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Presenting Shape Memory Polymers SMP and some Reinforcement materials for gaps filling in Archaeological Bones

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Abstract

Mummies and bones are potential materials since they retain the memories of the ancients and revealed the degree of their greatness. Bones are organic materials that include proteins like collagen, minerals including calcium hydroxyapatite, as well as other substances. By assisting with other factors (physical or chemical), the essence of bone allows microorganisms as well as insects to assault it. The aspects that can be formed as a result of this degradation process are known as holes. Gaps are also a challenging task for bone artifacts, especially in the excavation area. This current article review focused on the factors that create holes. In addition to the survey about the shape memory polymers aerogels (SMPA) and reinforcement materials which can be utilized to adapt to the old bones, as well as improved materials to render certain old reinforced polymers provide shape memory behavior. The examination and investigation analysis tools that could be utilized for evaluating the treated bones with certain shape memory polymers aerogels were also addressed in the article review.

Keywords: Archaeological bones; shape memory polymers; microorganisms; reinforcement materials

1. Introduction

Bones are made up of complex molecular structures; both organic and inorganic, making them more susceptible to degradation under inappropriate conditions. The regular and seasonal variations in relative humidity and temperature, as well as other factors, particularly biological factors, may trigger some facets of deterioration for bone artifacts. Bones are a hygroscopic material, which absorbs water and loses it to the surrounding air easily, in an ongoing attempt to reach a humidity balance and even contain a carbon element. All these conditions make it combustible, and its sensitivity to light rays, finally, containing an organic matter is one of the main reasons for many sources of deterioration, as it is an attraction for many microorganisms, some insects and rodents as a source of food [1], fungi, bacteria, cyanobacteria, burial environment, and termite may cause a lot of some forms of deterioration but gaps can be considered one of the biggest problems [2]. According to that, conservators should do a great effort to fill gaps resulted from the reasons mentioned above.

Through the importance of the consolidation process, there were various traditional materials and techniques used in the past, but these materials have proven to have many disadvantages, regardless of the characteristics that were attracted to use them. Since there weren't a variety of materials that old conservators could choose as the best suitable type to be used as gap fillers or even as consolidation material for archaeological bone, Natural resins like beeswax, Arabic gum, gelatin, animal glue and, shellac, were the common selection for its low cost and non-toxicity, but it only penetrated the bone structure and disguised its surface, also shows shrinkage which continued the bone damage. paraloid B72, polyvinyl acetate (PVAc), acrysol WS24, butvar B98, and cellulose nitrate were used for their high transparency, durability, super adhesive abilities, the

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resistance of changes in temperature and humidity, but their high cost, lost time during their application process, the possibility of deformation of the bone surface as a result of application errors, the possibility of swelling or shrinking during applying of the material or even color changes and the necessity of adding an adhesive, pesticide, microorganisms resistance and ultraviolet radiation resists, this long chain of materials which should be improved in the gap-filling paste, seems to be impossible to achieve in one mixture [3].

Since many scientists has turned to polymer science to design materials with a combination of qualities that open up a wide range of possible applications, sponge polymers [4] are the polymers that have the behavior of regaining shape when exposed to a particular effect under Appropriate conditions [5], sponge polymers can be defined as shape memory polymer nanocomposite aerogels (SMPA), Thus, it consists of two composites shape memory polymers and aerogels, SMPA are polymeric smart materials which have low density and a high ability to return from a temporary shape to their permanent shape induced by an external stimulus such as temperature changes, this happens when heated over polymer's thermal transformation temperature (Tg) if amorphous materials or melting temperature (Tm) if semi-crystalline polymers, to form the temporary shape which is easy-to-form and memory-preserving form for the permanent shape that forming after placing in the gap and cooled below its (Tg).

