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ORIGINAL CONTRIBUTION

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Influence of water on the dielectric behaviour of chitosan films

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Dedicated to Prof. F.J. Baltá-Calleja
on the occassion of his 60th anniversary

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Abstract The dielectric properties of chitosan films with a degree of deacetylation of 86% have been investigated in the frequency range of 10^3–10^6 Hz covering a broad range of temperatures from -150 to 150 °C. The variation of the dielectric properties with temperature has been associated with two dielectric processes: (a) a local relaxation attributed to the presence of hydrogen-bonded water appearing at low temperatures (b) a conduction process related to water molecules which becomes desorbed upon heating at $T > 80$ °C. Isothermal dielectric experiments have been performed in order to follow, in real time, the occurrence of both, the water sorption and desorption processes.

Key words Dielectric relaxation – water sorption – natural polymers – chitosan

Introduction

Chitosan (poly-$\beta(1 \rightarrow 4)$-2-amino-2-deoxy-D-glucose) is a polysaccharide which can be considered as a *N*-deacetylated derivative of chitin. After cellulose, chitin is the second most abundant natural polymer. Chitin can be extracted from the shell of lobsters and other crustacea. The process of *N*-deacetylation, schematically described in Fig. 1, is never complete rendering to chitosan samples with certain degrees of *N*-acetylation [1]. Chitosan, as compared with chitin, exhibit a lower degree of hydrogen bonding allowing its solubilization in organic acids. Depending on the solvent and on the casting procedure, films of chitosan with different levels of crystallinity can be obtained [2]. The association of water to polysaccharide systems containing the $\beta(1 \rightarrow 4)$ bond have been frequently reported [3]. In particular, the system water/chitosan has been shown to exhibit the existence of liquid crystalline mesophases for water weight concentration higher than 44% [3]. Chitosan in solution behaves like a polyelectrolite due to the presence of amino groups in the main chain [4]. The dielectric properties of chitosan solutions have been studied emphasizing the influence of both, counterions species and pH of the solution on the observed relaxation behaviour [4, 5]. On the contrary, the dielectric properties of bulk chitosan have not received so much attention until now [1].

In the present paper we focused our attention on the dielectric properties of chitosan films in an attempt to characterize the relaxation behaviour of chitosan in the solid state.

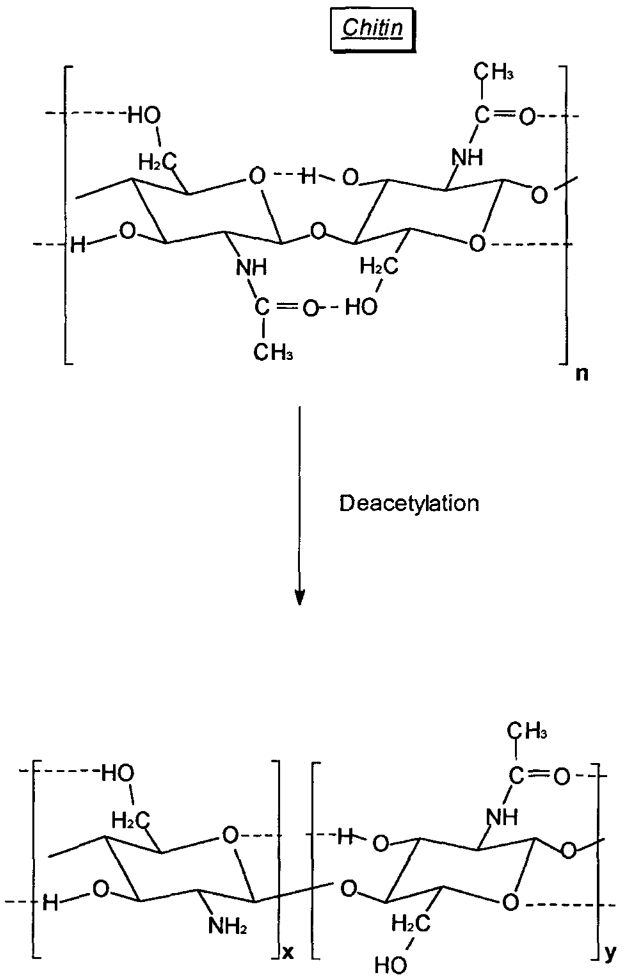

Fig. 1 Schematic description of the chitin deacetylation process rendering to chitosan

