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REVIEW ARTICLE

Nature-inspired Material – A Step Ahead in Dental Materials

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ABSTRACT

Glass-ionomer is first choice widely used biomaterial in caries disease. The evolution of dental material science includes insertion of new components into conventional material. A literature-based review outline of biomaterials for dental restorations development was presented in nature-inspired context. This article is a tribute to the entire research community, for all listed and unlisted, involved throughout the ages in the science of dental materials with the key inventions and milestones for humanity well-being on Earth. Results. Since the Neolithic, the human mind has been seeking for a matter to replace missing tooth tissue imitating/mimicking natural organ in appearance and function, what we call biomimetic/biomimicry approach. However, this restoring philosophy does not refer to the natural composition of hard tooth tissues. Possibly, there is another one concept of drawing inspiration from nature for the design of future dental materials. Nature-inspired synthesis goes beyond aesthetic/and anatomical similarities, and delves into the mechanistic, physico-chemical features or structure-phase of natural systems. In this context, pure glass-ionomer might be taken into consideration as a starting material. However, the search for synthetic nature-inspired mesomaterial with a structural-phase composition analogous to enamel/dentine/cementum, transforming into the original host hard tissues, should focus on elongated hydroxyapatite dipole control for creating and organizing into enamel prisms, and the interwoven alignment of perpendicular clusters/bunches in a picket-fence resembling three-dimensional order. The results of previous studies confirming the possibility of the formation of apatite-enamel-like tissue in glass-ionomer are promising. The concept of inclusion of calcium phosphate nanocrystals/substitution of glass filler seems to be forward-looking. The future role of polyelectrolyte organic matrix based on synthetic tooth polypeptides crosslinked with modified analogues of natural adhesives is still undiscovered.

Keywords: Apatite, Glass Ionomer, Nature Adhesive

1 Background

Human enamel has been defined as a distinctive tooth hard tissue that may be characterized by specific attributes or inherent beauty, in terms of its high content in calcium apatites oriented in prisms [1-4]. Teeth caries disease evoked by *Streptococci* the lineage of which goes back more than 3500 million years (3.5×10^9), was already tormenting Palaeozoic fishes, touching over the course of millions of years almost all dental animals, just like us today - contemporary *Homo sapiens*, for whom it has been become the most intense pandemic disease of human civilization [5-8]. When caries induces irreversible decalcification or proteolysis of the tooth skeleton, an optimal biomimetic restoration is desirable, with the utilization of biomaterials preventing recurrence.

Glass-ionomer (GI) may seem to appear like a mainstream of evaluating restoratives as it adheres chemically to the tooth structure, possess buffering abilities, as well as a thermal expansion coefficient which is similar to teeth, controls pH and releases fluoride and other ions, hence it not only contributes to the reduction in the number of residual bacteria underneath the restoration, but fundamentally favours remineralization of the affected dentin [9-12]. GI has been successfully introduced in Atraumatic Restorative Treatment (ART)

that is a minimally invasive approach to both the prevention and stop of dental carious lesions that was accepted by the World Health Organization (WHO) in 1994 as Basic package of Oral Care (BPOC) [13].
Although, archaeological traces of the first attempts to fill cavities in teeth might lead us to 13,000 years excavation at Riparo Fredian in the form of bitumen seals, or 6,500 years discoveries in Loka/Koper with beeswax fillings, notwithstanding real restorative philosophy of tooth mimesis/mimicry/mimetics moves us back to Old Kingdom of Egypt, over 2600 BP, when Hesy-Ra – ‘Great one of the dentists’, was able to prepare a mineral mixture of terebinthenic resin, powdered malachite and ochre from Nubian ground applied to the tooth cavity. However, the genuine synthetic era starts with Marggraf's invention of nonorganic phosphoric acid 308 years ago, and an organic one – an acrylic acid, the discovery of which owe to Redtenbacher 178 years ago. Linderer's son 170 years ago mentioned the use of semisynthetic cement: ground enamel of carnivorous animal made into a paste with phosphoric acid, while the first true synthetic cement was the zinc oxychloride invented by Sorel 166 years ago. Before 58 years, Smith researched on poly (acrylic acid) salt of sintered zinc oxide, which after 5 years has been fortunately introduced into dental practice as zinc polycarboxylate - first biomaterial with the intention of adhesive bonding to tooth hydroxyapatite calcium [14-17].
Contemporary discoveries presented by Wilson and Batchelor that dental silicate cement matrix was partially composed of aluminium or calcium phosphates have led to the suggestion to replace phosphoric acid with a less aggressive organic chelating acidic species [18].

