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Secondary relaxations in poly(allyl alcohol), PAA, and poly(vinyl alcohol), PVA. II. Dielectric relaxations compared with dielectric behaviour of amorphous dried and hydrated cellulose and dextran

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Abstract

This work deals with the characterisation of the dielectric secondary relaxations of poly(allyl alcohol) (PAA) and poly(vinyl alcohol) (PVA) and its comparison with the cellulose and dextran dielectric behaviour. Cellulose and dextran are two polysaccharides made of glucosyl repeat units. Cellulose has two hydroxyl groups (OH) and one hydroxymethyl group (CH_2OH) per glucose ring, while dextran has three OH groups and no CH_2OH group. PAA and PVA are the two simplest vinyl polymers containing CH_2OH and OH lateral groups, respectively. They exhibit only one broad dielectric secondary relaxation with characteristics in between those of the γ and β mechanical relaxations in dried PAA. Each of these apparently unique relaxations is successfully explained and modelled by the overlaps of two relaxation processes, γ' and β'. The γ' relaxation, related to the rotation of side groups (CH_2OH for PAA and OH for PVA), has characteristics close to those of the γ mechanical relaxation for dried PAA. The β' relaxation corresponds to more or less cooperative motions of main-chain segments. Furthermore, the influence of moisture on the secondary dielectric relaxations of PAA and PVA is discussed on the basis of a competition between γ' and β', where the intensity of β' (γ') increases (decreases) with increasing water content.

Keywords: Vinyl polymer; Polysaccharides; Thermal activation

1. Introduction

As a larger team project we are interested in the molecular simulation of thermally activated and localised motions in polysaccharides such as cellulose, dextran and amylose. All these polymers originate from the polymerisation of sugar units, so that they are all rich in hydroxyl and/or hydroxymethyl groups (see Fig. 1(a) and (c)). Like a great number of polymers bearing polar groups (for example polyamides), this makes them particularly susceptible to moisture [1–3]. Nevertheless, the complexity of polysaccharides presents a limitation for such modelling [4].

In a previous work [5], the two simplest vinyl polymers bearing hydroxyl or hydroxymethyl groups (poly(vinyl alcohol) (PVA) and poly(allyl alcohol) (PAA), respectively, see Fig. 1(b) and (d)) were studied by dynamic mechanical analysis. A γ relaxation was only observable at low temperature in the presence of a hydroxymethyl group (PAA). At higher temperatures, a β relaxation process occurred in both polymers. This β relaxation is highly cooperative and sensitive to polar solvents. The presence of a small amount of water or methanol induces a decrease of both the relaxation maximum temperature and the activation energy. The same trends were observed on cellulose and dextran [4].

Dielectric and mechanical spectroscopies are two complementary techniques classically used for the analysis of the sub-T_g molecular mobility. Dielectric spectroscopy is sensitive to orientation changes of dipole moments in material under an applied AC field. Mechanical spectroscopy is mainly sensitive to the anisotropy of the local volume change involved in the motion of molecular groups. Thus the rotations of small groups such as hydroxyl groups having a large dipole moment can be revealed by dielectric spectroscopy but they do not lead to significant effects detected by mechanical spectroscopy. In contrast, the

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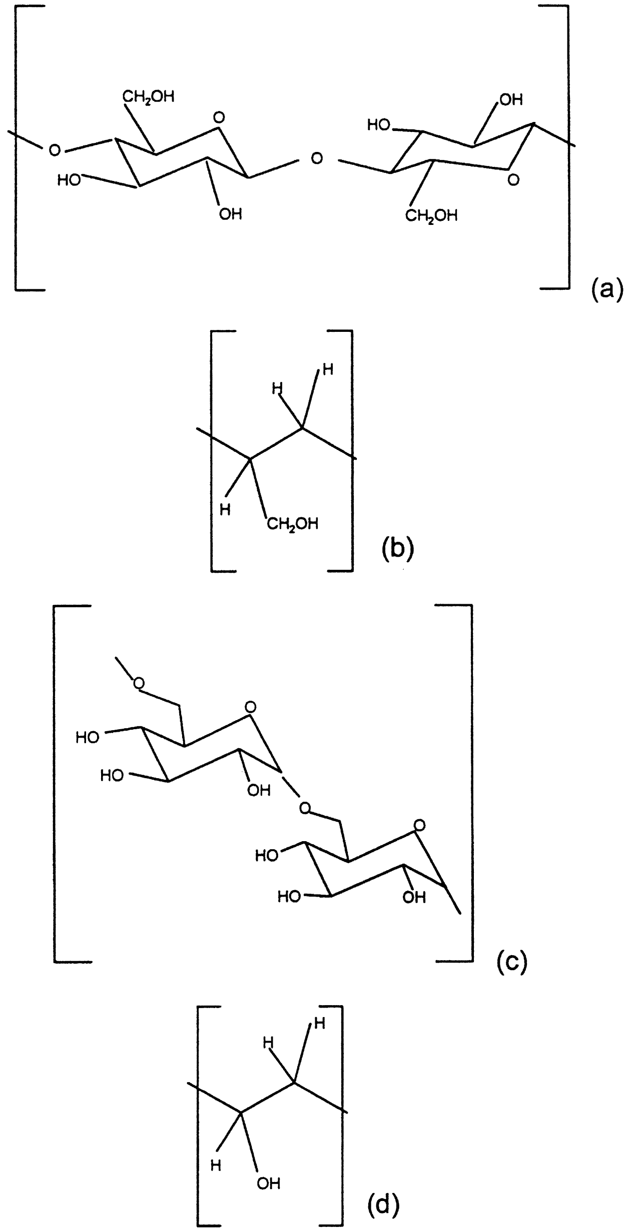

