Polymer 41 (2000) 7547–7557

polymer

Secondary relaxations in poly(allyl-alcohol), PAA, and poly(vinyl alcohol), PVA

Part I. Mechanical relaxations compared with mechanical behavior of cellulose and dextran in the presence of polar solvent

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Received 22 October 1999; accepted 12 January 2000

Abstract

As a team project, a molecular simulation study of thermally activated localized motions in polysaccharides, such as cellulose and dextran is required to determine the molecular origin of their secondary relaxations and the influence of polar solvents on these relaxations. Nevertheless, the complexity of polysaccharides led to the idea of testing the simplest polymer that could present similar mechanical behavior. Poly(allyl alcohol), PAA, and poly(vinyl alcohol), PVA, are the two simplest polymer containing hydroxymethyl and hydroxyl lateral groups, respectively. PVA is a commercial polymer, but PAA was synthesized by the reduction of poly(methyl acrylate) and characterized by infrared (IR) and ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy. PVA and PAA, with different water or methanol contents, were characterized by dynamic mechanical analysis (DMA). The dried PAA presents two secondary relaxations, the so called γ_{PAA} and β_{PAA}, whereas PVA presents only one secondary relaxation, β_{PVA}. For both polymers, characteristics and influence of polar solvent content on the β secondary relaxation are very close to the results obtained previously for cellulose and dextran. Such a comparison has been done to sort out the molecular origin of the γ secondary mechanical relaxation in polymers presenting polar side groups (vinyl polymers and polysaccharides). It appears that hydroxymethyl moieties are involved in this relaxation.

Keywords: Vinyl polymer; Polysaccharides; Thermal activation

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1. Introduction

Dynamics in amorphous polymers depend on the time–temperature scale at which they are studied [1]. The glass transition temperature (T_g) separates the liquid equilibrium state and glassy solid state. At low-temperature (below T_g) or at short times, amorphous polymers present secondary relaxation processes called β, γ, δ etc. These motions are often described as rotations of lateral groups (γ, δ etc. relaxations) or as motions of main chain segments (β relaxation, in most of the cases) [2].

Cellulose, dextran, amylose, pullulan etc. are biosynthesized polysaccharides made of repeated glucose units (see Fig. 1a and c). These polysaccharides differ by their glycosidic linkages and/or lateral groups (hydroxyl and hydroxymethyl groups) in the glucose ring. Complete studies on cellulose and dextran by mechanical and dielectric spectroscopy were made by Montès et al. [3,4]. On the basis of the comparison of mechanical and dielectric behaviors of these two polysaccharides having different chemical architectures (see Fig. 1), the γ and β relaxations were, respectively, associated with the non-cooperative rotation of CH_2OH and/or OH side groups and the slightly cooperative motion of the main chain segments (such as crankshaft motion) in agreement with other works [5–7]. As water is known to have an important effect on the mechanical properties of polysaccharides, the effect of polar solvent on these relaxations has also been investigated. From these studies, it appears that the presence of solvent induces, for all polysaccharides, a shift of the β relaxation towards lower temperatures together with an enhancement of its amplitude. These general trends have been observed with either methanol or water. In its effects, the presence of water in polysaccharides is comparable to what is observed in synthetic polymers exhibiting a strong inter-chain network of hydrogen bonds, such as polyamides [8–10].

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PII: S0032-3861(00)00061-6

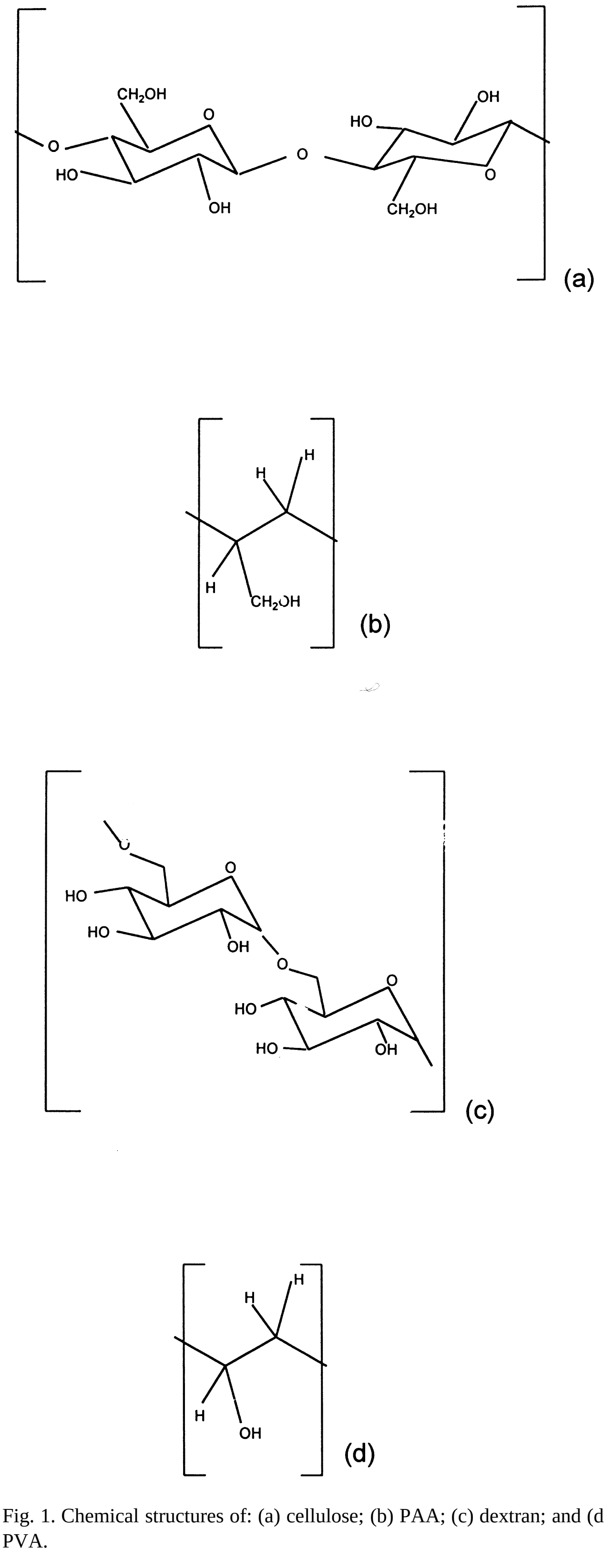

Fig. 1. Chemical structures of: (a) cellulose; (b) PAA; (c) dextran; and (d) PVA.