2 The lineage of glass ionomer cement

Original glass-ionomer dental cement (GIC) was being invented in 60s.of XX century C.E., with final patent in 1969 by chemical engineers Wilson and Kent with co-workers at the Laboratory of The Government Chemist (LGC) in London; GIC has been introduced into the dental clinical use by a dental physician Mc Lean, as a material to replace dental silicate cement; LGC is now a private company, based in Teddington but was originally established as a public sector laboratory in 1842 C.E., based in central London. GIC was developed as material that sets by neutralization reaction between substantial amount of unreacted, acid-decomposable glass, which acts as filler to reinforce the set cement, and a water-soluble weak polymeric acid. The term glass-ionomer covers two subgroups: glass-polyalkenoate and glass-phosphonate. The proper name for them, according to the International Organization for Standardization, ISO, is “glass polyalkenoate cement”, but the term “glass-ionomer” (including the hyphen) is recognized as an acceptable name [19-24].
Since glass ionomer has lunched firstly as commercial dental material, outside of dentistry began to find applications that exploit their good biocompatibility in otological and neuro-otological surgery or injectable bone cements as Al-free formulations with the inclusion of ZnO, GeO_2, ZrO_2, and Na_2O into the glass network, with potential metal cations release within a window of concentrations that promote osteoblast. These include artificial ear ossicles and bone substitute plates for craniofacial reconstruction. More recently, GIC has been suggested as materials for use as cement in orthopaedics surgery, for fixation of cochlear implants and, for sealing defects in the skull [25-31]. Over the decades, there have been further modifications of the pure GIC in the form of metal-reinforced, fast setting, cermet, semi- or anhydrous, high viscosity, visible-light-activated, resin-modified - dual or tree-cured, glass carbomers and ceramics- or zirconia-reinforced ones [21, 26, 32-38].
First experimental series were prepared by mixing series of pyruvic, tartaric, tannic, fluoroboric, glycerophosphoric and tetraphosphoric acids, at concentrations of 35–50% in solution and polyacrylic acid at a concentration of 25% in solution with G200 alumina-silicate glass powder of high basicity and fluoride content, with critical Si: Al ratio greater than 1:2, so the glass could be basic and capable to cement formation. Basicity of GIC may be explained with the use of a random stochastic crosslinking model described by Zachariasen. The resulting cement was known as ASPA I, the term ASPA being an acronym for Alumina Silicate Poly (acrylic Acid). ASPA was also the brand name of the very first commercial glass-ionomer cement, launched 46 years ago [39, 40]; as a result of the difficulties in operators reproducing the

manufacturers powder: liquid mixing ratio in a clinical simulation, there was launched an encapsulated version of ASPA three years later [41].

3 Organic matrix and glass filler of glass ionomer cement

The liquid component of the earliest experimental GIC (ASPA-I) was composed of an acrylic acid homopolymer solution (50% by mass) which had poor working and setting characteristics and was susceptible to gelation due to formation of intermolecular hydrogen bonds between the polymer chains [42]. Poly (acrylic acid) (PAA) is an example of weak polymeric carboxylic acids as the class of substances called polyelectrolytes. These are substances which combine the features of being both polymers and electrolytes. They derive the latter feature from the presence along the polymer chain of a substantial number of functional groups that are capable of carrying an electrical charge. In the case of most of the polyelectrolytes used to prepare glass-ionomer cements, these functional groups are carboxylic acids, −COOH. The physical chemistry of polyelectrolytes is complicated but can largely be neglected in considering the use of these substances for forming cement. However, the presence of the polar functional groups able to carry charge does confer one very important property, namely, that polyelectrolytes are generally soluble in water [43]. The polyelectrolytes used to prepare nowadays glass-ionomers are poly (alkenoic acid) s. This was recognized many years ago in the nomenclature agreed by the International Organization for Standardization (ISO) for these materials, where the formal name is glass polyalkenoate cement. In addition, 2:1 to the homopolymer of PAA, copolymers with unsaturated carboxylic acids (itaconic acid and maleic acid) were also studied with intention to reduce intermolecular hydrogen bonding owing to their reduced stereo regularity when compared with homopolymer. Poly (vinyl phosphonic acid) has been studied as a potential cement former, but its practical use is restricted to a single brand, where it is used in a mixture with poly (acrylic acid) and effectively acts as a setting rate modifier copolymer of acrylic acid and maleic acid have been reported. The latter has become commercially important, though the majority of commercial GICs are still formulated with PAA homopolymer [44]. Optimum properties are said to be achieved with PAA molecular weights of 11,000 (number average) and 52,000 (mass average) with polydispersity of 4.7 [45]. In an attempt to improve the setting characteristics of GI, investigations were focused on the role of a third component, a chelating agent, using citric acid, salicylic acid, acetylone, ethylenediaminetetraacetic (EDTA)/ sequestric acid, polyglycol and finally tartaric acid (5% by mass) that was added to the acrylic acid homopolymer (47.5% by mass) to form ASPA-II [46]. The overall effect of including either 5% or 10% by mass in cements (+)-tartaric acid in a glass-ionomer cement is that setting is delayed, so that the cement is easier to mix. It then sets sharply to give the finished, hardened material that can be completed within the tooth. As a consequence of the ability to promote these changes, (+)-tartaric acid is a very useful additive. However, its effectiveness varies between glasses, depending on their composition. It may have something to do with its ability to prevent the precipitation of aluminium salts, which it does by chelating Al^{3+} ions and keeping them in solution. By this mechanism, it may prevent the premature formation of ionic crosslinks involving Al^{3+}. Certainly, this is consistent with the fact that the bands due to aluminium polyacrylate appear later when tartaric acid is present than when it is absent [47]. Following the discovery of the role of tartaric acid in the setting reaction, especially its lyophilisate in high viscosity glass ionomers (HVGIC), glass formulations were no longer restricted to the opal G-200, providing opportunities for the use of more translucent glasses to produce aesthetic GIs. Today commercial glasses contain zinc, strontium, barium or lanthanum ions to impart radiopacity for increased detection and contrast with dental tissues and other restorative materials on dental radiographs [48]. It is vital that glasses for ionomer cements should be basic, i.e., capable of reacting with an acid to form a salt. In principle, several different glass compositions can be prepared that fulfil this requirement but in practice, only alumina-silicate glasses, with fluoride and phosphate additions, are fully satisfactory.