Fig. 1. Chemical structures of: (a) cellulose; (b) PAA; (c) dextran; and (d) PVA.

rotation of the larger hydroxymethyl group should induce a relaxation process detectable by both techniques. This has been shown through the comparison of dynamic mechanical and dielectric analyses on cellulose and dextran [4,6]. In the case of polysaccharides, the understanding of the contribution of each motion can be complicated by the presence of both side groups, as in cellulose. In this case, the broad dielectric relaxation arises from the contributions of both OH and CH_2OH side groups, while no motions corresponding to its β mechanical relaxation were detected. The study of the vinylic analogues of polysaccharides should simplify the analysis of the molecular origin of these relaxations.

Many experiments have already been devoted to the measurement of the dielectric properties of PVA [7–11]. They all characterised a single broad dielectric secondary relaxation around 220 K in the frequency range from 20 Hz to 1 MHz. Its apparent activation energy was estimated at 58 kJ mol^{-1} [12]. Moreover, this activation energy is little affected by the changes in degree of crystallinity: from 58 to 52 kJ mol^{-1} for a sample with from 37 (unheat-treated) to 58% crystallinity (heat-treated at 180°C). At any given temperature, however, the frequency of maximum loss increases slightly with increasing crystallinity. In contrast, no work has been reported on the dielectric relaxations in PAA.

The purpose of this paper is to analyse precisely the contribution of hydroxyl and hydroxymethyl moieties in the dielectric relaxation process with the same set of data. The influence of a polar solvent will be investigated too.

2. Experimental section

2.1. PAA synthesis

PAA is not commercially available, probably because the result of conventional radical polymerisation from allyl monomer is a polymer with a low degree of polymerisation. This comes from the high reactivity of these monomers to degradative chain transfer [13,14]. In this work, pure PAA was prepared according to the method of Cohen et al. [15], discussed in a previous paper [5], by the reduction of poly-(methyl acrylate) (PMA) (ALDRICH, with M_w 40,000) in toluene with lithium aluminium hydride ($LiAlH_4$) [15,16] and isolated with potassium sodium tartrate. The product of this reaction is completely soluble in 10% v/v methanol–water mixture.

2.2. PAA characterisation

The reduction of PMA into PAA was verified by infrared spectroscopy (IR) and nuclear magnetic resonance ^{13}C spectroscopy (NMR) [5]. The full conversion of the carbonyl bond into secondary alcohol bonds shows (by IR) the success of this reaction. The results obtained by NMR are consistent with the chemical structure of PAA. No detection of sub-products by these techniques confirms the purity of PAA. Finally, PAA was characterised by differential scanning calorimetry (DSC). At the scanning rate of 20 K min^{-1}, the glass transition temperature (T_g) was found at 75°C (348 K) for the dried polymer.

2.3. Sample preparation

2.3.1. PAA samples

PAA films were prepared from the solution of PAA in a 10% v/v methanol–water mixture. The films were then dried at 35°C (308 K) for 2 days at atmospheric pressure. Finally, they were maintained in the presence of dried P_2O_5

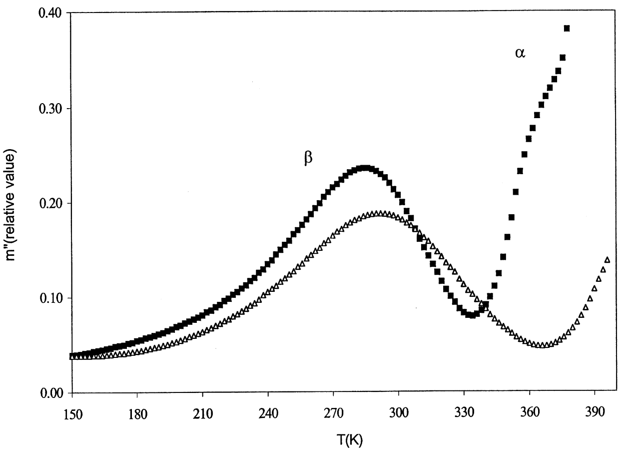

Fig. 2. Influence of solvent content on the secondary dielectric relaxation in PAA: m'' versus temperature ($f = 10$ kHz). PAA with 2.8% w/w of water (■) and dried PAA (△).

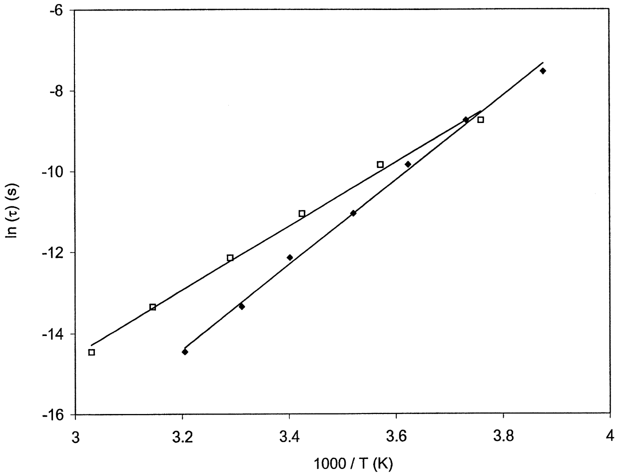

Fig. 3. Variation of $\ln(\tau)$ versus $1000/T$ for the dielectric relaxation of PAA. Comparison between PAA with 2.8% w/w of water (◆) and dried PAA (□).

during 2 weeks. The samples thus obtained contained a residual solvent fraction of 2.8% w/w as measured by weighing. To obtain dried PAA, the films were heat-treated at 90°C for 24 h inside the dielectric spectrometer.

