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Reduced physical aging rates of polylactide in polystyrene/polylactide multilayer films from fast scanning calorimetry

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A B S T R A C T

The physical aging behavior of amorphous polylactide constrained against polystyrene in layers of 300 nm, thanks to the layer–multiplying co–extrusion process, was investigated by fast–scanning calorimetry (FSC). By cooling down the sample from the liquid state to the glassy one at very fast scanning rates, it was possible to investigate the structural relaxation of the polymer glass at high temperatures for which the time needed to reach the equilibrium was shortened. Therefore it was possible to perform the study of physical aging in experimental conditions providing an expanded view of the structural relaxation for short aging times. Taking benefit of this property, it was highlighted that the aging kinetics of polylactide occurred significantly slower in the multilayer film, in comparison with a bulk amorphous film. The process of recovery in the multilayer system was found to occur at similar rates, or even slower, than in a three–layer film in which polylactide reached its maximum extent of crystallinity. This was attributed to mobility hindrance that might be inherent to the extrusion conditions or associated with the presence of capped interfaces with polystyrene.

1. Introduction

The environmental concern has increased the interest in the development of biodegradable packaging materials to replace petroleum–based plastic packaging. Polylactide (PLA) is easy to process, and has interesting use properties such as high transparency and gloss, and high tensile modulus. Several studies showed the potential of PLA in the packaging sector [1,2] although its brittleness is a limiting factor and its barrier properties need improvement [3]. Thermal crystallization can contribute to increase barrier properties, under the condition to limit the formation of a dedensified rigid amorphous fraction (RAF) during annealing [4,5].

The potential of layer multiplying co–extrusion to improve barrier properties has emerged recently [6–9]. This process combines two or three polymers into a continuous alternating layered structure with hundreds or thousands of layers, offering the possibility to decrease the individual layer thickness down to several nanometers, which yields confinement of one polymer by the other. This technique offers moreover the huge advantage of being able to produce objects at large scale and to be transferable to the industry for the fabrication of commodity materials. It has recently been shown with this technique that the crystallization of PLA under confinement can delay the formation of the RAF and therefore open new ways for property optimization [10].

PLA has a glass transition temperature (Tg) of approximately 60 °C and is therefore sensitive to physical aging at room temperature (i.e. storage below but near Tg), which can impact negatively its dimensional stability during service. Physical aging is caused by structural relaxation towards equilibrium and characterized by a decrease in thermodynamic quantities, such as specific volume, enthalpy and entropy [11–15]. It generally exacerbates the inherent brittleness of PLA [16] and increases its gas permeability [17].

Various methods have been used to study physical aging, including differential scanning calorimetry (DSC) [18,19], gas permeability measurement [20,21], dielectric spectroscopy
In DSC, physical aging is characterized by the enthalpy relaxation, which appears as the development of an endothermic peak superimposed to the heat capacity step of the glass transition. Recently, the development of fast scanning calorimetry (FSC) has received much interest regarding physical aging. This technique allows heating up and cooling down polymers as fast as thousand Kelvin per second. This performance requires a drastically reduced sample mass (typically tens to hundreds ng) to diminish the thermal lag (i.e., temperature gradients occurring in sample and instrument during the measurement). The major advantage of the very high cooling rates is that FSC can provide glasses with high level of enthalpy or specific volume. Physical aging can also be investigated at temperatures higher than in standard DSC conditions. Since the time to reach equilibrium depends only on the aging temperature \( T_{ag} \), this allows reaching the thermodynamic equilibrium much faster.