In order to investigate the molecular origin of the sub-T_g relaxations, the combination of both macroscopic measurements (DMA, dielectric) and molecular simulations appears to be a promising scheme; the effect of polar solvent may also be considered. As a large team project, we are then interested in the molecular simulation study of thermally activated and localized motions in polysaccharides such as cellulose, dextran, amylose. Nevertheless, the complexity of polysaccharides presents a limitation for this simulation [3]. This limitation led us to study the simplest polymers that can present similar molecular dynamics. As the presence of lateral groups such as hydroxyl or hydroxymethyl together with the occurrence of inter-chain hydrogen bonds are the main features of these polymers, we choose synthetic polymers with vinylic backbone exhibiting these characteristics. Poly(vinyl alcohol), PVA, and poly(allyl alcohol), PAA, are the simplest polymers having hydroxyl and hydroxymethyl lateral groups, respectively (see Fig. 1b and d). While PVA is a well-known commercial polymer, PAA has to be synthesized and has not been studied yet. In previous works [11,12] a unique secondary relaxation (β) and the main α relaxation were identified by DMA for different PVA/water systems. Nevertheless, these relaxations were not fully characterized. As a general trend, when PVA is dried (ca. from 30 to 0% (w/w) of water) the β and α relaxations shift towards higher temperatures. More precisely, the β relaxation shifts from 173 to 213 K and its amplitude decreases. For the dried PVA, the amplitude of this relaxation is very low. Additionally, the α relaxation shifts from 253 to 348 K. The influence of water on the β relaxation in PVA is similar to what is found for the β relaxation in cellulose, dextran and other polysaccharides [3,13]. This similarity supports the reliability of our scheme, but nothing seems to be reported in the literature on the relaxations of PAA. The main objective of this work is to determine precisely the characteristics of the relaxation in PVA and PAA and to specify the similarity between the mechanical behavior of different amorphous polymers (PVA, PAA, cellulose and dextran) exhibiting hydroxyl and hydroxymethyl group moieties. It could be then possible to understand better the role of the polar lateral groups and hydrogen interactions on the localized dynamics, and to sort out the role of polar solvents on their characteristics.

2. Experimental section

2.1. PAA synthesis

PAA is not a commercial polymer, and the unlikely result of conventional radical polymerization from allyl monomer is a polymer of low degree of polymerization due to the high reactivity of this monomer to degradative chain transfer [14,15]. In this work pure PAA was prepared according to the method of Cohen et al. [16], i.e. by the reduction of poly(methyl acrylate), PMA, (ALDRICH with $M_w = 40,000 \mathrm{g\ mol^{-1}}$ in toluene) with lithium aluminum hydride ($LiAlH_4$) [16,17]. To a refluxing (at 130°C) suspension of 3.8 g (0.1 mol) of $LiAlH_4$ in 200 ml of purified *N*-methylmorpholine, under nitrogen, was added dropwise, over a

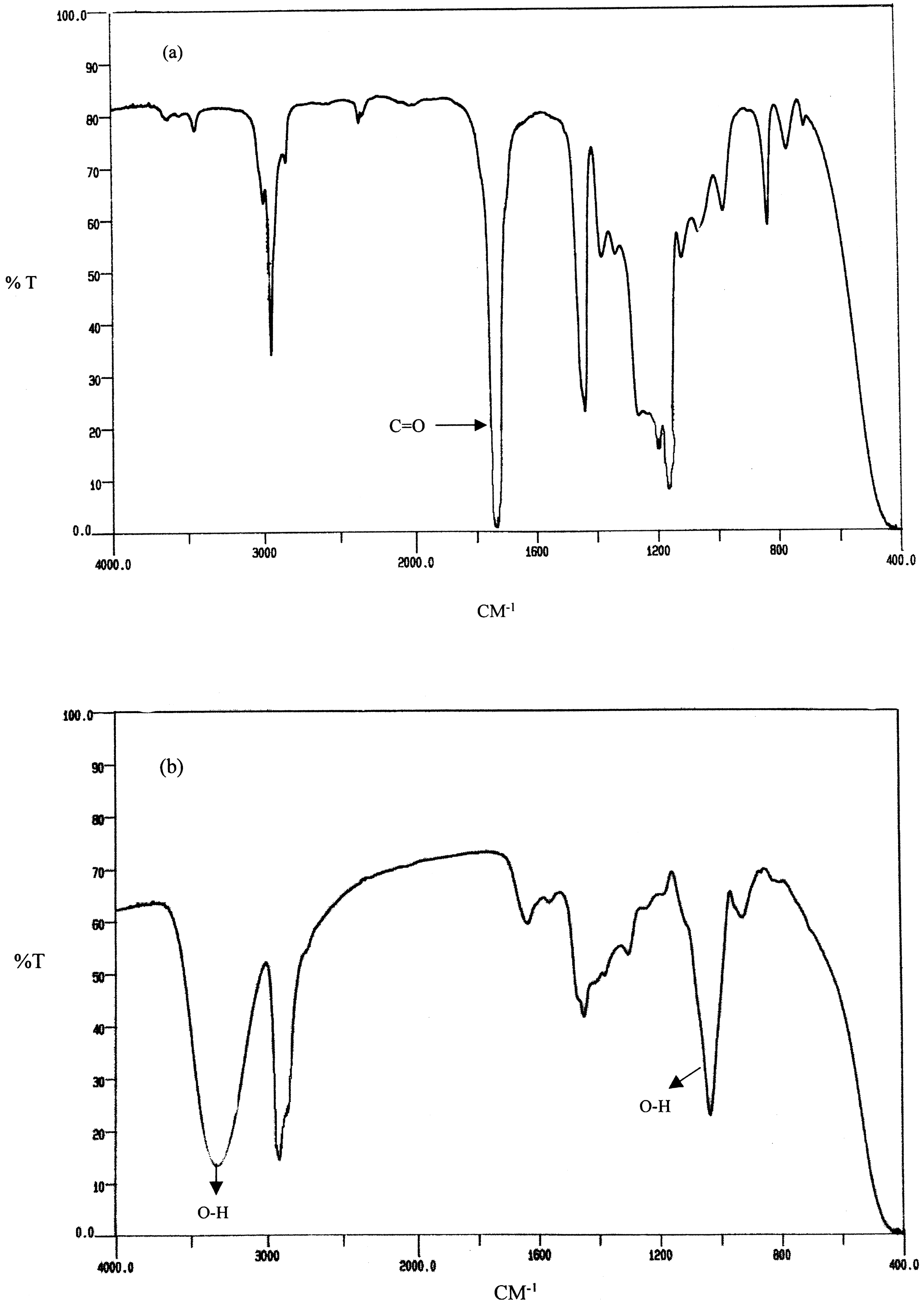

Fig. 2. Infrared (IR) spectrum for: (a) PMA; and (b) for PAA.

