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Local demixion in plasticized polylactide probed by electron spin resonance

Cécile Courgneau [a,b], Olivier Vitrac [a], Violette Ducruet [a], Anne-Marie Riquet [a,*]

[a] INRA, UMR 1145 Food Process Engineering, 1 Avenue des Olympiades, F 91300 Massy, France
[b] AgroParisTech, UMR 1145 Food Process Engineering, 1 Avenue des Olympiades, F 91300 Massy, France

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ABSTRACT

Improving the barrier properties to gas and organic compounds of biosourced polyesters, such as polylactides (PLAs), by increasing their crystallinity has been suggested by several authors. This paper investigates the risk of microphase separation for a technological approach that would involve a plasticization of PLA, to further its crystallization kinetics, with common plasticizers: Acetyl tributyl citrate (ATBC) and Poly(ethylene glycol) (PEG). Overplasticization effects following microphase separation were monitored along the film thickness by exposing dynamically thermo-compressed films to nitroxide spin-probes. The method enabled a scan of the local polymer mobility for different concentration profiles in spin-probes, with in particular a maximum moving continuously in time towards the geometric center. The results were interpreted as excess local temperatures that would give similar ESR spectra motion in the bulk. It was shown that measured excess temperatures could be related to local shifts in the glass transition temperature along the film thickness.

1. Introduction

The use of renewable resources for food packaging material producing is interesting for environmental reasons. Persistent pollution and limited fossil fuel resources are major concerns in our current society [1]. Bio-based polymers may offer solution to lessen our dependence to petroleum stocks while limiting the greenhouse gas emission [2]. Aliphatic polyesters such as polylactides (PLAs) offer an attractive alternative to synthetic polymers with similar mechanical properties [3–6]. Barrier properties to gas [7,8], water vapor [9] and organic compounds [10,11] have been studied extensively over the past decade. PLA is ranked between polystyrene and poly(ethylene terephthalate) (PET) for its barrier properties to oxygen with permeability values close to high density polyethylene ones. Permeability to gas or small solutes in thermoplastics tends to increase exponentially with the fractional free volume to cohesive energy density ratio [12]. In the case of PLA, few correlations have been proposed to correlate its structure with its transport properties. Available studies targeted the effect of crystallinity [13–19] on the sorption and diffusion of oxygen. It was shown that the permeability decrease with crystallinity, well-established on a polyester such as PET (down to 50% without orientation) [15,16], could not be easily reproduced at lab scale with PLA. Some groups showed an enhancement [14,17] and others non-significant effects [10]. The complication arises from the slow crystallization rate of unplasticized PLA with typical half time crystallization of 2 min at 110 °C for of poly(L-lactide) [20].

To get reproducible results at industrial scale, a possible strategy could be to plasticize PLA to accelerate cold crystallization. Previous results [21] showed, however, that the incorporation of linear plasticizers such as Poly(ethylene glycol) (PEG) led to significant exsudation. The current work aims at assessing possible microphase separation and heterogeneities in PLA blended with different plasticizers and concentrations: PEG and Acetyl tributyl citrate (ATBC), which do not yield detectable exsudation in differential scanning calorimetry (DSC).

To our best knowledge, few studies investigating the micro- or even nano-phase separation by ESR have been published. It was mainly carried out by the spin labeling method or on petro-sourced polymers [22–24]. Our motivation was to get an imaging of the molecular dynamics of small probes along the film thickness (half thickness: 75 μm) in well equilibrated PLA-plasticizer blends. Such profiles were obtained by introducing in a controlled manner a stable nitroxide radical acting as molecular probe and whose reorientation dynamics was detected by electron spin resonance (ESR). Different regions, either near the surface or deeper in the material, were monitored non-intrusively by changing the spin-probe concentration profiles along the material thickness via successive sorption and desorption of nitroxide radicals.

Microphase separations were detected by comparing the spin probe motion obtained with localized spin-probes to those obtained in the bulk. Local polymer chain dynamics were reconstructed from bidimensional ESR spectra (Temperature × Field)

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* Corresponding author. Fax: +33 1 69 93 51 85.
E-mail address: anne-marie.riquet@agroparistech.fr (A.-M. Riquet).

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and interpreted as excess temperature that would lead similar spin-probe motion.

The paper is organized as follows. Section 2 describes the methodology of preparation of blends and our ESR technique. Two spin-probes were used to increase the detectability of change in molecular dynamics for a same measurement temperature. Section 3 presents firstly the changes in spin probe motion spectra with time when a same processed film is exposed to decreasing probe vapor partial pressures. Exposure conditions were chosen to maintain during the whole experiment a strong disequilibrium between the surface and the ambience. The maximum concentration in the film was thus moving from the surface towards the material center. The concept of excess temperature was demonstrated by showing that localized 2D ESR spectra and bulk 2D spectra were almost invariant by temperature translation. An attempt of validation as a deviation of the local glass transition temperature (T_g) is proposed. Diffusional mechanisms of probes in neat and plasticized PLA are finally discussed in Section 4.

2. Materials and methods

2.1. Materials

Polylactide pellets were supplied by ECPM-LIPHT (France). The content in L-lactide was about 92 wt%. The average molecular weight was of $9.0 \times 10^4\ \mathrm{g\ mol^{-1}}$ with a polydispersity index of 2.75.

Plasticizers, Acetyl tributyl citrate (ATBC) and Poly(ethylene glycol) (PEG, $n = 7$), were purchased from Sigma Aldrich (France). Spin-probes, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (AminoTEMPO) were supplied by Aldrich (France) and Fluka (France) respectively. Table 1 lists the typical properties of plasticizers and spin-probes.