Two main factors are expected to govern molecular dynamics, and in particular physical aging, in multi-nanolayers films: the reducing of the domain accessible for relaxation which can be considered as a pure geometric confinement effect, and the nature of the interface between the layers. How physical aging occurs when the polymer dimension is reduced at the nanoscale is under debate. Because conflicting results have been recently reported, meaning acceleration \([33–39]\), slowing down \([40,41]\), or invariance \([25]\) of the physical aging rate. Therefore several parameters, with possibly antagonist effects, should be considered when investigating the structural relaxation in confined landscapes, such as confinement type, aging conditions, and interfacial interactions \([42]\). For example differences in physical aging kinetics were reported for free-standing thin films and multi-nanolayers films. Murphy et al. \([21]\) reported that polysulfone aged slower in multilayer films compared to free-standing thin films. Boucher et al. reported accelerated aging with decreasing the thickness of thin free-standing PS films \([43]\), whereas Langhe et al. \([44]\) observed a reduced aging rate of thin PS layers in multi-nanolayer films of PS and polycarbonate (PC). In this context the objective of the present work is to contribute to the discussion about the impact of the interface effects in multi-nanolayers films on the physical aging kinetics. We showed recently the possibility to use the layer--multiplying coextrusion process for the confinement of thin PLA layers (20 nm thickness) between PS films \([10]\). No interphase was evidenced in PS/PLLA films \([10]\), which allows here investigating the physical aging process of constrained PLA between slippery walls. We introduce furthermore amorphous and semi-crystalline samples to scale the aging rate in PS/PLLA films by comparing it with the aging rate in two different landscapes: an unconstrained amorphous phase and a constrained intra--lamellar amorphous phase with incomplete decoupling between amorphous and crystalline phases \([45]\).

2. Experimental

2.1. Material processing

Polylactide (PLA) pellets were purchased from Corbion Purac (PLA REVODE 190 L175). The content of \( l \)-lactide was higher than 99%. Polystyrene (PS) pellets were obtained from Total Petrochemicals (PS Lacqrene 1340). Due to the sensitivity of polylactide to hydrolytic degradation, PLA pellets were dried before extrusion in a Somos \(^{®}\) dryer while the residual humidity level was checked with an Abon \(^{®}\) PMXTM humidity tracer. Pellets were dried at 80 °C during 12 h to reach a humidity level between 250 and 300 ppm. After drying, PLA pellets were subsequently extruded by single screw extrusion with a 30 mm diameter extruder (with a 33 l/D (length on diameter) barrel) and a classical three sections screw. The extruder screw speed was set to 40 rpm. A mixer device containing 4 Sulzer SMX\(^{®}\) mixers was placed between the barrel and the die to ensure a better homogenization of the melt. A flat die of 200 mm width and a chill roll equipment were used to manufacture films of approximately 300 \( \mu \)m thickness. The temperature profile of the barrel for the six zones was 180–180–185–190–190–190 °C. The temperatures of the mixer device and the die were defined at 200 °C. The roll temperature was fixed at 20 °C to cool down the films. The resulting films are amorphous according to X-Ray diffraction and Differential Scanning Calorimetry (not shown there) and are called amorphous systems (AS) in the paper (see Table 1). A layer multiplying co-extrusion process was used to fabricate films of alternating layers of PLA and PS. The process is presented in Fig. 1. It consists in two single screw extruders of 20 mm diameter with gear pumps to regulate the composition, a three-layer feed block (A–B–A), a series of layer-multiplying elements, a flat die of 200 mm and chill rolls at 20 °C. PLA was extruded to form the central layer of the films initial structure and PS the external layers. The extrusion conditions are given in Table 2.

The composition of the PLA/PS films was fixed at 25/75 (w/w). The initial three--layer polymer flow entered a mixing section, followed by a sequence of layer--multiplying elements. The melt was initially cut in half vertically, and then both flows were superposed, compressed and stretched to its original width, hence doubling the number of layers with each layer--multiplying element. A series of \( n \) elements leads thus to \( 2^n+1 \) alternating layers. Using eight multiplying elements, a multilayer system (MS) of 300 \( \mu \)m in thickness with 513 alternating layers of PLA and PS was created. Atomic Force Microscopy (AFM) images showed that the integrity of both PS and PLA layers was respected as they were continuous and relatively uniform (Figure S1.1 in Supplementary Information). When no multiplying elements are added on the line, the three--layer film is collected as is and referred as amorphous 3--layer system (AS3). Its thickness was fixed at 120 \( \mu \)m. Post--processing crystallization was carried out by annealing AS3 at 85 °C for 180 min to form crystallized 3--layer systems (CS3). For the annealing treatment, the films were sandwiched between two sheets of Teflon and two stainless steel plates, and then thermo--compressed using a heat press (Darragon, France) at a pressure set to 5.10^6 Pa. The micrograph of the CS3 (Figure S1.1 in Supplementary Information) obtained from polarizing optical microscopy (POM) showed that the crystallization generates mostly small size spherulites with diameter less than 20 \( \mu \)m. According to Modulated Temperature Differential Scanning Calorimetry (MT--DSC) analyses, the crystallinity degree of the CS3 was about 35% and an important amount of rigid amorphous fraction, close to 40%, was generated. Details regarding MT--DSC protocols are given in Supplementary Information in Figure S1.2.

