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Molecular motions of chitosan in the solid state

Maria Pizzoli, Giuseppina Ceccorulli, and Mariastella Scandola
Dipartimento di Chimica "G. Ciamician" dell Universitá di Bologna and Centro di Studio per la Fisica delle Macromolecole del C.N.R., Via Selmi 2, 40126 Bologna (Italy)

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ABSTRACT

The relaxation behavior of chitosan has been investigated by dynamic mechanical and dielectric spectroscopy over a wide temperature and frequency range. Two dispersion regions are found in the spectrum of the dry polysaccharide: a relaxation (γ) at low temperature ($-102°$ at 3 Hz; $\Delta H = 47$ kJ/mol) and another relaxation process above room temperature (130° at 3 Hz; $\Delta H \sim 100$ kJ/mol). Absorbed water strongly modifies the relaxation spectrum of chitosan below room temperature, giving rise to a new relaxation (βd) at temperatures higher than the γ peak. With increasing water content, the γ peak is progressively depressed, while the βd relaxation intensifies and moves to lower temperatures. In room-stored samples ($\sim 10\%$ absorbed water) the βd peak is the only observable relaxation in the viscoelastic spectrum of chitosan below room temperature. The γ and βd loss processes are attributed to local motions of the polysaccharide backbone and of complex polymer–water units, respectively. The characteristic parameters of the high-temperature peak indicate that the relaxation originates from short-range rather than cooperative molecular motions.

INTRODUCTION

Attention has recently been given to polysaccharides as polymeric materials and a number of studies on the solid-state properties of these renewable polymers has appeared in the literature. The use of polysaccharides as constituents of copolymers containing synthetic polymer blocks[1–3] also attests to a growing interest towards polysaccharide-based materials.

From the practical point of view, fundamental information on the processability of polymers is usually obtained through thermal analysis, which provides knowledge of the main polymer transitions (melting and glass-to-rubber transition of the crystalline and amorphous phases, respectively). In addition to the well established calorimetric techniques, experimental methods capable of revealing the motional phenomena occurring in the solid state have attracted increasing attention. Both dynamic mechanical and dielectric spectroscopies, for example, allow determination of the viscoelastic spectrum of a polymer; as a result of a periodic excitation (either mechanical or electrical), molecular motions of increasing complexity are activated at progressively higher temperatures and give rise to the relaxations that make up the viscoelastic spectrum.

A number of theoretical studies have been conducted on isolated and solvated polysaccharide chains[4] to obtain information on chain dynamics. More recently, simulations have been extended to polysaccharides in the solid state[5]. On the experimental

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side, dynamic mechanical[6,7] and dielectric[8–10] spectroscopies have been successfully applied to a number of carbohydrate polymers.

In the case of chitosan, although its film-forming capability is well known and a number of practical applications have been suggested[11], the characterization of its solid-state properties is surprisingly limited. X-Ray studies have shown the existence of various polymorphs in chitosan, induced by solvent, film-preparation procedure, and annealing treatments[7,12,13]. The remaining solid-state studies regard the tensile properties of water-swollen films[14] as well as dynamic mechanical[7,15] and dielectric[10] measurements.

As an experimental contribution to the understanding of molecular motions in solid polysaccharides, we report here on the relaxation behavior of chitosan. The viscoelastic spectrum has been determined over a wide range of temperatures and frequencies by dynamic mechanical and dielectric spectroscopy. The effect of water – the ubiquitous solvent for biopolymers – on the relaxation spectrum of chitosan has also been investigated and compared with the behavior of other polysaccharides under analogous hydration conditions.

EXPERIMENTAL

Materials. — Chitosan, obtained by deacetylation of chitin from *Chionoecetes japonicus* (degree of deacetylation 85%), was supplied by Katakura Chikkarin Co. The polysaccharide was solubilized (12% wt/vol) in 1% aqueous HOAc. After vacuum degassing, the solution was cast on glass plates at 60° to afford films that were neutralized with 2M NaOH and subsequently thoroughly washed with water. The films were allowed to dry in air.