Experimental

Chitosan samples were obtained from Bioquimica Austral Chile with a degree of deacetylation of 86% and with viscosity average molecular weight of 1.14×10^6 g/mol. The samples were purified and extracted with acetone in a Soxhlet apparatus for 24 h, subsequently washed with methanol and diethyl ether and finally dried under vacuum at room temperature. Films with thicknesses of approximately 50 μm were prepared from a solution of 0.5 g of chitosan dissolved in 100 ml of 2% weight acetic acid solution. The solution was allowed to evaporate at room temperature in a Petri dish, then the formed film was rinsed with 100 ml of 5% sodium hydroxide solution and subsequently washed with enough distilled water. In order to get extended and flat specimens these films were placed between two stainless-steel plates and dried under vacuum at 150 °C for 3 h. These films were stored at laboratory conditions ($\approx$25 °C, humidity $\approx$25%) for 1 day before dielectric measurements.

Measurements of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$) were carried out in the frequency range of 10^3–10^6 Hz by using a Hewlett-Packard impedance analyzer HP 4192A. Circular gold electrodes, having diameters of 3 cm, were brought onto the sample surfaces by sputtering. The films were placed between two gold-plated stainless-steel electrodes. The dielectric cell was introduced in a home-made cryostat operating at a temperature-controlled nitrogen atmosphere. Dielectric measurements were made at constant temperature from − 150 °C up to 150 °C in 5 °C steps. Every single dielectric scan took about 10 min including heating, thermal equilibration and sweeping in frequency. The error of the absolute accuracy of the ε^* values can be estimated to be below 10%. The temperature accuracy involved during the ε^* measurements was estimated to be ± 0.1 °C.

Additional characterization of the samples was done by means of weight uptake, Fourier transform infrared spectroscopy (Perkin-Elmer 1725 X) and differential scanning calorimetry (DSC-4 Perkin-Elmer) as a function of the water content in the samples. DSC thermograms were obtained at a heating rate of 20 °C/min in $\approx$5 mg samples.

Results

Dielectric relaxation experiments

The dielectric relaxation behaviour of a chitosan film is illustrated in Fig. 2 which shows the dependence of the dielectric loss ε'', and dielectric constant ε' as a function of temperature and frequency in an isochronal fashion. Two main processes are detected in the investigated experimental region. At low temperatures, a relaxation appears centered around − 40 °C at 1 kHz whose maximum shifts towards higher temperatures as the frequency is increased. However, the intensity of the maximum remains almost constant. At higher temperature, an intense maximum in ε'' is observed around 80 °C at 1 kHz. In this high temperature region, ε'' decreases with increasing frequency in the characteristic manner observed for a conduction process. The above commented features can be visualized in Fig. 3 which shows ε'' data as a function of frequency at two given temperatures where both dielectric processes appear. Figure 2B shows that ε' increases continuously for temperatures in the region of the observed low-temperature relaxation. At higher temperatures ε' continues increasing to reach a maximum and subsequently decreases for

