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Secondary dielectric relaxations in dried amorphous cellulose and dextran

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Abstract

Cellulose and dextran are biosynthesized polysaccharides, made of glucose repeat units linked together by (β 1 → 4) and (α 1 → 6) linkages, respectively. Furthermore, cellulose has two hydroxyl groups and one hydroxymethyl group per glucose ring, while dextran has three hydroxyl groups and no hydroxymethyl group. This work deals with the characterization of dielectric secondary relaxations of amorphous dextran and cellulose. Dextran exhibits two dielectric secondary relaxations referred to as γ_{ddex} and β_{ddex}, while cellulose has only one very broad relaxation, γ_{dcell}. The γ_{ddex} relaxation process has an average activation energy and a pre-exponential time τ_o of 32 kJ mol^{-1} and 5×10^{-15} s respectively. This weakly cooperative relaxation process should be associated with the rotation of hydroxyl groups. The β_{ddex} relaxation has an average activation energy and a pre-exponential time τ_o of 82 kJ mol^{-1} and 10^{-20} s respectively. This activation energy has both enthalpic and entropic contributions. The comparison with mechanical relaxation data indicates that β_{ddex} results mainly from the motions of main chain segments. The analysis of the two dielectric relaxations of dextran leads to the conclusion that γ_{dcell} could result from the overlap of two processes corresponding respectively to the rotation of hydroxyl groups and to the rotation of hydroxymethyl groups.

Keywords: Polysaccharides; Activation energy; Activation entropy

1. Introduction

Cellulose and dextran are biosynthesized polysaccharides, made of glucose repeat units linked together by (β 1 → 4) and (α 1 → 6) linkages, respectively. Furthermore, cellulose has two hydroxyl groups and one hydroxymethyl group per glucose ring, while dextran has three hydroxyl groups and no hydroxymethyl group (see Fig. 1). They can be processed in such a way that they are amorphous. They exhibit secondary relaxation processes in their glassy state.

The sub-T_g molecular mobility in amorphous materials is generally attributed to localized, thermally activated motions. It leads to macroscopic mechanical or dielectric behaviour, so-called secondary relaxations (referred to as β, γ, δ, etc.) [1]. This work is focused on their analysis, not only because it is of interest to understand the exact molecular origin of such macroscopic behaviour, but also because recent work indicates that some of this process could be a precursor of the main (or α-) relaxation process which is associated with the generalized and cooperative motions involved in the glass transition [2–6].

Mechanical spectroscopy and dielectric spectroscopy are two complementary techniques classically used for the analysis of sub-T_g molecular mobility [7]. Mechanical spectroscopy is mainly sensitive to the anisotropy of the volume involved by the motion of molecular groups. Dielectric spectroscopy is sensitive to orientation changes of dipole moments in material submitted to a sine wave electric field. Thus the rotation of small groups such as hydroxyl groups which have a large dipole moment can be revealed by dielectric spectroscopy but they do not lead to any effect detected by mechanical spectroscopy. Thus the combination of mechanical and dielectric spectroscopies appears to be a powerful tool for the study of molecular mobility occurring in glassy polymers having a high density of polar groups. For example, cellulose which contains hydroxyl and hydroxymethyl groups does not exhibit the same relaxation processes by mechanical and dielectric measurements. Dynamic mechanical measurements performed on dried cellulose reveal two mechanical relaxations referred to as γ_{mcell} and β_{mcell} [8,9] while only one very broad dielectric secondary relaxation process,

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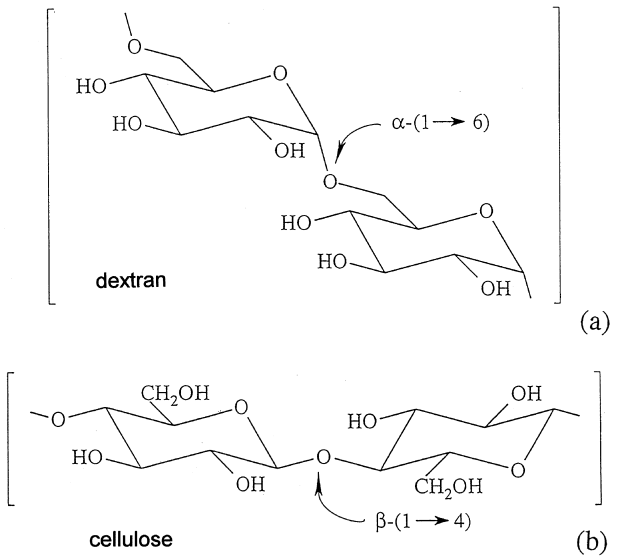

Fig. 1. Chemical structure of dextran (a) and cellulose (b).

called hereafter γ_{dcell}, is observed [10–14] by dielectric spectroscopy.

As is usually done, the secondary relaxation processes are characterized by their average activation energy E and their pre-exponential time τ_o using the Arrhenius analysis. The activation energy corresponds to the free energy barrier which must be jumped during the conformational transition involved in a relaxation process. The pre-exponential time τ_o is defined as the inverse of the vibration frequency of a particle in a potential well. Relaxation peaks measured on polymers are generally broader than a Debye peak [15,16], which means that there is a distribution of relaxation times. The complete characterization requires the fit of the relaxation time distribution, which could result from the distribution of the activation energy and/or of the pre-exponential time. Furthermore, secondary relaxations involve motions which can be more or less cooperative. The concept of cooperativity is often associated with a non-zero entropy in the total energy barrier involved in the conformational changes [17,18]. If the entropy contribution is negligible compared to the enthalpy contribution, the relaxation process corresponds to localized, non-cooperative motions. This is generally the case of side-group motions [19]. On the contrary, if the entropy contribution is large, motions are cooperative and probably involve segments of the main chain [19,20].

In previous work [21], it was shown that γ_{mcell}, which is detected at 150 K for 1 Hz and corresponds to the rotation of hydroxymethyl groups, has an activation energy mainly due to its enthalpic contribution. β_{mcell}, which appears at 220 K for 1 Hz and probably corresponds to localized motions of the main chain, has both enthalpic and entropic contributions for its activation energy. Other work available in the literature [10] concluded that γ_{dcell} and γ_{mcell} have the same molecular origin. γ_{dcell} would therefore correspond to the rotation of hydroxymethyl groups, but nothing is discussed about the role of the hydroxyl groups. Thus, in order to determine if they provide any contribution, dextran has also been studied here by dielectric spectroscopy.