Measurements. — The thermal properties were measured with a DSC DuPont 9900 Thermal Analyzer and a Perkin–Elmer TGA7 Thermogravimetric Analyzer (gas flow 20 mL/min, heating rate 10 deg/min).

Dynamic mechanical measurements were carried out with a DMTA (Polymer Laboratories) instrument operated in the tensile mode, at a frequency of 3 Hz and a heating rate of 3 deg/min, from -150 to 180°. In the DMTA instrument, a film sample is longitudinally deformed by a small sinusoidal stress and the resulting strain, which lags behind the applied force by a phase angle δ_E, is measured. The technique yields[16] values of the dynamic storage modulus E' (in-phase component), the loss modulus E'' (out-of-phase component), and the mechanical loss tangent $\tan \delta_E = E''/E'$.

Multifrequency dielectric measurements were performed with a DETA (Polymer Laboratories) instrument, at 1 deg/min, starting from -130°. In the DETA instrument, thin films held between circular electrodes are subjected to a small alternating electric field which produces an alternating polarization of the sample. The polarization lags behind the applied field by a phase angle δ_ε and the dielectric loss tangent is given by $\tan \delta_\varepsilon = \varepsilon''/\varepsilon'$, where ε' and ε'' are the real and imaginary components of the complex dielectric constant[16].

RESULTS AND DISCUSSION

1. *Thermogravimetric results.* — Figure 1 shows the thermogravimetric (t.g.) curve of chitosan powder, obtained both in nitrogen and in a flow of air. After an initial weight decrease due to water loss (10% from room temperature to 150°), the t.g. curve shows a main degradation-step in the vicinity of 320° (extrapolated onset 294°, maximum rate of weight loss 327°). After this abrupt weight-loss phenomenon, ~40% of residue is left, which volatilizes faster in the presence of air than when the inert gas is used. Under analogous experimental conditions, other polysaccharides such as xylan, amylose, pullulan, and dextran[17,18] show a main degradation-step in the t.g. curve at ~300°, that is, in the same temperature-range as found here for chitosan.

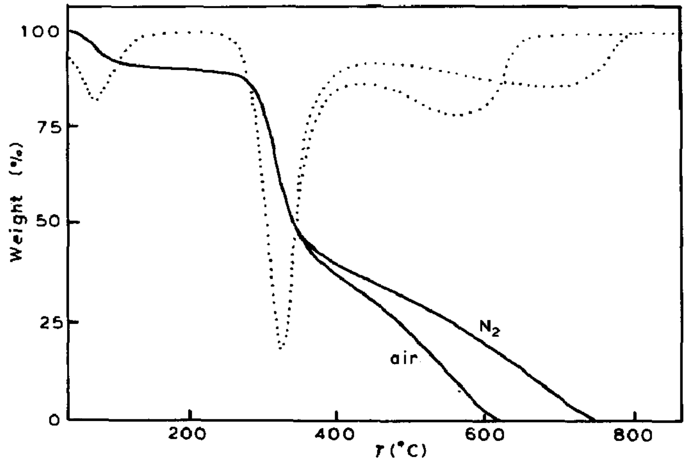

Fig. 1. Thermogravimetric curves of chitosan in nitrogen and in a flow of air. Dotted lines: derivative curves.

As regards the water loss, the 10% value obtained in dynamic experiments (Fig. 1) increases to 11.5% when chitosan is isothermally treated at 120° for 8.5 h; a water content of 10–15% can be reasonably expected and is commonly found in polysaccharides[17–19]. In polysaccharides, thermal degradation often prevents observation of the glass transition and melting which, owing to the remarkable rigidity of the sugar ring in the backbone, should occur at rather high temperatures. As a matter of fact, d.s.c. measurements on chitosan, apart from a large endotherm in the range 50–150° due to water evaporation, do not reveal any transition up to 280°, where complex exo–endothermal phenomena indicate the onset of thermal degradation.