period of 2 h, a solution of 8.6 g (0.1 mol) of PMA in 100 ml of *N*-methylmorpholine. Then the mixture was stirred under reflux for an additional 3 h. For the isolation process, while still hot, a solution of 30 g of potassium sodium tartrate in 150 ml of water was added dropwise very carefully, until the excess hydride had been decomposed. After the addition of all the tartrate solution, the hot mixture was stirred for one additional hour and then allowed to cool.

The filtered solution was evaporated (at about 70°C) to dryness on a steam bath under vacuum, leaving a soft residue. This was stirred with a mixture of 90 ml of methanol and 10 ml of water for 3 h. Most of the solid was dissolved, giving a viscous solution. The remaining powder was centrifuged and the polymer was precipitated in acetone. The purification process was repeated three times. The product obtained was completely soluble in methanol.

2.2. PAA characterization

The reduction of PMA to PAA was verified by infrared (IR) and nuclear magnetic resonance ^{13}C (NMR) spectroscopy. Fig. 2a and b shows the IR spectra for PMA and PAA, respectively. The spectrum for PMA (Fig. 2a) presents a typical band of carbonyl group, C=O at 1730 cm^{-1}, which disappeared in the spectrum of PAA (Fig. 2b). Additionally, the two absorption bands corresponding to secondary bonds O–H appear at 3338 and 1030 cm^{-1}. The full conversion of the carbonyl bond into the secondary alcohol bonds indicates that the reaction was complete.

Fig. 3a and b presents, respectively, the NMR ^{13}C spectra for PMA in solution in deuterated chloroform $CDCl_3$ and for PAA in solution in deuterated methanol (MeOD) at a frequency of 75 MHz. The PMA spectrum exhibits a characteristic peak for carbonyl groups around 175 ppm, one for O–CH_3 at 51 ppm and two at 41 and 35 ppm for the main chain groups CH and CH_2, respectively. The PAA spectrum does not show any carbonyl peak at 175 ppm in agreement with the IR analysis. A new peak at 74 ppm and a complex clump around 40 and 45 ppm arise in the modified polymer. According to the known secondary alcohol homologue series we can verify the presence of CH_2OH function around 75 ppm, CH from 35 to 45 ppm and CH_2 from 30 to 40 ppm. Thus, the results obtained are consistent with the chemical structure of PAA and as neither IR nor NMR could detect any of the sub-products, the good purity of the PAA synthesized in this work is confirmed.

Finally, PAA was characterized by Differential Scanning Calorimetry (DSC). At a scanning rate of 20 K min^{-1} a glass transition temperature (T_g) of 75°C (348 K) was measured.

2.3. Sample preparation

2.3.1. Poly(allyl alcohol)

PAA films were prepared by dissolving the polymer in methanol. First, the films were dried by evaporation of methanol at 35°C (308 K) for two days at the atmospheric pressure. Then, they were dried in an oven for 2 h at 70°C. The samples contained 6% (w/w) of methanol measured by thermogravimetry. In fact, completely dried films were too brittle to be tested by DMA.

On the other hand, PAA fibers were prepared by heating and spinning the polymer at 170°C. These samples presented about 4% (w/w) of water content. Samples with 1.5% (w/w) water were obtained by equilibration with a 0% relative humidity in the presence of P_2O_5 for two weeks. Finally, the completely dried samples of PAA were obtained by maintaining them at 60°C for 24 h under N_2 flow in the spectrometer before the experiment.

2.3.2. Poly(vinyl alcohol)

PVA was prepared in the form of either fibers or films. The PVA fibers were prepared by dissolving PVA (ALDRICH with M_w 124,000–186,000) in dimethylsulfoxide (DMSO) 40% (w/w) at 70°C. The gel obtained was spun at 80°C and precipitated into anhydrous methanol. The fibers were washed carefully by changing the solvent from DMSO to methanol. The PVA fibers were dried by successive thermal treatments and their solvent content was measured by gravimetry: from 30 min at 60°C (fibers with 30% (w/w) methanol content) to 24 h at 100°C (dried fibers).

Films of PVA were prepared by dissolving 40% (w/w) of the polymer in water at 70°C. They were dried at 0% relative humidity in the presence of P_2O_5 for two weeks. The samples retained about 2% (w/w) of water content. Finally, the completely dried PVA films were obtained by thermal treatment at 80°C for 24 h inside the mechanical spectrometer under N_2 flow before the experiment.

2.4. Mechanical spectroscopy

Dynamic mechanical measurements were carried out with a mechanical spectrometer (Mechanalyser from Metravib SA, Ecully, France) operating in torsional mode at different programming frequencies from 0.01 to 1 Hz and at a heating rate of 13 K h^{-1}, starting at 100 K. This instrument provides the complex shear modulus G^* and the loss angle tangent, $\tan \phi$ ($= G''/G'$). The samples were scanned from 100 to 300 K and from 100 to 360 K for PAA and PVA, respectively.

