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WATER EFFECT IN THE THERMAL AND MOLECULAR DYNAMICS BEHAVIOR OF POLY(*L*-LACTIC ACID)

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A detailed dielectric characterization of the relaxation modes found in a poly(*L*-lactic acid), PLLA, film containing 0.4 mass% of water is provided. The sub-glass relaxation process is a superposition of two processes, one highly influenced by water with activation energy of 50 kJ mol^{-1}, and another one, with longer relaxation times and lower intensity having activation energy of 38 kJ mol^{-1}. Dried PLLA exhibits an abnormally broad secondary β-relaxation that probably corresponds to the superposition of multiple processes. Upon water sorption the strength of the more mobile process significantly increases being shifted to lower temperatures which allows the detection of the underlying process. The glass transition relaxation process is deviated to higher frequencies almost one decade due to the water plasticizing effect. The reported results show that small quantities of water may have a profound impact in the relaxational features in PLLA, which should be taken in account when considering the properties and performance of this system.

Keywords: *dielectric relaxation, polyester, thermal treatment, water effect*

Introduction

Poly(*L*-lactic acid), PLLA (–[CH(CH$_3$)COO]$_n$–) has been widely used in environmental and biomedical applications, due to the biodegradable and biocompatible natures [1–4]. Besides its practical relevance, this polyester also owns interesting features that turns it appealing to be investigated in a broader perspective. For example, the crystallization rate of PLLA is rather slow, and it is possible to easily obtain this material with different crystallization degrees or crystalline morphologies [5–8]. The glass transition of PLLA is not far above room or body temperature. Therefore, the material will undergo structural relaxation in service, which will contribute for the time-dependent changing of relevant physical properties, such as volume or mechanical performance [9, 10]. The glass transition dynamics, that will determine such behaviour, was also found to be dependent on the crystallinity degree [11] and on the lamellar morphology [12], due to the confinement effect imposed by the crystalline lamellae to the amorphous phase. Another factor that will also determine the glass transition temperature and, in general, the segmental mobility, is the quantity of water inside the structure, that acts as a plasticizer. Different states of swollen water molecules can be envisaged, as commented by Puffr and Sebenda, including tightly bound molecules to the carbonyl groups, weakly bound water molecules, or in larger clusters, for the case of higher water contents [13]. Despite being essentially hydrophobic, PLLA is able to uptake small quantities of water that can affect the molecular dynamics. Some data already pointed out for the effect of humidity in the relaxational behaviour in PLLA [14], but more effort should be done in order to fully understand the plasticizing effect of water in this material. Information in this context could help to predict properties, such as mechanical and degradation profile, in relevant situations, including upon implantation in the body. Previous temperature scans showed that T_g could increase about 4°C when PLLA, initially in equilibrium at typical relative humidity, is dried. The activation energy of the β-relaxation was not effected by humidity, but the intensity of this secondary process was much higher for higher hydration levels, and presented a more complex shape. In this work we pretend to extend this study by detecting and characterise the relaxations on both dry and equilibrated PLLA using broad-band dielectric relaxation spectroscopy (DRS), covering temperatures from the subglassy state up to the region of the glass transition. DRS is able to probe dipolar fluctuations along a very large frequency range [15], being a very powerful tool to characterise molecular dynamic when temperature is also varied, covering the essential relaxation

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events. Our groups already used this technique to investigate the influence of water in the rotational/translational mobility of a polysaccharide, chitosan, also a biodegradable material widely used in biomedical applications [16]. In that work, it was detected the presence of a new relaxation assigned to the existence of water within the structure, labelled β_{wet}. It would be interesting to verify if such kind of process could be observed in other polymers, with a completely different structure. For example, in Nylon-6 it was found the existence of two local modes with intensities that depended on the water content in the sample, and two segmental modes, attributed to the wet and dry material [17]. It was not clear in previous studies if such findings could be extended to polyesters such as PLLA. Therefore, besides the finding of shifts in the loss peaks along the temperature (or frequency) axis, the detection of other relaxational processes related to the uptake of water molecules within the amorphous structure in PLLA will be also addressed.