Commercial glasses for glass-ionomer cements are typically based on calcium compounds, with some extra sodium. There are also materials in which calcium has been substituted by strontium. Ionomer glasses owe their basic character to the fact that both alumina and silica are used in their preparation. Glasses based on silica alone lack reactivity and also basicity, because their structure contains mainly SiO_4 tetrahedra linked at the corners to form chains that carry no charge. When alumina is added, the aluminium is forced to adopt a similar 4-fold tetrahedral geometry to silicon, i.e., AlO_4 tetrahedra. As aluminium carries a formal $^{3+}$ charge, it does not counteract the effect of the negatively changed oxygens as effectively as silicon, with its formal 4+ charge. To balance this, extra cations such as Na^+ and Ca^{2+} (or Sr^{2+}) have to be present. These create basic character and make the glass susceptible to attack by acids. Fluoride is also a vital component of the glasses used in glass-ionomer cements. Glasses, including G338, containing fluoride were among the earliest reported when glass-ionomers were first described, and were either of the SiO_2-Al_2O_3-CaF_2 system or the more complex SiO_2-Al_2O_3-P_2O_5-CaO-CaF_2 system. Practical ionomer glasses, including G338, are known to undergo at least partial phase separation as they cool. This leads to regions of varying composition and typically to the occurrence of one phase that is more susceptible to acid attack than the others. In principle, this might be expected to alter the optical properties of the glass, and in turn the cement, but there have been no studies reported exploring this point. Studies of ionomer glasses have been carried out using MAS-NMR spectroscopy and these have provided useful structural information about these materials. Aluminium has been shown to occur in both 4- and 5-co-ordination in various glasses, which confirms the effect of silica on the co-ordination state of aluminium. Fluorine occurs in these glasses bound exclusively to aluminium. The substitution of calcium with strontium in glasses of this type can be achieved by using the compounds SrO and SrF_2 in the place of CaO and CaF_2 in the glass-forming mixture. Strontium has the effect of increasing radiopacity compared with calcium in these glasses without any adverse effect on the appearance of these cements. Fluoride release is enhanced from these cements, though the reason for this is not known [49-54].

4 Water-activated acid-base neutralization polymerization of glass ionomer cement

Glass-ionomer polyelectrolyte sets within 2–3 min from mixing by an acid-base reaction. The first step is a reaction with hydrated protons from the polymeric acid at basic sites on the surface of the glass particles. This results in the movement of ions such as Na^+ and Ca^{2+} (or Sr^{2+}) from the glass into the placid solution, followed quickly by Al^{3+} ions. These ions then interact with acid molecules to form ionic crosslinks, and the insolubilized poly salt that forms become the rigid framework for the set cement. When this setting reaction occurs, all of the water becomes incorporated into the cement, and no phase separation occurs. Setting of glass-ionomer cements have been studied by various spectroscopic techniques, including infrared, FTIR and 13C NMR spectroscopy. The overall reaction appears to take place in two steps in a diffusion-controlled process. The first step is the formation of ionic crosslinks, as we have seen, and this is responsible for the immediate hardening process. Subsequently, there is a crosslinking process involving Al^{3+} ions that takes about 10 min to be clearly identified spectroscopically. This second step is slow and continues for approximately a day. After this initial hardening, there are further reactions, which take place slowly and are together known as maturation. Strength typically increases, as does translucency. In addition, the proportion of tightly bound water within the structure increases. The details of these processes are not known, and research continues on this question. Some years ago, it was shown that those hard, insoluble cements could be formed by reaction of ionomer glasses with acetic acid. This is in spite of the fact that metal acetate salts are soluble in water. It was also observed that these cements became progressively stronger in compression up to 3 months, though there were no discernible changes in the infrared spectra of the cements. This led to the conclusion that there was an inorganic setting reaction that complemented the neutralization reaction in the setting of these cements. Metal silicates were proposed as substances responsible for this setting, but subsequent work on what became called “pseudo-cements” (i.e., cements made from monomeric acids with ionomer glasses) showed that insoluble materials resulted only with phosphate glasses. In contrast, phosphate-free silicate glasses were shown not to undergo an equivalent setting reaction. This suggested that the proposed inorganic network is phosphate-based. Cement maturation include an increase in ionic crosslinking with time. In addition, there is an increase in the proportion of bound water within the cement, which has been attributed to greater binding of water to co-ordination sites around ions, or around neutralized polyanion molecules. There is also some evidence of the formation of silanol (Si-OH) groups on the surfaces of the glass particles, a process that involves hydrolysis of Si-O-Si (siloksan) groups. There is also evidence of some sort of inorganic network formation from the ion-depleted glass, probably involving phosphate groups from the latter. The freshly set cement is not completely fit for clinical service. It is susceptible to water exchange across its immature outer surface; it can dry out or alternatively, it can take in water [55-58].