SMPA's low cost, low density about 6:8g cm-3, durability, strain-tolerant, lightweight are very attractive but the high transition temperature is not completely suitable with artificial bone, Hence, a variety of aerogel polymers were used to modify a new low Tg that's more suitable for applying on bones [6]. Klister created aerogel in 1931 as a porous material produced by extracting gel solvent and changing it with gas while maintaining the overall porous structure. Aerogel has several of appealing features, comprising low dielectric constant, high surface area, low thermal conductivity, low density, and superior mechanical properties. Aerogel has a low thermal conductivity of 0.018 W/(mK) which improving more control for the transformation temperature process. Aerogels are also known as the lowest density material that has been produced with a range from 0.0011 to 0.5 g cm-3 [7–10]. However, some aerogels are opaque, which requires time to produce. Additionally, the manufacturing process causes errors mostly during the drying step, as capillary forces in the pores of the gel could shrink, triggering the walls of such pores to interact, resulting in a reaction between the polymers surface groups, inducing collapsing [11, 12].

However, there are ways to prevent these drawbacks by using freeze-drying mostly as a low-cost, one-of-a-kind method to remove water or other solvents from the aerogel, when compared to many other drying techniques, which are very costly, sophisticated, and require expensive raw materials as well as a lot of energy and CO2. Thus, the high surface area, controlled pore structure, excellent mechanical properties, relatively homogenous microstructural, and low specific shrinkage aerogels were produced using the freeze-drying process. Furthermore, the freeze-drying method has been demonstrated to be an efficient technique, with this technique being primarily used to generate aerogel polymers [13,14]. As a result, this article review was screened to represent several kinds of shape memory polymer aerogels (SMPA) that can demonstrate a millisecond-scale reaction to temperature as an external stimulus, massive elongation, high fixing ability, high recovery ratio, super elasticity, high thermal stability, resistant to ultraviolet rays and avoids to insects and microorganisms attack [15,16] providing with nanoparticles and cross-linked polymers, that can be applied to confirm archaeological bones to achieve that compatibility.

2. Formation of gaps on ancient bones

The most direct factors on the predicted fate of buried bones are burial and post-burial circumstances. It may be bone-preserving or bone-damaging and harmful [17]. Volcanic reactions, water oscillation, rock physical factors, salt crystallization, sand slopes, weathering, acidic reactions with plant roots in the soil, abrupt cooling, animal and rodent exposed to the loan, and the human factor of run over, cracking, and robbing are all buried [18].

2.1. Burial soil

Bone damage can be caused by a variety of factors that are concealed in the soil. By categorizing groundwater into diffuse, flowing, and renewable water, (Manifold et al., [19] clarified that the latter is in a constant dry and moisture cycle and results in increased bone porosity and holes, wherein chlorine decomposes and produces saline crystals. During droughts, bone components are under a lot of stress, which manifests itself in the forms of pits and tapes over time. There could also be chemicals and other compounds dissolved in water that reacts with bone structures and trigger bone material replacement. Johnson [20] documented that the perforation and erosion may well be exacerbated by the acidity of the soil. Acidic soil, which contains fulvic acid and some humic acids, can cause erosion resulting in increased concentration in the soil. Damage to superfluous tissue is obvious, given that the pH of this type of soil can range from 4 to 6, but Fernández-Jalvo et al., [21] asserted that the damage degree is related to the amount of time bone residues are visible.

In other cases, particularly, the soil contains numerous bacteria, fungi, and microorganisms [2] and Child [22] indicated that microbial decomposition of bone in this type of soil contributes to mineralization and inhibition of nitrogen and calcium in the soil, and then it is collected from buried bones, which will also be discussed further below.

2.2. Microbiological attack

Fungi, bacteria, and cyanobacteria in aquatic environments cause gaps in archaeological bones, as all these organisms influence the chemical structure and pore volume of bone tissue by acting as partial or total substitutes [23, 24]. That occurs when the bacteria secrete collagenase to disintegrate bone collagen, creating a series of tunnels with long linear diameters of 5: 10 m and 25:20 m. (**Fig. 1**).

Müller et al., [25] identified the most active and influencing bacteria on the bones, such as E. coli, Pseudomonas aeruginosa that leads to changing the composition of bone mineral as a which attributed to the exposure to chemicals produced by fungi that appear in circular pits with a diameter of 5: 10 m. Fungi, unlike bacteria, can reach bone fibers and leads to destroying the precise structure of bone tissue, but it really is unclear why they do so, given that they eat bones or feed on the material in the Haversian canal [26].

