3-Physical Chemistry and Properties of Polymers

Dynamic Mechanical and Dielectric Relaxation Behavior of Chitosan Films: Influence of Water Content

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Summary: The dynamic mechanical dielectric behavior of neutralized chitosan films has been investigated as a function of water content and temperature. Chitosan films exhibit three relaxation processes in the low frequency range: the first one between 86–102 °C, it corresponds to the α-relaxation process and shifts to higher temperatures with decreasing water content; a second relaxation was observed from 80 °C to the onset of thermal degradation (240 °C) and it is identified as the σ-relaxation often associated with proton mobility; and a third relaxation process in the 240–300 °C temperature range that corresponds to chitosan thermal degradation.

Keywords: chitosan; dielectric properties; glass transition; mechanical properties

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 polysaccharide that contains a considerable amorphous fraction. An important parameter of the amorphous state is the glass transition temperature T_g which plays an important role scientifically and 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 big controversy about the value of a glass transition temperature in polysaccharides, especially chitosan. Using several techniques including differential scanning calorimetry and dynamic mechanical thermal analysis (DMTA) reported elsewhere,[1–5] the reported values of T_g vary from 30 to 203 °C, while other authors[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.[8,9]

Recently, our group has reported,[10] for the first time, evidence for a relaxation

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process, which exhibits non-Arrhenius temperature dependence in dry α-chitin, and likely represents the primary α-relaxation. This evidence suggests a glass transition temperature for chitin of $62 \pm 10\,^{\circ}C$ estimated on the basis of the temperature dependence of the conductivity and of the relaxation time.

The aim of this work is to investigate the relaxation phenomena occurring in chitosan films in the low frequency range as a function of the water content using DMTA and dielectric spectroscopy analysis and to see if there exists a relationship between the glass transition temperature and these relaxation processes.

Experimental Part

Chitosan (82% 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 1 MHz were carried out using a Solartron in the vacuum cell.

Results and Discussion

Figure 1 shows the thermogravimetric results for the three types of samples with different water content analyzed in this work:

1) *wet* (at ambient conditions with no further treatment),
2) *annealed at 75°C* then cooled to 30 °C, and,
3) *annealed at 150°C* followed by cooling to 30 °C.

All measurements for *wet* and *annealed* samples were performed from 30 °C to 320 °C (TGA and DMTA) in dry air atmosphere. The amount of free water may be evaluated by the decrease of sample weight during the second heating scan. According to the results obtained, *wet* 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.

Figure 2a, 2b, and 2c show the temperature dependence of the *tan δ* obtained from DTMA measurements of the samples described above. Chitosan films exhibit three *tan δ* peaks at positions around 86–

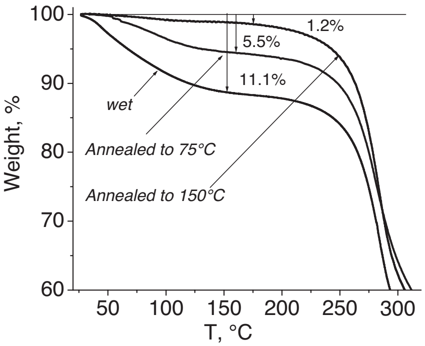

Figure 1.
Thermogravimetric analysis for the three types of samples obtained during second temperature scan: *wet, annealed at 75 °C, and annealed at 150 °C.*

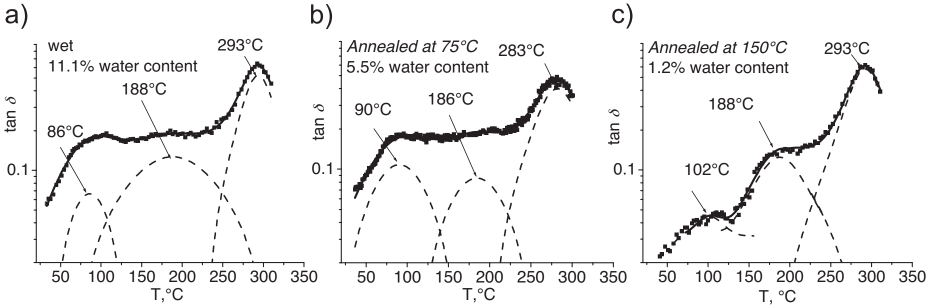

Figure 2.
Temperature dependence of *tan δ* of chitosan films: a*) wet*; b) *annealed at 75 °C*; and c) *annealed at 150 °C*. Solid squares: experimental data; lines: data fitting; dash lines: peak position found from fitting procedure.