2.3.2. PVA samples

PVA films were prepared by dissolving PVA (ALDRICH with M_w 124,000–186,000) in 40% w/w of water at 70°C. PVA films were dried in the presence of P_2O_5 for 2 weeks. The samples thus obtained contained a residual water fraction of 1.2% w/w as measured by weighing. Finally, fully dried PVA films were obtained by a further thermal treatment at 90°C for 24 h inside the spectrometer. The heat required for melting of 100% crystalline PVA is 138.6 J g^{-1} [17]. Thus a crystallinity of 45.7% (melt heat of 63.5 J g^{-1}) was calculated by DSC for the dried sample of PVA.

2.4. Dielectric spectroscopy

Dielectric measurements were carried out with a dielectric spectrometer (HP 4284A from Hewlett–Packard) operating here in the frequency range of 0.3–300 kHz and at a heating rate of 2 K min^{-1}. Interfaced with a personal computer including home-made software, this instrument provides the complex dielectric capacitance Cp* ($= \varepsilon_0 \varepsilon_r^*(S/e)$, where ε_r^* is the complex relative permittivity and ε_0 is the permittivity of free space, S and e the area and the thickness of the sample, respectively) and the loss tangent (tan δ). PVA and PAA samples (hydrated and dried) were scanned from about 140 to 400 K. In order to decrease the effect of the overlap with the α relaxation, especially on the imaginary part of the permittivity, ε'', we have worked with the complex dielectric modulus m^* ($m^* = 1/\varepsilon^*$). 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 T the temperature for which the imaginary part of the dielectric modulus, m'', passes through a maximum.

3. Results and discussion

3.1. PAA

For dried and hydrated PAA (and for the whole frequency range) only one broad relaxation peak was observed at lower temperature than the main relaxation, α, associated with the glass transition. Fig. 2 presents the comparison of dielectric results, at 10 kHz, for dried PAA and with 2.8% w/w of water. The secondary dielectric relaxation, denoted here as β_{dPAA}, as well as the α relaxation shifts to higher temperature and its intensity decreases slightly when the solvent is removed. At 10 kHz, β_{dPAA} shifts from 285 K for PAA with 2.8% w/w of water to 295 K for the dried polymer.

As a first approximation, it is usual to describe the variation of the characteristic time τ of a relaxation process by the Arrhenius equation,

$$\tau = \tau_0 \exp\left[\frac{E}{RT}\right] \qquad (1)$$

where τ_0 is the pre-exponential factor and E is the apparent activation energy. Fig. 3 shows the plot of $\log(\tau_{\beta_{dPAA}})$ versus $1/T$, for hydrated and dried PAA. The activation energy, $E_{\beta_{dPAA}}$, decreases after thermal treatment from 87 kJ mol^{-1} for the hydrated sample (2.8% w/w of water), to 65 kJ mol^{-1} for dried PAA. Simultaneously, the pre-exponential time, $\tau_{0\beta_{dPAA}}$, becomes larger: it is close to 10^{-20} s for hydrated PAA and around 1.6×10^{-16} s for anhydrous PAA.

It is clear that the molecular mobility of PAA is influenced by moisture. However, it is well known that the polar water molecules modify the total polarisation of the system. The modelling of the dielectric relaxation would rely on the approximation that motions of water are not counted in the total relaxation processes. Moreover, the relaxation processes measured

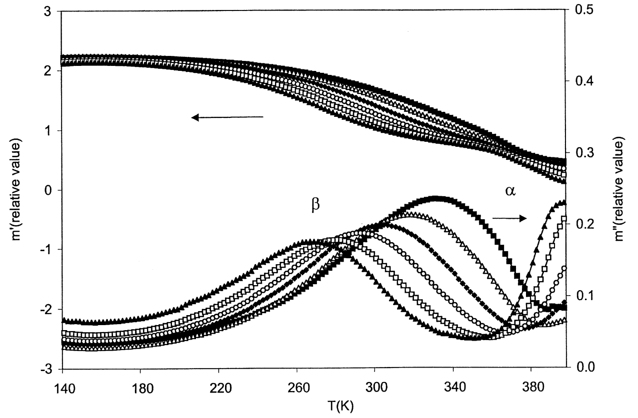

Fig. 4. Dielectric data for dried PAA: real (m') and imaginary (m'') part of the dielectric modulus versus temperature. For 300 (■), 100 (△), 30 (◆), 10 (○), 3 (□) and 1 kHz (▲).