2. *Low-temperature relaxations.* — Figure 2 shows the dielectric spectrum at six selected frequencies (0.2–50 kHz) of "dry" chitosan, namely, of a chitosan film that has been heated under vacuum up to 180° in the DETA instrument prior to measurement, in order to eliminate the humidity absorbed from the environment. Below room temperature a dielectric relaxation, whose temperature increases with increasing frequency, is observed. The insert in Fig. 2 shows that the peak temperature (open circles) follows the Arrhenius equation:

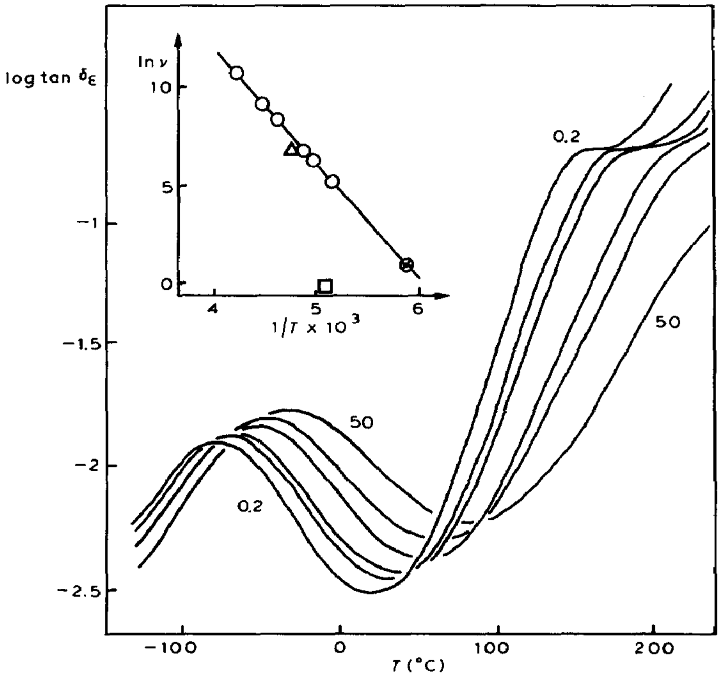

Fig. 2. Dielectric curves of "dry" chitosan at different frequencies (0.2, 0.6, 1, 5, 10, and 50 kHz). [Insert: Arrhenius plot of the γ relaxation from dielectric data (open circles). Dynamic mechanical result, from this work: crossed circle. Lit. data: (square) ref. 8; (triangle) ref. 15].

$$\ln(\nu/\nu_0) = -\Delta H/RT \qquad (1)$$

as expected for a secondary relaxation caused by local motions of small molecular units[16].

The dynamic mechanical spectrum of high-temperature dried chitosan is shown in Fig. 3. Two relaxations are observed, one at about −100°, the other in the high-temperature range. The peak temperature of the former is reported, for the sake of comparison, in the ln ν *vs.* $1/T$ plot of Fig. 2 and is seen to fit satisfactorily the linear dependence extrapolated from the dielectric data. This result indicates that the low-temperature peak of Figs. 2 and 3 refers to the same relaxation phenomenon, which is denoted γ relaxation.

From the slope and intercept of the straight line in Fig. 2, the following values of the apparent activation energy of the process ΔH and of the limiting frequency ν_0 (representing the characteristic frequency of molecular motions at infinitely high temperature) are obtained: $\Delta H = 47$ kJ/mol; $\nu_0 = 10^{14}$ Hz.

Heijboer[20] has shown that, for a wide variety of polymers having secondary relaxations due to *local motions* of either main or side chains, the activation energy ΔH is directly proportional to the peak temperature T, according to Eq. *1*, with $10^{13} < \nu_0 < 10^{15}$. The ΔH and ν_0 values for chitosan clearly indicate that the origin of the γ relaxation has to be sought in a local motion of the polysaccharide chain.

