Impedance spectroscopy characterization of relaxation mechanisms in gold–chitosan nanocomposites

Alexandra Neagu [a,b], Lavinia Curecheriu [a,*], Mirela Airimioaei [a], Ana Cazacu [c], Adrian Cernescu [d], Liliana Mitoseriu [a,*]

[a] Department of Physics, Al. I. Cuza University, Bd. Carol I, no. 11, Iasi 700506, Romania
[b] Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
[c] Department of Sciences, "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine, 3, M. Sadoveanu Alley, 700490 Iasi, Romania
[d] Center for NanoScience (CeNS), Faculty of Physics, Ludwig-Maximilians-Universität, Geschwister-Scholl-Platz 1, 80539 Munich, Germany

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ABSTRACT

Au–Chi nanocomposites with different AuNPs additions were investigated. The dispersion of AuNPs in polymer matrix was observed using s-SNOM analysis. The dielectric properties as a function of temperature show two relaxation processes: (1) a primary α-relaxation process, at low temperatures; (2) a second low frequency relaxation at temperatures between 70 °C and 150 °C identified as the σ-relaxation often associated with short range ion mobility. In nanocomposite films, the σ-relaxation process overcomes the α-relaxation process so that the glass transition is no longer detected. The dielectric nonlinear properties (tunability) shown an increase of dipolar moment with AuNPs additions and this results are in good correlation with matrix modification in FTIR investigation.

1. Introduction

The recent advances in flexible and green electronics led to an intense research activity in the area of multifunctional flexible materials [1]. The main requirements are related to the obtaining of inexpensive, flexible, environmentally friendly and light-weighted electronic components. These types of electronic components can be used in a large number of applications such as: energy storage devices, radiofrequency sensing platforms, actuators, biosensors, wearable healthcare devices, and flexible antennas for wireless applications [2]. The mechanical and electrical requirements of flexible electronic devices can be achieved using Polymer Matrix Composites (PMCs). The idea of any composite is to combine the best properties of its constituent phases, so that enhanced or even new properties to be generated. Polymers are appealing as matrices due to their flexibility, high dielectric strength, low cost and easy processing. Their major drawback for electronics applications is their low value of permittivity. However, using different types of fillers, such as ferroelectric [3–5] or conductive [6–8] nanoparticles (NPs), a significant increase in permittivity values can be obtained.

The combination of metallic NPs-polymer matrix, attracted recent interest for low-cost flexible electronics with potential use in a large number of applications such as: supercapacitors, sensors, flexible non-volatile memories, optoelectronics, and electromagnetic shielding [9].

Chitosan (Chi) is a good option as polymer matrix due to its biodegradability, biocompatibility, non-toxicity, easy processing into the shape of membranes and films and high flexibility at room temperature [10]. Additionally, it should be highlighted that chitosan possesses several polar groups (OH, NH_2) in its molecular structure that makes it a good candidate for non-linear dielectric properties, *i.e.* a permittivity-field $\varepsilon(E)$ dependence, as demonstrated in a previous work [11,12]. As conductive filler, gold (Au) NPs were chosen, due to the high electrical conductivity of the order of 10^6 cm^{-1} Ω^{-1}. Even though gold is slightly less conductor than copper or silver, it is preferred to the other two conductors because is less reactive and thus, less likely to corrode or oxidize. Other appealing properties of Au NPs are their biocompatibility, non-toxicity and the ability to be readily bound to a large range of biomolecules, such as polysaccharides, amino acids and proteins/enzymes [13–17]. As demonstrated in our previous study [11], the combination gold–chitosan (Au–Chi) composites are expected to show an increased effective permittivity by comparison with the matrix, while maintaining relatively low dielectric losses. To use such composites in real device structures, their low and high field dielectric properties at various frequencies and temperatures need to be investigated.

* Corresponding authors.

The aim of the present study is to investigate the temperature dependence and different relaxation mechanisms of Au–Chi nanocomposites by means of Impedance Spectroscopy (IS) technique. The low and high field electrical properties are discussed in correlation with microstructural data revealed by scattering scanning near-field optical microscopy (s-SNOM) analysis and by FTIR investigations of Au–Chi thin films.

2. Materials and experimental procedures

Au–Chi nanocomposites have been prepared by using the dry phase inversion method [11], in which acetic acid (CH_3-COOH), chloroauric acid ($HAuCl_4 \cdot 3H_2O$) and chitosan (75% N-deacetylation degree, 263 836 g/mol average molecular weight and 2.70 polydispersity index) were used as raw materials. More details on the preparation procedure were given elsewhere [11]. Films with different Au concentrations (ranging from 0.0% to 2.5%) and uniform Au NPs volume distribution were obtained by stirring and heating precursor solutions in an ultrasonic field of 20 kHz with amplitude of 50%, for 10 min, using a Sonoplus Bandelin device. The samples are denoted as following: Chi 0 (pristine chitosan), Chi 1.5, Chi 2.0 and Chi 2.5 which corresponds in the final composite film Au volumic fractions.