The first part of this work analyses the two dielectric relaxations of dextran. The enthalpy and entropy contributions in the total energy barrier of these processes, as well as the width distribution of their relaxation times, are evaluated by fitting experimental data. The second part is a discussion on the molecular origin of γ_{dcell} based on the comparison of data obtained from dielectric measurements on dextran and mechanical measurements on cellulose.

2. Experimental

2.1. Sample preparation

Cellulose, from Buckeye (UK), with an average degree of polymerization $\overline{DP}$ of 600, was dissolved in monohydrate *N*-methyl morpholine *N*-oxide (NMMO) with a cellulose concentration of 10% (w/w). Then the solution, which is solid at room temperature, was extruded at 363 K (90°C) and precipitated in anhydrous methanol in order to completely remove NMMO. In previous work [22–24], these conditions were optimized so that no trace of NMMO could be detected by mass spectrometry. Thus, wholly amorphous cellulose films were obtained [22]. The samples were then dried for 24 h at 373 K and thereafter cut into discs of area 100 mm^2. The thickness of the films was 0.1 mm.

Commercial dextran powder from Sigma (with $\overline{DP} \approx 1000$) was dissolved in water. Solutions containing 20% (w/w) were dried slowly at room temperature to obtain homogeneous films with a thickness of 0.1 mm suitable for study of the dielectric behaviour. The films were then dried at 373 K for 24 h.

2.2. Dielectric spectroscopy

Dielectric measurements were carried out with a dielectric spectrometer (Hewlett-Packard HP 4284A) operating in the frequency range of 0.5 to 70 kHz and at a heating rate of 2 K min^{-1}. Interfaced with a PC compatible computer including home-made software, this instrument provides the real ε' and imaginary ε'' parts of the complex relative permittivity. The relaxation time τ was determined as a function of temperature T using the relationship $\omega\tau = 1$ where ω is the angular frequency and the T temperature for which ε'' passes through a maximum [7].

3. Results

The study of dextran by dielectric spectroscopy shows the existence of two relaxation processes. Fig. 2 shows dielectric thermograms for different frequencies. At first

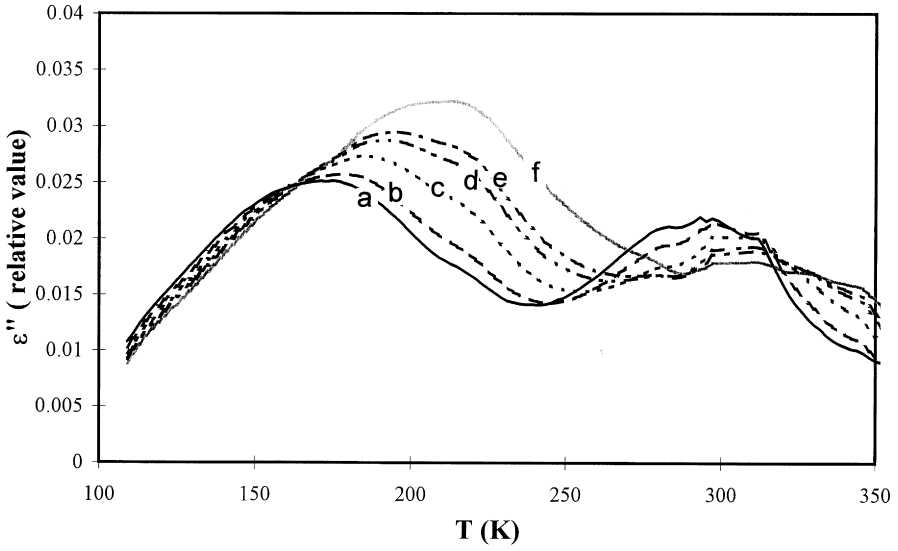

Fig. 2. Dielectric data for anhydrous dextran: ε'' versus temperature. From right to left: (a) 0.5, (b) 1, (c) 3, (d) 5, (e) 10 and (f) 30 kHz (see also Figs 6 and 7).

the low temperature relaxation γ_{ddex} appears as a large peak of ε'' at 170 K for 1 kHz. A second dielectric relaxation process referred to as β_{ddex} appears at 300 K at 1 kHz. Its amplitude is smaller than for γ_{ddex}. A plot of ln τ versus $1/T$ exhibits linear behaviour for both relaxations. As shown in Fig. 3, our data are in agreement with those available in the literature [10,25]. Thus, the temperature dependence of τ can be fitted by the Arrhenius equation:

$$\tau^{\text{d}}_{\gamma\text{dex}} = \tau^{\text{d}}_{0\gamma\text{dex}} \exp\left(\frac{E^{\text{d}}_{\gamma\text{dex}}}{RT}\right) \quad (1)$$

$$\tau^{\text{d}}_{\beta\text{dex}} = \tau^{\text{d}}_{0\beta\text{dex}} \exp\left(\frac{E^{\text{d}}_{\beta\text{dex}}}{RT}\right) \quad (2)$$

where $E_{\gamma\text{ddex}}$ and $E_{\beta\text{ddex}}$ are the apparent activation energies and $\tau_{0\gamma\text{ddex}}$ and $\tau_{0\beta\text{ddex}}$ the pre-exponential factors of γ_{ddex} and β_{ddex} respectively. $E_{\gamma\text{ddex}}$ was found to be 32 kJ mol^{-1} and $\tau_{0\gamma\text{ddex}}$ around 10^{-15} s. $E_{\beta\text{ddex}}$ was found to be 82 kJ mol^{-1} and $\tau_{0\beta\text{ddex}}$ of the order of 10^{-20} s.