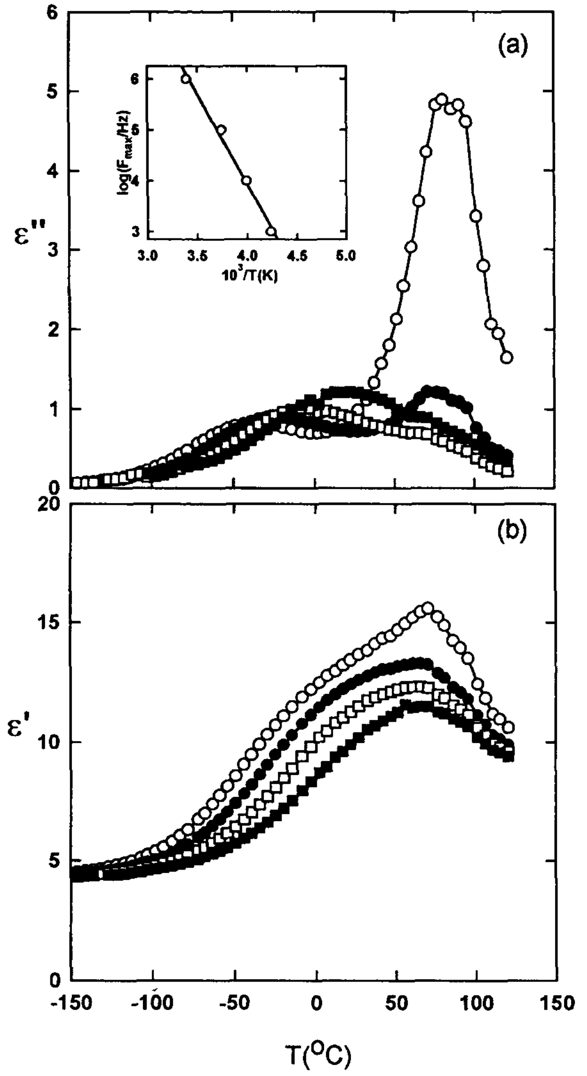

Fig. 2 Isochronal plots of ε'' **A** and ε' **B** for four selected frequencies: 10^3 (○), 10^4 (●), 10^5 (□), 10^6 (■) Hz. The inset shows the frequency of maximum loss as a function of the reciprocal temperature for the low-temperature process

temperatures higher than 70 °C. The dependence of the frequency of maximum loss (F_{max}) for the low-temperature process follows an Arrhenius dependence as shown in the inset of Fig. 2A. From the slope of this curve an activation energy of about 17 kcal/mol (71 J/mol) can be derived.

Presence of water in chitosan films

DSC scans of the chitosan samples from the same batch as those employed for the dielectric experiments are shown in Fig. 4. The first heating cycle shows the appearance of a broad maximum centered about 80 °C. The subsequent second heating scan exhibits an absence of any thermal transition.

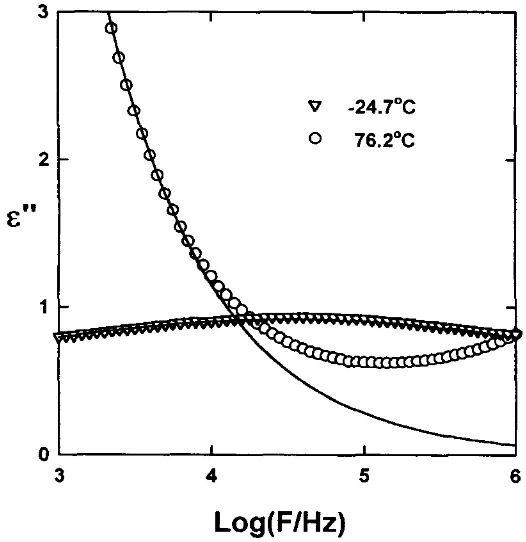

Fig. 3 Dielectric loss, ε'', as a function of frequency for two selected temperatures. Continuous lines are theoretical fits according to the Cole–Cole equation ($T = -24$ °C) and to a conduction process ($T = 76.2$ °C)

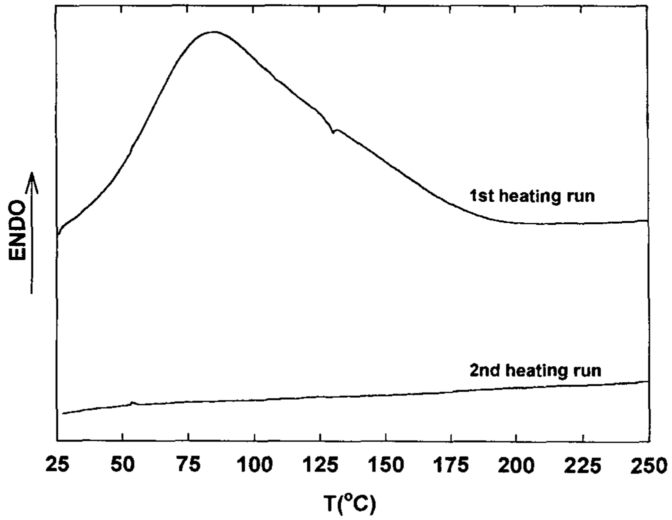

Fig. 4 Consecutive first and second DSC scans of chitosan films

Figure 5 shows Fourier transform infrared spectra of a chitosan film (≈ 25 μm) before (A) and after (B) drying under rotatory pump vacuum for 1 day. Both spectra show the expected bands of chitosan [6]: the very strong bands at about 3400 and 1100 cm^{-1} are associated to the stretching and deformation vibration modes of alcoholic groups