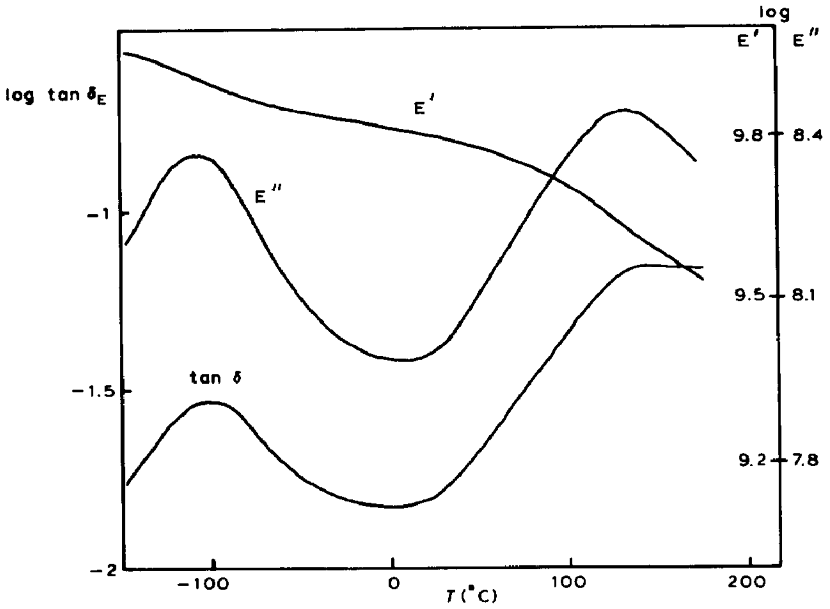

Fig. 3. Dynamic mechanical spectrum of "dry" chitosan.

It is well known that it is extremely difficult to eliminate completely the water absorbed by polysaccharides; thus, before venturing to suggest an assignment of the γ relaxation to a specific molecular motion, it is worth considering how the viscoelastic spectrum of chitosan is affected by absorbed water. The most convenient way to vary systematically the water content of chitosan is to heat the film up to different temperatures directly in the DMTA instrument in subsequent cycles, starting with a sample equilibrated under "room humidity" conditions. Loss of water is monitored through measurement of the sample length, which is seen to decrease instead of increase with increasing temperature. Unfortunately, no quantitative evaluation of the water content is possible during the thermal run, nor is a reliable *a posteriori* estimate available.

Figure 4 shows the dynamic mechanical curves relative to five consecutive runs on the same chitosan sample: each thermal scan reaches a progressively higher temperature, so that the water content gradually decreases going from curve A (room conditioning) to curves B, C, D, and E, respectively. Curves B, C, D, and E are relative to measurements under dry nitrogen purge. Chitosan containing the amount of humidity normally absorbed from the atmosphere (curve A) shows a secondary relaxation (βd) centered at $-80°$, that moves to higher temperature and decreases in intensity with decreasing water content. In curve D, the peak has moved up to $-32°$ and another relaxation appears at lower temperature, in a region where, in curve C, a slight asymmetry is observed. After further drying up to 120°, the upper peak disappears (curve E), while the lower relaxation centered at about $-100°$ becomes fully evident. This latter relaxation phenomenon is the γ relaxation of dry chitosan, already evidenced in both Fig. 2 (dielectric) and Fig. 3 (mechanical).