In the case of cellulose, a single very broad relaxation process (Fig. 4) occurs around 205 K at 1 kHz. The linear plot of ln τ versus $1/T$ (Fig. 5) leads to the apparent activation energy $E_{\gamma\text{dcell}}$ of 50 kJ mol^{-1} and the average pre-exponential time $\tau_{0\gamma\text{dcell}}$ of 10^{-17} s, which is in agreement with data available in the literature [11,13,14]. This relaxation is thus closer to the mechanical γ relaxation of cellulose (40 kJ mol^{-1}) than to its mechanical β relaxation (80 kJ mol^{-1}) [21]. For this reason, this relaxation peaks will be referred to as γ_{dcell} in the following.

4. Discussion

4.1. Analysis of the dielectric secondary relaxations of dextran

As is clearly shown in Fig. 2, the two secondary dielectric relaxations of dextran are rather broad. This means that the relaxation times $\tau_{\gamma\text{ddex}}$ and $\tau_{\beta\text{ddex}}$ are distributed.

The molecular understanding of both mechanisms requires that precise characterization of the distribution of the relaxation times $\tau_{\gamma\text{ddex}}$ and $\tau_{\beta\text{ddex}}$ be made. This may be done by fitting the experimental curves of the complex relative permittivity ε^* of amorphous dextran versus temperature for several frequencies. First, it is assumed that the γ_{ddex} and β_{ddex} processes act independently each other. Thus, the total permittivity should be the sum of both γ_{ddex} and β_{ddex} contributions, so that the real and imaginary parts of $\varepsilon^*_{\text{dex}}$ can be written:

$$\varepsilon'_{\text{dex}} = \varepsilon'_{\gamma\text{dex}} + \varepsilon'_{\beta\text{dex}}$$
$$\varepsilon''_{\text{dex}} = \varepsilon''_{\gamma\text{dex}} + \varepsilon''_{\beta\text{dex}} \quad (3)$$

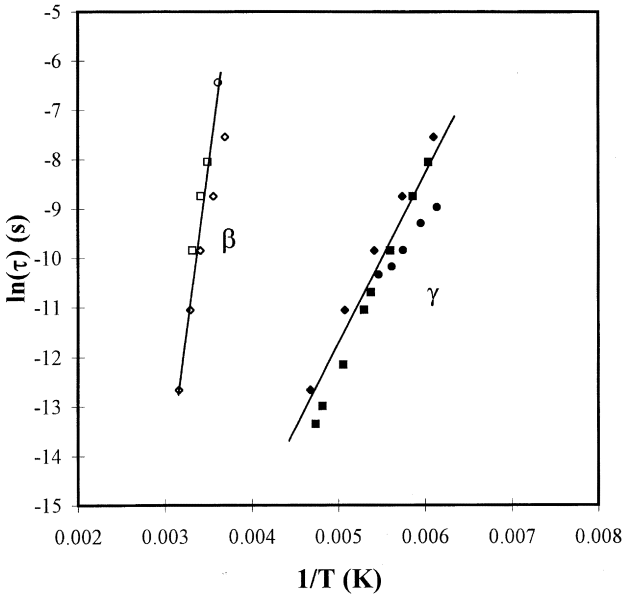

Fig. 3. Comparison of γ and β dielectric relaxation of anhydrous dextran: ln τ versus $1/T$ for the γ dielectric relaxation (■, our results; ◆, [10]; ●, [25]) and for the β dielectric relaxation (□, our results; ◇, [10]; ○, [25]).

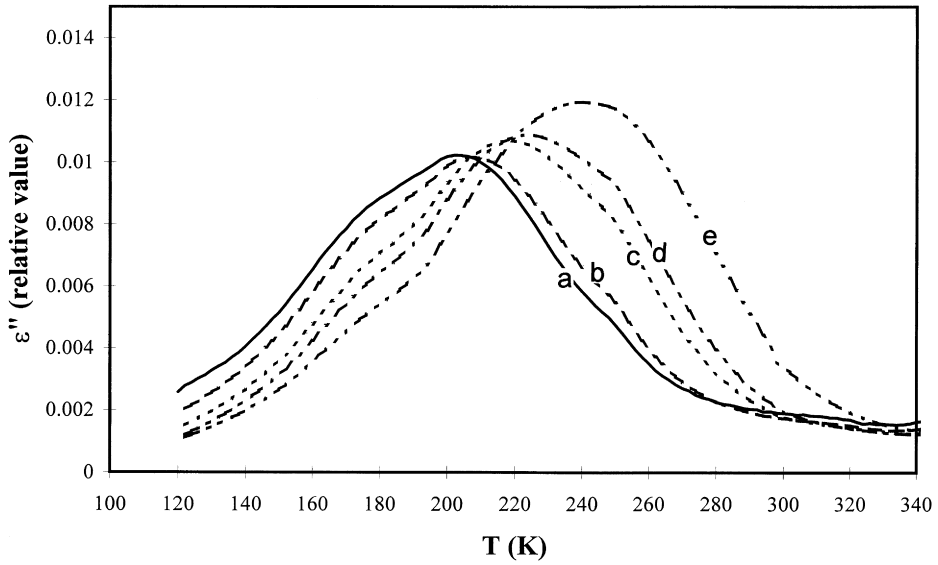

Fig. 4. Dielectric data for anhydrous cellulose: ε'' versus temperature. From right to left; (a) 0.5, (b) 1, (c) 5, (d) 10 and (e) 50 kHz (see also Fig. 9).

The distribution of $\tau_{\gamma\mathrm{ddex}}$ and $\tau_{\beta\mathrm{ddex}}$ can result from the distribution of the activation energies $E_{\gamma\mathrm{ddex}}$ and $E_{\beta\mathrm{ddex}}$ and/or from the distribution of the pre-exponential times $\tau_{0\gamma\mathrm{ddex}}$ and $\tau_{0\beta\mathrm{ddex}}$ [15–20]. In this study and for the sake of simplicity, we assume that $\tau_{0\gamma\mathrm{ddex}}$ and $\tau_{0\beta\mathrm{ddex}}$ are not distributed. Thus, the distribution of the relaxation times $\tau_{\gamma\mathrm{ddex}}$ and $\tau_{\beta\mathrm{ddex}}$ results from the distribution functions $\Phi_{\gamma\mathrm{ddex}}$ and $\Phi_{\beta\mathrm{ddex}}$ of the activation energies $E_{\gamma\mathrm{ddex}}$ and $E_{\beta\mathrm{ddex}}$. Assuming further that these activation energies have a Gaussian distribution, $\Phi_{\gamma\mathrm{ddex}}$ and $\Phi_{\beta\mathrm{ddex}}$ can be written as:

