

Dynamic mechanical and dielectric relaxation behavior of chitosan films: influence of water content

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Introduction

Chitosan is an N-deacetylated polysaccharide derived from chitin and it is widely used for biomedical applications, tissue engineering, controlled drug delivery, biotechnology, and food industry. Its widespread use is due to its biocompatibility and solubility in acidic aqueous media. In addition, the modification of chitosan may be a convenient and effective method to obtain new materials for practical utilization.

Chitosan is a semicrystalline polyssacharide that contains a considerable amorphous fraction. An important parameter of the amorphous state is the glass transition temperature T_g which plays important role in the development of new composite materials based on chitosan. In polymers, above T_g , the bonds between the polymer chains become weak in comparison to thermal motion, and the polymer becomes rubbery. This change leads to large changes in some physical properties, such as density, specific heat, mechanical modulus, dielectric constant, etc.

In the literature exists a large controversy about the value of a glass transition temperature in chitosan. Using several techniques including differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) reported elsewhere [1-5], the values of T_g vary from 30 to 203°C, while other works [6, 7] have not observed a glass transition.

Another problem in the investigation of chitosan's properties is a strong influence of water content. The presence of water can distort significantly the relaxation processes in polysaccharides, giving rise to an additional relaxation process [9].

The aim of this work is to investigate the relaxation phenomena occurring in chitosan using DMTA and dielectric spectroscopy as a function of the water content.

Experimental

Chitosan (89 % of degree of deacetylation) films with thickness of 30 μm were obtained by dissolving 1 wt % of chitosan in a 1 wt % aqueous acetic acid solution. Films were prepared by the solvent cast method by pouring the solution into a plastic Petri dish and allowing the solvent to evaporate at 60°C. Because of the films preparation technique, the chitosan have the amino side group protonated (NH_3^+ groups), therefore the films need to be neutralized. The films were immerse into a 0.1 M NaOH solution during 30 min and washed with distilled water until neutral pH. A thin layer of gold was vacuum-deposited onto both film sides to serve as electrodes.

Free water content was determined by thermogravimetric analysis (TGA) using a Mettler Toledo apparatus with heating rate 5°C/min.

DMTA measurements were carried out using RSAIII, TA Instruments with a heating rate of 5°C/min at a frequency of 0.1 Hz, in an atmosphere of dry air. These conditions were the same as those for TGA measurements.

The dielectric measurements in the frequency range from 0.1 Hz to 110 MHz were carried out using a Solartron and Agilent Precision Impedance Analyzer 4294A in the vacuum cell.

Results and discussion

Fig. 1a shows the thermogravimetric results for the three types of samples: 1. *as prepared*, 2) annealed during the first temperature scan at 75°C, and 3) annealed at 150°C followed by cooling to 30°C, in the TGA system in a dry air atmosphere, and then a second temperature scan up to 150°C is performed. The amount of free water may be evaluated by the decrease of sample weight during the second heating

scan. According to the results obtained, *as prepare* films have free water content about 11.1%. Water content for films annealed to 75°C and 150°C are about 5.5% and 1.2% respectively.

Using the same annealing methodology and measurements condition in the DTMA and TGA measurements, we can monitor the water content in all samples.

Figs 1b, 1c, and 1d show the temperature dependence of the $\tan \delta$ (black points – experimental data, red lines–results of fitting, green lines–peak position found from fitting procedure) obtained from DTMA measurements at the samples described above. Chitosan films exhibit three $\tan \delta$ peaks at positions around 86-102°C (which dependent on free water content), 188°C and 293°C, respectively.

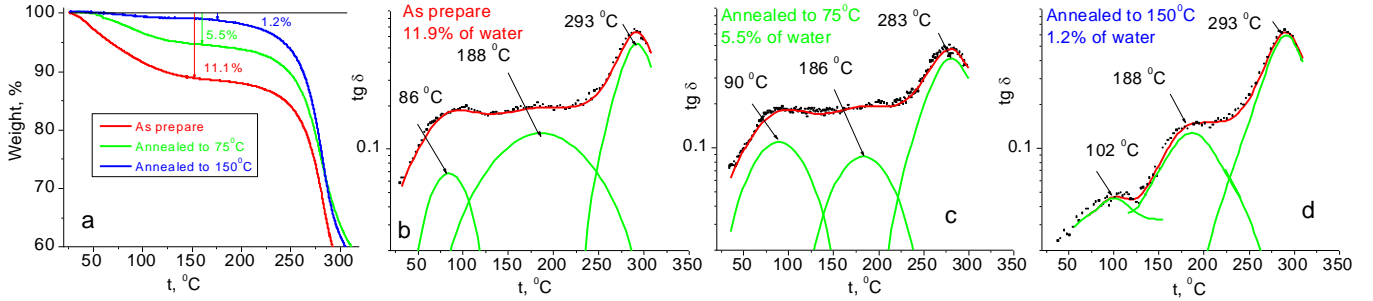


Fig. 1 a) Termogravimetric analysis; temperature dependence of $\tan \delta$ of chitosan films: b) *as prepare*; c) annealed at 75°C; d) annealed at 150°C.

