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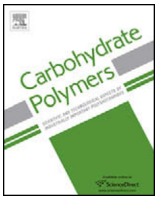

Dielectric and electric properties of new chitosan-hydroxyapatite materials for biomedical application: Dielectric spectroscopy and corona treatment

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ABSTRACT

Chitosan-hydroxyapatite composite materials were synthesized and the possibility to make their surface charged by corona discharge treatment has been evaluated. Dielectric and electric properties of the materials were studied by dielectric spectroscopy, including application of equivalent circuits method and computer simulations. Dielectric spectroscopy shows behavior of the materials quite different from that of both chitosan and HA alone. The obtained dielectric permittivity data are of particular interest in predicting the materials' behavior in electrostimulation after implantation. The ε values observed at physiological temperature in the frequency ranges applied are similar to ε data available for bone tissues.

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1. Introduction

Carbohydrate biopolymers attract attention because of their unique physico-chemical and biological properties. They allow one to create a variety of materials. An important area of their application is medicine: the creation of biologically active agents, materials for drug encapsulation, the preparation of scaffolds for tissue engineering, etc. In this case, it is important that these polymers are non-toxic, biocompatible, and able to provide optimal conditions for adhesion, expansion and cell immobilization thus promoting the integration of an implant with the surrounding tissue. One of the most promising polymers in this respect is chitosan, derived from natural chitin (Dutta, Dutta & Tripathi, 2004; Kumirska, Weinhold, Thöming & Stepnowski, 2011). Chitosan is a product of chitin deacetylation; its macromolecule comprises 2-amino-2-deoxyglucopyranose and 2-acetamido-2-desoxyglucopyranose monomers; their percentage is called the degree of deacetylation of chitosan. Chitosan possesses antioxidant, antibacterial, radioprotective, immunomodulatory properties, fibre- and film-forming ability, it is non-toxic, can be easily modified or used in making composite materials capable of biodegradation. Its electrical characteristics (e.g. volume resistivity and electret properties), poorly studied at present, strongly influence the properties and biological activity of chitosan-based materials.

One of the most effective ways of varying the characteristics of various polymers is to create composites based on them. In this paper, chitosan-based composite materials with nanoscale hydroxyapatite (HA) are studied. HA, the mineral component of bone, is absolutely harmless to a living organism non-toxic polarizable material. HA is a crystalline form of calcium phosphate with either monoclinic or hexagonal crystal symmetry. The stoichiometric formula of HA is $Ca_5(PO_4)_3(OH)$, although the crystal structure can exist in a wide range of nonstoichiometric compositions. The chemical composition of HA can be widely varied by partial substitution by other ions of calcium, phosphate, or hydroxyl at their positions in the crystal lattice. The hydroxyl groups form linear columns along the crystallographic c-axis that give rise to the dielectric properties of HA, including high temperature proton conductivity,

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ferroelectricity, piezoelectricity, pyroelectricity and electret behavior. Hydroxyapatite is the primary mineral component of bone tissue, and the osteoconductive properties of synthetic HA have led to its widespread use as coating or additive in bone grafts, scaffolds, and orthopedic implants. It has been shown that electrical polarization of HA enhances bioactivity and osseointegration, both *in vitro* and *in vivo* (Nakamura, Kobayashi, Nakamura, & Yamashita, 2009; Toda & Monma, 2009; Kumar, Gittings, Turner, Bowen, Bastida-Hidalgo, & Cartmell, 2010).

Generally, a surface with net positive or negative charge, compared to neutral one, is expected to be more hydrophilic, facilitating interfacial processes and protein adsorption (Boyan, Hummert, Dean, & Schwartz, 1996). Furthermore, surface charge has been shown to increase osteoblast adhesion and early stage bone mineralization at the bone-implant interface with two main mechanisms suggested for surface charge's positive affecting of materials' osseointegration: by forming an apatite layer (adsorbing Ca^{2+} and ${PO_4}^{3-}$) and by adsorbing certain types of proteins with desirable reactions with bone-forming cells (Shelton & Davies, 1991; Guo, Matinlinna, & Tang, 2012). Thus, surface charge modification of bone scaffold materials is a promising new direction for improving their biological properties and performance. Although it is a relatively new approach, it has been rapidly gaining attention, with a lot of research focusing on effective and practical techniques that create a long-lasting electric field on the material surface. All applied methods can be roughly categorized in two main groups: chemical modification of the surfaces, producing charged groups along them with one predominating polarity (Hoven, Tangpasuthadol, Angkitpaiboon, Vallapa, & Kiatkamjornwong, 2007), and physical methods, producing electret materials – quasi-permanently polarized and having accumulated surface charge of opposite polarity on two opposite sides (Sessler & Gerhard-Multhaupt, 1999). One of the physical surface charge modification methods for obtaining electrets is the corona discharge treatment (also known as air plasma treatment) of the materials (Yovcheva, 2010), a surface modification method that utilizes a low temperature corona discharge plasma, generated at a sharp tip electrode with the application of high voltage, to impart changes in the properties of a surface.