Experimental

The material studied in this work is from Purac Biochem with an inherent viscositiy of 5.87 dL g^{-1}.

The molecular masses, M_n and M_w, of the polymer, evaluated from gel permeation chromatography (Shimadzu, LC 10A, Japan) using polystyrene as standard and chloroform as solvent, are 269000 and 301000, respectively. PLLA films were prepared by melting the material in a hot plate (at ca. 200°C), compressed between two metallic disks and quenching it in cold water. The PLLA films obtained are amorphous as checked by DSC and X-ray diffraction.

In order to evaluate the water influence, a PLLA film exposed to about 50% of relative humidity, here designate as $PLLA_{wet}$ was used and its behaviour compared with a PLLA sample previously evacuated at 323 K for 48 h to remove absorbed water, named $PLLA_{dry}$; the cooling down to room temperature of this later sample was accomplished under vacuum. Duplicate samples of each type were measured assuring reproducibility. The water content in $PLLA_{wet}$ was determined in a control sample as 0.4 mass% by mass loss (precision of 0.01 mg) after drying. The chosen temperature for water removal is conditioned by the onset of crystallization that occurs around 353 K [18].

Samples were placed between two gold-plated electrodes (diameter 10 mm) of a parallel-plate capacitor for dielectric measurements that were carried out using a broadband impedance analyzer, α-N analyzer from Novocontrol GmbH, covering a frequency range from 10^{-1} Hz to 1 MHz.

The sample cell (BDS 1200) was mounted on a cryostat (BDS 1100) and exposed to a heated gas stream being evaporated from a liquid nitrogen dewar. The temperature control was performed within ±0.5°C, with the Quatro Cryosystem. Novocontrol GmbH supplied all these modules.

The amorphous sample was cooled down to –120°C and dielectric spectra were collected in increasing temperature steps from –120 up to 25°C: in the temperature range $-120°C \leq T \leq -70°C$ the dielectric spectra were recorded every 2°C; in the remaining temperature region the spectra were recorded every 5°C.

After this procedure a dielectric spectrum was acquired, isothermally at 80°C, for each sample type.

Dielectric results and discussion

Sub-glass processes

In a complementary study, the complex permittivity of a $PLLA_{dry}$ was measured following the same experimental procedure described here. Both imaginary and real components of complex permittivity were fitted by using Havriliak–Negami (HN) function [19]:

$$\varepsilon^* = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{[1+(i\omega\tau)^{\alpha_{HN_j}}]^{\beta_{HN_j}}} \tag{1}$$

where j is the number of relaxation processes, $\Delta\varepsilon$ is the dielectric strength, $\tau \approx (2\pi f_{max})^{-1}$ is the characteristic relaxation time, and α_{HN} and β_{HN}, the shape parameters describing the symmetric and asymmetric broadening of the complex dielectric function, respectively [15] ($0<\alpha_{HN}<1$, $0<\alpha_{HN}\beta_{HN}<1$).

A secondary relaxation occurring at temperatures below the glass transition, here designated β_{dry}, was characterized, and the temperature dependence of relaxation times, estimated from HN fitting, led to Arrhenian behaviour with activation energy of 50 kJ mol^{-1}. The α_{HN} and β_{HN} shape parameters determined were 0.28±0.02 and 0.79±0.03, respectively. The low value of α_{HN} indicates that the β relaxation is rather broad being complex in nature. Due to the inexistence of polar side groups in the PLLA chain, this secondary process has been assigned to twisting motions in the main chain. Combining dielectric and dipolar moment calculations, Ren *et al.* estimated that the amplitude of such motions in poly(*d*,*l*-lactic acid) could be described by an average twisting angle of around 11° [20].