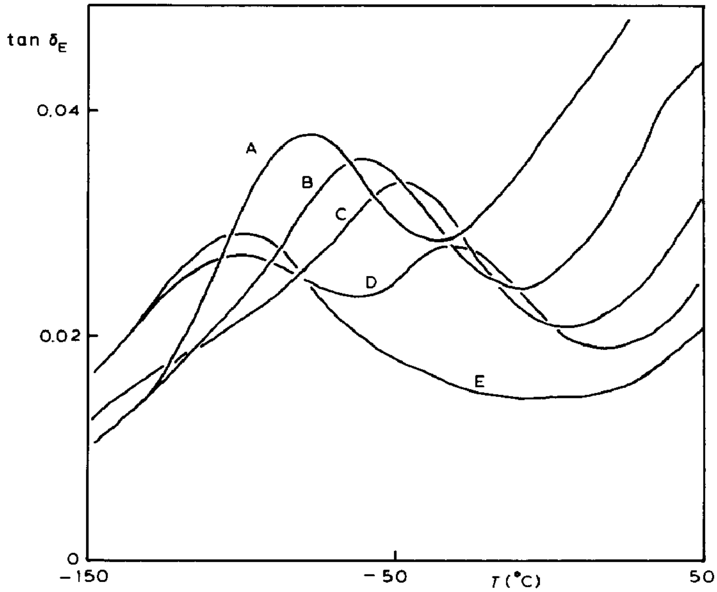

Fig. 4. Dynamic mechanical curves of chitosan having different water contents. A: "room" humidity; B, C, D, and E: after heating up to 30, 60, 90, and 120°, respectively, under dry nitrogen purge.

As regards the assignment of this relaxation process, it may be recalled that a relaxation at −75° (1 Hz) for so-called "dry" chitosan[15] and at −61° (1 kHz, activation energy 38 kJ/mol) for chitin[8] dried under vacuum for 3 h at 100° have been reported in the literature. While for chitosan no molecular attribution was given, in the case of chitin the relaxation was assigned to motion of residual tightly bound water[8].

Both data from the literature are shown in the insert of Fig. 2, where the result on chitosan by Ogura *et al.*[15] clearly falls very far from the straight line that fits the present γ relaxation data. Close inspection of Ogura's paper, however, indicates that the datum reported is obtained from a curve similar to our curve D of Fig. 4 and therefore concerns a sample still containing some water. The peak temperature is taken from the high-temperature side of the absorption region and is clearly relative to the βd instead of the γ relaxation: for this reason Ogura's result cannot fit the Arrhenius plot. On the other hand, a close fit is shown in Fig. 2 for the datum on chitin by Fukada *et al.*[8], a finding that throws some doubt on Fukada's assignment of the chitin relaxation to motion of residual water in the "dried" polysaccharide. As a matter of fact, expecting for chitin in the presence of absorbed water a behavior analogous to that found for chitosan, no fit to the Arrhenius plot should be found if residual water were present in Fukada's chitin.

We may therefore conclude that the γ relaxation of chitosan that occurs at about −100° at 3 Hz, with activation energy 47 kJ/mol, is comparable to that reported for chitin[8] and refers to a molecular motion characteristic of the dry polysaccharide.

It is worth pointing out that such polysaccharides as dextran, pullulan, amylose, and xylan[17,18] in the dry state also show a low-temperature secondary relaxation (γ) that evolves as a consequence of water absorption in much the same way as the γ relaxation of chitosan, that is, it is depressed and finally disappears, while another water-induced relaxation (βd) grows at a higher temperature. This latter moves to lower temperature with increasing water content and becomes the dominant relaxation-process in normal "room" humidity conditions. The existence of diluent-induced relaxations, commonly termed βd, has been frequently reported in the literature. These relaxations arise not only as a consequence of water absorption by hydrophilic polymers[21,22], but also when other low-molecular-weight diluents are incorporated in polymeric materials[23].