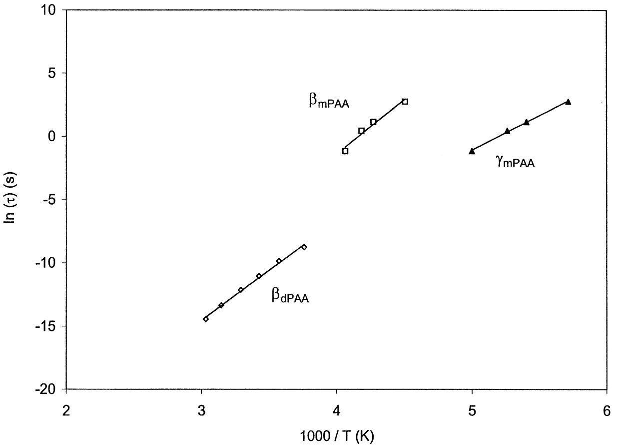

Fig. 5. Variation of $\ln(\tau)$ versus $1000/T$ for the secondary relaxations measured by dielectric and mechanical spectroscopy in dried PAA: (▲) for γ_{mPAA} (activation energy of 45 kJ mol^{-1}); (□) for β_{mPAA} (activation energy of 71 kJ mol^{-1}); and (◇) for β_{dPAA} (activation energy of 65 kJ mol^{-1}).

by mechanical spectroscopy in the polymer–solvent system cannot be compared directly with their corresponding dielectric behaviour. For these reasons, the following results will be focussed on dried PAA in order to characterise more precisely its relaxation process.

Fig. 4 shows the evolution of m' and m'' versus temperature for the dried sample at 1, 3, 10, 30, 100 and 300 kHz. The broad secondary relaxation lies between 220 and 330 K. As previously determined for ε'' versus T, the activation energy and pre-exponential time of the dielectric relaxation were found to be 65 kJ mol^{-1} and 2×10^{-16} s, respectively. These characteristics are in between the data obtained for the γ and β relaxations measured by mechanical spectroscopy [5].

Fig. 5 summarises and compares the characteristics of the secondary relaxations measured by mechanical and dielectric spectroscopies for dried PAA. One possible explanation of the only dielectric relaxation peak, is the overlap of the two relaxation processes at the measuring frequencies. Thus, the measured dielectric relaxation could result from the superposition of two relaxation processes, γ'_{PAA} and β'_{PAA}. In this hypothesis, the parameters for γ'_{PAA} should correspond to the γ mechanical relaxation of dried PAA (see Fig. 5), i.e. to the rotation of the hydroxymethyl groups, and those of β'_{PAA} to the β mechanical relaxation, i.e. to the motions of its main-chain segments.

In order to check this hypothesis, a simple modelling of their respective contribution was performed. As for the dynamic mechanical measurements [5], a distribution of the relaxation times is assumed. The relaxation time distributions for γ'_{PAA} and β'_{PAA} may result from the distribution of the activation energy and/or of the pre-exponential time [18–22]. In this study (as in Ref. [5]) and for the sake of simplicity, we assume that the distribution of the relaxation times results from the distribution functions $\Phi_{\gamma_{PAA}}$ and $\Phi_{\beta_{PAA}}$ of the activation energies $E_{\gamma_{PAA}}$ and $E_{\beta_{PAA}}$. Moreover, if we assume that these activation energies have a Gaussian distribution, we can write Φ in the general form as:

$$\Phi(E) = \frac{1}{B\sqrt{\pi}} \exp\left[-\left(\frac{E - \langle E \rangle}{B}\right)^2\right] \qquad (2)$$

where B and $\langle E \rangle$ are the corresponding Gaussian distribution width and average activation energy, respectively. The formalism used for modelling the dielectric complex modulus m^* is the same as that already used for the complex compliance J^* [4,5] or complex permittivity [6,23]. The fit of m^* requires the following parameters for the two relaxation processes γ' and β': $(m_r - m_u)$, m_u, $\langle E \rangle$, τ_0 and B, where m_u and m_r are the unrelaxed and relaxed dielectric modulus, respectively. This represents a great number of parameters. To avoid any fitting artefact, the initial set of activation energies and pre-exponential times was chosen to be the same as in the mechanical study [5]. A strong constraint was the accuracy of the fit to all the measured frequencies. This drastically reduces the degrees of freedom in the fitting procedure. Fig. 6(a) and (b) shows the result of this modelling. Parameters for γ'_{PAA} are summarised in Table 1. Parameters for β'_{PAA} remain close to those of β_{dPAA} for dried PAA (see Table 2). This probably comes from the fact that the amplitude of β'_{PAA} is always higher than the amplitude of γ'_{PAA}. The same trend was observed with the mechanical experimental results, suggesting that the reorientation of the dipoles is very large during the β relaxation process.

3.2. PVA

Fig. 7 shows the dielectric thermogram of dried (bottom) and with 1.2% w/w water content (top) PVA. As for PAA, PVA presents only one very broad secondary relaxation peak, β_{dPVA}, in agreement with data available in the literature [5,8–11]. The intensity of β_{dPVA} decreases with decreasing water content. This secondary relaxation does not shift in temperature (in contrast with the α relaxation