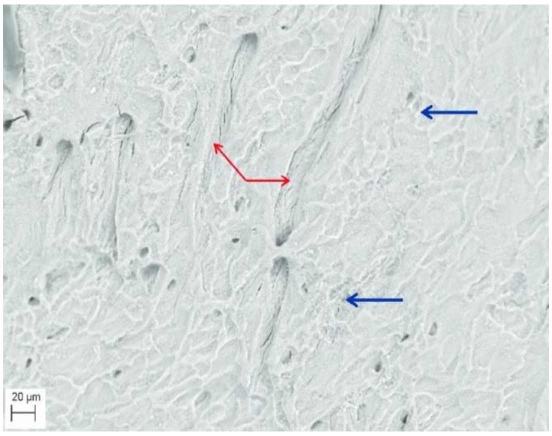

Fig. 2: Holes in bones by microbiological factor

2.3. Termite attack

Backwell et al. revealed that throughout Milne's studies, a termite mound in tropical Africa detected 2 tons of calcium carbonate in calcareous soils as well as another twenty tons of calcium carbonate at a depth of six meters in non-calcareous soils.

Termite assaults on bones in the form of pits and tapes were documented by Queiroz et al., [28] as stars as revealed in **(Fig. 2)**. Huchet et al., [29] referred to the development of a type of termite known as Isoptera in the Peruvian state, but he believed that it did not dig bone to obtain calcium carbonate from the bones, instead of concluding that it not only nourished him due to a lack of cellulose in the soil as well as the presence of bones as an impediment in the range of this type of termite. However, according to Wrobel and Biggs, termite species that feed on bones are nitrogen-free and, burying bones becoming a proper source of nitrogen when nitrogen is presented at a ratio of 3:4 % of bone formation.

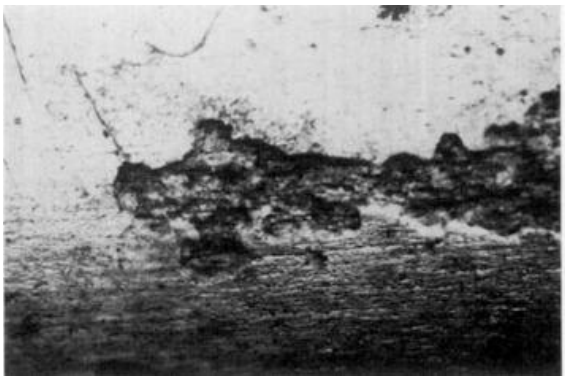

Fig. 1: Termite pits on bones [30].

3. Consolidation:

Consolidation and completion, particularly in the case of filling gaps, rely on the utilization of fillers for filling these gaps and completing the missing areas with flexible substrates that can establish and weaker than the bones so that it doesn't create anxiety, but this process used to be bright and clear color compared with the utilized materials in the past [31]. Natural and synthetic polymers are well-known in all aspects of everyday life, but since industrial polymers can change the properties of the polymer, they are suitable for a wide range of applications. However, these materials have proved to have numerous drawbacks, regardless of the attributes that attracted researchers to use them.

Natural resins have been the most popular choice because there was a lack of variety of materials that old conservators can choose from to use as gap fillers or even as consolidation material for archaeological bone. Beeswax, like many other natural resins including such Arabic gum and gelatin animal glue, has been used since 1929, according to British Museum guidelines. Many of these materials were presented as outstanding adhesives, but they only entered the bone structure and masked its surface; they also shrank with natural aging, prolonging the damage of bone [3].

Thermoplastic resins are solid materials that soften to a liquid at high temperatures and then harden when cooled. They are made up of long chains of repeating molecules and could be produced in crystalline or semi-amorphous forms. These features allow thermoplastics to be molded into a variety of forms and architectures. Polyethylene, Poly (methyl methacrylate) polyvinyl chloride, polystyrene, polypropylene, polyamides, polyesters, and polyurethanes are thermoplastic resins that are typically dissolved in organic solvents. However, owing to excessive crystallization, they can become insoluble even in organic solvents, which are considered a fault in such polymers [32-38].