3. Results and discussion

3.1. Mechanical analysis of the secondary relaxations

3.1.1. Experimental data for poly(allyl alcohol)

By mechanical spectroscopy, a clearly visible $\tan \phi$ relaxation peak of high amplitude is observed at 240 K for dried PAA, at 230 K for PAA with 1.5% (w/w) water content, and at 200 K for PAA with 6% (w/w) methanol content (see Fig. 4). At higher temperature, the increase in $\tan \phi$ corresponds to the beginning of the main or α relaxation associated with the glass transition of PAA more or less plasticized by water or methanol. Thus, the relaxation peak of Fig. 4 is assigned to the secondary β

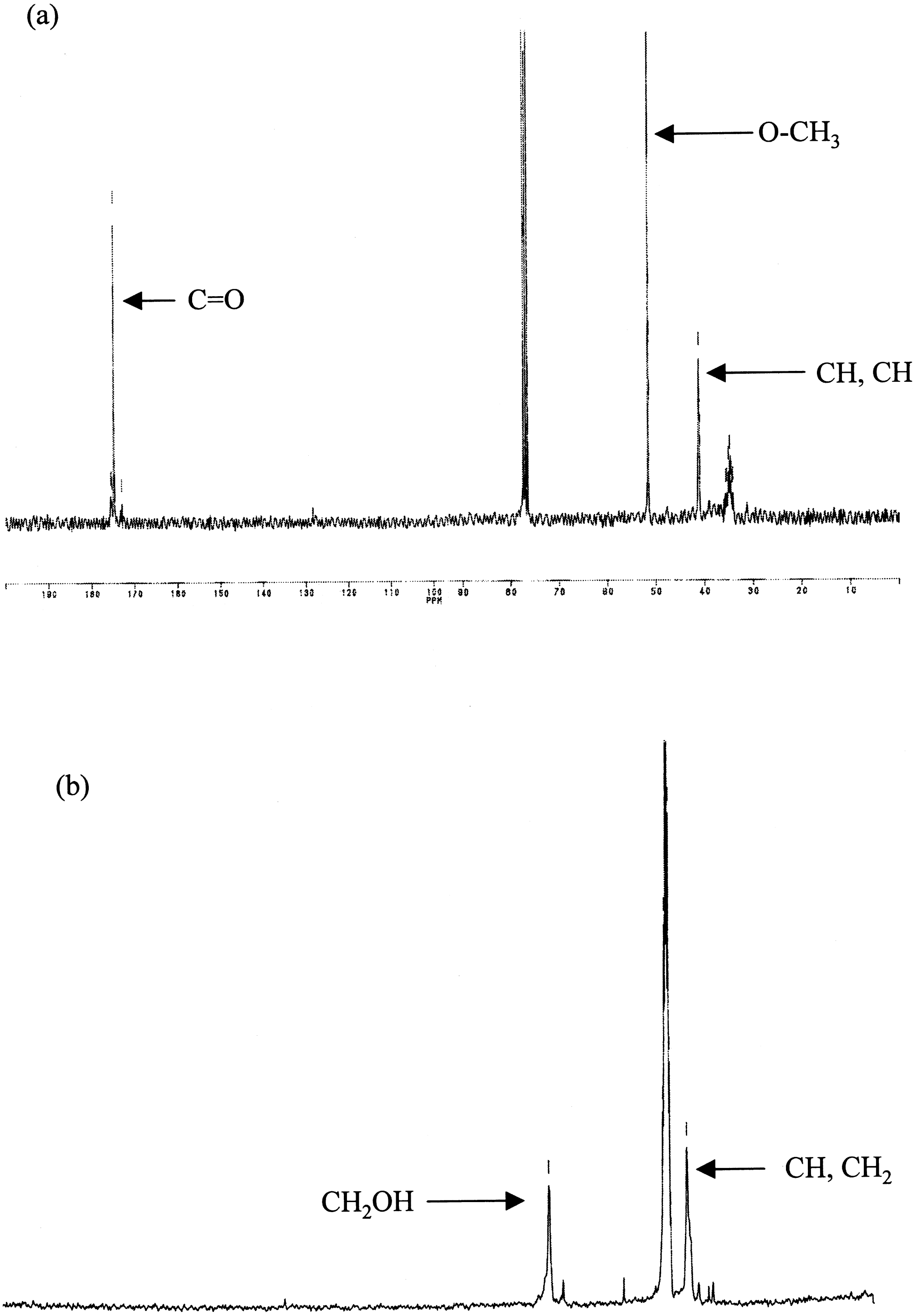

Fig. 3. Nuclear Magnetic Resonance (^{13}C NMR) spectrum (75 MHz) for: (a) PMA; and (b) PAA.

mechanical relaxation, here after referred to as β_{PAA}. It shifts to higher temperature with decreasing content of the solvent. However, the dried sample exhibits an additional low temperature shoulder. Fig. 5 details the evolution of the real and imaginary parts of shear modulus G' and G'' versus temperature for the dried sample at four different frequencies: 0.01, 0.05, 0.1 and 0.5 Hz. A first low-temperature relaxation, γ_{PAA}, appears around 175 K with a low intensity compared with the β relaxation. This relaxation disappears on increasing the solvent content.

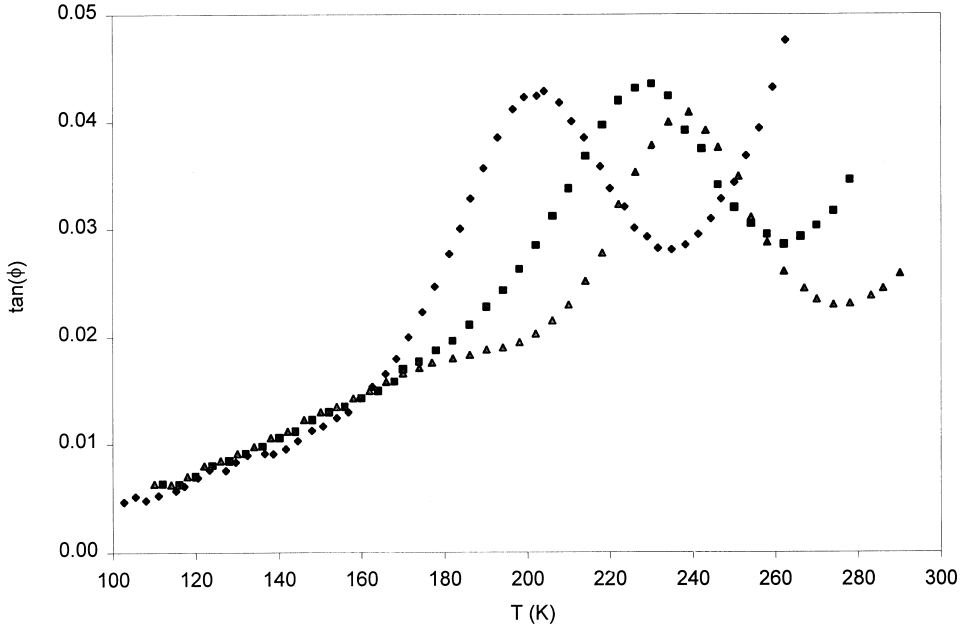

Fig. 4. Influence of the solvent content on the secondary mechanical relaxations in PAA: tan ϕ versus temperature. Dried sample (▲), 1.5% (w/w) water content (■), and 6% (w/w) methanol content (◆).