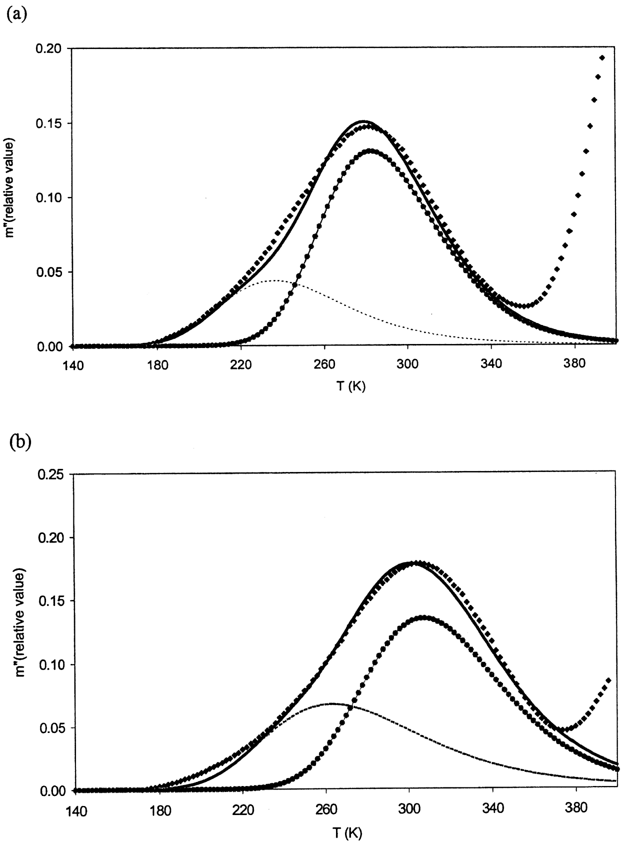

Fig. 6. Secondary β'_{PAA} and γ'_{PAA} dielectric relaxations for dried PAA, at (a) $f = 3$ kHz; and (b) $f = 30$ kHz. m'' versus temperature. (◆) Experimental data; (—) calculated data; (- - -) calculated contribution of γ'; and (●●●) calculated contribution of β'.

which shifts from 350 to 400 K), when dried from 1.2% w/w of water to dried PVA. Nevertheless, the β_{dPVA} activation energy decreases from 74 (for PVA with 1.2% w/w of water) to 59 kJ mol^{-1} (for dried PVA).

The pre-exponential time increases from 10^{-20} to 8.3×10^{-16} s. m' and m'' thermograms for dried PVA for different frequencies are shown in Fig. 8. The apparent activation energy and pre-exponential time for this relaxation are thus 59 kJ mol^{-1} and 8×10^{-16} s, respectively. Fig. 9 compares the characteristics of the secondary relaxation measured by mechanical [5] and dielectric spectroscopy. The activation energy of β_{mPVA} was estimated [5] around 88 kJ mol^{-1} and its pre-exponential time was found to be about 10^{-22} s. It is clear that β_{dPVA} is very broad and has a much lower activation energy than $\beta_{mPVA.}$

Recalling that PVA presents only hydroxyl groups and that it was concluded [5] that OH groups are too small to lead to mechanical relaxation, it can be understood that PVA does not exhibit a γ mechanical relaxation like PAA. Nevertheless, in dielectric spectroscopy, motions of OH groups may be detected, because the dipole moments of both hydroxyl and hydroxymethyl groups are similar. As for PAA, the dielectric relaxation observed in PVA should result from the overlaps of two different processes called here after γ'_{PVA} and β'_{PVA}. γ'_{PVA} should result from the rotation of OH side groups while β'_{PVA} should come from more or less cooperative motions of main-chain segments.

In order to check this assumption, dielectric experimental curves for dried PVA were fitted by the two independent relaxations γ'_{PVA} and β'_{PVA}. γ'_{PVA} has characteristics close to the PAA γ mechanical relaxation (see Table 1) and β'_{PVA} has characteristics close to those of the unique dielectric relaxation measured, except its amplitude (see Fig. 9 and Table 2). Experimental and calculated plots of m'' versus temperature for 3 and 30 kHz are shown in Fig. 10(a) and (b). The amplitude of β'_{PVA} is close to or lower than the amplitude of γ'_{PVA}, in accordance with the idea that β_{mPVA} disappears with decreasing water content [5]. This can explain that the apparent energy is lower than for β_{mPVA} and also that the dielectric relaxation does not move with

Table 1
Characteristics of the secondary γ' dielectric relaxation (in two relaxations — γ' and β' — model) for dried PAA and PVA. Comparison with dried cellulose and dextran

Polymer	Side groups	$\langle E_{\gamma'} \rangle$ (kJ mol^{-1})	$\tau_{0\gamma}$ (s)	B_γ (kJ mol^{-1})	ΔS_γ (J K^{-1} mol^{-1})	Ref.
PAA	CH_2OH	44	10^{-14}	3.5	15	This work
PVA	OH	40	10^{-13}	4	0	This work
Dextran	OH	32	5×10^{-15}	9	–	[6,24]
Cellulose	CH_2OH	32	5×10^{-15}	9	–	[6]
	OH	34*	$9 \times 10^{-13*}$	7[a]		

Table 2
Characteristics of the secondary β' dielectric relaxation (in two relaxations — γ' and β' — model) for dried PAA and PVA. Comparison with the secondary β dielectric relaxation in dried dextran

Polymer	$\langle E_\beta \rangle$ (kJ mol^{-1})	$\tau_{0\beta}$ (s)	B_β (kJ mol^{-1})	ΔS_β (J K^{-1} mol^{-1})	Ref.
PAA	68.5	1.2×10^{-17}	3.5	70	This work
PVA	66	5×10^{-17}	5.5	65	This work
Dextran	82	3×10^{-19}	10	–	[6]