2.2. Fast scanning calorimetry (FSC)

The fast scanning calorimetry (FSC) analyses were performed using a power compensation twin--type chip--based fast scanning calorimeter Flash DSC 1 (Mettler Toledo) equipped with a Huber TC1000 intra--cooler. The samples were placed on the sensitive area of a MultiSTAR UFS 1 MEMS chip sensor (Fig. 2A). Prior to use, the chip was conditioned and corrected according to Mettler Toledo procedures. A thin layer of silicone oil was used to promote adhesion of the sample onto the chip and to improve thermal contact. Samples were continuously flushed with a 20 mL/min \(^{−1}\) flow of gaseous nitrogen to prevent condensation from environmental moisture and to ensure temperature control. Sample mass was estimated from the step change in heat flow at the glass transition by assuming that the heat capacity value step \( \Delta C_p \) obtained by FSC
at $\beta_h = 1000 \text{ K s}^{-1}$ is identical to the value obtained on another sample from the same material by MT–DSC at $\beta_h = 2 \text{ K min}^{-1}$. The mass of the samples typically ranged between 50 and 200 ng.

The use of FSC required several steps of calibration for a given heating rate ($\beta_h = 1000 \text{ K s}^{-1}$ in the present case). In a first time, the temperature calibration of the sample sensor was performed. To do so, a piece of indium was placed on the reference sensor as schematized in Fig. 2B. This allowed checking the temperature calibration of the sensor. At $\beta_h = 1000 \text{ K s}^{-1}$, an onset melting temperature of 156.6 °C, consistent with the theoretical value, was measured (see Fig. 3A). Then, on the sample sensor, a second piece of indium was disposed on the top of the sample to estimate the static thermal lag $\Delta T_{S}$. This thermal lag was due to the thickness of the sample which creates heat transfer delay and temperature gradients. Its value was estimated from the difference in the onset temperature of both indium melting peaks, as depicted in Fig. 3A, then extrapolated to a theoretical heating rate equal to zero. In addition, the dynamic thermal lag $\Delta T_{D}$ was estimated from a symmetric correction based on the half of the difference in the glass transition temperature measured upon cooling and heating at the same scanning rate $\beta_h = |\beta_s|$, using the area matching method.

### Table 1

Processing characteristics and microstructure parameters of monolayer, 3–layer, and multilayer films.

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Film Type</th>
<th>Processing method</th>
<th>PLA/PS composition (w/w)</th>
<th>Number of multiplying elements</th>
<th>Number of layers</th>
<th>Total film thickness (µm)</th>
<th>Nominal PLA thickness (nm)</th>
<th>Xc (%)</th>
<th>XMA (%)</th>
<th>XRA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>Amorphous system</td>
<td>Single screw extrusion</td>
<td>100/0</td>
<td>/</td>
<td>1</td>
<td>300</td>
<td>300,000</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>A3S</td>
<td>Amorphous 3–layer system</td>
<td>Layer multiplying co–extrusion</td>
<td>25/75</td>
<td>0</td>
<td>3</td>
<td>120</td>
<td>30,000</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>R3S</td>
<td>Rejuvenated 3–layer system</td>
<td>Layer multiplying co–extrusion</td>
<td>25/75</td>
<td>0</td>
<td>3</td>
<td>120</td>
<td>30,000</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>C3S</td>
<td>Crystallized 3–layer system</td>
<td>Layer multiplying co–extrusion</td>
<td>25/75</td>
<td>0</td>
<td>3</td>
<td>120</td>
<td>30,000</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>MS</td>
<td>Multilayer system</td>
<td>Layer multiplying co–extrusion</td>
<td>25/75</td>
<td>8</td>
<td>513</td>
<td>300</td>
<td>300,000</td>
<td>0</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

*Rejuvenated in fast scan DSC by consecutive thermal cycles from 0 to 230 °C.

