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Intelligent Material: the essence of smart materials

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Abstract
There is no single material in dentistry that is ideal in nature and fulfils 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''. These smart materials are materials that have properties which may be altered in a controlled fashion by stimuli, such as stress, temperature, moisture, pH, and electric or magnetic fields. Thus, smart materials respond to stimuli by altering one or more of their properties. Smart behaviour occurs when a material can sense some stimulus from its environment and react to it in a useful, reliable, reproducible, and usually reversible manner. The use of smart materials has revolutionized dentistry such as smart composite, NITI smart alloy, smart seal obturation system and self-healing composite.

Keywords: smart composites, Nickel-Titanium alloy, smart seal obturation, self-healing composite.

1. 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 [1]. 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
By definition, 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. Smart materials are highly responsive and have a great capacity to sense and respond to any environmental change. Hence these materials are also known as "Responsive Materials [2]. Today it is one of the challenging tasks to manufacture new multifunctional materials which possess intelligence at the material level. Material intelligence is classified in to three functions: sensing changes in environmental conditions, processing the sensed information and finally making judgment (actuating) by moving away from or to the stimulus [3].
This article, aims to describe the various materials in dentistry that exhibit some sort of smart behaviours.

2. Smart Composites
Generally, Boskey mentioned that Aaron S. Posner to have firstly described amorphous calcium phosphate (ACP) [4] in the mid-1960s. It was obtained as an amorphous precipitate by accident when mixing high concentrations (30mM) of calcium chloride and 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 [5].
Smart composites contain Amorphous Calcium Phosphate (ACP), one of the most soluble of the biologically important calcium phosphates. The basic building blocks of tooth enamel is hydroxyapatite; it is also an inorganic component of dentin. In the case of carious attack hydroxyapatite is removed from the tooth 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 at neutral or high pH remains ACP. When low pH values i.e., at or below 5.8 occurs during a carious attack, ACP converts in to HAP and precipitates, thus replacing the HAP lost to the acid. 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 calcium and phosphate ions [3].
Ex: Ariston pH control — introduced by Ivoclar — Vivadent (Liechtenstein) Company.

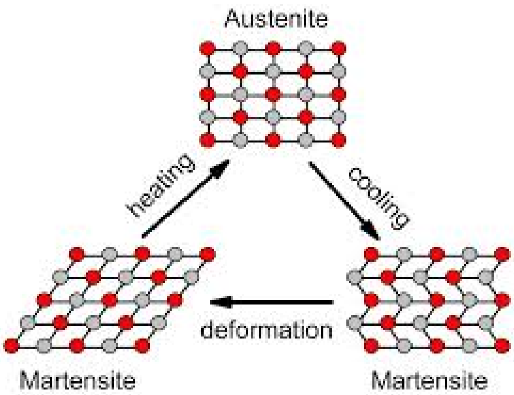


Fig 1: Nickel-Titanium Smart Alloy

3. Nickel-Titanium Smart Alloy

The term "smart material" or "smart behaviour" in the field of dentistry was probably first used in connection with Nickel-Titanium (NiTi) alloys. In 1938, Greninger and Mooradian observed the shape memory effect in Cu-Zn and Cu-Sn alloys. In 1962, Buehler and co-workers, of the U.S. Naval Ordnance Laboratory, discovered the shape memory effect which began to be known as Nitinol [3]. In 1975, Andreasen, of Iowa University, made the first implant of a superelastic orthodontic device [6]. In endodontic, 55 wt.% Ni and 45 wt.% Ti are commonly used, referred to as "55NiTiNOL." introduced by Walia *et al.* in 1988 [2]. The smart behaviours of NITI alloy because of their exceptional superelasticity, shape memory, good resistance to fatigue and wear, and relatively good biocompatibility [7]. The ability of resisting stress without permanent deformation, going back to initial lattice form, is called superelasticity. The ability of the NiTi file to come back to its original straight form without showing any sign of lasting deformation called shape memory [8].
When an SMA is cold, or below its transformation temperature, it has a very low yield strength and can be deformed quite easily into any new shape, which it will retain. However, when the material is heated above its transformation temperature, it undergoes a change in crystal structure which causes it to return to its original shape [2]. The superelasticity of NiTi rotary instruments provides improved access to curved root canals during cleaning and shaping, with less lateral force exerted. It gives more centered canal preparations with less canal transportation and a decreased incidence of canal aberrations [2] 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 (Figure 1) [2]. When the material is in its martensite form, it is soft and ductile and can easily be deformed. SE NiTi is highly elastic, whereas austenitic NiTi is quite strong and hard [9]. In martensitic phase, only a light force is required for bending. If the stress is released, the structure exist to an austenitic phase and its original shape. This phenomenon is called stress-induced thermoelastic transformation [10].