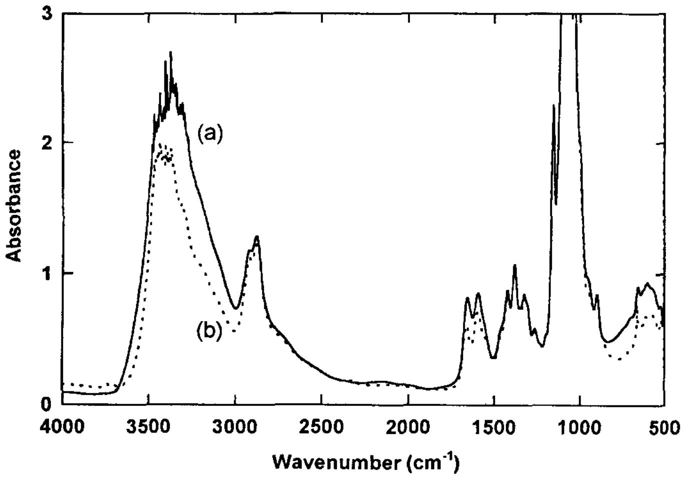

Fig. 5 Transmission FTIR spectra of a chitosan film before **A** and after **B** application of rotary pump vacuum for 1 day

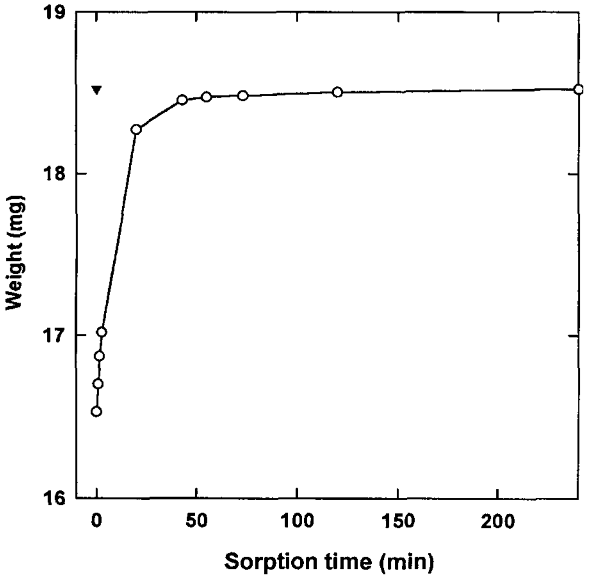

Fig. 6 Weight uptake of a vacuum dried chitosan film exposed to air. The inverse triangle (▼) corresponds to the film before drying

(–OH), respectively. The less-intense band at about 1300 cm^{-1} is also characteristic of alcoholic groups. The shape of the band at 3400 cm^{-1} reveals the presence of hydrogen bonds involving likely both alcohol (–OH) and amine (–NH_2) groups present in chitosan. In addition, the doublet at $\approx$1700–1500 cm^{-1} must be related to the amide I and amide II bands of the remaining acetamide groups, and to the –NH deformation vibration mode of the primary amine group.

By applying vacuum to the samples, an important intensity reduction of the 3400 cm^{-1} as well as of the doublet at 1700–1500 cm^{-1} occurs. This fact can be explained by an elimination of water affecting the hydrogen-bonded structure of the polymer. Figure 6 illustrates quantitatively the weight loss of the films (about 11%) after 1 day vacuum. It also shows the weight uptake of the "dried" film when it is exposed to air. It is noteworthy that the recovery of the initial weight of the film occurs in the first 30–40 min.

Discussion

Low-temperature process

The dielectric relaxation process observed at low temperatures has been presented as Cole–Cole plots, ε'' vs. ε' in Fig. 7.

An attempt has been made to fit the experimental results to symmetric relaxation process described by the Cole–Cole equation [7]

$$\varepsilon^* = \Delta\varepsilon^* + \varepsilon_u \tag{1}$$

with

$$\Delta\varepsilon^* = \frac{\varepsilon_r - \varepsilon_u}{[1 + (i\omega\tau_0)^b]} , \tag{2}$$