Several works are devoted to the preparation of electret chitosan films and the study of their biological properties (Wang et al., 2010; Wang et al., 2012). Chitosan electret membranes exhibit stable surface charges, with good bioactivity and biodegradability. Wang et al., (2010) studied the effects of chitosan bioelectret membrane on bone regeneration in a rabbit cranial defect model. The bioelectret was fabricated by film casting and polarized by grid-controlled corona charging (−1 kV). The bioelectret membrane recipients had a significantly higher volume of newly formed bone and greater rate of material degradation than the non-polarized membrane recipients. Furthermore, the bioelectret membrane induced new bone formation not only around the host bone but also in the center of the defect. Chitosan bioelectret membranes have been shown to have an apparent potential for guided bone regeneration applications. Additionally, some data suggest that chitosan surfaces, that have been chemically modified to be positively or negatively charged, can increase protein adsorption on the material surface, explained in terms of electrostatic attraction and repulsion, and, as a result, mediate cell-scaffold interactions and improve cell adhesion (Hoven et al., 2007).

There is some data published on dielectric/impedance spectroscopy and related methods of chitosan materials in the form of films. Bobritskaya, Castro, & Temnov, 2013; Bobritskaya, Kubrakova, Temnov, & Fomicheva, 2013 investigatad chitosan polymer films by dielectric and thermally activated spectroscopy. The same authors studied chitosan films with a mineral filler by dielectric spectroscopy, showing that the conductivity of the biopolymer decreases with the addition of filler particles. In the work of Atif Islam et al. the effect on conductivity of chitosan-silane crosslinked-poly(vinyl alcohol) blended films due to change in the concentration of PVA and temperature was investigated by impedance spectroscopy and showed good conductance properties. The ionic conductivity of the films initially increased with the increase in temperature for all synthesized samples, which showed an increase in the number of effective charge carriers, and decreased at a specific higher temperature for each film. Murugaraj, Mainwaring, Tonkin, & Al Kobaisi, 2011 studied the hydration of chitosan films by dielectric spectroscopy in a conventional constraining plate configuration and did comparison with free standing films. In the study of Zhao and Asami, (2002) the dielectric properties of chitosan microsphere beads in aqueous electrolyte solutions were investigated in the 1–500 MHz frequency range. Distinct dielectric relaxation was observed around 10 MHz in weakly acidic solutions (pH 4–6) and the relaxation intensity depended on the electrolyte concentration. Using the relatively nondestructive electrochemical impedance spectroscopy method, that also can be performed under physiologically relevant conditions, some authors were able to obtain data on pore characteristics of chitosan materials comparable to that of scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP), two commonly used methods for scaffold characterization which require dry samples and vacuum conditions for measurement (Tully-Dartez, Cardenas, & Ping-Fai, 2010).

Much more research has been done on surface charged HA and HA-based materials. Electric and dielectric properties of HA can be influenced significantly by the orientation of OH^- ions in HA crystals. Fu et al. (2015) demonstrate that hydroxyapatite retains surprisingly large stored charge when synthesized electrochemically from aqueous solution. Some publications describe the production of surface-charged HA by polarization by proton transport under DC fields in the order of few kV/cm at high temperatures (200–400° C), where large surface charges can be induced. The surface-charged HA scaffolds have shown a significantly increased osteoblast adhesion, cell proliferation and metabolic activity compared to non-charged controls and performed much better in *in vitro* and *in vivo* tests, accelerating new bone formation (Tarafder, Bodhak, & Bandyopadhyay, 2011; Bodhak, 2009; Dekhtyar, Polyaka, & Sammons, 2008; Itoh, Nakamura, Kobayashi, Shinomiya, and Yamashita, 2006; Itoh, Nakamura, Kobayashi, Shinomiya, Yamashita, & Itoh 2006). The study of the electric and dielectric properties of HA, to big extent by dielectric/impedance spectroscopy and related methods, has also been of interest for a number of potential applications, including bone grafts (Gittings et al., 2009; Zakharov, 2001). Importantly, HA materials exhibit piezoelectric and pyroelectric properties (Gittings et al., 2009; Tofail, Baldisserri, Haverty, McMonagle, & Erhart, 2009; Baxter, Turner, Bowen, Gittings, & Chaudhuri, 2009), just as bones do, and which are important in bone growth and remodelling (Telega & Wojnar, 2002; Fukada, 1981). Electric and dielectric properties of HA have also been studied in regard of materials' interaction with electrical fields applied to improve fracture healing and enhance bone growth (Gittings et al., 2009).

A lot of studies have examined the electrical and dielectric properties of HA and HA-based materials (Horiuchi et al., 2013; Horiuchi et al., 2014). However, the studies of dielectric characteristics of chitosan/HA composites are virtually absent. There are only scarce reports about obtaining electret composites. Nakamura et al. (2010) evaluated the effects of composite wound dressing films made of silk fibroin (SF) containing hydroxyapatite (HA) or polarized HA (pHA) powders on endothelial cell (EC) behaviors that have important roles in the wound-healing process. In the investigation of Qu et al. (2014), chitosan/nanoHA electret membranes with negative charges were fabricated by grid-controlled constant voltage corona charging. In this study chitosan/nHA membranes

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