A plot of log (τ) versus $1/T$, where $\omega\tau = 1$, is linear for the β_{PAA} relaxation (see Fig. 6). Thus, as a first approximation and though the overlap of the two relaxations is not taken into account, it is usual to describe the variation of the relaxation time by the Arrhenius equation

$$\tau = \tau_0 \exp\left[\frac{E}{\mathrm{R}T}\right] \tag{1}$$

where τ_0 is the pre-exponential factor and E is the apparent activation energy. For the dried PAA, the amplitude of γ_{PAA} is too small and broad to determine its peak position as the relaxation appears as a shoulder on the low temperature side of the β relaxation. Nevertheless, apparent activation energy, $E_{\gamma\mathrm{PAA}}$, and pre-exponential factor, $\tau_{0\gamma\mathrm{PAA}}$, may be roughly evaluated from the shift of this shoulder versus frequency. Thus, $E_{\gamma\mathrm{PAA}}$ is found close to 45 kJ mol^{-1} and $\tau_{0\gamma\mathrm{PAA}}$ is in the order of 3×10^{-12} s. For the β relaxation, the evaluation of the activation energy and pre-

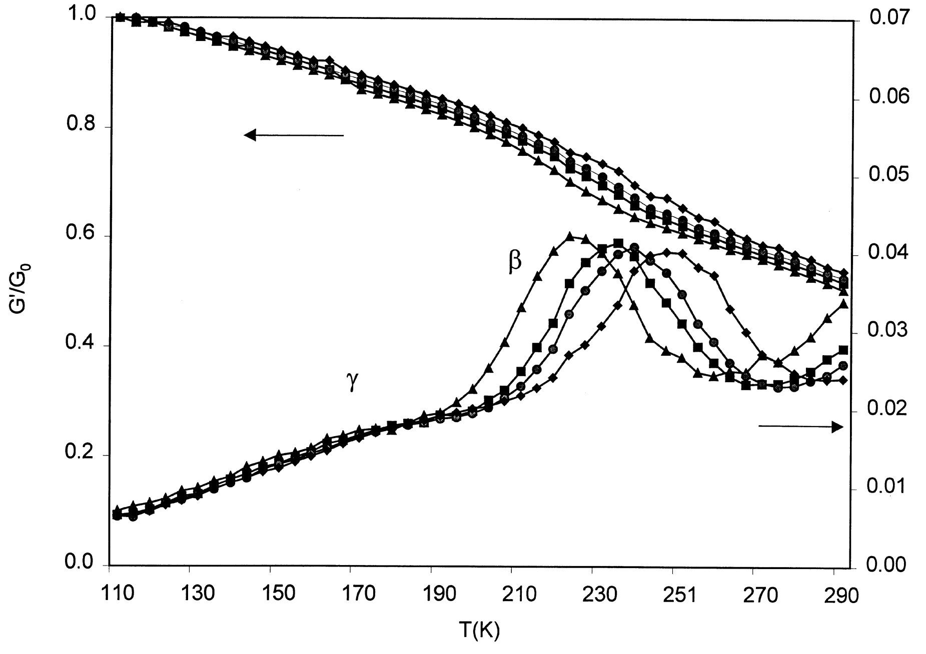

Fig. 5. Mechanical data for dried PAA: storage (G') shear modulus and loss tangent (G''/G') versus temperature. 0.5 Hz (◆), 0.1 Hz (●), 0.05 Hz (■) and 0.01 Hz (▲).

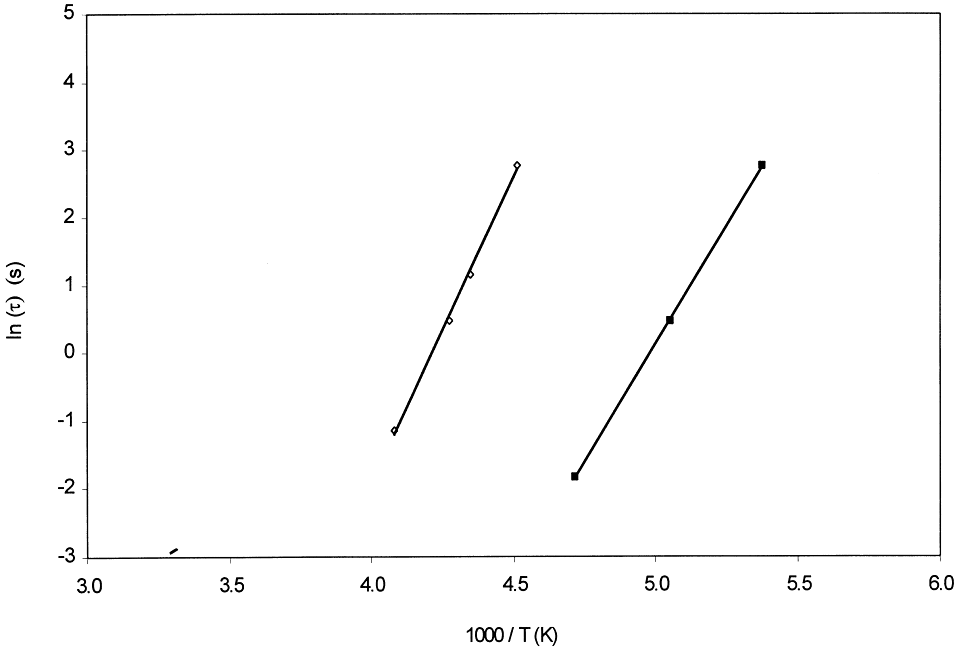

Fig. 6. ln $(1/f)$ versus $1000/T$ for the β mechanical relaxation of PAA. Dried sample (◇) sample with 6% methanol content (■).

exponential time is more straightforward. $E_{\beta\mathrm{PAA}}$ increases after successive thermal treatments from 68 kJ mol^{-1} for MeOH containing sample to 73 kJ mol^{-1} for the dried PAA.