5 Biological aspects of glass ionomer cement

There is today a trend towards the use of tooth-coloured restorative materials, particularly composite resins. The use of amalgam as a restorative material has been in decline in recent years and this can be attributed partly to the public's concern regarding the controversy on its safety. On the other hand, concerns about the estrogenecity of bisphenol -A (BPA), bisphenol-A-dimethacrylate (BPA-DMA) and other aromatic components leached from bis-GMA- and bis-EMA-based composites have been expressed. BPA is an organic compound used in the industrial production of polycarbonates and epoxy resins. However, BPA is an endocrine disruptor, with potential toxicity. Pure BPA is not a component of dental composite resins. However, derivatives of BPA - from pure BPA – are widely used: bisphenol A diglycidyl methacrylate (bis-GMA) especially, but also bisphenol A dimethacrylate (bis-DMA), polycarbonate-modified bis-GMA (PC bis-GMA), ethoxylated bisphenol A glycol dimethacrylate (bis-EMA) and 2,2-bis [(4-methacryloxy polyethoxy) phenyl] propane (bis-MPEPP). Filling and sealing material including RMGICs often contains the toxic (co)monomers hydroxyethylmethacrylate (HEMA), triethyleneglycoldimethacrylate (TEGDMA), urethanedimethacrylate (UDMA) and bisglycidylmethacrylate (bis-GMA). The resin (co)monomers may be released from restorative dental materials and can diffuse into the pulp, the gingiva, the saliva and the circulating blood. Numerous cytotoxic responses to dental composite resins have been described. It can lead to a variety of adverse biological effects in the patient, from persistent inflammation to sensitization and potential allergic reactions. There are potential problems of long-term exposure to HEMA in particular for dental personnel. Besides contact dermatitis and other immunological responses, HEMA is volatile, and its vapor can be readily inhaled, causing adverse reactions in the respiratory system. One essential advantage of pure glass-ionomer cements is that it is biocompatible as monomer free compared to RMGICs [59-74].

There is a subtle distinction between safety and biocompatibility – two important features of dental materials. Safety is concerned with the fact that materials when in contact with the human body should not cause any adverse effect, whereas biocompatibility is the quality of being non-destructive in the biological environment maintaining the beneficial effect to the patient. So far, few materials can be regarded as completely safe and fully biocompatible in the oral environment. Most dental materials interact with the oral environment and this interaction might involve a release of components with undesirable side effects for oral tissues [75].

GIC bioactivity can be defined as 'materials that elicit a specific biological response at the interface between tissues and the material, which results in the formation of a bond' [76]. Bioactivity is also an important feature of these materials, a phenomenon that has appeared in several observations. In saliva, glass ionomers have been shown to fluoride, calcium and phosphate ions release and recharge ions with a resulting increase in hardness. At the interface with the tooth, an ion-exchange process occurs over time that leads to the formation of a distinctive layer that provides a highly durable and strong bond between the cement and the tooth. Lastly, at the bottom of pits and fissures, the morphology of the glass ionomer changes, and a structure is formed, which is reported to be "enamel-like". Moreover, glass-ionomer, thanks to the bioactivity indeed, can contribute directly to the remineralization of carious dentine [64, 77-80].

6 Glass carbomer cement

Glass-carbomer cement has been a relatively novel generation of glass-ionomer, which has been augmented to enhance the bioactivity first of all by incorporation of hydroxyapatite (HAp: $Ca_{10}[PO_4]_6[OH]_2$) that is a typical abundant biomineral in humans. Confirmed fluorosilicate glass powder of GCC (SiO_2 54.6 Mol%,