To analyze the water influence, a $PLLA_{wet}$ was measured from –120 up to 25°C to characterize sub-glass behaviour. The respective dielectric loss spectra are shown in Fig. 1a. Figure 1b presents the isochronal plot at 1 kHz taken from the isothermal measurements (full symbols).

It is obvious the bimodal character with a pronounced process detected at the highest frequencies/lowest temperatures partially merging another broad and less intense process centred at lower frequencies/higher temperatures. Two HN functions were used to treat the results as shown dashed lines that depict the individual functions used in the fit of loss data at –25°C whose sum is represented as a dark solid line. Included in Fig. 1b is the isochronal plot of PLLA$_{dry}$ (open circles) evidencing its broadness, being located in between the two sub-glass processes. The process located at the lowest temperatures will be designated as β_{wet} since it seems to be significantly enhanced upon water sorption as deduced from Fig. 1b. The underlying sub-glass process will be named simply β.

Thus, two individual HN functions were used to fit PLLA$_{wet}$. The respective curves obtained at –25°C are included in Fig. 1a as dashed lines where the sum is represented as a dark solid line; solid lines in grey correspond to the overall fit of the remaining temperatures.

Figure 2 presents the temperature dependence of a) α_{HN} and $\alpha_{HN}\beta_{HN}$ and b) dielectric strength. The alpha parameter slightly decreases with the increasing temperature for the β_{wet} process, indicating a broadening of this process that becomes more symmetrical when temperature increases (increasing of $\alpha_{HN}\beta_{HN}$); a broadening of the relaxation is also found for the underlying β process although keeping more or less the same symmetry. Its dielectric strength increases with temperature as usual in localized molecular mechanisms, while the dielectric strength, Δε, for the β_{wet} process is almost temperature invariant (some compensation occurs between Δε of both β_{wet} and β which should be attributed to the fit procedure), being more intense relatively to the β process due to the higher number of dipoles able to reorient.

Figure 3 presents the temperature dependence of the relaxation times estimated from HN fitting for both relaxation processes. The linearity denounces an Arrhenian behaviour, which activation energy was estimated to be 50 and 38 kJ mol^{-1}, for β_{wet} (squares) and β (circles) processes respectively.

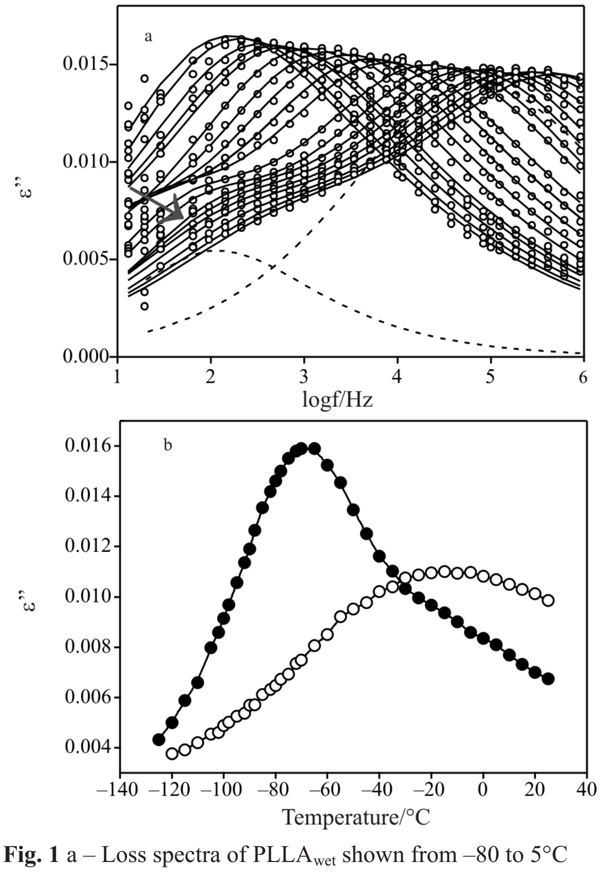

Fig. 1 a – Loss spectra of PLLA$_{wet}$ shown from –80 to 5°C every 5°C (also included –78 and –72°C) (○); dashed lines depict two individual HN functions used in the fit of loss data curve as shown at –25°C indicated by the arrow. All solid lines represent the global HN fit. b – Isochronal cut at 1 kHz for ● – PLLA$_{wet}$ and ○ – PLLA$_{dry}$, taken from the isothermal measurements

