vicinity of that crack tip. In this case, the 4.4% volume increase becomes beneficial hindering crack propagation.¹

The result is that a compressive or crack closure stress is produced which slows down or stops the crack. This crystallographic transformation in response to stress makes zirconia a smart material fig.4.¹



1

Fig.4 Phase transformation in Zirconia.

V. Smart impression material

These materials exhibit following characteristics:

1. They are hydrophilic to get a void-free impression.
2. They possess Shape memory so during elastic recovery it resists distortion for more accurate impression and toughness resists tearing.
3. They have a snap - set behavior those results in precise fitting restorations without distortion.
4. They cut off working and setting times by at least 33%.
5. They have low viscosity and hence high flow. E.g.: Imprint TM 3 VPS, ImpregimTM, Aquasil ultra (Dentsply).

2

Chromatic alginates (Alginates with color indicators)

The problem observed among some of the undergraduate students is difficulty in identifying the ideal consistency of alginate material during manipulation. Various color indicators were added to the alginate impression materials to identify the different stages of manipulation. These color indicators change the color of the alginate mix as setting reaction taking place due to the change in the pH. This change in the color of the alginate mix facilitates identification of the ideal consistency to load it into the tray and make accurate impressions.¹⁴

VI. Smart glass ionomer cement

The scientist «Davidson» first suggested the smart behavior of GIC. It is related to the ability of a gel structure to absorb or release solvent rapidly in response to a stimulus that can be temperature, change in pH etc. GICs are described as “smart materials” with respect to their thermal behavior, since it is a desired feature, when restorative materials undergo thermally induced volumetric changes close to those of the tooth substance.²

Wide temperature fluctuations may occur in the oral cavity due to the intake of hot or cold food and fluids. Hence, the restorative materials placed in this environment may show thermal expansion or contraction in response to thermal stimuli. When dealing with thermally induced volumetric changes, comparison of coefficient of thermal expansion and contraction CTE values of the restorative material and the tooth substance is more important than the CTE value of the material itself. The mismatch of thermal expansion and contraction between a restoration and the tooth structure may cause stresses to develop at the interface and this may have unfavorable effects on the margins and finally lead to microleakage.¹

For glass-ionomers, little or no change in dimension was observed when heating and cooling between 20°C and 50°C in wet conditions. In dry conditions, the materials showed a marked contraction when heated above 50°C. The explanation for this behavior 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 behavior is similar to that of human dentine 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 behavior of human dentine through a type of smart behavior.¹⁵

The mass loss of glass-ionomer cements (GICs) in wet conditions is significantly less than that in dry conditions. The GICs, as water-based materials, have the ability to exchange fluid with the environment. The “loosely” bound water is readily lost and regained as a result of changes in the environmental conditions (e.g., temperature). The loss of “loosely bound” water is likely to be a reversible process; that is, the water may be reabsorbed on cooling. The water gained from the environment may compensate for the contraction of the GIC matrix. Therefore, the final dimensional change of GICs in wet ambient conditions may be minimal as a net result of thermal expansion and contraction, water loss, and water gain. Hence, the reaction of GICs to their environment is active and they may be considered as having “smart” behavior. The initial water loss caused by environmental temperature change may be considered as the “trigger” to this “smart” behavior.¹⁵

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. Hence, this aspect of the smart behavior of dental cements can be controlled by the operator.^{1, 15}

The other issue of the smart behavior of GIC is the **fluoride release and recharging ability**. Commonly the fluoride release is seen as a high initial fluoride release followed by a moderate reduction over a period.¹⁶

VII. Smart burs

These are polymeric burs that remove only infected dentin. The affected dentin, which has the ability to remineralize, remains intact. Overcutting of tooth structure, which is usually seen with conventional burs, can be avoided by the use of these smart preparation burs. The polymer cutting edges wear down on coming into contact with harder materials, such as healthy dentin and become blunt. They are open in three sizes 010, 014, and 018 and are proposed for single use.^{2, 16}