102 °C (depending upon on free water content), 188 °C and 293 °C, respectively.

The first peak at ca. 100 °C has been previously reported by DTMA measurements elsewhere [9,11], but there is no theoretically sound explanation about its nature and its relationship with water content. Also, other studies[12,13] claim that this peak is related to the glass transition temperature of chitosan, which shifts to lower temperatures with increasing moisture content [13]. Our study focuses on the mechanical response of chitosan films to water content (Figure 1) in order to determine the effect of water content on chitosan molecular motion.

The peak in the *tan δ* curve at ca. 150–190 °C has already been observed in many studies,[2,3,9,14] and it has been also designated as the glass transition temperature of chitosan related to the molecular motion in the amorphous region with no further explanation.

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

In summary, only by means of DTMA measurements a direct interpretation about the nature of relaxation process in chitosan films as a function of water content would be doubtful. Hence, complementary techniques such as impedance spectroscopy[10] and spectroscopic ellipsometry[15] are needed to fully connect data to molecular relaxations.

Figure 3a shows the complex impedance spectra of chitosan films. These spectra

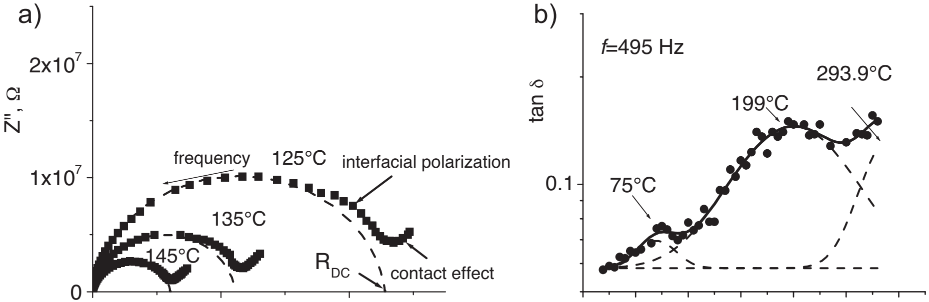

Figure 3.
a) Impedance spectra of chitosan and b) tan δ obtained from dielectric spectroscopy measurements at 495 Hz. Solid squares and circles: experimental data, dash line: model fitting.

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-Silliars polarization effects, signaled as a "bulge" on the semicircle. For further consideration in the analysis, we take into account only a so-called depressed semicircle that does not include contact and interfacial polarization effects. Preliminary impedance data treatment includes the subtraction of the *dc* conductivity contribution, the exclusion of contact and interfacial polarization effects, and obtaining a condition of minimum moisture content for further analysis. Details on data manipulation and fitting are reported elsewhere [10].

Due to a large conductivity contribution in the low frequency range, a *direct current (dc)* conductivity correction must be applied to experimental data. This *dc* conductivity strongly modifies the dielectric loss factor ε'' in the low frequency side of the spectra. In this case it can be expressed as: $\varepsilon'' = \varepsilon''_{\text{exp}} - \sigma_{dc}/w\varepsilon_0$, 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 of the impedance plane (as shown in Figure 3a). More details are given in [10].

Similarly as observed by DMTA, measurements in dielectric spectra exhibit three different relaxations (Figure 3b). The little difference in the peak positions of these two independent measurements (DTMA and dielectric spectroscopy) is explained as follows: dielectric spectroscopy is sensitive to fluctuations of dipole moments and mechanical relaxation monitors the fluctuations of internal stresses. Such effect has been observed in many polymers. i.e., mechanical relaxations processes are observed at temperatures different than the corresponding dielectric relaxation [16].

After *dc* correction of the complex permittivity has been fit using Cole-Cole empirical correlation[17] as follows:

$$\varepsilon * -\varepsilon_\infty = \frac{(\varepsilon_s - \varepsilon_\infty)}{[1 + (j\omega\tau)^{1-\alpha}]}, \qquad (1)$$

where ε_s and ε_∞ are limiting values for low and high frequency (intersections with real ε' axis), τ is the mean relaxation time, α is the constant phase element (*CPE*) power. The *CPE* is an empiric impedance function with impedance $Z_{\text{CPE}} = A(jw)^{-\alpha}$, where A is the *CPE* constant, α is the *CPE* exponent.