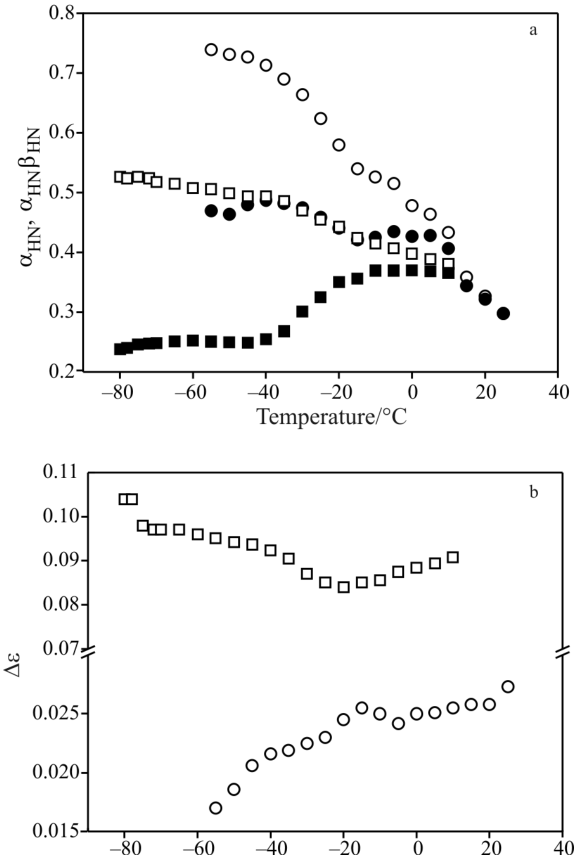

Fig. 2 Evolution of the HN parameters of the two processes detected in PLLA$_{wet}$ a – shape parameters: α_{HN} (open symbols) and $\beta_{HN}\alpha_{HN}$ (filled symbols) for β_{wet} (squares) and β (circles) processes; b – dielectric strength for the □ – β_{wet} and ○ – β processes

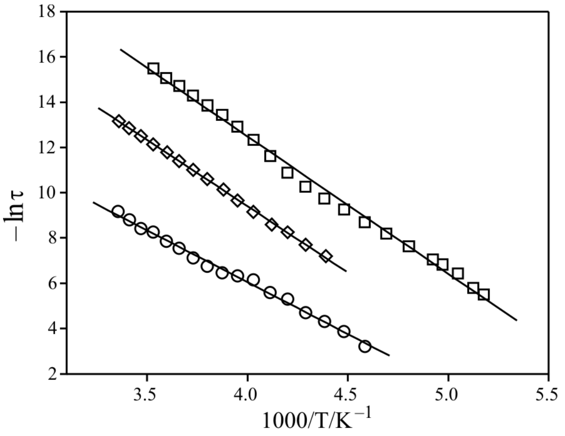

Fig. 3 Relaxation map of the two components of the sub-glass relaxation of PLLA$_{wet}$, namely □ – β_{wet} and ○ – β, compared with the β relaxation observed in ◇ – PLLA$_{dry}$