4. Smartseal Obturation System

Obturation of root canals should prevent reinfection of the canal space and prevent periradicular disease. This objective may be achieved by three-dimensional filling of the instrumented canal, accessory canals, and dead spaces different canal filling techniques are currently available to achieve this goal [2]. Guttapercha is an impermeable material, leakage between sealer and dentin and gutta-percha and sealer and presence of voids leads to failure of treatment. To overcome these problems and improve the treatment outcome, a root canal obturating system called Smartseal TM (known as Prosmart TM outside UK) was developed.
It is hydrophilic endodontic point and an accompanying sealer. It consists of propoint and smart paste/smart paste bio. It is available in different tip sizes and tapers. One propoint covers all tip sizes and it is available in the following sizes:
6% taper - ISO tip sizes 25 to 45
4% taper - ISO tip sizes 25 to 45
ProTaper™ - F1, F2, F3, F4 & F5
Sendoline™ S5 - S2, S3, S4. (Figure 1)[11]

Fig 2: Propoints: S range

Propoint Also known as C points, these obturation points are constructed in two parts:
Central Core: It consists of a combination of two proprietary nylon polymers, Trogamid T and Trogamid CX. It is considered to provide the point with the flexibility and can be easily inserted into curved canals.
Outer Polymer Layer: It consists of a cross-linked copolymer of acrylonitrile and vinylpyrrolidone, which has been cross-linked using allyl methacrylate and a thermal initiator. This hydrophilic, hydrogel layer allows the point to swell and adapt the canal wall [12] and expand laterally without expanding axially by absorbing residual water from instrumented canal space and from naturally occurring intraradicular moisture [13].
The lateral expansion of C Point is claimed to occur nonuniformly, 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). As claimed by the manufacturer, although C Point is capable of achieving a relative good fit of an irregular canal space, gaps may still remain between the walls of the canal and the expanded point. Consequently, an accompanying sealer must be used to seal those areas [2].
Smartpaste Bio
Smartpaste bio is a resin based sealant designed to swell through the addition of ground polymer. The manufacturer claims that the addition of bioceramics, gives the sealer exceptional dimensional stability and makes it non-resorbable inside the root canal. Smartpaste bio produces calcium

hydroxide and hydroxyapatite as byproducts of the setting reaction, rendering the material both anti-bacterial while setting and very biocompatible once set. Also, it has a delayed setting time (4-10 hr), and is hydrophilic in nature, allowing the propoint to hydrate and swell to fill any voids.

The sealant is delivered in a pre-mixed syringe and does not require mixing as it can be applied directly into the canal using an intra-canal tip minimising wastage of material. The cement absorbs water from within the canal and once set smartpaste bio produces a radiopaque biocompatible cement [12]. It gives less voids and greater efficiency in filling simulated lateral canals and a comparable homogeneity of obturation using Smart Seal system over Gutta-percha [13].

Eid *et al*. (2013) evaluated the biocompatibility of C Point and commercially available gutta-percha points using a rat odontoblast-like cell line (MDPC-23) by measuring cell viability and mineralization potential o fMDPC-23 cells. They concluded that the in vitro biocompatibility of C Point is comparable to gutta-percha with minimal adverse effects on osteogenesis after elution of potentially toxic components [14].

The single‐ cone technique utilizing matched taper Propoint PT combined with Smartpastebio showed the lowest amount of glucose leakage [15]

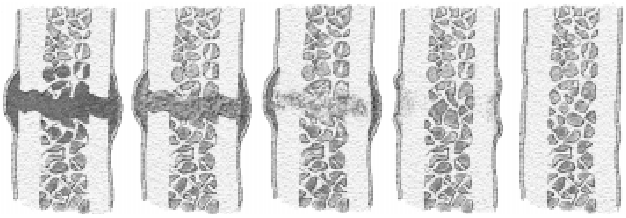
The study concluded that bond strength of Smart-Seal system to root canal dentin may improve with UA (ultrasonic activation) in the coronal and middle thirds and MDA/EndoActivator in the apical third [16].