VIII. Smart sutures

These 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 are fixed. When the temperature is raised above the thermal transition temperature, the suture shrinks and tightens the knot, applying the optimum force. The 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 are made of plastic or silk threads covered with temperature sensors and microheaters, which can detect infections. E.g.: Novel MIT Polymer (Aachen, Germany).¹⁷

IX. Pheromone guided smart antimicrobial peptide

A new class of pathogen selective molecule called specifically (or selectively) Targeted Antimicrobial Peptides (STAMP) have been developed based on the fusion of a species-specific targeting peptide domain with a wide spectrum antimicrobial peptide domain. This pheromone-guided “smart” material peptide is targeted against the killing of *Streptococcus mutans*, the principal microorganism responsible for dental caries. Utilizing Competence Stimulating Peptide (CSP), a pheromone produced by streptococcus mutans, can be eliminated from multi-species biofilm without affecting the nation cariogenic microorganisms. Their molecules have the potential to be developed into antibiotics that will selectively eliminate pathogens while preserving the protective benefits of a healthy oral flora.²

X. Smart seal obturation system

a smart seal obturation system; The C Point system (EndoTechnologies, LLC, Shrewsbury, MA, USA), is a point-and-paste root canal filling technique that consists of prefabricated, hydrophilic endodontic points and an accompanying sealer. The deformable endodontic point (C Point) is available in different tip sizes and tapers and is designed to expand laterally without expanding axially, by absorbing residual water from the instrumented canal space. Its inner core consists of a mix of two proprietary nylon polymers: Trogamid T and Trogamid CX. The polymer coating is a cross-linked copolymer of acrylonitrile and vinyl pyrrole, which are polymerized and cross-linked using allyl methacrylate and a thermal initiator. The lateral expansion of this Point occurs non-uniformly, with the expandability depending on the extent to which the hydrophilic polymer is prestressed (i.e., contact with a canal wall will reduce the

rate or extent of polymer expansion). This nonisotropic lateral expansion enhances the sealing ability of the root canal filling, thereby reducing the possibility of reinfection.¹⁸

XI. Smart coatings for dental implants

Researchers have developed a “smart coating” that helps surgical implants bond more closely with bone and prevents infection reducing the possibility of implant rejection. The coating creates an inner crystalline layer next to the implant and an amorphous outer layer surrounding bone. The amorphous layer dissolves over time and releases calcium and phosphate, which encourages bone growth. The bone grows into the coating resulting in improved bonding osseointegration. This bonding also makes the implant more functional, because the bonding helps the bone and the implant to share the load. The researchers have also incorporated *silver nanoparticles* throughout the coating to reduce infections. As the amorphous layer dissolves, silver incorporated into the coating is released which acts as an antimicrobial agent. This will limit the amount of antibiotics patients will need the following surgery, and will provide protection from infection at the implant site for the life of the implant. Moreover, the silver is released more quickly after surgery, when there is more risk of infection, due to the faster dissolution of the amorphous layer of the coating. The silver release will slow down while the patient is healing; therefore, it is called as smart coating.¹⁹

XII. Smart fibers for laser dentistry

Hollow core photonic crystal fibers (PCFs) for the delivery of high-fluence laser radiation capable of removing tooth enamel have been developed. Sequential laser radiation pulses are transmitted through a hollow-core photonic crystal fiber with a core diameter of approximately 14 micrometers and are focused on a tooth surface to cut dental tissue. The same fiber is also used to transmit emission from plasmas, which is produced by laser pulses on the tooth surface in the backward direction for detection and optical diagnostics.^{2, 20}

Conclusion

In recent years there has been a huge development of materials in various fields. In dentistry, the use of smart materials promises improved reliability and long-term efficiency because of their potential to have specific functions intelligently in response to various local changes in the environment, thereby significantly improving the quality of dental treatment.

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