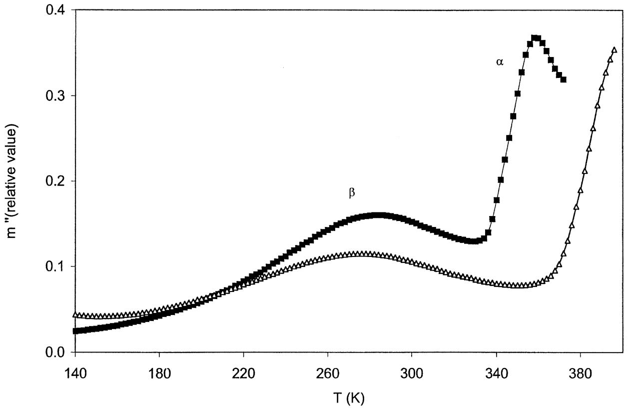

Fig. 7. Influence of solvent content on the secondary dielectric relaxation in PVA: m'' versus temperature ($f = 10$ kHz). PVA with 1.2% w/w of water (■) and dried PVA (△).

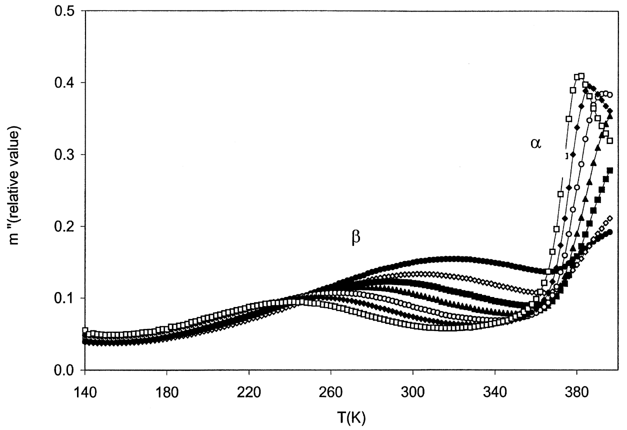

Fig. 8. Dielectric data for dried PVA: m'' versus temperature. For 300 (●), 100 (◇), 30 (■), 10 (π), 3 (○), 1 (◆) and 0.3 kHz (□).

the solvent content, as a result of the competition between the behaviour of γ'_{PVA} and β'_{PVA} versus the effect of solvent. A good agreement between experimental and calculated curves was obtained for all the frequencies using the assumption of two relaxation processes.

3.3. Comparison with polysaccharides

3.3.1. General characteristics for secondary relaxation in polysaccharides

Dielectric spectroscopy data show that amorphous dried cellulose exhibits only one dielectric secondary relaxation process [6,25–27] with characteristics closer to those of the γ mechanical relaxation (γ_{mcell}) than to those of the β mechanical relaxation (β_{mcell}). It was thus referred to as γ_{dcell} [6]. In contrast, dried dextran presents two secondary relaxation processes at frequency less than 10 kHz, called γ_{ddex} and β_{ddex}. These relaxations have characteristics close to those of γ_{mcell} and β_{mcell}, respectively (see Tables 1 and 2). At higher frequencies than 10 kHz, γ_{ddex} and β_{ddex} overlap and only one peak is observed.

Dextran possesses only hydroxyl lateral groups (OH). The motion of this moiety is unable to produce a mechanical relaxation, but should give rise to the γ_{ddex} dielectric relaxation. Cellulose has two kinds of lateral groups, i.e. hydroxymethyl groups (CH_2OH) and hydroxyl groups (OH). Its γ mechanical relaxation is attributed to the motion of CH_2OH groups and the broad γ dielectric relaxation was attributed to the overlap of two relaxation processes, referred to as γ_{OH} and $\gamma_{CH_2}OH$. They have close activation energies (Table 1) and correspond, respectively, to the rotation of hydroxyl and hydroxymethyl groups.

On the other hand, the amplitude of the β_{mcell} peak for dried cellulose, is very weak, three times lower than for the β_{mdex} of dextran [4]. Following Montès and Cavaillé [6], this could explain why no dielectric β relaxation is observed in dried cellulose. This is not the case of β_{mdex} for which a corresponding dielectric relaxation β_{ddex} is observed.

3.3.2. γ Dielectric relaxation

The two vinylic analogues PAA and PVA have only one kind of lateral group. The γ dielectric relaxation should then arise from the motion of one group only. Unfortunately, the γ and β relaxation processes already merge at low frequencies, as in the case of dextran at frequencies greater than 10 kHz. These broad relaxations can be deconvoluted in two sub-relaxations γ' and β', with the aforementioned cautions. The results thus obtained are compared to the characteristics of the γ dielectric relaxation in polysaccharides (see Table 1). Both activation energies and pre-exponential times are comparable in the two series. This confirms the existence of a dielectric relaxation process involving the rotation of a polar side group, either hydroxymethyl or hydroxyl. However, the activation energies are slightly higher for the vinylic analogues PVA and PAA than for the polysaccharides. This suggests that the OH groups are more constrained in the synthetic polymers. This indeed explains why the merging of the two relaxation processes γ and β occurs at lower frequencies for PVA and PAA.

