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Influence of chitin nanocrystals on the dielectric behaviour and conductivity of chitosan-based bionanocomposites

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ABSTRACT

A series of bionanocomposite films based on chitosan, reinforced with chitin nanocrystals, were developed, and assessed in terms of dielectric behaviour and conductivity by using an experimental methodology that allows avoiding the conductivity contribution and the exclusion of contact and interfacial polarization effects. The dielectric relaxations at low and high frequency and temperatures were modeled by Havriliak-Negami functions. Below the glass transition temperature (Tg), the γ and β relaxations were observed, which were related to intramolecular and non-cooperative segmental movements. At higher temperatures, an intermolecular and co-operative macromolecular movement, related to the glass transition, gave rise to α-relaxation. In addition, two over-Tg ρ_I and ρ_{II} relaxations were found, which were related to the displacement of dipoles in the disordered structure of bionanocomposites. The addition of chitin nanocrystals did not affect the apparent activation energy *Ea* of the γ-relaxation. However, it decreased the *Ea* of the β-relaxation and increased the free volume at temperatures in the vicinities of the α-relaxation. Finally, the electric conductivity of the bionanocomposites was lower than that of neat chitosan and chitin due to the interaction between the −OH and $-NH_2$ groups that reduced the ionic mobility, along with the increase of free volume, with the subsequent separation of phases.

1. Introduction

The biomass-derived materials are suitable for their use in many applications as a consequence of their biodegradability properties, biocompatibility, high availability and low cost, which makes them interesting for many industries. Materials from natural resources are hence developed in order to replace the petroleum-based ones by means of using products such as cellulose, starch, lignin, chitosan, chitin, among many other biopolymers, a mixture of these and composites with the aim of optimizing the long-term properties of the final material [1].

Within biomass polymers, chitin can be found in different living systems as crustacean shells, insect cuticles and cell walls of fungi, yeast and green algae [2]. This polymer, considered the second most abundant biopolymer on earth after cellulose, is composed of *N*-acetyl-2-amido-2-deoxy-D-glucose units linked by β(1–4) bonds [3,4]. Chitin nanostructures, obtained by chemical or mechanical treatments, are increasingly considered as suitable building blocks for the design of functional bionanocomposite materials, owing to their nanosized dimensions and unique rod-like or fibrous structure. Their unique properties – such as their extremely small size, low density, chemical stability, biological activity, and non-cytotoxicity-, make them excellent candidates for use in extensive applications [5–10].

Chitosan is the major and simplest chitin derivative, also with a high-molecular-weight linear polymer obtained by deacetylation of chitin. While chitin lacks of solubility in the most common solvents, the advantage of chitosan is its capacity to be dissolved in diluted aqueous solutions with $pH < 6.5$ [4]. In this sense, it has been blended with polymers such as poly(acrylic acid) [11], poly(vinylidene fluoride) [12] or poly(vynily alcohol) [13], as well as composited with fillers such as montmorillonite [14], carbon nanotubes [15], nanosilica [16], silver triflate [17], sodium triflate or alumnia [18].

The design of biocomposites based on chitin and chitosan therefore represent a unique resource. On the one hand, matrixes, fillers and biocomposites could be fabricated at the same place, with low environmental impact due to transport of raw materials. On the other

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hand, their residues could be easily managed without the usual difficulties of sorting or dismantling, since they have the same chemical nature. As a whole, the chitosan/chitin bionanocomposites can be ecodesigned from a cradle-to-cradle perspective [19,20]. In this line, the preparation of specific bionanocomposites based on chitosan matrix reinforced with chitin nanocrystals and whiskers has been proposed [21–23]. A general improvement of the thermal stability, mechanical stiffness and antifungal activity of the biocomposites has been shown as a function of the presence of chitin nanocrystals [23].

Chitin–based materials are useful to prepare scaffolds, hydrogels and wound dressings, as adsorbents in industry, water purification, for protein immobilization, transformation of bacteria by exogenous genes, stabilization of oil-in-water emulsion and nematic gels, formation of $CaCO_3$/chitin-whisker hybrids and as carbon precursors [24]. In the field of composites, chitin nanocrystals and nanofibres have been reported to reinforce biocomposites of different matrixes such as poly (lactic acid) [25–27], thermoplastic starch [28], chitosan [23] or carrageenan [29] and as poly(vinyl alcohol) [30] among other. The use of chitin and chitosan actually stand up as a promising bioplastic alternative within the tendency of eco-design of materials [31]. There is a challenging area of innovation to the use of these bio-nanocomposites as in packaging for smart applications or, in the field of low temperature direct alcohol fuel cells, the preparation of membranes as polyelectrolyte. Among its advantages, it is worth mentioning its low-cost and eco-friendly nature; its hydrophilicity to perform at high temperatures and low relative humidity conditions; low permeability to alcohol molecules; and high capacity of functionalisation, due to the chemical $-OH$ and $-NH_2$ groups present in its structure [31]. For these applications, an exhaustive characterization of dielectric and conductive properties is necessary during the design of these materials [32].