2.2. Methods

2.2.1. Film preparation

Before use, PLA pellets and plasticizers were dried at 80 °C overnight in a vacuum oven. Films were possibly formulated with plasticizers and spin-probes in molten state within an internal mixer (Haake Rheocord 9000) at 160 °C and 60 rpm for 15 min. Two different levels of plasticizers, either PEG or ATBC, were considered: 9 and 17 wt%. When directly incorporated to formulation, a concentration of 0.15 wt% was used for both spin-probes. Final blends were dried during a minimum of 4 h at 80 °C.

Neat and plasticized PLA films were processed by thermo-compression (press model: 15 tonnes, Telemecanique, France) at 185 °C and 150 bars in a multistep process. PLA blends were first molten between both hot plates without pressure for 3 min. They were subsequently successively pressed under 10 bars for 30 s, 50 bars for 30 s and finally 150 bars for 1 min to remove air bubbles. The final film thickness was approximately of 0.15 mm for surface area of ca. 100 $\mathrm{cm^2}$. All films were quenched in water at ambient temperature.

2.2.2. Dynamic exposure to spin-probe vapors

2.2.2.1. Experimental. Variable concentration profiles in spin-probes with a maximum moving towards the center of films were obtained out by exposing the films to probe vapors within a sorption vessel at 343 K (above the melting point of probes and above the glass transition temperature of the tested PLA). The sorption experiment was carried in a finite volume (ca. 1200 $\mathrm{cm^3}$) in equilibrium with a finite amount of liquid probes (ca. 20 mg) and subjected to a periodic renewal (14 renewals, initially every day and subsequently every 3 days) of the whole gas phase by fresh air at 343 K. The design ensured that a complete consumption of the liquid probe amount (by either sorption or due to air renewal) was achieved after 8 days of contact. As a result, the profiles during the first 8 days corresponded to a sorption situation with a maximum at the immediate surface whereas profiles after 8 days obeyed to a desorption situation with a maximum translating progressively towards the center. Samples consisted in small $20 \times 2 \times 0.15\ \mathrm{mm^3}$ strips. All neat and plasticized samples were exposed to the same enriched probe vapor ambience in the same flask to get comparable results with exposure time.

Renewal times were used to acquire the ESR spectrum of each sample at 298 K. All acquisitions were performed in less than 20 min with an initial cooling time of 5 min. Last acquisition occurred after 29 days of residence time in the sorption vessel at 343 K.

Such conditions ensured that the maximum intensity of the paramagnetic signal for different exposure times was related to probes located at different depths. As the diffusion coefficients of the probe within PLA varied plasticization level, ESR measurements for a same exposure time corresponded, however, to different positions between samples except for small contact times.

2.2.2.2. Interpretation. The principles of mass diffusion of a spin-probe into the sample under dynamic exposure were interpreted with the help of a simple diffusion model. At time $t = 0$, a probe-enriched atmosphere with partial pressure equal to $p_\infty(t = 0)$ is put in contact with a sample of thickness $2l$. The atmosphere is subjected to kinetic losses due to either transfer to the sample or to some leakages with an atmosphere with a probe partial pressure $p_0 = 0$. By assuming that mass flux at the sample-air interface ($x = 0$) is controlled by a mass transfer coefficient, h, and a Henry constant, k, the transport and mass balance equations become in one dimension:

$$\begin{cases} \frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\frac{\partial}{\partial x}C(x,t)\right) \text{ for } 0 \leqslant x \leqslant l \\ \frac{\partial C(x=0,t)}{\partial x} = \frac{h}{RT}\left(kC(x=0,t) - p_\infty(t)\right) \\ \frac{\partial C(x=l,t)}{\partial x} = 0 \\ \frac{dp_\infty(t)}{dt} = \frac{A}{V_\infty}\left[\alpha(p_0 - p_\infty(t)) + h(kC(x=0,t) - p_\infty(t))\right] \end{cases} \tag{1}$$

where α is a constant controlling the dilution rate of the probe-enriched atmosphere, R and T the gas constant and the absolute temperature respectively, and A and V_∞ are the surface contact area and the volume of the atmosphere in contact respectively.

Fig. 1 presents the simulated probe concentration profile along the film half-thickness $C(x,t)$ for typical chemical affinities of the probe (i.e. k values) for the film while keeping constant all other parameters. Without changing the conclusions, a uniform diffusion coefficient in the film, $D(x)$, and large mass Biot number $Bi = hl/D > 100$ were assumed. System of Eq. (1) was discretized in space according to a finite volume discretization method (strictly verifying the mass balance) and integrated in time via a second order backward difference scheme. Scaling parameters A/V_∞ and α were chosen to fit the discontinuous experimental dilution profile with a theoretical continuous one (Fig. 1a). Depletion time, $t_{depletion}$, was defined as the time to reach a maximum bulk concentration in the film (Fig. 1c) and used as time scale to plot simulated results. Corresponding concentrations profiles are plotted in Fig. 1b for times shorter and longer than depletion time. Important features such as the position of maximum of concentration in the film and the position of 99th percentile (first position x_{99} such that $\int_0^{x_{99}} C(x,t)dx = 0.99\int_0^1 C(x,t)dx$) are depicted in Fig. 1d. For times shorter than depletion time, probes were located within a region positioned at the interface and thickening linearly with the square root of time. By contrast, depletion time triggered