Shellac is a thermoplastic substance made from the secretions of a small insect called *Laccifer lacca*. This is the only industrial resin of animal origin, and this is made up of polar and non-polar components. Shellac is relatively inexpensive, non-toxic. Nevertheless, as a natural material, it is susceptible to a variety of factors, which may cause it to become brittle over time. The standards that should be satisfied the features of materials used in the reinforcement and treating the archaeological bones, as described by Bracci and Melo, are including. The importance of preserving the surface of the antique from any deformation or morphological change in terms of color and composition for a long period.

- Having the ability to eliminate the hardening material without creating any impact damage;
- The material ought to have a high transparency and therefore should not cause any artificial change in color.
- Operator toxicity must be taken in to account.
- It's best to use a homogeneous, low-viscosity material.
- An evaluation of the new materials' durability and aging after they've been installed. However, prior handling, several issues need to be considered in order to ascertain that material can be used, such as;
- The organic or inorganic aspect for the utilized reinforcement material.
- Determine the chemical, mechanical, physical, and other properties of the material.
- Select the best type of solvent for the artificial substance, examine the consolidation materials to determine their attributes, the decay time, and melting temperature, and so on.
- Make the decision whether immersion, brushing, or spraying is the best technique for applying the material. Determine the appropriate concentration before applying using different tests and examination methods.
- Paying attention to some of the most acceptable application period, this ranges depending on the materials, particularly while using the spray method
- Determine the best application conditions, taking into account the ambient humidity and temperature, in order to avoid affecting the polymer's or solvent's efficiency.

3.1. Shape Memory Polymers

Shape memory behavior was first discovered in alloys in 1932 when it encouraged the lander gold-cadmium alloy to investigate the rubber impact [39]. This dazzling occurrence has caught the interest of many researchers, as Chang and Read noted in 1951 when they mentioned the alloy's recovery. Due to gold-original cadmium's form, resistance to change, and ability to acquire shape memory, many goods with similar properties as "alloys which maintain shape memory" have been designed [40]. This property has attracted a lot of attention, allowing scientists to discover it in a variety of materials such as ceramics, gels, and polymers. It first appeared when an American decided to name Vernon assumed to manufacture a dental treatment material made up of resins Ester metha acrylic acid, which has characteristics comparable to the form and was used as a seed for implementation.

All SMP polymers have a low density of about 3:6-8g, are eco-sustainable and excellent biocompatibility, and have a high form recovery capability, which also occurs after passing via two stages of thermal reflection and freezing capacity [41]. The sponge polymer should be intended to take the shape of the missing part and heat up to temperatures greater than the degree of thermal conversion or the melting takes a temporary form that is easier to form and poured into the part to be finished but maintains the memory for the final form [6, 42].

3.2. Aerogels can be made of wide variety of substances including:

3.2.1. Polycaprolactone

Polycaprolactone (PCL) is an aliphatic polymer consisting of mono-caprolactone polymerization using catalysts such as alcohol or Sn (Oct)2 [43] as the average molecular weight of the polymer from 3000 to 80,000 g/ mol (Fig. 4). PCL has many good properties such as elasticity, but it lacks many mechanical properties that make it suitable to withstand pressures suitable for its application in bone tissue [44], which can be treated with reinforcement and multiple fillers, including the addition of hybrid nanofibers with creatine [45].

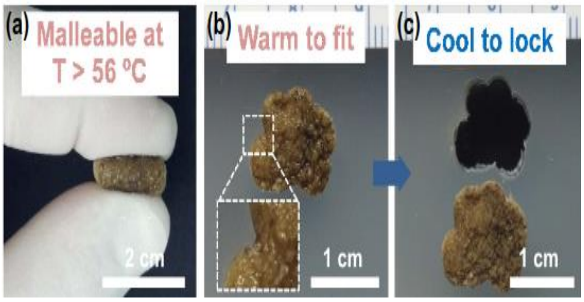

Fig. 3: Self-fitting behavior of a polydopamine-coated PCL SMP scaffold when heated above the Tm of PCL, the cylindrical scaffold softened, allowing it to be mechanically fitted into a model irregular defect. After cooling, the new temporary shape was retained, even after the scaffold was removed from the defect [46].