Concerning the identification of dielectric relaxations, *Viciosa* et al. analysed the macromolecular motions of wet and annealed chitosan by dielectric spectroscopy and found two Arrhenius-like β-relaxation, related to the interaction of $-NH_2$ with water and the migration of conductive species, in an increasing temperature order [33]. These analyses were performed without a conductive barrier and the molecular relaxation masked by the conductive deviation could not be observed. *Gonzalez-Campos* et al. proposed a mathematical methodology to suppress the contribution of the direct current (DC) conductivity and interfacial polarization effects, and found in addition a VFTH-like α-relaxation, correlated with the glass-rubber relaxation [34]. In the present work, a methodology to suppress the masking effect of the DC conductivity is carried out experimentally in the sample electrode assembly, which permits a deeper identification of dielectric relaxations. Thus, the focus of the present work was to correlate the relative amount of chitosan and chitin nanocrystals in the bionanocomposites in terms of dielectric and conductive properties. This study might contribute to optimise the knowledge about the success of chitin nanocrystals in the elaboration of proper bionanocomposites for a broad range of applications.

2. Experimental procedure

2.1. Materials

The bionanocomposite materials studied in this work was elaborated using *Cervimunida Johni* lobster as raw material for the extraction of chitin (CHNC, DA = 95 ± 3%) and chitosan (CS, DA = 10 ± 3%) materials. Chitosan-chitin nanocrystals (CS/CHNC) bionanocomposite films were prepared by solvent/evaporation technique. First 1% CS solutions in acetic acid were prepared and filtered to eliminate any residues of chitosan powder. Then, three different amounts of CHNC were added in each solution and stirred during 30 min at 20.000 rpm until homogeneous mixture, as reported in a previous work [23]. The bionanocomposites were labelled according to the CS:CHNC proportion, as follows: CS/CHNC0.5 for a 1:0.5 (33.33% CHNC), CS/CHNC1 for 1:1(50% CHNC) and CS/CHNCS for a 1:2(66.66% CHNC). The formulations were poured into acrylic plates and the solvent was evaporated in a ventilated oven over night at 30 °C. All films were kept in a desiccator containing allochroic silica gel at room temperature for 1 week prior to any test.

2.2. Dielectric and conductivity measurements

The dielectric spectra (DS) of the samples were obtained using an Alpha mainframe frequency analyser in conjunction with an active cell (Concept 40, Novocontrol Technologies BmgH & Co. Kc, Hundsangen, Germany). The sample electrode assembly (SEA) consisted of two stainless steel electrodes filled with the neat polymers and bionanocomposites. The methodology to prepare the SEA was directly placed in the cell a sandwich with a Teflon™ film of (132 μm thick) inserted as blocking layer between the sample and one electrode. The sample/Teflon™ sandwich is a Maxwell-Wagner-Sillars [37–39] layer capacitor, which suppresses the direct current and avoids at low temperatures the dipole motion and the charge accumulation at the electrode interface [40–42]. It has been found that the dielectric response of the Teflon™ film is approximately 100 times less than the response of the studied bionanocomposites.

The diameters of the electrodes were 20 mm and the thickness was kept around 300 μm. The relative response was measured under isothermal conditions in the frequency range $f = 10^{-2} – 10^6$ Hz, at temperatures of −150 °C to above melt temperature, controlled by the Quatro system (Novocontrol Technologies, Germany) by increasing steps of 10 °C under inert nitrogen atmosphere and using liquid nitrogen as coolant.

The complex conductivity was analysed by means of the same experimental set with a sample electrode assembly (SEA) consisting of two stainless steel electrodes filled with the neat polymers and bionanocomposites without Teflon™, at a frequency range of $f = 10^{-2}$ - 10^7 Hz under isothermal conditions at temperature of 298 K under inert nitrogen atmosphere.

2.3. Thermal properties

The thermogravimetric and calorimetric properties were carried out by means of a TGA/SDTA 851 and a DSC822^e Mettler Toledo instruments, respectively. The thermogravimetric scans were performed heating at a constant rate of 10 °C·min^{-1} from 25 °C to 900 °C under a nitrogen atmosphere of 20 mL min^{-1}. The calorimetric first and second heating scan were performed in a semi hermetic-pan from −50 to 200 °C with a heating rate of 5 °C·min^{-1} under a nitrogen atmosphere.

2.4. Structural analysis

The crystallinity index was measured from the X-ray diffraction patterns obtained with a Philips Pert Pro automatic diffractometer using Cu-Kα radiation (operating at 40 kV and 40 mA) over the angular range of 5–70° 2θ (step size = 0.04 and time per step = 353 s) at room temperature. The crystallinity index of nanocomposite films were calculated using equation (1)

$$C.\ I.\ (\%) = [(I110 – Iam)/I110]\ X\ 100 \tag{1}$$

where I_{110} is the maximum intensity (arbitrary units) of the 110 crystallographic plane and I_{am} is the amorphous portion diffraction, which usually is found about 2θ = 12.5°–13.5°

3. Results and discussion

3.1. Phenomenological description of dielectric relaxations

The dielectric behaviour of chitosan CS, chitin nanocrystals CHNC