The most interesting results have been obtained in the low frequency range (10^{-1}–10^3 Hz). Figure 4a shows dependence of *dc* conductivity versus *1/T* and low frequency relaxation time (Figure 4b) obtained using the Cole-Cole model. These dependencies

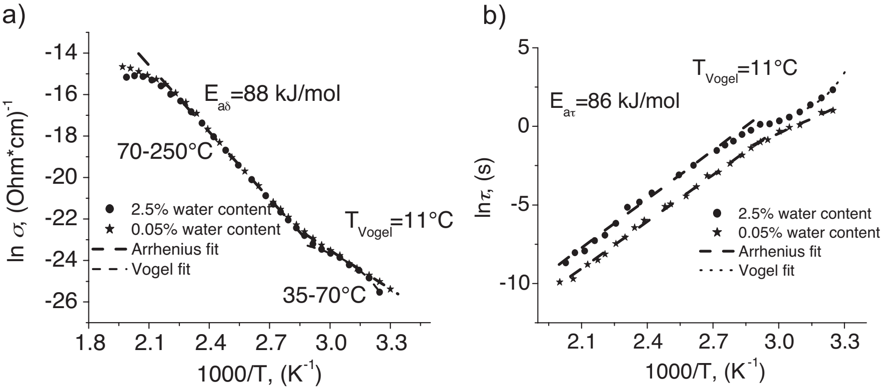

Figure 4.

a) *dc* conductivity *versus 1/T*; b) low frequency relaxation time *versus 1/T*, obtained using the Cole-Cole model for samples with different water content.

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 of ca. 2.5%, 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 [18]:

$$\sigma = \sigma_0 \exp\left(-\frac{DT_0}{T - T_0}\right), \qquad \tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right), \tag{2}$$

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 is a distinctive feature of the α-relaxation behavior also called dynamic glass transition.[10,18] In many polymers T_0 is usually 50 °C lower than glass transition temperature T_g.[14] In the present study the $T_0 = 11\,^\circ\mathrm{C}$ have been obtained. Once T_0 is calculated, a T_g of ca. $61 \pm 10\,^\circ\mathrm{C}$ for neutralized chitosan was obtained. This value correlates well with DMTA results (the fist peak dependent on free water content observed between 86 and 102 °C). As explained above, it has been previously reported in literature[16] that for many polymers, mechanical relaxation processes are observed at temperatures different than the corresponding dielectric relaxation, this is in part because dielectric spectroscopy is sensitive to fluctuations of dipole moments and mechanical relaxa tion monitors the fluctuations of internal stresses.

It is noteworthy that a relaxation for α-chitin[10] reported, for the first time, by our group is close in value to the one observed for neutralized chitosan. To the best of our knowledge, our studies are the first one to report theoretically sound values for α–relaxations in chitin and neutralized chitosan.

In samples annealed at 120 °C, this low temperature relaxation vanishes. Water is a small polar molecule that gives aid in breaking H-bonding in chitosan by a plasticizing effect. By carefully looking at Figure 4b, one can see that the Vogel-type relaxation (α-relaxation) seems to vanish, to give an Arrhenius-type relaxation (sigma-relaxation) as water content is close to ca. 0%. It is possible, although not understood, a superposition of these two relaxations when water is absent. This speculation may be related to the fact that no study has claimed to observe an α–relaxation in dry polysaccharides. The issue remains to be studied in more detail.

For the temperature range 80–220 °C both conductivity and relaxation time measurements show an Arrhenius-type behavior (Figure 4a and 4b) 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.[19] This process is associated with the hopping motion of ions in the disordered structure of the biomaterial and is called σ-relaxation.[19]

These results obtained from dielectric spectroscopy measurements allow concluding that the second peak observed in the *tan* δ curve near to 188 °C is related to the σ-relaxation which exhibits a weak dependence on the water content.

In dielectric measurements, a change in the slope at 240 °C and above denotes as well as the third peak in DMTA measurements the beginning of chitosan thermal degradation.

Conclusions

Dielectric and dynamic mechanical molecular relaxations of neutralized chitosan films have been investigated as a function of water content. On this basis, the α-relaxation process related to the glass transition temperature was observed in the 86–102 °C temperature range. The glass transition temperature shifts to higher values with decreasing water content and vanishes in dry-chitosan films. A second low frequency relaxation was observed from

80 °C to the onset of thermal degradation (240 °C) and it is identified as the σ-relaxation often associated with proton mobility. This relaxation exhibits Arrhenius-type temperature dependence with activation energy values of 86–88 kJ/mol; showing a weak dependence on water content. Additionally, in the temperature range between 240–300 °C, the relaxation process corresponding to the beginning of thermal degradation had been observed.

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