where ε_r and ε_u are the relaxed and unrelaxed dielectric constant values, τ_0 is the central relaxation time and b is the parameter which describes the symmetric broadening of the relaxation time distribution function [8]. In order to estimate the accuracy of the fitted parameters, their values were varied. The maximum variation which is possible without provoking a significant deviation between the measured and calculated curves was determined. In all cases this maximum variation was less than $\pm 3\%$ for b and $\Delta\varepsilon = \varepsilon_r - \varepsilon_u$, and $\pm$ 10% for τ. The continuous lines in Fig. 7 represent the best fit to the Cole–Cole equation. The fitting parameters corresponding to Fig. 7 are presented in Table 1. The small value of the parameter b of $\approx$0.2 indicates the existence of a broad distribution of relaxation times. The high degree of deacetylation achieved in these samples reduces the overall amount of acetamide dipole groups to $\approx$14%. As revealed by the weight variation of chitosan films after drying and subsequent exposure to ambient atmosphere, chitosan films present an important amount of water of about 11% at room humidity levels ($\approx$25%). Considering that after vacuum the FTIR bands associated to water are reduced (spectrum (B) in Fig. 5), then we can correlate the weight

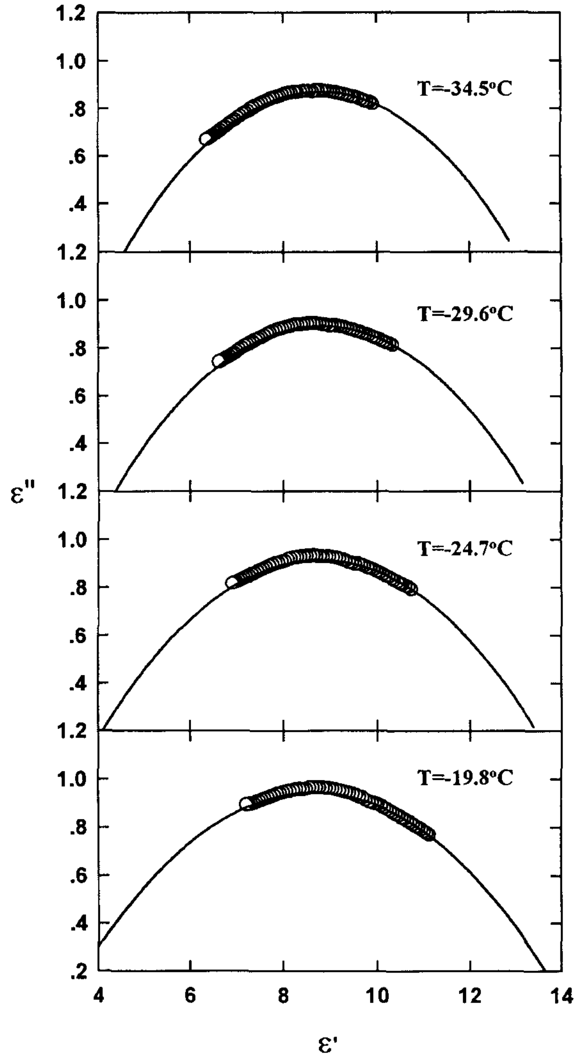

Fig. 7 Cole–Cole diagrams of the low-temperature relaxation at temperatures. Solid curves denote best fits calculated according to Cole–Cole equation. Parameters of the fits are shown in Table 1

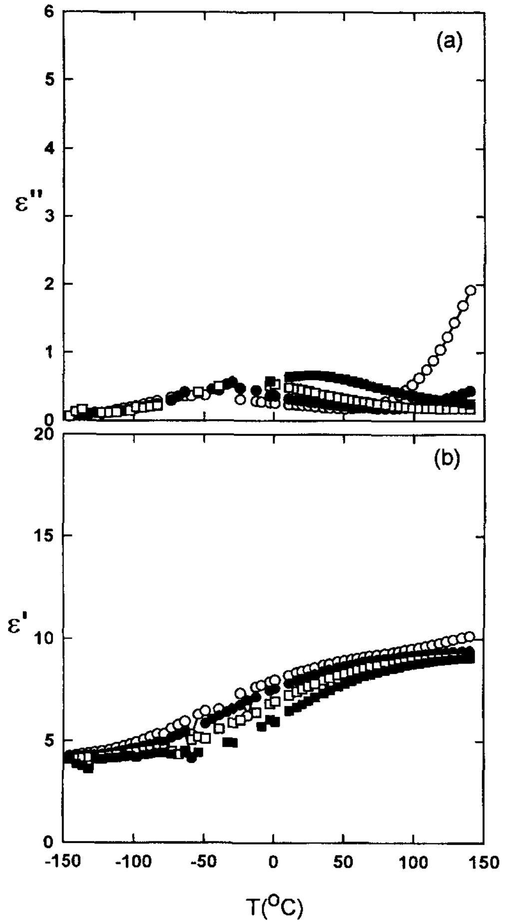

Fig. 8 Isochronal plots of ε'' **A** and ε' **B** for four selected frequencies for a sample dried at 143 °C. Same symbols as in Fig. 2