**Crystallized in press at 85 °C during three hours.*

### Table 2

The extrusion conditions to fabricate PLA/PS films.

<table>
<thead>
<tr>
<th>PLA extruder temperature profile (°C)</th>
<th>PS extruder temperature profile (°C)</th>
<th>Pump and feed block temperature (°C)</th>
<th>Layer multiplier block temperature (°C)</th>
<th>Flat die temperature (°C)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Material temperature (°C)</th>
<th>PLA screw speed (rpm)</th>
<th>PS screw speed (rpm)</th>
<th>PLA throughput (g/h)</th>
<th>PS throughput (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>22</td>
<td>57</td>
<td>600</td>
<td>1800</td>
</tr>
</tbody>
</table>

![Fig. 1. Principle of the layer multiplying co–extrusion process.](image)
2.3. Physical aging

The aging kinetics was studied by means of FSC and with this respect a methodological question needed to be solved. The rate of the recovery process is not linearly correlated with the aging temperature \( T_{ag} \) and typically shows a maximum [49]; it results from a competition between the driving force, i.e. the degree of undercooling, and the macromolecular mobility (higher at lower undercooling). Physical aging studies are generally performed at a fixed distance from \( T_g \) in the vicinity of the maximum rate. This recommendation is difficult to follow when studying constrained systems (MS and C3S), for which the glass transition appears very broad in FSC. In that case, the glass transition temperature can hardly be defined and it is more convenient to consider a glass transition domain. Previous work on PLA showed that an aging temperature \( T_{ag} \) equal to 50 °C led to a strong signature of recovery when crossing the glass transition during subsequent heating [31]. By performing aging at 50 °C, \( T_g = T_{g cool} - 16 °C \) for both AS and A3S. For constrained systems, by considering the uncertainties on the determination of \( T_{g cool} \) it was established that \( T_{ag} \) situated for each sample between \( T_g \) - 15 °C and \( T_g \) - 25 °C. From the methodological point of view, the investigation of the structural dependence of the physical aging was still possible under the condition to ascertain data by considering the role of the aging temperature.

The physical aging experiments were performed with the aging times \( t_{ag} \) varying from 0.001 to 100 min. Prior to the annealing, a good thermal contact was ensured by a consecutive heating and cooling at 1000 K s\(^{-1}\), up to 125 °C, and down to -80 °C. Then the sample was heated at 1000 K s\(^{-1}\) up to 125 °C, just below the FSC signature of the glass transition of polystyrene to obtain zero-aged PLA, before being cooled down to \( T_{ag} = 50 °C \) at 1000 K s\(^{-1}\). Such a procedure allowed preserving the integrity of the layers and consequently the hard confinement of polylactide by polystyrene. The enthalpy of recovery associated to the physical aging of the PLA for the different materials was calculated by integrating the difference between the scans of an aged sample and a sample with a nil aging time as depicted in Supplementary Information in Figure SI.3.

3. Results and discussion

3.1. Physical aging of unconstrained PLA by means of FSC

Fig. 4A displays FSC normalized heat flow of AS after aging at 50 °C. The endothermic peak related to the enthalpy relaxation of AS was superimposed to the glass transition and shifted to higher temperatures when the aging time increases from \( t_{ag} = 0.001 \) min to \( t_{ag} = 100 \) min. This is classically observed in physical aging experiments. \( \Delta C_p \) did not change with the aging time, suggesting that the sample remained wholly amorphous despite the successive crossings of the glass transition. To compare the behavior of neat PLA (AS) with the behavior of PLA in the neighboring of PS, the analysis of the physical aging of the A3S was performed. This experiment was complicated by the thickness of the PLA layer in A3S which was close to 30 μm. Consequently taking a representative sample of the 3-layer system with a mass of a few mg was challenging. Thus, a piece of A3S was selectively cut in an area where both PS and PLA coexisted in the material and a FSC analysis was carried out by heating up to 230 °C in order to check the
presence of the glass transitions of PS and PLA. This procedure caused the rejuvenation of the 3-layer system. The rejuvenated sample (R3S) (Fig. 4B) exhibited an aging behavior similar to AS (Fig. 4A) despite its different thickness. The enthalpy relaxation of PS was of relative low intensity in comparison to PLA. This result might be attributed to a lower content of PS in the cut sample. Besides PS is aged 80°C below its glass transition temperature. At larger undercooling (higher $T_g - T_{ag}$), the rate of densification decreases due to lower molecular mobility, which effects a smaller enthalpy loss within the time-scale of the aging experiment [50].