3.3.3. β Dielectric relaxation

The β dielectric relaxation process for both PVA and PAA arises from the higher part of the deconvolution and is referred to as β'. Their activation energies and pre-exponential times are shown in Table 2. According to Heijboer [22,28], their apparent activation energies are too high (and pre-exponential time too short compared to the Debye time) to be attributed to local motions. As in dynamic mechanical analysis, they should arise from cooperative motions of the backbone. The confusion with the α relaxation is impossible as it clearly appears at higher temperature as shown for example in Figs. 2 and 7. Tables 1 and 2 report the activation enthalpies and entropies according to Starkweather analysis [20,29] for each simulated relaxation of both PVA and PAA. The total activation energy can be separated in entropic (ΔS) and enthalpic (ΔH) contribution by the

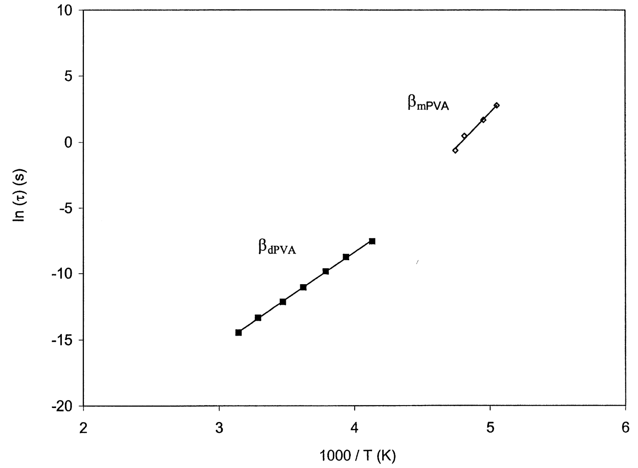

Fig. 9. Variation of $\ln(\tau)$ versus $1000/T$ for the secondary relaxation measured by dielectric and mechanical spectroscopy in dried PVA: (◇) for β_{mPVA} (activation energy of 88 kJ mol^{-1}); and (■) for β_{dPVA} (activation energy of 58.5 kJ mol^{-1}).

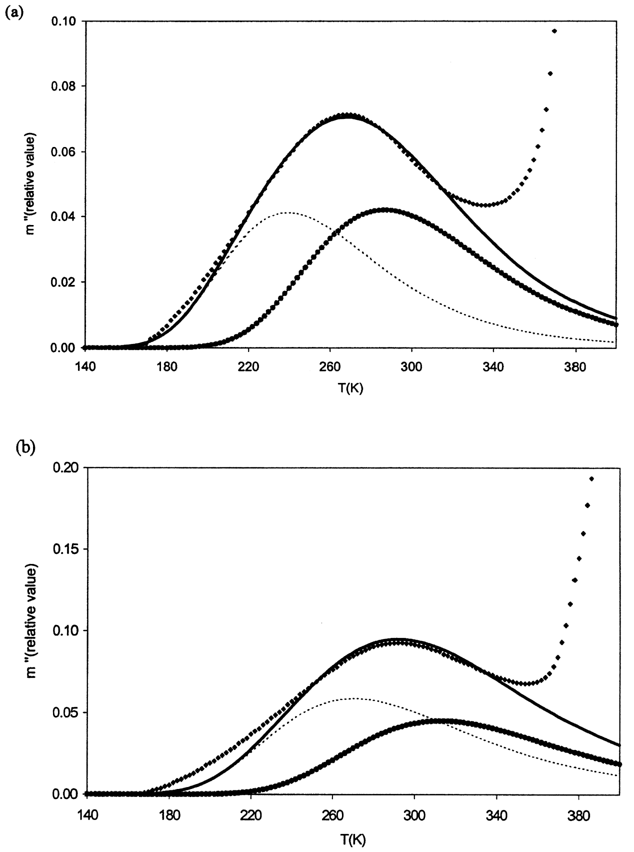

Fig. 10. β'_{PVA} and γ'_{PVA} dielectric relaxations for dried PVA, at (a) $f = 3$ kHz; and (b) $f = 30$ kHz. m'' versus temperature. (◆) Experimental data; (—) calculated data; (- - -) calculated contribution of γ'; and (●●●) calculated contribution of β'.

relations:

$$E_a = RT[1 + \ln(kT/2\pi hf)] + T\Delta S \quad \text{and}\ \Delta H = E_a - T\Delta S$$

In this analysis, low activation entropies (less than 20 J mol^{-1} K^{-1}) are related to localised motions, whereas higher values (more than 50 J mol^{-1} K^{-1}) correspond to cooperative motions. For both systems, the γ' relaxations have very low entropic contributions in agreement with their attribution to localised motion of the lateral groups. In contrast, the higher values found for the β' relaxations in PVA and PAA corroborate the idea of more cooperative motions implying the main chain.

Their characteristics are very close, and slightly different from those of dextran (see Table 2). Although the differences are not very strong, activation energies are a little lower and pre-exponential times longer for the synthetic polymers compared to the polysaccharides. This small effect, already observed for the dynamic mechanical measurements [5], are probably due to the differences in the rigidity in the vinylic and polysaccharidic backbones. Indeed, the cooperative character of the β relaxation in both series remains.