To determine the sample morphology and the AuNPs distribution inside the Chi films, a commercial s-SNOM (NeaSNOM, neaspec.com) employing a sharp metalized tip (NanoWorld) externally irradiated by the focused beam of a CO_2 laser (emission frequency is set to a wavelength of 11.2 μm) was employed. Efficient suppression of background light is achieved by vertical tip oscillation (40–50 nm amplitude) at the cantilever's mechanical resonance frequency $\Omega \sim 250$ kHz and demodulation of the detector signal at higher harmonics Ω. In order to determine how AuNPs bond to the chitosan matrix, FTIR analyses were carried out at room temperature, using a Bruker Tensor 27 FTIR Spectrometer. The FTIR spectra were recorded in the range of 4000–500 cm^{-1}. For the electrical measurements, Ag electrodes were used in order to ensure a good electrical contact. The complex impedance spectra, in the frequency range of 20–2 × 10^6 Hz and at different temperatures between (20–150 °C), were determined using an impedance bridge Agilent E4980A Precision LCR Meter. The high field tunability $\varepsilon(E)$ was determined using a circuit fed by a high dc voltage from a function dc-generator coupled with a TREK 30/20A-H-CE amplifier [18] superimposed on a small ac testing voltage (1 V), with a frequency of 3 × 10^4 Hz.

3. Results and discussions

3.1. Morphology investigations

Simultaneously recorded AFM and IR near-field images directly show a homogeneous distribution of AuNPs inside the chitosan matrix compared to the pure polymer film (Fig. 1). The average height of the AuNPs above the film level is around 15 nm. Broadening effects of the particles lateral size can be observed in topography as indication of a chitosan covering layer. The AuNPs distribution can be also observed according to the optical contrast determined with spatial resolution ≈20 nm. Specifically, the scattering amplitude signal demodulated at the third harmonic of the tapping frequency of the tip is related to the local value of the complex dielectric function $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ of the sample. The amplitude of the scattering signal is expected to increase in metallic regions compared with that in the insulating areas [19]. In the same time, the signal intensity scales with the polarizability $\alpha = r^3(\varepsilon - 1)/(\varepsilon + 1)$ of the particles like the scattered field from isolated spheres [20]. Such combined effects lead to a dark contrast on the NPs
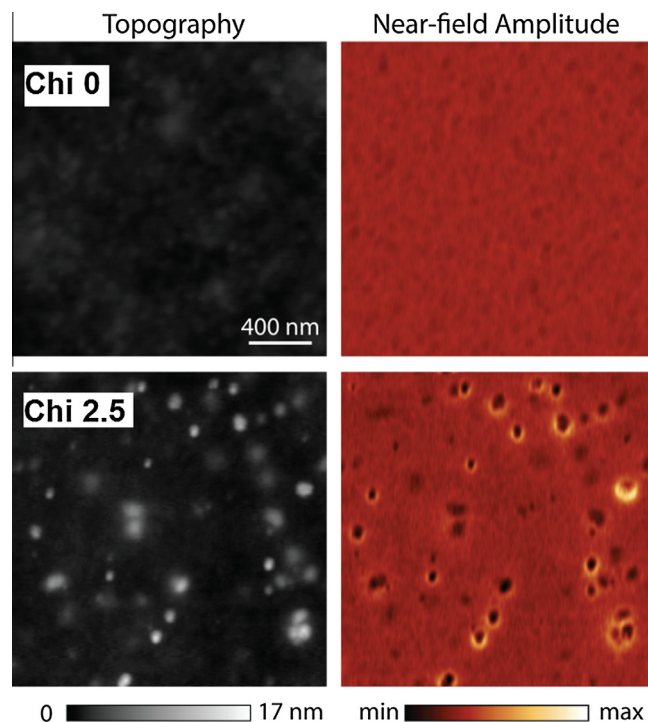

Fig. 1. s-SNOM images (2 × 2 μm²) of pure Chi and Au–Chi composite films. In the left side is presented the topography, and in the right side the backscattered IR amplitude recorded at 3rd order demodulation frequency.

surrounded by a bright rim showing a change in the local dielectric function of the AuNPs and increase concentration of the collective free-carrier oscillations (plasmons).

3.2. FTIR spectra of Chi and Au–Chi nanocomposites

Fig. 2 shows the FTIR spectra of Chi and Au–Chi composite films. The spectrum of the Chi 0 shows a broad and unstructured band at 3650–3000 cm^{-1} attributed to the superposition of O—H and N—H stretching vibrations, and peaks at 2876, 2130, and 1062 cm^{-1} ascribed to C—H, C—NH$_2$, and C—O stretching vibrations,

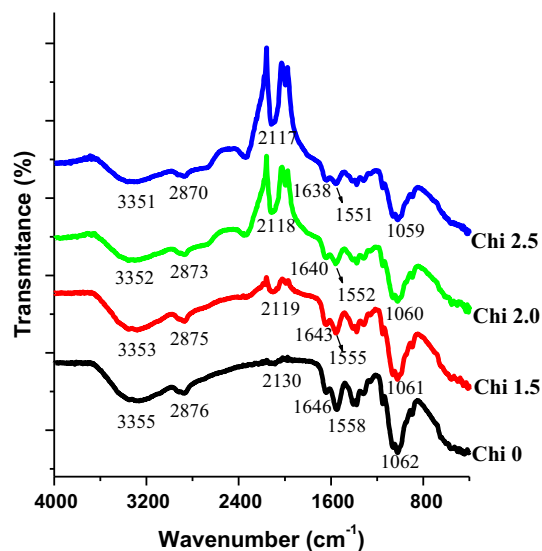**Fig. 2.** FTIR spectra of pristine Chi and Au–Chi nanocomposites with different Au concentrations.