Table 1 $\Delta\varepsilon$, b, and τ_0 obtained from the fitting of Eq. (1) in the case of the low-temperature relaxation process

T [°C]	$\Delta\varepsilon$	b	τ_0[s]
−34.5	9.6	0.23	2×10^{-5}
−29.6	10	0.22	1×10^{-5}
−24.7	10.5	0.22	5×10^{-6}
−19.8	11.2	0.21	2×10^{-6}

uptake to a sorption of water by the sample. This assumption is consistent with the calorimetric data which exhibit, in a first scan, a broad endotherm centered at about 80 °C. Here, this endotherm can be associated to the existence of a water elimination process. The immediate consecutive DSC scan does not present such an endotherm because the sample has been already dried and it is kept under nitrogen flow within the calorimeter. The presence of water may give rise to the formation of hydrogen bonds with the –OH and $-NH_2$ groups affecting the low-temperature relaxation. Activation energies for the local motion of ester and acetone groups of about 13 kcal/mol have been reported in the literature [9, 10]. Different activation energy values for hydrogen-bonded water ranging from 9 to 13.3 kcal/mol for elastin [11], 12.2 kcal/mol for polyimides [12], 13.6–14.5 kcal/mol for nylon-6 [13, 14], 18 kcal/mol for nylon-12 [15] can be found in the literature. Thus, the value derived in the present paper for the activation energy, ≈ 17 kcal/mol, is consistent with a local relaxation of water even though the influence of the acetamide group cannot be fully discarded on the only basis of the measured activation energies. In order to further verify this

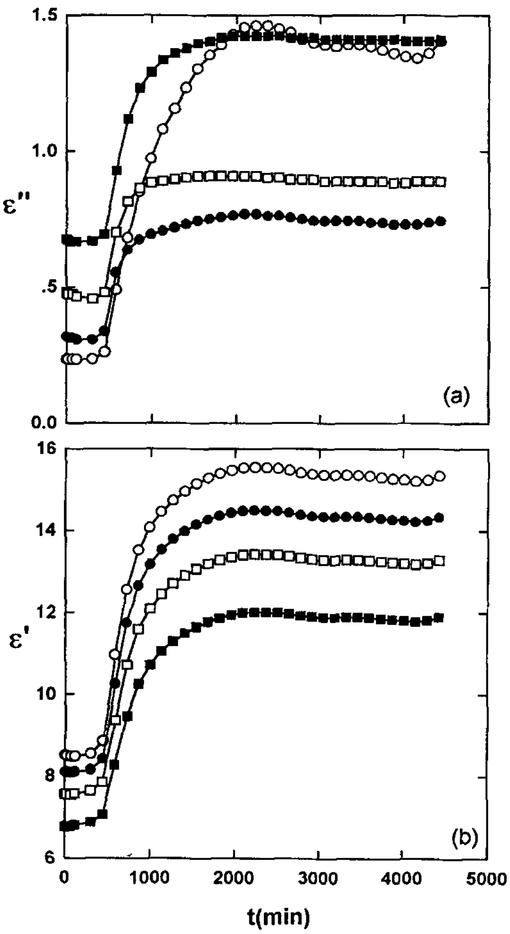

Fig. 9 Variation of ε″ **A** and ε′ **B** with time for different frequencies at room temperature after thermal treatment 143 °C. Same symbols as in Fig. 2