Al_2O_3 20.0Mol%, P_2O_5 3.2Mol%, SrF_2 11.9 Mol%, CaF_2 4.1 Mol%, NaF 5.4 Mol%, ZnO 0.7 Mol%, BaO 0.2 Mol%) obtained in the sintering process at temperature above 950 °C, followed by hardening and grinding, has been finally washed by strong hydrochloric acid so that the surface layer of the particles is substantially depleted in calcium, whereby most of calcium ions lie well inside the particles towards the core. The highly proportion glass used contains strontium, relatively high amounts of silica compared with the glasses used in the well-established brands of conventional glass-ionomer, but it contains comparable amounts of aluminium, phosphorus and fluoride. Due to the acid-washing process, the glass is fairly unreactive towards poly (acrylic acid) or acrylic/maleic acid copolymer with a broad halo which is indicative of the amorphous nature of the glass phase. Glass powder consists of two types of particles of average diameter size 1-20 µm, and even seemingly 200 µm as was mentioned, marked with ‘*S*’ (smooth) and small ‘*I*’ (irregular) particles, lying on a smooth particle; ‘*S*’ has a typical alumina-silicate composition, while ‘*I*’ contains more Ca and P. Confirmed composition of the powder include fluoroaluminosilicate glass >90%, Apatite < 6%, Polyacids < 4%. Nominally up to 20 masses %, optimally 8 masses%, of nanoscale fluorine/hydroxyapatite particles, which also behave as secondary filler that greatly increases the reactive surface, and improves high polishing ability, is to promote the neutralizing effect and remineralization of caries-damaged enamel and dentin. Solid state NMR spectroscopy has shown that this filler is mostly hydroxyapatite, and it is included to promote the formation of enamel-like material at the interface with the tooth. Nanocrystals of calcium FAp, that is slightly less soluble at 25 °C than Hap, can act as nuclei for the remineralization process and initiate the formation of FAp. FAp nanocrystals showed sharp lines characteristic of a crystalline phase. The diffraction pattern of the FAp sample matched both calcium HAp and calcium FAp impossible to distinguish by XRD because of their almost identical lattice parameters. Polymeric acid contained in powder refers to carbomer - the traditional brand name in commercial nomenclature, i.t. the water-absorbing homopolymer of poly (acrylic acid), – (CH2-CH(COOH)) n-. Important novel component of glass carbomer is silicone oil - an organic carbon chain additive, which is completely biocompatible, added to provide the material with greater strength and increased transparency. It is consisting of linear polydimethylsiloxane molecules with functional hydroxyl groups. These hydroxyl groups can form hydrogen bonds with other cement components, thus preventing the silicone oil from leaching from the cement after being set. This allows the silicone oil to form hydrogen bonds with other components of the cement, so that it remains bound in the cement after setting influencing the final mechanical properties enhancing the toughness of the material. Silicone oil incorporated into the glass powder becomes adsorbed onto the surface of the glass, and this also interferes with the reaction with polyacid. Nanoparticulate fluoride/hydroxyapatite may cause the set material to be more brittle; to overcome the silicone oil is added. It toughens the material and remains bound within the material by hydrogen-bonding. Glass-carbomer is easy to auto-mix and only a little reaction occurs as these two components are blended. Working time is 3’30”. Secondary hardening reaction continues up to 10 days, and full maturation reaches 3 years. GCC is capable of setting in an auto-polymerization mode that is the reaction of the basic glass with the aqueous acid in a neutralization reaction. However, the manufacturers recommend that it be treated for 60-90 s with a high-energy dental polymerization light of 1400mW/cm^2, (60 °C) not to promote a photochemical reaction, but to accelerate by heat the acid-base reaction. In general, such accelerated setting allows for shorter chair time and improved clinical outcome. Set material is to be covered with special monomer-free gloss, based on siloxanes. The setting reaction in glass carbomer cement was followed by multinuclear 27Al, 31P, 19F and 29Si MAS-NMR. The conversion of the Al (IV) into Al (VI) is well approximated by a linear function of logarithm of aging time. At least two different Al (VI) species formed as a result of the cement formation. The data showed that secondary setting reaction still continues up to 10 months. Combination of the 27Al and 31P MAS-NMR data indicates presence of the Al–O–P linkages in the initial glass. The acid pre-washing of the glass powder is thought to affect the formation of the surface species and also alter the amount of Al–O–P linkages per phosphorus. Setting of glass carbomer involves two parallel reactions, one between the ion-leachable basic glass powder and poly (acrylic acid), the other apatite that are being partially consumed during this stage. Both are acid-base reactions result in an ionically crosslinked polyacid matrix containing embedded filler. In this case, however, the filler is not ion-depleted glass only, but also partially reacted hydroxyapatite. The resulting matrix is similar to that which occurs in conventional glass-ionomer cement, though differs in that it also includes poly (dimethyl siloxane) oil. It comes to cross-linking through the creation of hydrogen bonds with oxygen-silicon chains (Si-O-Si), what is an idea closer to matrix formation in ormocers. This leads to the formation of interpenetrating polymer networks (IPN) with set polysalt/siloxane matrix described by cracks and voids with the content of small glass filler particles. Complex structure is to have an impact on declared flexural strength (FS = 122 MPa), shear bond strength to enamel (SBS = 13.7 MPa), compression strength (CS = 260 MPa), modulus of elasticity of (E = 8.3 GPA), nanohardness (nH = 0.603 GPa), hardness without gloss with the formula of modified polysiloxanes (HV = 61.262 MPa) and with gloss (HV = 56.800 MPa), surface roughness (Ra = 0.81 nm) without gloss and (Ra = 1.54 nm) with gloss [81-104].