The following discussion is focussed on the dried PAA in order to characterize more precisely the two relaxation processes, but it is clear that the molecular mobility of PAA is influenced by the moisture content. Although γ_{PAA} and β_{PAA} in dried sample were characterized using the Arrhenius law, the experimental data, plots in Fig. 5, show that the relaxation peaks are much broader than a Debye peak, which means that the distribution of the relaxation times [18,19] has to be accounted for. Calling $\Psi(\ln \tau)$ the distribution function of $\ln(\tau)$, the compliances, J' and J'', can be written as

$$J'(\omega) = J_{\mathrm{u}} + (J_{\mathrm{u}} - J_{\mathrm{r}}) \int_{-\infty}^{\infty} \frac{\psi(\ln \tau)}{1 + \omega^2 \tau^2}\, \mathrm{d}(\ln \tau)$$
$$J''(\omega) = (J_{\mathrm{u}} - J_{\mathrm{r}}) \int_{-\infty}^{\infty} \frac{\psi(\ln \tau)\omega\tau}{1 + \omega^2 \tau^2}\, \mathrm{d}(\ln \tau) \qquad (2)$$

where J_{r} and J_{u} are the relaxed and unrelaxed shear compliances, respectively. The relaxation time distribution of $\tau_{\gamma\mathrm{PAA}}$ and $\tau_{\beta\mathrm{PAA}}$ could result from the distribution of the corresponding activation energy and/or of the pre-exponential time [18–22].

In this study and for sake of simplicity, we assume that $\tau_{0\gamma\mathrm{PAA}}$ and $\tau_{0\beta\mathrm{PAA}}$ are not distributed. Hence, the distribution of the relaxation times results from the distribution functions $\Phi_{\gamma\mathrm{PAA}}$ and $\Phi_{\beta\mathrm{PAA}}$ of the activation energies $E_{\gamma\mathrm{PAA}}$ and $E_{\beta\mathrm{PAA}}$. Moreover, if we assume that these activation energies have a Gaussian distribution, we can write Φ in the general form as:

$$\Phi(E) = \frac{1}{B\sqrt{\pi}} \exp\left[-\left(\frac{E - \langle E \rangle}{B} \right)^2 \right] \qquad (3)$$

where B and $\langle E \rangle$ are the corresponding Gaussian distribution width and the average activation energy. The fit of J^* requires the following parameters: $(J_{\mathrm{r}} - J_{\mathrm{u}})$, J_{u}, $\langle E \rangle$, τ_0

Table 1
Characteristics of the secondary β mechanical relaxation in dried PAA and PVA and with methanol content, a comparison with dried and hydrated cellulose and dextran

Polymer	Side groups	Solvent content (% w/w)	$\langle E_\beta \rangle$ (kJ mol^{-1})	$\tau_{0\beta}$ (s)	B_β (kJ mol^{-1})	Reference
PAA	CH_2OH	6[a]	68	2.7×10^{-18}	8	This work
		0	73	9×10^{-17}	3.5	This work
Cellulose	CH_2OH and OH	6[b]	60	5×10^{-17}	–	[3]
		0	85	5×10^{-20}	10	[3]
PVA	OH	15[a]	58	6×10^{-18}	10	This work
		0	80	10^{-18}	14	This work
Dextran	OH	7[b]	60	10^{-18}	–	[3]
		0	86	10^{-19}	10	[3]

[a] % (w/w) methanol content.

[b] % (w/w) water content.