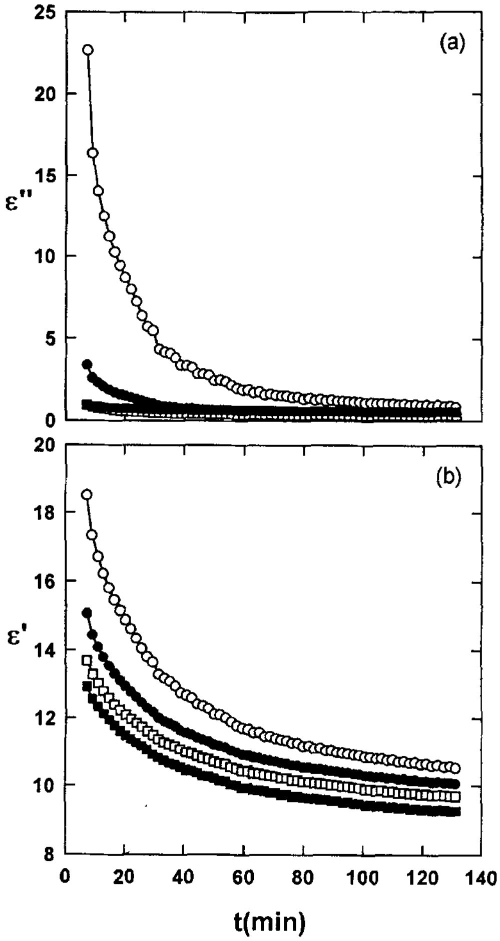

Fig. 10 Variation of ε″ **A** and ε′ **B** with time for different frequencies at $T = 85$ °C. Same symbols as in Fig. 2

assumption we performed experiments on samples dried at 143 °C during several hours and subsequent cooling to −150 °C under nitrogen flow. Figure 8A and B show ε″ and ε′ values as a function of both, temperature and frequency. As one can see, the strength of the low-temperature process, as characterized by the step in ε′, is reduced in about one-half after the drying process indicating that water may play an important role on this low-temperature process. It is worth to emphasize that some bounded water always remains after the drying process as it is known to occur in polyamides [16].

High-temperature process

The dielectric process observed at high temperatures (Fig. 2A) presents up to 80 °C the features of a conduction process characterized by an increase of ε″ at low frequencies (Fig. 3). The conductivity contribution to ε″ can be described by the power law: $\varepsilon'' = \sigma/(\varepsilon_0\omega^s)$ were "σ" is related to the direct current electrical conductivity, ε_0 is the vacuum dielectric constant and "s" is related to the nature of the conduction mechanism. A value of $s < 1$ is related to a non-ohmic transport [17]. Such a dependence has been found to be valid for different polymeric materials [17, 18]. A fitting of this equation ($s = 0.62$ and $\sigma = 9 \times 10^{-9}$ S/cm) to the experimental results is shown in Fig. 3 by the continuous line. The departure of the experimental data from the calculated curve for frequencies $F > 10$ kHz is due to the existence of the low-temperature relaxation. For temperatures $T > 80$ °C, ε″ exhibit an anomalous behaviour characterized by a dramatic reduction.

As commented above, the investigated chitosan films contain a considerable amount of water. Upon heating the absorbed water is likely removed as revealed by the broad endothermic peak observed in the first heating DSC scan

(Fig. 4). According to these observations we must attribute the maximum observed in ε'' at ≈ 80 °C to a water desorption process. Indeed, the maximum disappears in the dried sample (see Fig. 8A). In order to verify this assumption two different experiments were performed. Firstly, a chitosan sample was heated up to 143 °C and immediately cooled down to room temperature. Then, isothermal measurements of both, ε'' and ε' were recorded at room temperature as a function of time. As shown in Figs. 9A and B both, ε'' and ε' exhibit, after a certain induction time, a dramatic increase which levels off at longer times. Once the steady state was achieved, a second heating of the sample up to 85 °C was done and then isothermal measurements of ε' and ε'' were performed. Here, a clear decrease of both magnitudes is observed (Figs. 10A and B). Therefore, results presented in Figs. 9 and 10 can be interpreted as due to a water sorption/desorption process. The relative long induction period (≈ 600 min) observed in Fig. 9 in contrast to the rapid water sorption process shown in Fig. 6, can be explained by considering the restriction imposed to water by the experimental arrangement of the chitosan films in the dielectric measurements.

Conclusions

Chitosan films in equilibrium with air ($\approx 25\%$ humidity) contain about 11% of water. Dielectric experiments performed in chitosan films reveal the existence of two dielectric processes. The lower-temperature process presents a temperature-activated character and can be interpreted as being due to the local relaxation of hydrogen-bonded water. The higher-temperature process must be related to a water desorption mechanism upon heating of the sample. Due to this fact, this process is strongly dependent on sample history.

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