In Fig. 5, the enthalpy of recovery $\Delta H$ calculated for AS and R3S is presented in terms of a structural relaxation function $\phi(t_{ag}) = (\Delta H_{\infty} - \Delta H) / \Delta H_{\infty}$ where $\Delta H_{\infty}$ is the total enthalpy loss, representing the distance to equilibrium. The structural relaxation function is the same for AS and R3S. The vicinity of PS, like the thickness of the film, did not seem to impact the kinetics of the structural relaxation of amorphous PLA. Fig. 5A shows in addition the structural relaxation function from data reported in previous works [31,51,52] and measured by classical DSC at $T_{ag} = 15^\circ C$, meaning at constant value of total enthalpy loss. The structural relaxation kinetics were much lower than the ones reported from FSC, and the signature of physical aging was detected only after a few minutes aging in DSC, while an increase in the enthalpy of recovery was recorded after a few seconds aging in FSC. This result should find its explanation in the fact that the aging temperature is higher in FSC, leading to shorter relaxation times. The aging rate $R_a$, obtained by FSC and classical DSC, was $R_a = 1.6 \pm 0.1$ and $R_a = 0.7 \pm 0.1$ J/decade respectively, $R_a$ being defined from the enthalpy of recovery variations with aging time (Figure SI.4 in Supplementary Information). $R_a$ was already used to compare the physical aging kinetics of various polymer glasses [15,53,54], polymer nanoparticles [55], nanocomposites [40], free-standing films [25,36,56], stacked films [38], co-extruded multilayers [44,57]. In Fig. 5B the structural relaxation function obtained from DSC and FSC are compared for identical temperature of aging $T_{ag}$. Data obtained in the present study at $T_{ag} = 50^\circ C$ position well in consistence with the data previously obtained from FSC at $T_{ag} = 52, 47, 44^\circ C$ respectively. It is also observed that, at constant aging temperature, the recovery function obtained from DSC approaches the one obtained from FSC, but the aging still proceeds slower. Since this result does not perfectly follow theoretical predictions assuming that the time to reach equilibrium will be the same, other causes explaining this difference should be considered. A difference of equilibration time when PLA is vitrified in FSC at 0.17 K s$^{-1}$ or 1500 K s$^{-1}$ has been reported previously [31]. Time scale to reach equilibrium has been observed to be longer when PLA is vitrified at lower rate. On the other hand, when the same cooling rate was used in both FSC and DSC, the time needed to reach equilibrium was the same. In FSC the sample is significantly thinner compared to the standard bulk sample analyzed in DSC. Therefore, its surface/volume ratio is higher.
which facilitates the free volume hole diffusion (FVHD) at the free interface. This peculiar property is only observed for high cooling rates. Thus it has been assumed that critical thickness resulting in acceleration of the physical aging was cooling rate dependent. Therefore, from amorphous samples, it is shown that FSC gives more enthalpy recovery and allows investigating physical aging within shorter times at higher temperatures. In the following, benefit of this property has been used to investigate constrained PLA.