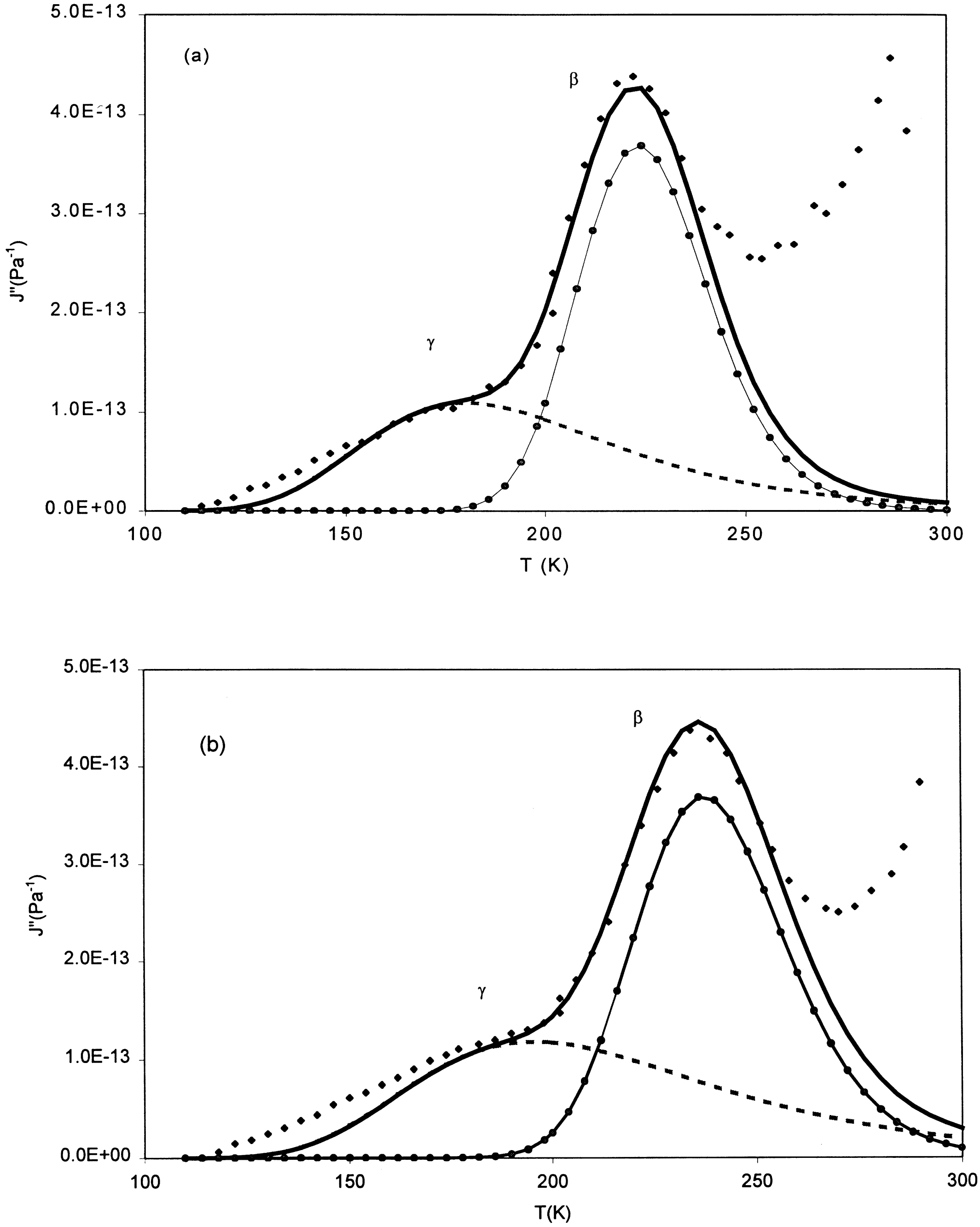

Fig. 7. β and γ mechanical secondary relaxations in dried PAA. Model of γ and β relaxation at (a) $F = 0.01$ Hz and (b) $F = 0.1$ Hz. J'' versus temperature. Experimental data (◆); calculated curve (—); calculated contribution of the γ relaxation (– – –); and calculated contribution of the β relaxation (–●–●–).

and *B*. Each of these parameters is deduced from the experimental data, except *B*, which is adjusted by fitting the experimental curves. The experimental and calculated plots of J' versus temperature for 0.01 and 0.1 Hz are shown in Fig. 7a and b. A good agreement between the experimental and calculated curves is obtained for all the frequencies with the same set of parameters. The values for β_{PAA} and γ_{PAA} calculated curves are summarized in Tables 1 and 2, respectively.

3.1.2. Experimental data for poly(vinyl alcohol)

Fig. 8 shows the dynamic mechanical thermogram of PVA films containing 0, 15 and 30% (w/w) methanol at 0.1 Hz. Every sample presents only one secondary relaxation peak, β_{PVA}, in agreement with the general trend observed in presence of water in the literature [11,12]. The intensity of β_{PVA} decreases strongly with decreasing fraction of the polar solvent and its width increases. On the other hand, as for PAA, the β_{PVA} peak shifts to higher

Table 2
Characteristics of the secondary γ mechanical relaxation in dried PAA, a comparison with dried cellulose

Polymer	Side groups	$\langle E_\gamma \rangle$ (kJ mol^{-1})	$\tau_{0\gamma}$(s)	B_γ (kJ mol^{-1})	Reference
PAA	CH_2OH	45	10^{-12}	7	This work
Cellulose	CH_2OH and OH	36	10^{-12}	7	[3]

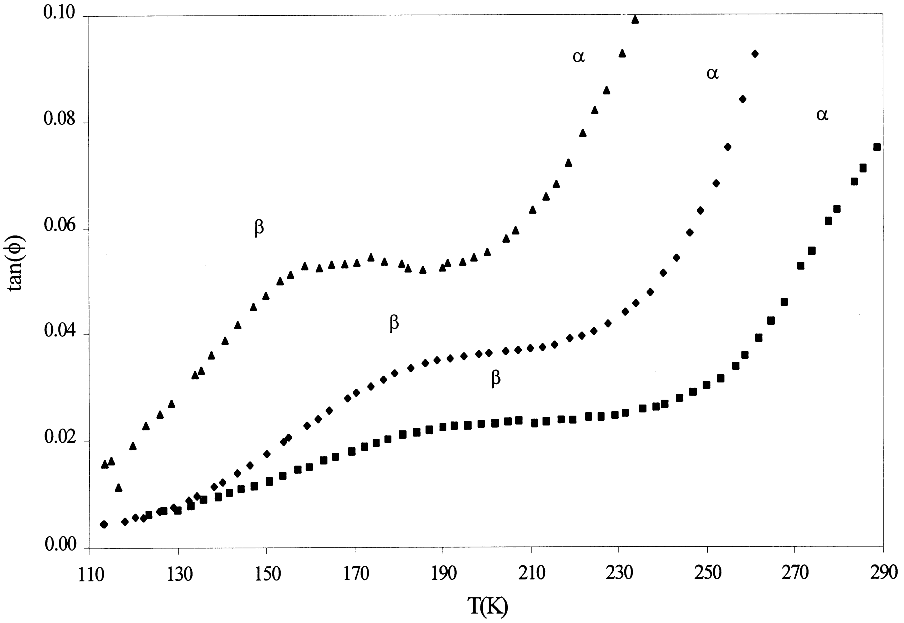

Fig. 8. Effect of methanol on the secondary mechanical relaxation of PVA: tan ϕ versus temperature. 30% (w/w) methanol content sample (▲), 15% (w/w) methanol content sample (◆), and dried sample (■).

temperature. It is observed at about 220 K for the dried PVA and around 190 and 170 K for PVA with 15 and 30% (w/w) methanol content, respectively (see Fig. 8). Its activation energy, $E_{\beta PVA}$, increases slightly after each thermal treatment and reaches 80 kJ mol^{-1} for the anhydrous sample with the pre-exponential time, $\tau_{0\beta PVA}$, of about 10^{-18} s. Water presents a similar influence on the β relaxation in PVA with 2 and 0% (w/w) water content. The experimental data of the dried PVA and PVA with 15% solvent content are fitted as discussed above. The parameters are summarized in Table 1.

3.2. Comparison with polysaccharides

3.2.1. General characteristics of secondary relaxations in polysaccharides

The analysis by mechanical and dielectric spectroscopy for cellulose and others polysaccharides [3,4,13] shows that the intensity and position of their secondary relaxations are strongly influenced by the water content. Mechanical spectroscopy data show that the amorphous cellulose exhibits two mechanical secondary relaxation processes [3,5,22–24] (referred to as γ_{mcell} and β_{mcell}) but the dried dextran presents only one secondary relaxation process, called β_{mdex}. The amplitude of β_{mcell} decreases strongly with the water content. For dried cellulose, the amplitude of β_{mcell} peak is three times lower than that for dextran. Following a previous work [3], this could explain why no dielectric β relaxation is observed in dried cellulose. On the other hand, dielectric spectroscopy experiments [4] show that the dried cellulose exhibits only one dielectric secondary relaxation with characteristics close to γ_{mcell} and so was referred to as γ_{dcell}. Finally, dextran exhibits two dielectric secondary relaxations (called γ_{ddex} and β_{ddex}).