The first peak at 100°C has been reported, by DTMA measurements, in refs. [9, 10], but there is no theoretically sound explanation and relation to water content. Also references [11, 12] claim this peak has been attributed to the glass transition temperature, which shifts to lower temperatures with increasing moisture content [12]. Our study focuses on the above same properties to investigate sample response to water content (Fig. 1).

The peak in the $\tan \delta$ curve at 150-190 °C has already been observed in refs. [2, 3, 9, 13] and it has been designated as a glass transition relaxation which is related to the molecular motion in the amorphous region.

The peak at around 293°C and a second weight loss at the TGA measurements begins at 240°C pointing out the degradation process (this value is closely related to degradation temperature as reported in the literature for chitosan [2-4]).

In summary DTMA measurements alone do not allow a direct interpretation about the nature of relaxation process in chitosan films as a function of water content. Additional dielectric spectroscopy measurements are needed to fully characterize relaxation process in chitosan films.

Fig. 2a shows the complex impedance spectra of chitosan films. These spectra show three different behaviors: 1) a typical semicircle at “high” frequencies, which corresponds to the bulk material properties; 2) a straight line in the low frequency range, which relates to the contacts effects, and 3) interfacial Maxwell-Wagner-Sillars polarization effects, signaled as a “bulge” on the semicircle. For further consideration in the analysis, we take in account only a so-called depressed semicircle that does not include contact and interfacial polarization effects.

Due to large conductivity contribution in the low frequency range, the dc correction must be applied to samples. This dc conductivity strongly modifies the dielectric loss factor ϵ'' on the low frequency side. In this case the ϵ'' can be expressed as $\epsilon'' = \epsilon''_{exp} - \sigma_{dc} / \omega \epsilon_0$, where ϵ''_{exp} is the experimental loss factor value, σ_{dc} ($\sigma_{dc} = d / (R_{dc} S)$), R_{dc} is direct current resistance which has been obtained from the intersection of the “high” frequency semicircle and the real-part axis on the impedance plane (as shown in Fig. 2a).

After dc correction two different relaxations can be identified through a simple Cole-Cole plot diagram (ϵ'' versus ϵ' , Fig. 2b). These two relaxations are recognized by two well-resolved semicircles at low (10^0 - 10^3 Hz) and high frequency (10^4 - 10^8 Hz). The fitting of the complex permittivity in samples were carried out using Cole-Cole empiric correlation [15] as follows:

$$\epsilon^* - \epsilon_\infty = \frac{(\epsilon_s - \epsilon_\infty)}{[1 + (j\omega\tau)^{1-\alpha}]},$$

where ϵ_s and ϵ_∞ are limiting values for low and high frequency (intersections with $\epsilon' = 0$ axis), τ is the mean relaxation time, α is the constant phase element (CPE) power. The CPE is an empiric impedance

function with impedance $Z_{CPE} = A(j\omega)^{-\alpha}$, where A is the CPE constant, α is the CPE power. The two semicircles are separate in the frequency range which makes it possible to fit and investigate low- and high-frequency relaxation processes independently (green lines on Fig. 2b).