To go further into detail, a general trend is observed in the two series. The polymers exhibiting broad and weak β mechanical relaxations (PVA and cellulose) present low (PVA) and even undetectable (cellulose) β dielectric relaxations. In contrast, the strong β mechanical relaxation of PAA and dextran are related to stronger dielectric processes. In the dynamic mechanical experiments, the amplitude of the relaxation should be related to the sum of the local volumes involved in the molecular motions. In dielectric experiments, the amplitude should rely on the total change of polarisation, and then to the amplitude of the motions. In both PVA and cellulose, the presence of crystalline (PVA) and paracrystalline (cellulose) regions should constrain the cooperative motions of the β relaxation. This could lead to weaker relaxation processes either in dynamic mechanical or dielectric experiments.

3.3.4. *Influence of water*

The analysis by dielectric and mechanical spectroscopy for cellulose and other polysaccharides [4,6,24] shows that the intensity of secondary relaxation peaks is influenced by the moisture content. Dielectric spectroscopy data show that amorphous hydrated cellulose exhibits only one dielectric secondary relaxation process [6,24–27]. For hydrated dextran (and for all frequencies), γ_{ddex} and β_{ddex} overlap and only one peak can also be observed.

The influence of water on the unique observable dielectric relaxation in PAA and PVA (see Figs. 2 and 7) is similar to its influence on the dielectric relaxations in dextran. The apparent energies increase with increasing water content and simultaneously pre-exponential times decrease (see Tables 2 and 3). This effect is apparently opposed to what is observed by mechanical spectroscopy.

Nevertheless, an important point is that the influence of water molecules on dielectric relaxations is very similar for all the polymers studied here and the interpretation of experimental dielectric data for PAA and PVA allows us

Table 3
Characteristics of the secondary β relaxation measured by dielectric spectroscopy in hydrated PAA, PVA and dextran

Polymer	Water content (% w/w)[a]	$\langle E_\beta > \rangle$ (kJ mol^{-1})	$\tau_{0\beta}$ (s)	Ref.
PAA	2.8	87	10^{-20}	This work
PVA	1.2	74	1.9×10^{-18}	This work
Dextran	< 5	111	10^{-24}	[24]

[a] Characteristics for hydrated sample are obtained from m'' assuming an Arrhenius behaviour.

to explain this behaviour. Each of the γ and β relaxations measured by mechanical spectroscopy (for example in PAA and in cellulose) has an opposite behaviour with water. Mechanical experiments show that the amplitude of the γ relaxation decreases while the amplitude of the β relaxation increases with increasing water content. Conjointly, the maximum of the β relaxations shifts to lower temperature, and their activation energies diminish [4,5]. In the dielectric experiments, the effects should be the same, with the difference that the two relaxations overlap. The apparent relaxation measured by dielectric spectroscopy (which results from the overlap of the two processes, γ' and β') has characteristics closer to the stronger relaxation. These combined effects can explain why for hydrated samples, the activation energy of the apparent dielectric relaxation is close to the activation energy of β (around 85 kJ mol^{-1}) and for dried samples, it is closer to γ (45 kJ mol^{-1}). This scheme is supported by the general trend observed in both synthetic and natural polymers.

4. Conclusions

Secondary dielectric relaxations in PAA and PVA were characterised by dielectric spectroscopy. For PAA and PVA (with and without moisture content) only one relaxation (referred to as β_{dPAA} and β_{dPVA}) was observed. The dielectric relaxation in PAA and PVA presents characteristics in between those of the γ mechanical relaxation of PAA (and of cellulose), and of the β mechanical relaxation of PAA, PVA, cellulose and dextran. For this reason and because of the large half-width of the dielectric relaxation, a unique relaxation was modelled from the overlap of two relaxations (γ' and β') for PAA and PVA, where β' corresponds to main-segment rotation and γ', to side-group rotation. This overlap is enhanced in dielectric measurements, mainly because the frequency range is much higher (100 Hz to 1 MHz) than for mechanical measurements (10^{-4}–1 Hz).

After this deconvolution, the characteristics of both synthetic and polysaccharidic polymers are similar. A general scheme for polymers bearing polar side groups is proposed. The γ (or γ') dielectric relaxation is related to the localised motions of the lateral groups, either CH_2OH or OH. The γ dielectric relaxation measured for dextran and PVA confirms that OH side groups can produce a relaxation process measurable by dielectric spectroscopy, although this motion does not give rise to a mechanical relaxation. The β (or β') dielectric relaxation process corresponds to cooperative motions of the main chains. Small differences between the β activation energies of the two series should depend on the different backbone rigidity of vinyl and sugar units, even if this factor is difficult to evaluate and hence questionable.

The effect of polar solvents like water on the unique dielectric relaxation is a consequence of their effect on each γ' and β' relaxation. The intensity of γ' decreases with increasing water content, while the opposite occurs for β'. The result is then an increase in the apparent energy of the dielectric secondary relaxation. Similar effects observed in polysaccharides lead to the idea that polymers bearing polar groups have a general behaviour towards solvents.

Nevertheless, these conclusions rely on the indirect observation of the motions and of the effect of polar solvents via an external stimulus. However, the results obtained with either mechanical or dielectric experiments, on both polysaccharides and vinyl polymers appear very similar. This general scheme shared by polymers bearing hydroxyl and/or hydroxymethyl groups allows us to call the vinyl polymers PAA and PVA ‘models of polysaccharides’ in the restricted area of secondary relaxation processes, including the effect of polar solvents. Future effort will be concentrated on a complete molecular modelling of the dense structure of these ‘model polymers’.

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