3.2.2. γ Mechanical relaxation

In this work, only PAA presents a γ mechanical relaxation (see Fig. 5). With characteristics similar to the cellulose γ mechanical relaxation (see Table 2), γ_{PAA} relaxation apparently disappears when PAA contains a small amount of solvent. On the basis of the comparison between mechanical and dielectric behavior of cellulose and dextran (polysaccharides with different chemical architectures) [3,4], γ_{mcell} is associated with the motion of side groups. Cellulose has two kinds of lateral groups, i.e. hydroxymethyl groups (CH_2OH) and hydroxyl groups (OH) (see Fig. 1a). So, this relaxation could be associated with the rotation of CH_2OH and/or of OH. However, mass transfer by rotation of OH around the C–OH axis is extremely small and therefore would not be able to produce any relaxation signature. Thus, the only group involved in the mechanical relaxation should be CH_2OH. Moreover, PAA presents only one kind of side group, i.e. CH_2OH (see Fig. 1b). So, if the γ mechanical relaxation involves the rotation of side groups in both cellulose and PAA, this should come from CH_2OH. This is also consistent with the fact that no similar γ mechanical relaxation can be seen either in dextran or in PVA, and they only have OH groups (see Fig. 1c and d). Nevertheless, dextran presents a γ dielectric relaxation. This is consistent with the fact that in dielectric measurements, the motion of OH groups is clearly visible because the dipole moments of both primary and secondary OH groups are similar. Thus the very broad γ_{dcell} peak has been attributed to the overlap of two relaxation processes referred [4] as to γ_{OH} and γ_{CH2OH}, and correspond to the rotation of hydroxyl and hydroxymethyl groups, respectively.

3.2.3. β Mechanical relaxation

Table 1 shows the influence of the solvent content on the β mechanical relaxation for PAA and PVA as well as for cellulose and dextran [3,4]. A similar plasticizing effect of polar molecules of the solvent (water or methanol) in cellulose, dextran, PAA and PVA is verified. In fact, after each thermal treatment this relaxation shifts to higher temperature and its intensity decreases for all polymers (see Figs. 4 and 8). The apparent activation energy increases from approximately 60 to 80 $\mathrm{kJ\,mol^{-1}}$, starting with 6% (w/w) solvent content to reach the dried samples and simultaneously, the pre-exponential time decreases from about 10^{-17} s to about 10^{-20} s (see Table 1). According to Heijboer [25,26], the apparent activation energies are too high (and pre-exponential time too short compared to the Debye time) to ascertain that only lateral groups are responsible for these relaxations. On the other hand, it is clear that none of these processes could correspond to the glass transition (for PAA and PVA the α relaxation appears clearly at much higher temperature (see, for example Fig. 8)). Thus, they should be associated with localized motions of the main chain. Montès et al. [3] showed, from the evaluation of enthalpy and entropy contributions in the relaxation time temperature dependence, that the activation entropy is nonzero for the β relaxation. This should be also the case for β_{PAA} and β_{PVA} as the pre-exponential time $\tau_{0\beta PAA}$ and $\tau_{0\beta PVA}$ are much shorter than the Debye time. (see Table 2). The origin of this value can be found in either intra and/or intermolecular interactions, since it is difficult to imagine that the rotation of a main chain segment can occur without any contribution from their first neighbors. In fact, more probably, the two effects, i.e. intra and intermolecular, have to be considered. However, the only way to determine the value and the molecular origin of this relaxation would be to perform their molecular simulation, in order to model the thermoactivated motions. Thanks to the mechanical behavior similarities shown here between simplified structures of vinyl polymers presented in this work and complex polysaccharides, the molecular simulation study should be relevant. It could provide new insights in the relaxation mechanisms in hydrogen bonded polymers, and more precisely for the complex polysaccharides. Molecular modeling data will be presented in the near future.

4. Conclusion

Secondary mechanical relaxations in PAA and PVA were characterized by mechanical spectroscopy. The dried PAA exhibits two secondary relaxations (γ_{PAA} and β_{PAA}). The humidified PAA sample does not present any evidence for a γ relaxation. PVA (with and without solvent) presents only one relaxation (β_{PVA}). The influence of the polar solvent (methanol and water) was also observed for β_{PAA} and β_{PVA}. Due to a shift towards low temperature in β_{PAA}, it completely overlaps the small γ_{PAA} in presence of the solvent. The characteristics of γ_{PAA} in dried PAA are comparable with the γ mechanical relaxation of dried cellulose. The mechanical γ relaxation is probably the signature of the rotation of CH_2OH groups. On the other hand, OH groups cannot be at the origin of such relaxation, as in both dextran and PVA (polymers containing only OH side groups) no γ relaxation can be detected. These preliminary results show that PAA can be a simple model for the simulation of the molecular dynamics of the γ relaxation in cellulose and others polysaccharides with similar side groups. It should be also possible to characterize the influence of solvent in cellulose on the cooperativity of localized motions.

In a more surprising manner, characteristics of β_{PAA} and β_{PVA} are also comparable with the β mechanical relaxation of cellulose, dextran, amylose etc. The influence of polar solvents on these relaxations is similar. Nevertheless, if the β relaxation is due to the cooperative motions of segments of the main chain, the question of this similarity still remains. Indeed, the flexibility of vinyl chains is very different from that of sugar rings. However, the general similarity observed in both synthetic and natural polymers containing hydroxyl and hydroxymethyl moieties is promising. An appropriate molecular simulation of PVA and PAA will allow us to get information on the way: (i) the molecules of polar solvent are distributed; (ii) these molecules modify the energy barrier between two metastable conformers; and (iii) this solvent modifies the cooperativity of these motions.

Acknowledgements

A. De La Rosa gratefully acknowledges CONACyT (Consejo National de Cencia y Tecnologia, Mexico) for the economic support during this work.

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