$$\Phi_{\gamma\mathrm{ddex}}(E_{\gamma\mathrm{ddex}}) = \frac{1}{B_{\gamma\mathrm{ddex}}\pi^{1/2}} \exp\left[-\left(\frac{E_{\gamma\mathrm{ddex}} - \langle E_{\gamma\mathrm{ddex}}\rangle}{B_{\gamma\mathrm{ddex}}}\right)^2\right]$$

$$\Phi_{\beta\mathrm{ddex}}(E_{\beta\mathrm{ddex}}) = \frac{1}{B_{\beta\mathrm{ddex}}\pi^{1/2}} \exp\left[-\left(\frac{E_{\beta\mathrm{ddex}} - \langle E_{\beta\mathrm{ddex}}\rangle}{B_{\beta\mathrm{ddex}}}\right)^2\right] \quad (4)$$

where $B_{\gamma\mathrm{ddex}}$ and $B_{\beta\mathrm{ddex}}$ are the corresponding Gaussian distribution widths. $\varepsilon_{\mathrm{u}\gamma}$ and $\varepsilon_{\mathrm{u}\beta}$ are the unrelaxed permittivity of cellulose for each process. The fit requires that the following parameters are determined: $(\varepsilon_{\mathrm{r}\gamma} - \varepsilon_{\mathrm{u}\gamma})$, $\varepsilon_{\mathrm{u}\gamma}$, $(\varepsilon_{\mathrm{r}\beta} - \varepsilon_{\mathrm{u}\beta})$, $\varepsilon_{\mathrm{u}\beta}$, $B_{\gamma\mathrm{ddex}}$, $B_{\beta\mathrm{ddex}}$ $\tau_{0\gamma\mathrm{ddex}}$, $\tau_{0\beta\mathrm{ddex}}$, $\langle E_{\gamma\mathrm{ddex}}\rangle$ and $\langle E_{\beta\mathrm{ddex}}\rangle$, where $\varepsilon_{\mathrm{r}\gamma}$ and $\varepsilon_{\mathrm{r}\beta}$ are the relaxed permittivities for the two processes. The parameters $\varepsilon_{\mathrm{u}\beta}$, $\varepsilon_{\mathrm{u}\gamma}$, $\varepsilon_{\mathrm{r}\gamma}$, $\varepsilon_{\mathrm{r}\beta}$ are determined through Cole–Cole diagrams giving ε'' versus ε'. By neglecting any change of $B_{\beta\mathrm{ddex}}$ and $B_{\gamma\mathrm{ddex}}$ with temperature, ε' and ε'' can be calculated for all the temperature range between 100 to 300 K and for different frequencies. Experimental and calculated plots of ε' and ε'' versus temperature for 1 kHz are shown in Figs 6a and 6b. Good agreement between experimental and calculated curves is also obtained for other frequencies (Figs 7a and 7b). The best fit was obtained with $\langle E_{\gamma\mathrm{ddex}}\rangle$ of 32 kJ mol^{-1} and $\tau_{0\gamma\mathrm{ddex}}$ of 5.10^{-15} s, with $B_{\gamma\mathrm{ddex}}$ of 9 kJ mol^{-1} (see Table 1). $\langle E_{\beta\mathrm{ddex}}\rangle$ and $\tau_{0\beta\mathrm{ddex}}$ were found to be 82 kJ mol^{-1} and 3×10^{-19} s respectively. $B_{\beta\mathrm{ddex}}$ was estimated around 10 kJ mol^{-1}. Values for $\langle E_{\gamma\mathrm{ddex}}\rangle$ and $\langle E_{\beta\mathrm{ddex}}\rangle$ are close to the previous values determined directly from the data. This indicates that the overlap between the γ and β relaxation can be neglected. Furthermore, this fit allows the width of each relaxation to be determined separately, which will be used in the following sections.

Once the activation energy of a relaxation process is precisely determined, it is possible to discriminate its

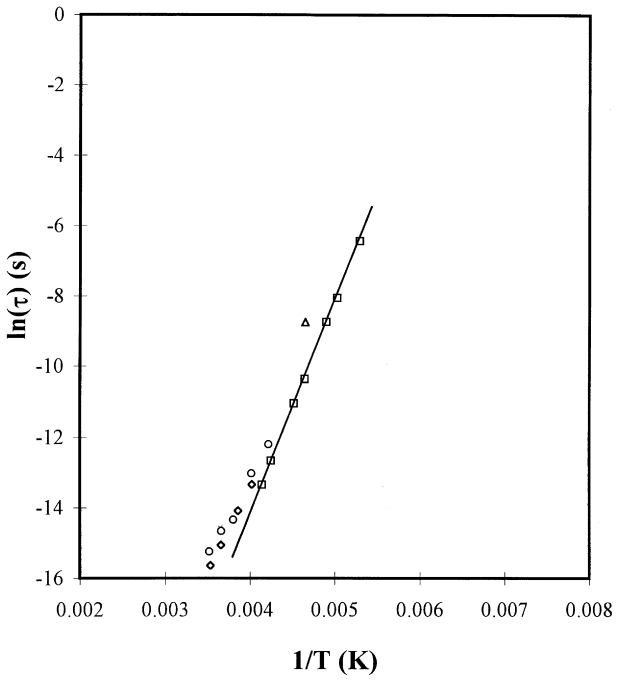

Fig. 5. Variation of ln τ versus 1/T. Comparison of γ dielectric relaxation of anhydrous cellulose: □, our results; △, [13]; •, [14]; ○, [12].