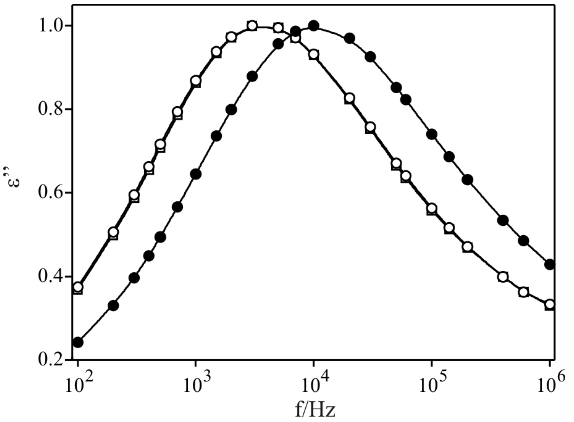

Fig. 4 Loss peaks obtained at 80°C for: ● – PLLA$_{wet}$, PLLA$_{wet}$ after being heated up to 200°C and cooled again at ○ – 80°C and for □ – PLLA$_{dry}$

The activation plot of PLLA$_{dry}$ was inserted in Fig. 3 (losanges). The relaxation is deviated to higher relaxation times relatively to the β_{wet} process, having the same activation energy (E_a=50 kJ mol^{-1}). The residual β process, with lower intensity, is located at higher relaxation times. Ongoing studies of sub-glass relaxations in PPLA, crystallized at different temperatures, show that the secondary relaxation of both wet and dried samples acquires a multiple modal character for crystallization temperature above 95°C. A low frequency flank evolves from the β_{dry} relaxation with a location very close to the β process is now detected. Thus, the presence of water seems to have a plasticizing effect on the more mobile component of the β_{dry} process, enhancing this relaxation and shifting it to lower temperatures, allowing the detection of the underlying less intense β process. According to these observations, the residual β process is less sensitive to water content.

It must be emphasized that similar traces (in tanδ) are found by Starkweather *et al.* [14] for poly-lactide exposed to different levels of relative humidity. However, no comments are made about the residual process observed at the high temperature side of the main secondary relaxation.

Glass transition process

In order to evaluate water if also influences the glass transition relaxation process if adsorbed, a dielectric spectrum was collected at 80°C, a temperature that lies above T_g (60.8°C, obtained by DSC measurements at +10°C min^{-1}) after the measurements in sub-room temperature range.

Figure 4 presents the normalized loss curves for PLLA$_{wet}$ (open circles) and PLLA$_{dry}$ (full circles) both measured at 80°C. The PLLA$_{wet}$ was further heated up to 200°C to assure water removal, cooled down to 80°C and re-measured (open squares). The loss curve collected after this treatment matches with the loss spectrum of PLLA$_{dry}$. The comparison between dry and wet spectra shows that water shifts the loss maximum almost one decade to higher frequencies evidencing the important influence of water contents as low as 0.4 mass%. Nevertheless the shape of the loss peak in the wet sample is exactly the same as the dried one; same shape parameters were used to obtain the overall fit depicted as solid lines in Fig. 4, where two relaxations were used: the alpha process and the β process. Additionally the coincidence of the loss curve of the wet sample after heating up to 200°C with the spectrum of a previously dried sample shows that no decomposition of the sample occurred during heating and that the temperature treatment was efficient to warrant the elimination of water.

Conclusions

The results reported here evidence the existence of two sub-glass relaxation modes in the wet material. Both modes can also be present in dried PLLA, since an abnormally broad process is detected in between the two relaxations mentioned, although with less resolution. The water sorption dramatically increases the strength of the more mobile component of the secondary relaxation detected in dried PLLA shifting it to lower temperatures and allowing the detection of the underlying secondary process located at higher temperatures.

Concerning the glass transition relaxation process, the usual plasticization water effect is felt by shifting the α process almost one decade to higher frequencies. However, no changes are observed in the shape parameters of the loss peaks of the α-relaxation due to the effect of water.

In conclusion, small quantities of water may have a profound impact in the relaxational features in PLLA, which may have consequences in the properties and performance of this system.

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