Glass ionomer cement has a wide application area because of its advantages. However, its use on permanent teeth at locations facing occlusal forces is restricted, and that is why several strategies are followed to enhance the mechanical properties, such as incorporation of powdered silver-tin amalgam alloy, cermet, stainless still, gold, oxides of titanium, palladium, niobium, strontium or zirconium, ytterbium fluoride, barium or magnesium sulphate, whiskers/fibres/crystals of aluminium silicate, silicon carbide, zirconia, aluminium, carbon, or cellulose, reactive glass/bioglass, fluorinated graphene, hydroxyapatite, fluorapatite, N-vinyl pyrrolidone, bioactive apatite with zirconia or nanosilica complex, nanochitosan, organic derivative of montmorillonite or even chicken eggshell powder [105-114].

7 Zirconia glass ionomer cement

Good chemical and dimensional stability, mechanical strength and toughness, coupled with a young's modulus in the same order of magnitude of stainless-steel alloys is the origin of the interest in using ZrO_2 as a filler. ZrO_2 has been widely used for the toughening and strengthening of brittle HAp and bioglass in biomedical applications. In 1969, zirconia was first used for medicine purposes in orthopaedics as a material for hip head replacement [115-118]. 3-8 wt. % addition of Y_2O_3 stabilized zirconia (YSZ) exhibits good chemical and dimensional stability, mechanical strength and toughness of material. The accessible zirconia powders have different grain sizes and different additives, such as yttrium oxide and alumina, which can be distributed homogeneously throughout the whole material or higher concentration at grain borders. YSZ–glass ionomer may serve as a potential silver amalgam or metal-reinforced GIC because it is tooth-coloured, and it has better mechanical properties [119-121]. Since the first glass ionomer cement (GIC) was marketed in 1975, limit for restorative GICs compression strength is reduced by 23% from 130 MPa in 1991 to 100 MPa in 2003. When the first non-metallic reinforced GIC appeared on the market, it was guaranteed all batches to comply with the 300 MPa limit of ISO1559:2001. The typical value of this material of 323 MPa was to be exceeded by a ceramic reinforced version. This material consists of powdered fluoroaluminosilicate glass with particle size 5–10 μm, polyacrylic acid, tartaric acid and ceramic reinforcing filler; it has been shown elsewhere that zirconia is the major if not the only (crystalline) component of the additive of this product, that is able to react partially with the matrix, which may produce some bonding (and so matrix constraint) and also possibly an altered polysalt matrix. Liquid includes polyacrylic acid in distilled water [122-124].

Lately, new zirconia-reinforced glass ionomer cement has been introduced. It is a new class of restorative glass ionomer cement that exhibit the strength of amalgam and at the same time maintain the fluoride releasing capacity of GICs and completely eliminating mercury hazards. Addition of zirconia as filler particle in the glass component improves mechanical properties of the restoration by reinforcing structural integrity of the restoration in load-bearing areas. The wide distribution of Zirconia fillers allows a high packing density of the powder with the hydrogel salt matrix. The slightly decreased microhardness could be attributed to the composition of this zirconia reinforced GIC, which has particulates of zirconia in a lattice of glass ionomer, though it showed higher mean VHN values at 1 week than at 1 day, because of the hardening phase of the setting reaction in case of glass ionomer due to continued formation of aluminium salts bridges. Solubility of in saliva amounted to 10.70 ± 3,15μg/mm^3. The powder contains 10/15-20 weight % glass filler of average 0,8 μm granulation, tartaric acid (1-10%), polyacrylic acid (20-50%), homogeneously incorporated zirconium dioxide, and deionized water as its liquid. Zirconium oxide results from Baddeleyite (ZrO_2) that contains high levels of zirconia ranging from 96.5 to 98.5%. The powder liquid ratio is 8:1 P/L. The glass component of zirconia-reinforced is subjected to controlled micronization, to acquire optimum particle size and characteristics. The grain size has an effect on an exclusive characteristic of zirconia called transformation toughening, which gives it higher strength, toughness, high hardness, and corrosion resistance; thus, when it is homogeneously incorporated in the glass component, it further reinforces the material for lasting durability and high tolerance to occlusal load. Homogeneity of the glass particles further reinforces the durability of the material and the strength to withstand occlusal load. Zirconia-reinforced glass ionomer cement has confirmed compressive strength of 160.91 MPa. This material shows relatively poor polishing. This may be due to large filler particle incorporated in the cement. Increase in surface roughness results in alterations in light reflection and material surface turn opaque. Studies showed that material with large particle size possess high surface roughness. The SEM analysis indicated voids and cracks on their surfaces. The voids may be incorporated during the sample preparation and cracks during the processing of samples for SEM analysis (125-136).