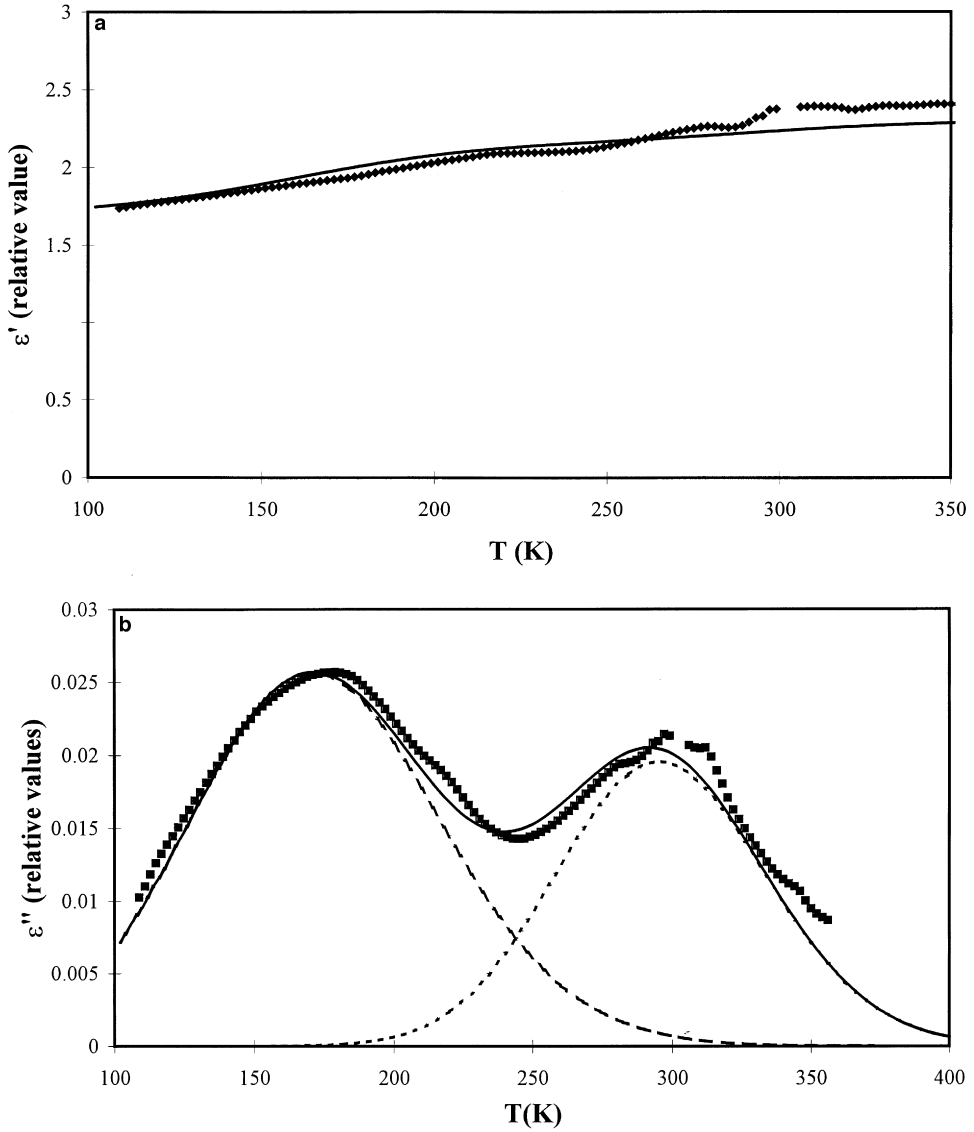

Fig. 6. Comparison of dielectric data at 1 kHz for dextran: ε' (a) and ε'' (b) versus temperature: ———, calculated data (ε' or ε''); - - -, contribution of the γ_{ddex} relaxation; — —, contribution of the β_{ddex} relaxation; ■, experimental data.

enthalpic and entropic contributions. According to most work on sub-T_g relaxations (see, for example, Ref. [2]), γ_{ddex} and β_{ddex} should be due to localized motions of groups of atoms or of molecular segments. In particular, local regions which contain the smallest group capable of reorientation should lead to γ_{ddex} relaxation and local regions which contain larger groups should lead to β_{ddex} relaxation.

Table 1
Parameters used for the fit of the γ_{ddex} and β_{ddex} relaxation processes of anhydrous dextran

Parameter	γ_{ddex}	β_{ddex}
$\langle E \rangle$ (kJ mol^{-1})	32	82
B (kJ mol^{-1})	9	10
$(\varepsilon_r - \varepsilon_u)$	0.3	0.15
ε_u	1.7	2.1
τ_o (s)	5×10^{-15}	3×10^{-19}

The thermodynamic origin of the activation energy associated with each relaxation process may lead to information on the corresponding molecular motions. The entropy contribution of $E_{\gamma ddex}$ and $E_{\beta ddex}$ can be determined using the approach developed by Starkweather [17,18]. Thus the Eyring theory [26] can be used to describe a relaxation time τ as follows:

$$\tau = \frac{2\pi h}{kT} \exp\left(\frac{-\Delta S}{R}\right) \exp\left(\frac{\Delta H}{RT}\right) \quad (5)$$

with ΔS and ΔH the entropy and enthalpy contributions of the free activation energy of a thermoactivated motion, respectively, k the Boltzmann constant and h the Planck constant. On the other hand, the apparent activation energy E corresponds to the derivative of ln τ versus $1/T$:

