

Advanced Glass-Ceramic Materials for Biomedical Applications

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Biomaterial science studies the interactions that occur between materials and tissues in order to understand the mechanisms that lead to material integration in biological systems for medical purposes. It is a field that requires a multidisciplinary approach, integrating materials science, chemistry, biology, engineering and medicine. Its development arose out of the requirement for new materials with high performance in terms of tolerability and integration capability that can be used to replace or restore function to a body tissue. Despite advances in the biomaterials field, at this point in time a satisfactory combination between the properties of the materials (mechanical, chemical and tribological) and their biocompatibility has not yet been achieved. This is the cause of early failure of implants, which necessitates subsequent replacement of prosthetic devices, especially in young patients. Glass-ceramics are an important family of materials proposed for bone repair and substitution. They have the capability to bond with living bone by forming a hydroxyapatite layer with a composition similar to that of the mineral phase of bone [1]. The first bioglass (45S5) was discovered in 1971 by Hench et al. [2]. Afterwards many other glasses with various compositions were explored [3]. Kokubo et al. [4] developed Apatite-Wollastonite (A-W) glass-ceramics which retains a high mechanical strength *in vivo* for a long period and is able to bond to living bone in a short space of time. Moreover, published literature [5] shows that the preparation method, in addition to the material composition, also affects the resulting structure and, thus, the biological properties of the materials obtained. An ideal technique to prepare bioglass is the sol-gel method, a versatile synthesis technique used to produce glasses and ceramics at low temperatures. The process starts when water is added to a solution of metal alkoxide precursors in alcohol. The hydrolysis of the metal alkoxide and the polycondensation of the oligomers formed cause a transition of the system from a mostly colloidal liquid ('sol') into a solid 'gel'. By drying the obtained wet gel, it is possible to prepare xerogels (by exposure to low temperatures) or aerogels (by solvent extraction under supercritical conditions) or dense ceramic and glass by means of a further heat treatment at higher temperatures. Glasses and ceramics synthesized via the sol-gel method exhibit higher bioactivity and biocompatibility than materials with the same composition but prepared using other techniques [6]. Indeed, sol-gel-derived glasses have an inherent mesoporosity that gives them a larger surface area and degradation rates potentially more rapid than melt-derived glasses of similar composition. Moreover, the presence of -OH groups on their

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surface stimulates hydroxyapatite nucleation, promoting their easier Osseo integration. Sol-gel glasses and ceramics have been proposed for many biomedical applications, such as artificial dental roots, bone regenerative materials, coatings to improve biological performance of bio inert implants and drug delivery systems [7-12]. In particular, silica, calcium silicate and calcium phosphate glasses and ceramics are attracting interest due to their ability to stimulate osteogenesis via both their dissolution and degradation products [10]. Indeed, soluble silica and calcium ions are able to activate and stimulate osteoprogenitor cells at the implant site, promoting bone tissue growth. These materials have also demonstrated the ability to form hydroxyapatite on their surface *in vitro* [13,14]. However, the brittleness of sol-gel materials limits their use in several load-bearing applications. To overcome these problems, many strategies have been proposed. The sol-gel method is easily coupled with different coating techniques like spray coating, spin coating and dip coating for the surface modification of bio inert implants with the aim of inhibiting wear, reducing corrosion and improving biological properties, as bioactivity and biocompatibility [15]. This allows the optimization of surface properties while retaining favourable bulk properties of the bio inert implants used. Recently, polymer-based composite materials, consisting of poly (ϵ -caprolactone) in which inorganic sol-gel fillers are embedded, have been proposed [16,17] to develop composite 3D scaffolds. This strategy allows the mechanical performance of the neat PCL to be improved and, at the same time, advantage to be taken of the well-known

bioactive features of inorganic sol-gel particles. Moreover, the low processing temperatures of the sol-gel method allows thermo labile molecules (e.g. polymers, drugs, biomolecules, etc.) to be entrapped in the inorganic glassy matrix, making the sol-gel processes an ideal technique to prepare organic-inorganic hybrid (OIH) materials. The leading idea in their development has been to combine the favourable properties of each individual component forming the hybrid, and at the same time attempting to decrease

or eliminate each component's drawbacks through a synergistic effect, thus resulting in a generation of new materials with new properties. Several OIH systems, consisting of an inorganic matrix in which a polymer and a drug were encapsulated, have been proposed as drug delivery systems. In this case, the polymer displays a dual function: improving the mechanical properties of the glassy matrix and modulating the release kinetics of the drug by the sol-gel matrix [18].

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