3.2. Physical aging of constrained PLA by means of FSC

In comparison to AS and R3S, the glass transition of C3S (Fig. 6A) was wider and the enthalpy recovery peak broader. Moreover the peak maximum was situated 15 °C higher at the longest aging time. The molecular dynamics of the MAF is strongly influenced by the microstructure in semi–crystalline PLA [51]. The amplitude of the heat flow step remained unchanged after the successive passages above the crystallization temperature \((T_c = 85 \, ^\circ C)\), which showed that the microstructure was not significantly modified. The crystallization of A3S (leading to C3S) decreased the heat capacity step from 0.48 to 0.16 J g\(^{-1}\) K\(^{-1}\), and the MAF only represented 33% of the quantity material (Table 1). The intensity of the endothermic peaks related to physical aging of C3S decreased in consequence. Fig. 6B shows surprisingly that the endothermic peak related to physical aging of the multi–nanolayer sample MS, although wholly amorphous, presented the same characteristics as for C3S, i.e. broadened and shifted towards higher temperatures. This behavior has been reported by Poel et al. [58] when positioning the sample too far from the center of the heating area, or when the thermal contact between the sample and the sensor changes during the analysis. In the present study the samples were positioned as close as possible to the center of the sensor like in Fig. 2A and oil was used to ensure a good contact with the sensor. Therefore the shift of the glass transition to higher temperatures could result from the constraining of PLA between the layers of polystyrene. Due to the low mass of PLA in MS, the endothermic peak was of weak intensity. The measurement sensitivity was however sufficient to determine the maximum temperature of the recovery peak \(T_{peak}\) and the value of the enthalpy of recovery notwithstanding the signal noise. Fig. 7A plots the increase of \(\Omega_{peak} = T_{mid}\) with the aging time. It rose faster in the constrained systems, C3S and MS, the effect being more pronounced for MS. It is possible that in constrained systems, the local density increase during physical aging induces stronger restrictions of mobility, shifting the recovery process to higher temperatures. It was also observed that the enthalpy recovery values were significantly lower in constrained systems (Fig. 7B). They increased to about 8 J/g for AS and R3S, but only to 2 J/g for C3S and to 1 J/g for MS (Fig. 7B).

However, the direct comparison of the enthalpy of recovery is insufficient to understand the impact of the processing on the physical aging kinetics. Two criticisms can be formulated: i) due to the difficulty to measure the \(T_g\) of the constrained systems upon cooling the strict equivalence of the undercooling conditions of all samples cannot be asserted, ii) the quantity of PLA relaxing at the glass transition is lower in constrained samples. The MS included PLA and PS and the C3S was semi–crystalline. That is why the enthalpy recovery values were rescaled in the following to the quantity of PLA relaxing at the glass transition. By rescaling the enthalpy of recovery to the content relaxing at the PLA glass transition, the total enthalpy loss becomes the same for all materials independently on their microstructure (uncertainties being related to the determination of \(T_g\)). Thus it allows comparing the enthalpy of recovery in materials exhibit different relaxing contents. Furthermore the effects of different undercooling degrees were taken into account.

3.3. Influence of the constraint nature on the physical aging kinetics of MAF

As shown in Fig. 8, the rescaling to the quantity of PLA relaxing at the glass transition leads to an increase of the enthalpy of recovery in C3S and MS. It is worth mentioning that the participation of RAF to the structural relaxation in PLA has been discussed by Righetti et al. [50]. To consider both possibilities of the structural relaxation of the only MAF, and of the whole amorphous phase, the two rescaling procedures have been performed for the C3S.

However, the values are still lower than those of AS and R3S. If the microstructure does not impact the physical aging, all curves in Fig. 8 should be superimposed. One could attribute this difference in terms of structural causes linked to the mobility constraints induced by crystals or layer multiplying co–extrusion process. As mentioned above, this hypothesis is only valid when the physical aging conditions are comparable, which is hard to certify due to the uncertainties around the glass transition temperature of constrained systems. Therefore, in addition to the experimental data, a physical aging map is proposed in Fig. 8 as a reference. The values of the enthalpy of recovery were calculated with the help of the physical aging data of amorphous PLA (FSC data) published in our previous work [31]. For each undercooling conditions (\(dT = T_g, cool ~