$$E = R\frac{\mathrm{d}(\ln \tau)}{\mathrm{d}(1/T)} \quad (6)$$

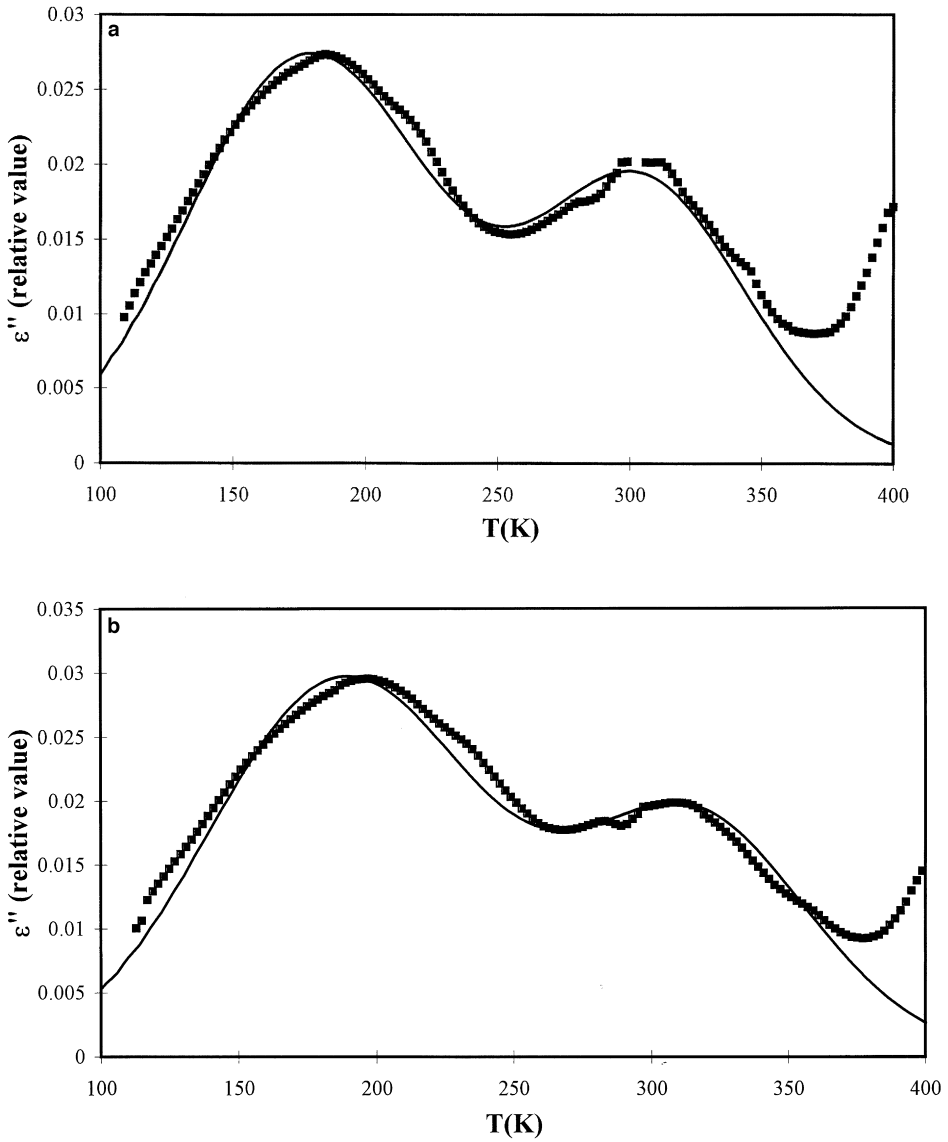

Fig. 7. Comparison of dielectric data for anhydrous dextran at 3 kHz (a) and 10 kHz (b): ———, calculated data (ε″); ■, experimental data.

It is worthy of note that from Eqs. (5) and (6), if $\Delta S = 0$, $E = \Delta H + RT$ and is, in fact, very close to ΔH. According to Starkweather [17,18,20], the apparent activation energy of a relaxation occurring at temperature T and frequency f can be written as a function of its apparent activation entropy ΔS:

$$E = RT\left[1 + \ln\left(\frac{kT}{2\pi hf}\right)\right] + T\Delta S \tag{7}$$

For γ_{ddex}, ΔS is found to be negligible (i.e. $\tau_{0\gamma\mathrm{ddex}}$ is close to the Debye time). On the contrary, for β_{ddex}, $T\Delta S$ was found to be 100 J mol^{-1} K^{-1}.

Thus, the analysis shows that the activation energy associated with γ_{ddex} has essentially an enthalpy contribution. As recalled above, this type of relaxation involves localized, non-cooperative motions and is often associated with the motions of side-groups, i.e. for dextran, hydroxyl groups. No γ mechanical relaxation process is observed on dextran [10,21], probably because its very small size does not provide a macroscopic effect. Thus, it is confirmed that dielectric spectroscopy more is sensitive to motions of smaller size molecular groups if they have a dipole moment than mechanical spectroscopy. The large width of the γ_{ddex} energy distribution could come from the fact that the energy barrier to be jumped during the rotation of hydroxyl groups depends mainly on the local balance of hydrogen bonds [27,28]. This depends in turn on the local chain conformation in the amorphous material.

As seen above, the entropy contribution of β_{ddex} is not negligible compared to the enthalpic contribution. This indicates that the motions associated with this relaxation process are cooperative. According to Heijboer [18], the apparent activation energy is too high, i.e. the pre-exponential time is too short compared to the Debye time,

for only side-groups to be responsible for this relaxation. On the other hand, it is clear that this process does not correspond to the glass transition of dextran and is probably associated with localized motions of the main chain. It is of interest to compare β_{ddex} with the secondary mechanical relaxation of dextran β_{mdex}. In previous work [9,21], dynamic mechanical measurements have been performed on anhydrous dextran. β_{mdex} appears at 220 K for 0.1 Hz. Fig. 8 shows a plot of ln τ versus $1/T$ where the mechanical and dielectric β processes of dextran are compared. It appears that the data conform to a single line, i.e. β_{mdex} and β_{ddex} have similar characteristics (activation energy and pre-exponential time) and may have the same molecular origin.

4.2. Analysis of the dielectric secondary relaxation of cellulose

Anhydrous cellulose exhibits only a single, broad secondary dielectric relaxation (γ_{dcell}). Although two secondary mechanical relaxations γ_{ddex} and β_{ddex} are observed [21], the strength of the β relaxation is strongly dependent on water content and, in the dry state, the β relaxation is very weak, the peak height being only one-third of that observed with dextran. It is therefore not very surprising that the β relaxation cannot be observed dielectrically in dry cellulose.