Didato *et al*. (2013) compared the time-based lateral expansion of two sizes (25 and 40) of C Point obturation points with a similar-sized gutta-percha point (control) at various distances from the point apex: 5, 10, and 15mmunder 50xmagnification, using a binocular microscope. Changes in C Point dimension were significantly higher for both sizes at each tip distance after 20min of water immersion but gutta-percha did not significantly change from the dry value during water immersion [17].

4. Self-Healing Composites

Materials usually have a limited lifetime and degrade due to different physical, chemical, and/or biological stimuli. These may include creep or dynamic (fatigue) forces, internal stress states, corrosion, dissolution, erosion, or biodegradation. This gradually leads to a deterioration of the materials structure and finally failure of the material [18].

Self-healing composite which are inspired by biological system such as bone. Fracture of the bone provides an excellent model for developing a synthetic healing process for structural materials. For a bone to heal, nutrients and undifferentiated stem cells must be delivered to the fracture site and sufficient healing time must elapse. The healing process consists of multiple stages of deposition and assembly of material, as illustrated (Fig. 3). The network of blood vessels in the bone is ruptured by the fracture event, initiating autonomic healing by delivering the components needed to regenerate the bone [19].



(a) (b) (c) (d) (e)

Fig 3: Healing stages of bone; (a) internal bleeding, forming a fibrin clot, (b) development of unorganized fiber mesh, (c) calcification of the fibrocartilage, (d) calcification converted into fibrous bone, (e) transformation into lamellar bone.

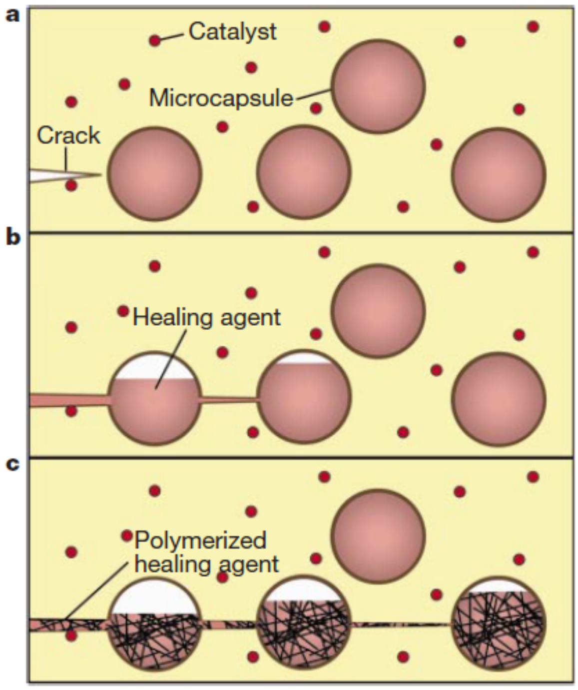


Fig 4: Basic method of the microcapsule approach (White *et al*., 2001)

In recent research, White *et al*. have developed a self-healing polymer. It is first self-healing synthetic material. It is resin based material.
This was an epoxy system which contain resin filled microcapsule Dicyclopentadiene (DCPD), a highly stable monomer with excellent shelf life, was encapsulated in thin shell made of urea formaldehyde [20].
If crack occur in epoxy composite material, near some of microcapsules rupture and release resin. These resin fills the crack by react with Grubbs catalyst in epoxy composite, (figure4) [7] resulting ring opening metathesis polymerization (ROMP) reaction take place and repair the crack [20]
It can be expected that dental composites using this technology would have a significantly longer duty cycle and enhanced clinical performance. The main problems may occur from the potential toxicity of the resins in the microcapsules and from the catalyst. However, seem to be rather small, and may well be below the toxicity threshold [2]

5. Conclusion
With the availability of these intelligent materials, which possess multifunctional capabilities, it will be easy and comfortable to cope up with dental therapy and execute specific function smartly to respond to changes in the local environment. This will benefit for the patient and the quality of treatment by using this most sophisticated class of multifunctional material, in the near future, will undergo a significant improvement.

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