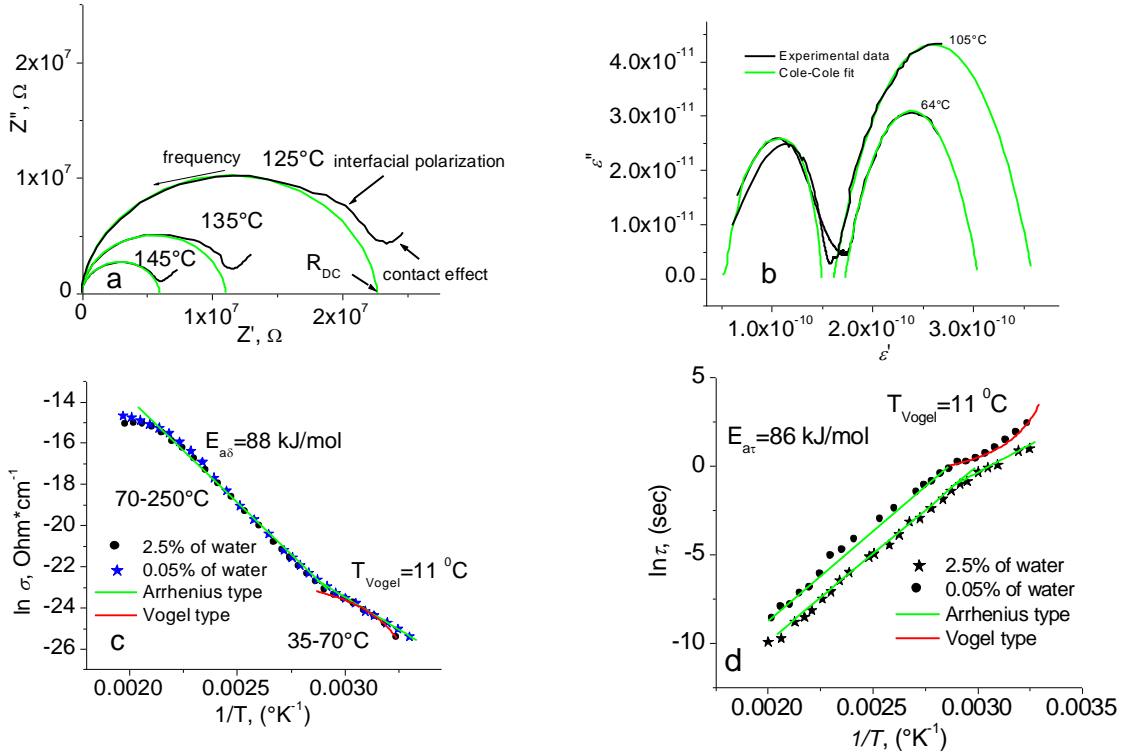


Fig. 2. a) Impedance spectra of chitosan; b) Cole-Cole plots (the data were corrected for dc conductivity contribution); c) dc conductivity vs $1/T$; d) low frequency relaxation time vs $1/T$, obtained using the Cole-Cole model for samples with water contents indicated on Figs.

In the high frequency region (10^4 - 10^8 Hz) for all chitosan films a secondary relaxation process is identified with Arrhenius-type dependence of the relaxation time as a function of $1/T$ and activation energy equal 46 kJ/mol (which do not depend on the water content). This relaxation process can be related to side-group motions by means of the glucosidic linkage and is called β -relaxation. The activation energy values calculated from dielectric measurements is in excellent agreement with reported in the literature [14].

The most interesting results have been obtained in the low frequency range (dc- 10^3 Hz). Fig. 2c shows dependence of dc conductivity versus $1/T$ and low frequency relaxation time (Fig. 2d) obtained using the Cole-Cole model. These dependencies can be analyzed in two different temperature ranges, the "low temperature relaxation" from 20 to 70°C and the "high temperature relaxation" from 80 to 240°C.

The low temperature relaxation is highly affected by water content. In the film with water content about 3%, a non-Arrhenius behavior appears in both conductivity and relaxation time dependencies versus $1/T$, which can be described by the Vogel-Fulcher-Tammann (VFT) equation:

$$\sigma = \sigma_0 \exp\left(-\frac{DT_0}{T-T_0}\right), \quad \tau = \tau_0 \exp\left(\frac{DT_0}{T-T_0}\right),$$

where σ_0 and τ_0 are the pre-exponential factors, D is material constant and T_0 is the so-called Vogel temperature. This non-linear dependence has the typical α -relaxation behavior also called dynamic glass transition [15]. In many polymers T_0 is usually 50°C lower than glass transition temperature T_g [13]. In the present study the $T_0 = 11$ °C have been obtained. Once a T_0 is calculated, a T_g value, for neutralized chitosan, is ca. 61 ± 10 °C. This value correlates well with DMTA results (the first peak has been obtained at the position dependent on free water contents between 86 and 102°C). As explained above, it has been reported in literature [16], that for many polymers, mechanical relaxation processes are observed at temperatures 10 ± 15 °C higher than the corresponding dielectric relaxation. This is in part because

dielectric spectroscopy is sensitive to fluctuations of dipole moments and mechanical relaxation monitors the fluctuations of internal stresses.

In annealed samples at 150°C (water content < 0.05%), this low temperature relaxation vanishes. For the temperature range 80-220°C both conductivity and relaxation time measurements show an Arrhenius-type behavior (Figs. 2b and 2c) for all water contents with activation energy 86-88 kJ/mol. These values are in good agreement with previous reports for neutralized and non neutralized chitosan and for other polysaccharides [14]. This process is associated with the hopping motion of ions in the disordered structure of the biomaterial and is called σ -relaxation [14].

Results obtained from dielectric spectroscopy measurements allow to conclude that the second peak in the $\tan \delta$ curve with position (near 188 °C) relate to σ -relaxation which does not depend on the water content.

A change in the slope at 240°C and above denotes as third peak in DMTA measurements can be relate to the beginning of material degradation.

Conclusions

The dielectric and dynamic mechanical behaviors of neutralized chitosan films have been investigated as a function of water content. On this basis the glass transition temperature was obtained in the range 86-102°C which shifts to higher temperature with decreasing moisture content and the glass transition vanishes in a dry material. A second low frequency relaxation was observed from 80°C to the onset of thermal degradation (240°C) and identified as the σ -relaxation often associated with proton mobility. This relaxation exhibits a normal Arrhenius-type temperature dependence with activation energy of 86-88 kJ/mol and it is independent of water content. In the temperature region between 240-300°C have been observed relaxation process which corresponded to the beginning of the degradation.

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