As discussed above, γ_{dcell} could result from motions of side-groups. Cellulose contains two kinds of side-groups whose motions are known to lead to a macroscopic dielectric effect: hydroxyl groups and hydroxymethyl groups. The dielectric analysis of dextran shows that the hydroxyl group rotations appear at 170 K at 1 kHz. On the other hand, the motion of hydroxymethyl groups in cellulose is observed by mechanical measurements at 150 K at 1 Hz [21]. From the knowledge of its activation energy, it appears that this motion would lead to a relaxation phenomenon at 225 K at 1 kHz. If we consider the temperature range of γ_{dcell}, the motions of both hydroxyl and hydroxymethyl groups could be at the origin of this relaxation. Thus γ_{dcell} could result from the overlap of two relaxation processes referred as to γ_{OH} and γ_{CH2OH}, where γ_{OH} corresponds to the rotation of the hydroxyl groups while γ_{CH2OH} comes from the motions of hydroxymethyl groups. In order to check this hypothesis, the complex permittivity ε^* of cellulose can be calculated assuming $\varepsilon^* = \varepsilon^*_{\gamma CH2OH} + \varepsilon^*_{\gamma OH}$, if we neglect all interactions between the two processes. γ_{OH} can be assumed to have the behaviour of γ_{ddex}, so that the average activation energy $\langle E_{\gamma OH}\rangle$, the pre-exponential $\tau_{o\gamma OH}$ and the width of the energy distribution are taken equal to those determined for γ_{ddex}. Furthermore, and at a very qualitative level, it is assumed that γ_{CH2OH} has the same characteristics as the γ mechanical relaxation of dried cellulose. Thus, $\varepsilon_{u\gamma OH}$ and $\varepsilon_{r\gamma CH2OH}$, which are the unrelaxed value of $\varepsilon'_{\gamma OH}$ and relaxed value of $\varepsilon'\gamma_{CH2OH}$, respectively, can be determined from the Cole–Cole diagram of γ_{dcell}. $\varepsilon_{u\gamma CH2OH}$ and $\varepsilon_{u\gamma OH}$ have been evaluated in order to obtain the best fit of the experimental data. Plots

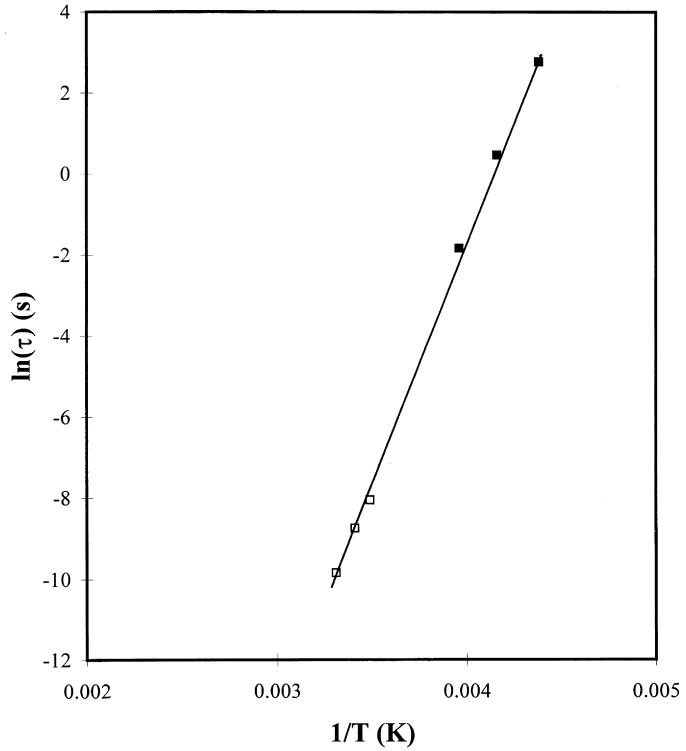

Fig. 8. Variation of ln τ versus $1/T$. Comparison of the β dielectric relaxation and β mechanical relaxation data of anhydrous dextran: ■, β_{ddex} dielectric relaxation; □, β_{mdex} mechanical relaxation.