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Fig. 6. FSC normalized heat flows of C3S (A) and MS (B) after physical aging at \(T_{cool} = 50 \, ^\circ C\) for aging times ranging between 0.001 and 100 min. All scanning rates were \(\dot{\theta}_0 = \theta / t = 1000 \, K \, s^{-1}\). The sample mass is \(m = 170 \, ng\) for C3S and \(m = 60 \, ng\) for MS.
The aging rate of $\text{MS}$ decreased to $0.6 \pm 0.2$ J/decade. This result is consistent with reports on multilayer samples by other authors [44]. Murphy et al. [21] observed that the effect of physical aging in nanolayers obtained by co-extrusion stands in contrast to studies with thin, freestanding films. It can be explained by the presence of capped interfaces in multilayer systems instead of free surface. Indeed, the existence of free surface facilitates the free volume hole diffusion. In these systems, an acceleration of physical aging is typically reported [63,64], that can affect macroscopic properties, permeability for example. Several studies have highlighted that the glass transition of bulk samples does not evolve under confinement when the free surface is suppressed by hard confinement [65], irreversible adsorption [66], and crystallization [67]. Physical aging may also be hindered due to attractive interactions of the polymer with the neighboring surface [68–70] or, using an alternative hypothesis, slowing down of the free volume hole diffusion (FVHD) at the surface [22,71]. It has been observed that the acceleration of physical aging, occurring in thin freestanding films and in stacked films, in terms of the time required to reach equilibrium, associated the depression of the glass transition temperature [30]. Furthermore Fukao et al. [38,72] have shown that the rate of physical aging in stacked films could evolve from thin film like to bulk like with interlayer diffusion. In the multilayer system investigated in the present study, it is interesting to observe that the constraints generate an increase of the glass transition, in contrast to the behavior of stacked films. In addition to that the structural equilibrium in these aging conditions is only dependent on the total enthalpy loss $\Delta H_{\text{tot}}$. As discussed before, the undercooling conditions ($\Delta T = T_{g, \text{cool}} - T_{g}$) for C3S and MS aging could not be precisely controlled due to the measurement uncertainty on their $T_g$. It was nevertheless possible to observe modifications in their structural relaxation (Fig. 8). The physical aging kinetics of C3S and MS were clearly delayed compared to A5 and R3S.

The aging rate of C3S was $0.6 \pm 0.2$ J/decade when rescaled to the total content of amorphous phase (MAF + RAF) and it was $R_a = 0.9 \pm 0.1$ J/decade, when rescaled to the MAF content only. The decrease of the physical aging rate with increasing crystallinity degree has been reported for several semi-crystalline polymers, including polypropylene [59], poly (phenylene sulfide) [60], or PEEK [61]. Monnier et al. [62] observed that the structural recovery functions between semi-crystalline PLAs crystallized under quiescent or flow-induced conditions were similar, with an aging rate of $1.1 \pm 0.1$ J/decade, if rescaled to the MAF content. These results are consistent with ours.
relaxation can be impacted by the fabrication process [73], which can, like in the multi—nanolayer coextrusion process, impose high elongation and shear rates on the polymer melt. Ghazaryan et al. [74] reported that both uniaxial and biaxial plastic deformation, in excess of 150% plastic strain, decelerates, and possibly prohibits the physical aging process. Finally, the thickness of the PLA layer is in excess of 150% plastic strain, decelerates, and possibly prohibits the physical aging process. The reported that both uniaxial and biaxial plastic deformation, in elongation and shear rates on the polymer melt. Ghazaryan et al. might be multiple, possibly involving the role of capped interfaces and the internal stress linked to confinement about the structural relaxation kinetics in a magnification.

4. Conclusion and perspectives

The use of fast scanning calorimetry allows obtaining information about the structural relaxation kinetics in a magnified scale. It is shown here that the layer multiplication co—extrusion process is able to slow down the physical aging in amorphous PLA on a level equivalent or higher than thermal crystallization. This observation is however limited to one PLA layer thickness and it would be interesting to investigate this property in an extended range. The causes explaining the slowing down of the structural relaxation might be multiple, possibly involving the role of capped interfaces and the internal stress linked to confinement and orientation of the macromolecules. The possibility of restricting the structural damages caused by physical aging would be of interest for industrial development of multilayer films.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.polymerr.2018.07.017.

References