In the case of the polysaccharides mentioned, the γ relaxation of the dry polymer was assigned[17,18] to local motions of the main chain, such as small-amplitude oscillations of the sugar rings about the glycosidic bonds, on the basis of considerations of conformational freedom and of the absence in both xylan and dextran of the primary alcohol group that has been often invoked[6,9,24] as responsible of low-temperature relaxations in polysaccharides. The same attribution to a local motion of the backbone is here proposed for the γ relaxation of chitosan, a polysaccharide lacking bulky substituent groups. The residual *N*-acetyl groups (15% in the sample investigated) are very unlikely to give rise to a well-resolved loss phenomenon such as the γ peak, as peak intensity is known to reflect the number of molecular groups, on a volume basis, that undergo mobilization[16].

Concerning the effect of absorbed water, the following scheme for the water–polysaccharide interaction is suggested: at the initial stages of hydration, H-bond formation between water and the polysaccharide results in a strengthening of the H-bond network. The motion responsible for the γ relaxation is hindered and as a consequence the γ peak is depressed. Because of the higher energy required to activate the molecular motion in the presence of bound water, the new βd relaxation is seen to occur at a higher temperature. As the water content increases further, most of the newly added molecules are likely to bind to previously absorbed ones, forming water–water bridges that loosen the H-bond network. In this context, the motion of the chitosan–water relaxing units becomes easier and the temperature of the βd relaxation decreases.

In conclusion, the γ relaxation of chitosan is attributed to a local motion of the polymer main-chain, whereas the βd dispersion is classified as a water-induced relaxation.

3. *High-temperature relaxation.* — One more absorption region that deserves discussion appears in the viscoelastic spectrum of chitosan above room temperature. The relaxation phenomenon, earlier reported by Ogura *et al.*[15], is distinctly observed in the dynamic mechanical E″ curve (Fig. 3) as a well-resolved loss modulus peak, less clearly defined in the tan δ curve. Furthermore, the dielectric spectrum of Fig. 2 suggests the presence of a high-temperature relaxation. Comparison of the frequency and temperature location of the peak indicates that the molecular motion evidenced by both experimental techniques is the same. A crude estimate of the activation energy through application of Eq. *1* to the experimental data yields a value of ~ 100 kJ/mol (ν_0 of the order of 10^{14} Hz).

As far as the assignment of the relaxation is concerned, Ogura *et al.*[15] attributed a peak appearing at 140° (1 Hz) in the dynamic mechanical spectrum of dry chitosan to the glass transition of the polysaccharide. Moreover, Kurita *et al.*[25] reported, for crosslinked water-soluble (partially deacetylated) chitin, a softening phenomenon at 145°.

As regards chitosan, the present results bring no evidence in favor of the glass-transition attribution: the d.s.c. measurements show no stepwise increase of the specific heat at temperatures corresponding to the dynamic mechanical relaxation. Moreover, both the intensity of the tan δ peak and the associated modulus drop (see Fig. 3) are very modest indeed for a glass-to-rubber transition, involving large-scale cooperative molecular motions in the amorphous phase, unless the polysaccharide contains a very limited amorphous fraction. To ascertain if a conspicuous crystalline phase is present, X-ray investigations on the same chitosan films used in the dynamic mechanical experiments were performed, but very little crystallinity was found. Therefore, since a substantial amorphous phase should exhibit a readily detectable transition, it seems unlikely that the relaxation in question can be attributed to amorphous chitosan undergoing the glass-to-rubber transition. In this connection, we point out that dextran, a polysaccharide having a more flexible backbone than chitosan, shows[18] a T_g at 220°, well above the high-temperature relaxation of chitosan. The result on dextran suggests that the T_g value of chitosan probably lies at rather high temperatures, where degradation phenomena prevent its determination.

The unlikeliness of the previous attribution[15] of the high-temperature relaxation of chitosan to the glass transition is further supported by examination of the parameters derived from the frequency–temperature dependence of the relaxation. Both the ΔH and ν_0 values actually conform to Heijboer's predictions[20] for secondary loss-processes associated with local molecular motions. Though no conclusive assignment is currently given, the results of this work suggest that the relaxation arises from a molecular motion having a less co-operative character than the glass-to-rubber transition.

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