Furthermore, polycaprolactone is the softer of these polymers because it is heated higher than Ttarns, which is around 56°C. As a result, it can even be squeezed by hand, which is called a transient form, and during that time we can put the modeling shape in the missing part of the bone (gap). Due to the polymer shape memory behavior, the scaffold is extended to suit the gap mostly during the cooling period, enabling it to recover its permanent shape as shown in (**Fig. 3**) [47].

3.3. Aerogel based on synthetic and inorganic compounds

3.3.1. Polyurethane:

It's an AB-type polymer with solid molecules like dioxins, diamines, as well as other thin-shaped blocks of soft polyether ether strips running through it [48]. Polyurethane's ability to be affected by heat, as well as its durability and versatility, meet the requirements for bone harvesting. However, such sponge material, which has several interconnected pores that enable bone cells to expand, cannot occur in dead cells bone [49].

3.3.2. Silica Aerogels

Silica aerogels are the most thoroughly investigated subclass of aerogels, having been developed in the 1930s using the sol-gel method, which entails the synthesis of an inorganic network by a chemical reaction in solution at low temperatures. Large surface area (600-1600 m2g-1), small pore size, low thermal conductivity (0.01w/m.K), high thermal conductivity (0.01w/m.K), and moderate thermal conductivity (0.01w/m.K) are some of the excellent properties of silica aerogels. Using silica aerogel has a number of disadvantages: Aerogels containing alkoxide precursors are extremely costly and time consuming to make, as well as easily shrinking and even destroying the gel [12].

3.3.3. Metal Oxide Aerogels

Many metal oxides, including zirconia (ZrO_3), iron oxide, tantalum oxide (Ta_2O_5), vanadium oxide (V_2O_5), alumina (Al_2O_3), tin oxide (SnO_2), and manganese oxide MnO_2, molybdenum oxide (MoO_3) are used for aerogels preparation. Metal oxide aerogels are made by drying metal salts or alkoxide at pressure and temperatures above 50ºC [50]. Indeed, aerogels are a natural porous structure that really can stimulate cells to reconstruct and supplying pores in cancellous bone tissue-in live bone. Nevertheless, aerogels have lack adhesion and mechanical properties that match those of bone, which can be addressed by incorporating reinforcements and crosslinked polymers [51].

3.3.4. Aerogels based polysaccharides

Because of their biodegradability, low toxicity, and ease of production from natural resources, polysaccharide-based aerogels have piqued interest in a variety of research areas, comprising separation methods, catalysis, drug delivery, and tissue engineering. Although a few polysaccharide-based aerogels contain cationic or anionic functional groups. They can be used as hosts in applications that include greater methods most commonly for guest atoms/molecules [52].

3.3.5. Cellulose nanocrystals aerogel

Nanocellulose, also known as cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs), is a nanoscale derivative of natural cellulose which has been used to produce cellulose-based aerogels, emulsions, composites, and coatings. Mechanical processes, often combined with chemical/enzymatic pretreatments, produce CNFs, which have been approximately 5 nm wide and up to many micrometers long fibrils made up of ordered and disordered cellulose regions and are comparatively versatile. As a result, even at low concentrations, CNFs entangle readily, allowing them to form highly porous gel networks with excellent mechanical properties. CNCs, on the other hand, are highly crystalline and rigid rod-shaped particles with diameters of 5–10 nm and lengths of 100–200 nm, with a limited ability to "entangle." Both CNFs and CNCs are made from renewable resources and are non-toxic [14], and can be readily functionalized using common surface chemistry [15]. This latter property is used to introduce cross-linking groups to the CNC surface, allowing them to covalently construct a networked structure, allowing us to regulate the internal aerogel structure and maintaining that the final materials do not diffuse in liquid environments [53].