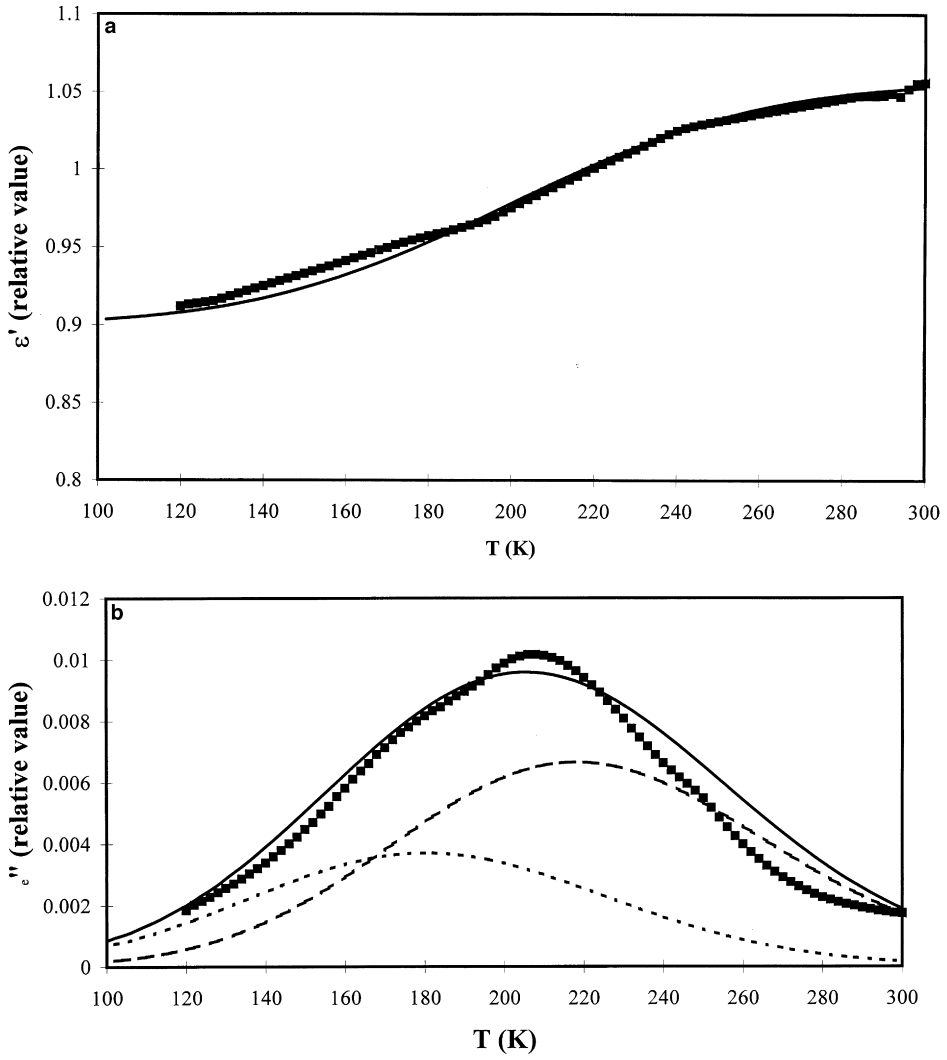

Fig. 9. Comparison of dielectric data at 1 kHz for anhydrous amorphous cellulose: ε' (a) and ε'' (b) versus temperature: ———, calculated data (ε' or ε''); - - -, contribution of the γ_{OH} relaxation; — —, contribution of the γ_{CH2OH} relaxation; ■, experimental data.

of ε' and ε'' versus temperature are shown in Figs 9a and 9b and the corresponding parameters are displayed in Table 2. Dielectric thermograms of ε'' and ε' versus temperature have been calculated for different frequencies. The good agreement between experimental and calculated plots indicates that the hypothesis of two contributions coming from the rotation of OH and CH_2OH groups is a possible explanation for the broadness of γ_{dcell}.

Table 2
Parameters used for the γ_{OH} and γ_{CH2OH} relaxation processes to fit γ_{dcell}

Parameter	γ_{OH}	γ_{CH2OH}
$\langle E \rangle$ (kJ mol^{-1})	32	34
B (kJ mol^{-1})	9	7
$(\varepsilon_r - \varepsilon_u)$	0.04	0.06
ε_u	0.9	1
τ_o (s)	5×10^{-15}	9×10^{-13}

5. Conclusion

Dried cellulose presents only one secondary relaxation process (γ_{dcell}) while two relaxation processes (γ and β) are observed by mechanical measurements. The absence of a dielectric β relaxation in dried cellulose may be related to the fact that its mechanical β relaxation is drastically dependent on the moisture content and nearly disappears for dried cellulose. On the contrary, dextran keeps a dielectric and mechanical β relaxation, even at very low moisture content. Furthermore, γ_{dcell} can be analysed from the comparison of data obtained from (i) dielectric measurements performed on dried dextran and (ii) mechanical measurements performed on dried cellulose. This broad relaxation peak could correspond to the overlap of two relaxation processes involving distinct molecular groups: the rotation of hydroxyl groups and the rotation of hydroxymethyl groups. This is the main difference between the dielectric γ relaxation of cellulose and its mechanical γ

relaxation. In fact, the mechanical γ relaxation of cellulose is mainly due to the rotation of the hydroxymethyl groups, while dielectric measurements are sensitive to both the motions of hydroxymethyl and hydroxyl groups.

The approach developed in this paper only attempted to analyse the dielectric γ relaxation process observed in anhydrous cellulose. It would be of interest to apply it to hydrated amorphous cellulose. This would allow one to evaluate more accurately the role of water molecules on the dielectric behaviour of this polymer, whose viscoelastic behaviour is particularly sensitive to the presence of water.

References

[1] Ferry JD. Viscoelastic properties of polymers, 3rd edn. New York: Wiley, 1980.
[2] Perez J, Muzeau E, Johary GP. Macromolecules 1991;24:4713.
[3] Ngaï KL, Rendell RW, Rajagopal AK, Teitler S. Annals of the New York Academy of Sciences 1986;484:150.
[4] Ngaï KL, Rendell RW, Yee AY. Macromolecules 1988;21:3396.
[5] Cavaillé JY, Perez J, Johary GP. Phys Rev B 1989;39(4):2411.
[6] Perez J, Cavaillé JY, Etienne S, Jourdan C. Rev Phys Appl 1988;23:125.
[7] McCrum NG, Reed BE, Williams G. Anelastic and dielectic effects in polymeric solids. New York: John Wiley, 1967.
[8] Bradley SA, Carr SH. J Polym Sci: Polym Phys Ed 1976;14:111.
[9] Montes H, Mazeau K, Cavaillé JY. J Non-Cryst Solids 1994;172-174:990.
[10] Scandola M, Ceccorulli G, Pizzoli M. Int J Biol Macromol 1991;13:254.
[11] Boutros S, Hanna AA. J Polym Sci: Polym Chem Ed 1978;16:89.
[12] Ishida Y, Yoshino M, Takayanagi M. J Appl Polym Sci 1959;1:227–235.
[13] Crofton DF, Perhrick RA. Polymer 1981;22:1048.
[14] Seidman R, Mason SG. Canadian Journal of Chemistry 1955;32:744.
[15] Nowick AS, Berry BS. IBM Journal Res Dev 1961;5:297.
[16] Nowick AS, Berry BS. IBM Journal Res Dev 1961;5:312.
[17] Starkweather HW. Polymer 1991;32:2443.
[18] Starkweather HW. Macromolecules 1988;21:1798.
[19] Heijboer J. In: Meier DJ, editor. Molecular basis of transitions and relaxations. Midland Macromolecular Monographs, 4. New York: Gordon and Breach, 1975.
[20] Starkweather HW. Macromolecules 1981;14:1277.
[21] Montes H, Mazeau K, Cavaillé JY. Macromolecules, 1997;30:6977.
[22] Paillet M, Cavaillé JY, Desbrieres J, Dupeyre D, Peguy A. Colloid Polym Sci 1993;271:311.
[23] Garcia Ramirez M, Cavaillé JY, Dupeyre D, Peguy A. J Polym Sci: Polym Phys 1994;32:1437.
[24] Lenz J, Schurz J. J Appl Polym Sci 1988;5:1987.
[25] Nishinari K, Shibuya N, Kainuma K. Makromol Chem 1985;186:433.
[26] Eyring H. J Chem Phys 1936;4:283.
[27] Johary GP, Pahmanathan K. Physics and Chemistry of Glasses 1988;29 (6):219.
[28] Johary GP. J Mol Struct 1991;250:351.