The newest formula with 3% mass of Yttrium Trioxide Partially Stabilized Tetragonal Polycrystalline Zirconia (3YTZP) has been approved for use in dental clinic. The powder consists of fluoroaluminosilicate glass, nanoparticles of zirconia oxide, pigments; liquid includes polyacrylic acid, tartaric acid; powder liquid ratio rates 3.6:1.0. This material exhibits CS varying from 302.23 to 326 MPa. It is possible that the zirconia fillers would cause interference in the chelating reaction between the carboxylic group (-COOH) of polyacrylic acid and the calcium ions ($Ca^{2+)}$ of tooth apatite. Hydroxyapatite (HAp), the main mineral component of the tooth structure and bone is bioceramics containing calcium and phosphorus. The HA particles were added to glass-ionomer powder due to their biocompatibility and similar composition to apatite in human dental and skeletal systems. The compositions 4 and 12 vol. % HAp/ZrO_2-GICs exhibited superior mechanical properties than the original GICs. The mechanical properties of HAp/ZrO_2-GICs were found to be much better than those of HAp-GICs because ZrO_2 has the attributes of high strength, high modulus, and is significantly harder than glass and HAp particles. Furthermore, ZrO_2 does not dissolve with increasing soaking time. Addition of nano-sized zirconia fillers to the HAp-GIC has led to a significant increase in modulus, strength and hardness by keeping improved dissolution stability with increased soaking time. Incorporation of 5 and 15 wt.% of microhydroxyapatite to nanozirconia-reinforced GIC improved microhardness, while adding 25 wt.% of HAp decreased hardness compared to the control groups (without HAp). Although nanoparticles of HAp are more similar to the mineral phase of tooth structure than micro-particles as far as crystal size is concerned, nano-HA considerably prolongs the setting time of GICs. Volume of HA can change the amount of liquid needed to complete the reaction of particles. Since HAp/ZrO_2 particle size is smaller than glass powder, the surface area is much larger compared to glass; therefore, it might need a greater amount of liquid for interaction. Incorporation of nano- and micro-particles of HAp could enhance the hardness of conventional glass-ionomer. Due to high surface area and good mechanical interlocking with the polymer matrix in nano HAp, it is recommended that different percentages of nano Hap be used in future studies [137-142].

8 Dental regeneration, biomimetics or nature-inspired restoration

Since has turned attention to the possibility of using living matter, e.g. stem cells or extracellular matrix, regenerative dentistry including transplantation and cloning, has become an important concept, in which multiple approaches have been introduced to generate or regenerate tooth enamel through synthesis using physic-chemical means, protein matrix-guided enamel crystal growth, biomineralization, cell-based enamel engineering, and biological enamel regeneration based on *de novo* induction of tooth morphogenesis [143-146]. On the other hand, for thousands of year’s humanities has been using an inanimate matter to replace missing tooth tissue imitating/mimicking natural organ in appearance and function, what we call biomimetic/biomimicry approach [147-149]. However, this restoring philosophy does not refer to the natural composition of hard tooth tissues.

Possibly, there is another one concept of drawing inspiration from nature for the design of future dental materials. Nature-inspired synthesis, because that's what we are being discussed about, goes beyond aesthetic/and anatomical similarities, and delves into the mechanistic, physico-chemical features or structure-phase of natural systems (150). In this context, pure GICs, also in coats/gloss [151-154] might be taken into consideration as a starting material.

9 Calcium phosphates/carbonates

The first articles describing the structure and composition of bones, teeth and other types of calcified tissues appeared less than 350 years ago. After 100 years Swedish chemist and metallurgist Johan Gottlieb Gahn discovered the existence of calcium and phosphorus in the bones. Thanks' to Tomes's research 130 years ago, we know that the unique physicochemical properties of enamel result from the high content of hydroxyapatite. Modern knowledge has established that the organic matrix of enamel (EOM) and the combination of enamel with dentine (DEJ) can have a structural and functional relationship with basal membranes, e.g., in the skin, by the presence of collagen type IV or VII and metalloproteinase-20. Calcium phosphates are an integral component of geological and biological systems. They occur in virtually all rocks and are the main structural component of vertebrates. There are several formulas for calcium phosphate: monocalcium (MCPM) $Ca(H_2PO_4)_2 \cdot H_2O$, monocalcium anhydrous (MCPA) $Ca(H_2PO_4)_2$, calcium phosphate dihydrate (DCPD, brush) $CaHPO_4 \cdot 2H_2O$, anhydrous dicalcium phosphate (DCPA, monenite) $CaHPO_4$, eight-calcium phosphate (OCP) $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, α-tricalcium phosphate (α-TCP) $\alpha\text{-}Ca_3(PO_4)_2$, β-tricalcium phosphate (β -TCP) $\beta\text{ -}Ca_3(PO_4)_2$, amorphous calcium phosphate (ACP) $Ca_x(PO_4)_y \cdot nH_2O$, calcium deficiency hydroxyapatite (CDHA) $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$, hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$, tetra calcium phosphate (TTCP) $Ca_4(PO_4)_2O$. Calcium phosphates with a Ca/P atomic ratio between 1.5 and 1.67 are called apatites (e.g. hydroxyl-, fluor-, chloroapatite) [155-160]. Synthetic HAp ceramics, modelled after natural hydroxyapatite, seem to be the most suitable material for tooth and/or bone substitution due to their excellent biocompatibility and bioactivity. The mechanical properties of pure HAp ceramics are poor; fracture strength (K1c) doesn't exceed 1.0 MPa x $m^{1/2}$ (human bone 2-12 MPa x $m^{1/2}$). In addition, the Weibull module (n) is low in a humid environment (n = 5-12) [161]. Therefore, science began to look for patterns/alternatives in nature. Chicken egg powder can be an alternative and hint. It consists of 94-98.2% calcium carbonate, 0.9% magnesium and 0.9-1.0% phosphate, and about 5% other organic substances. Egg shells are 3-layered structures with an outer membrane, inner spongy and lamellar layers of protein fibers, connected by calcium carbonate crystals. Natural HAp can be obtained not only from eggshells, but also from fish, chicken, beef or coral bones [162-165]. This was used experimentally, e.g., in a study in which it turned out that the mechanical properties of conventional glass ionomer cement for restoration were enhanced by the addition of CESP. In addition, CESP enrichment did not diminish fluoride and calcium release (166).