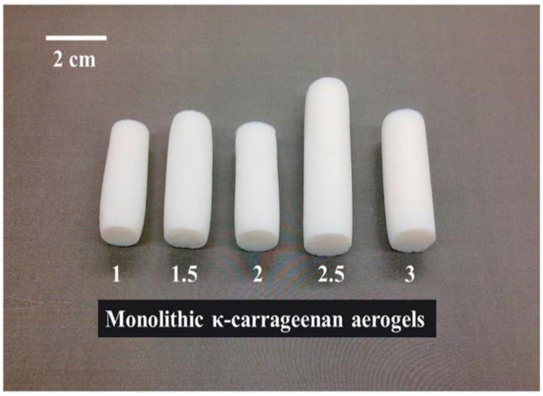

Fig. 4: Photographic image of k-carrageenan aerogels, prepared by adding 0.3 M of KSCN. The concentration of k-carrageenan (in wt%) is tagged below the corresponding sample [55].

3.3.6. Carrageenan aerogel

K-Carrageenan is a sulphate polysaccharide that contributes to the carrageenan family as displayed in (Fig. 4). In the presence of specific cations including cesium, rubidium, potassium or it forms a hard gel. It dissolves in a hot aqueous solution above 80ºC. Carrageenan forms a gel when cooled well below mid-point temperature, which would be determined by the concentration of unique cations, because of the structural transition from the coil to helix, forming of double helices, and aggregate of double helices. The special cations aid in the structural transition and efficiently stabilize the helices throughout that process [54].

3.3.7. Pectin aerogel

Pectin aerogels have recently proven to be highly promising bio-based materials for high added-value technologies including such thermal insulation, and they also have a lot of potential in the life sciences. Considering the significance of controlling aerogel structure for application performance little is known about the interactions between polysaccharide type, processing conditions, and aerogel texture and properties. Pectin has appealing characteristics including certain non-toxicity, biodegradability, and renewability, in addition to its interesting bio-active effects and gelling abilities: a “human-friendly” image that is required for life sciences applications [56, 57].

3.3.8. Chitosan aerogel

Chitosan is a significant component in the preparation of aerogel materials in life science because it has a lot of functional groups. Chitosan aerogels are potential carriers for many domains due to their biodegradability and biocompatibility, as well as the variety of chemical functionalities they contain. Furthermore, owing to their highly porous network, large specific surface area, and polycationic feature, chitosan aerogels as vehicles can increase the bioavailability [58, 59].

3.3.9. Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) is created when cellulose is carboxylated. Simple cellulose dissolution, solution blending, and freeze-drying processes were used to make CMC aerogels with different porous structures. For CMC aerogels, the effects of the DS value and the amount of CNTs on the surface structure, specific surface area, compressive modulus, adsorption capabilities, and density, and were investigated. Due to the uneven distribution of the substituents, the DS value has little effect on the surface structure, density, and mechanical properties of the CMC aerogels. The unique surface area of the aerogels reduces as the quantity of CNTs increases due to CNT agglomeration. The adsorption capacity of the CMC aerogel to the liquid increases as the viscosity of the liquid increases because the high viscosity liquid has good adhesion to the pore wall [60-62].

3.3.10. Starch aerogel

Aerogels made of starch are a type of advanced biomaterial with a low density and a large special surface area. Starch gelatinization, retrogradation, organic solvent exchange, and supercritical CO2 drying are some of the most prevalent methods for making aerogels. The starch-based aerogels that resulted are nanoporous and have a wide spectrum of applications [63].

4. Conclusions and future outlook

Pores, holes, and gaps are examples of widespread degradation in bones that can occur even in archaeological sites or museums. Because more than one factor, such as soil impact, microorganisms, and termites, would cause these types of damage. These remains represent a record full of information about human life in this period, the extent of well-being or poverty that may live, the aspects of health care, the form of nutrition they can get, and even the sex and age of these remains, making them important to maintain. While SMPAs has a long and successful history of commercial use, the ability to change their forms. They “preserve” a permanent or original form, undergo deformation to store a temporary shape, and then return to their original “preserved” form when exposed to stimuli. A variety of catalysts can be used for operation, such as heat. Since the shape memory polymers aerogels have never been used with the archaeological bones, therefore, many tests will be conducted to make these polymers suitable for the nature of artificial bones also using fillers and reinforcement materials is an appropriate procedure to obtain this convenience. Many polymers which are commonly used in the restoration of ancient bones also have shape memory behavior which can be highlighted either by adding other polymers as copolymers, adding fillers, using crosslinked polymers, or even by converting it to a nanoparticle’s polymer.

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