10 Natural adhesive/cohesive organic matrixes

As for the organic matrix, clearly related to the cohesion and adhesion of the material, in the past the possibility of using coniferous natural resins in the form of liquid or fossils has been mentioned many times [167]. The first known examples of coal pitch and wood tar glue were used and dated 200,000 years to join two pieces of stone tools together [168]. In nature, many marine organisms such as mussels, *Pharmacopeia californica* marine worms and barnacles produce a strong wet grip mechanism by cleverly combining chemistry of catechol, polyelectrolyte complexes and supramolecular structures. The attachment of mussels to various surfaces was the subject of one of the earliest observations regarding bioadhesion. Aristotle noticed that clinging to cosmopolitan mussels (*Pinna nobilis*) was due to a durable fibre bundle with sticky ends. The term fine linen, as a pattern of bioadhesion, was accidentally used by Aristotle (from Greek *byssos* - linen), and to this day has gained universal acceptance [169, 170].

Sea mussels have mastered the ability to attach to various surfaces in sea water through the use of adhesive proteins. These mussel foot proteins (Mfps) are known to cure quickly to form adhesive plates with high interfacial bond strength, durability and strength. At least six Mfps (Mfp-1 to Mfp-6) have been identified from the adhesive plates of several mussel species (*Mytilus edulis, Mytilus galloprovincialis, Mytilus californianus*). The modern search for molecules responsible for the adhesion of fine linen began 67 years ago with a ground-breaking article on *Mytilus byssus*, which referred to the peculiar occurrence of 3,4-dihydroxyphenylalanine (DOPA), which is modified from tyrosine by post-translational hydroxylation. The availability of the full primary sequence of a number of proteins inspired attempts to produce complete or partial synthetic analogues.

Adhesive strategies based on DOPA are probably quite rare in nature because they have been positively detected only in sea and freshwater mussels, tunicates, reef-building polychaete and some flukes. Notwithstanding this, it is proposed that a deeper understanding of the molecular mechanism of fine linen adhesion should lead to fundamental insights into nature's adhesion. The DOPA catechol side chain has the ability to form various types of chemical interactions and crosslinking, which gives Mfps the ability to solidify on site and tightly bind to various types of substrate surfaces [171-175]. The amazing, moisture-resistant property of Mfps has inspired scientists to develop a wide range of advanced functional materials. DOPA's ability to create strong reversible and irreversible interactions has been used to create a unique and versatile platform for developing adhesive polymers with improved material properties (i.e., Composite hydrogels, smart materials and self-healing materials). For mussels, these self-adhesive fluids consist of Mfps highly concentrated, internally unstructured polyelectrolytes, which quickly solidify on contact with seawater. These interfacial Mfps have an unusually large number (28-34 mol%) of aromatic residues, including tyrosine (Y), tryptophan (W) and DOPA (post-translational modified tyrosine), as well as nitrogen-containing lysine (L) and arginine (A) [176, 177]. In the cement of marine worms, in the presence of both polyanions (polyphosphoserine-rich proteins) and polycations (lysine-rich proteins), liquid-liquid phase separation is modelled as a complex coacervation process leading to a lean balance in polyelectrolytes [178]. The causes of the gecko's foot, *Hemisphaerota cyanea* or *Ceratophrys ornata* frogs are very interesting in terms of their ability to attach strongly to various surfaces, and at the same time to adapt and recover from extreme mechanical stress. Gecko-inspired, biodegradable and biocompatible adhesive was developed from surface modified poly (glycerol-co-sebacate acrylate), in a system of pillars on a nano scale, used in conjunction with a thin tissue-responsive surface [179-181].

11 Conclusion

The results of previous research confirming the possibility of creating apatite–enamel-like tissue in GIC are promising. The concept of different calcium phosphate nanocrystals inclusion/glass filler substitute in GIC compound seems to be forward-looking. However, the search for synthetic nature-inspired mesomaterial with a structural-phase composition analogous to enamel/dentine/cementum, transforming into the original host hard tissues, should focus on elongated HAp dipole control for creating and organizing into enamel prisms, and the interwoven alignment of perpendicular prisms in a picket-fence resembling three-dimensional order. In this respect, the future role of polyelectrolyte organic matrix based on tooth polypeptide equivalents crosslinked with modified analogues of natural adhesives is probably still undiscovered.

12 Declarations

12.1 Competing Interests

The author declares that this study has not been ordered, financed and there is no conflict of interest.

12.2 Publisher's Note

AIJR remains neutral with regard to jurisdiction claims in institutional affiliations.

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