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Molecular dynamics in electrospun amorphous plasticized polylactide fibers

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ABSTRACT

The molecular dynamics in the amorphous phase of electrospun fibers of polylactide (PLA) has been investigated using the cooperative rearranging region concept. An unusual and significant increase of the cooperativity length at the glass transition induced by the electrospinning has been observed. This behavior is attributed to the singularity of the amorphous phase organization. Electrospun PLA fibers rearrange in a pre-ordered metastable state which is characterized by highly oriented but non-crystalline polymer chains, and the presence of highly cohesive mesophase which plays the role of an anchoring point in the amorphous phase. The successful processing of electrospun fibers of plasticized polylactide is also demonstrated. It is shown that the plasticizer remains in the polymer matrix of the nanofiber after electrospinning. When PLA is plasticized, the loosening of the macromolecules prevails over the preferential orientation of the chains; therefore no mesophase is formed during the electrospinning and the cooperativity length remains the same. When the content of plasticizer increases, the inter-chain characteristic distances estimated from wide angle X-ray scattering (WAXS) are redistributed, suggesting a change in the level of interactions between macromolecules. It is assumed that the resulting decrease of the cooperativity length is driven by the progressive reduction of the number of inter-chain weak bonds. It is shown that in a non-confined environment, the number of structural entities involved in the alpha relaxation is strongly dependent on the level of physical interactions in the amorphous phase.

1. Introduction

In the theory of Adam and Gibbs [1], the relaxation process related to the glass transition is cooperative, and the motion of a structural unit is only possible if a given number of neighboring units are also in motion. Among the different models used to estimate the size of the Cooperative Rearranging Region (CRR) or cooperativity length, is the thermodynamic approach proposed by Donth [2] which relates the CRR to the dynamic heterogeneity deduced from the temperature fluctuation associated with the glass transition. This approach provides a picture of the relaxation time at the glass transition which is directly observable through calorimetric measurements [3]. According to this approach [2], the cooperativity volume $\xi^3_{T\alpha}$ at the dynamic glass transition temperature T_α can be estimated from the following equation:

$$\xi^3_{T\alpha} = \frac{(1/C_p)_{Glass} - (1/C_p)_{Liquid}}{\rho(\delta T)^2} k_B T^2_\alpha \quad (1)$$

With k_B the Boltzmann constant, δT the average temperature fluctuation related to the dynamic glass transition of a CRR, ρ the density, and C_p the heat capacity at constant pressure. Two causes for cooperativity changes have been observed so far. The first relates to changes in thermodynamic variables such as temperature, and the second to structural modifications of the material. In the first case, it is well known that the cooperativity length increases

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when the temperature decreases from the crossover temperature for which the cooperativity arises to the glass transition temperature [4–6]. In the second case, the approach of Donth has widely been used to investigate the decrease of cooperativity for two kinds of structural hindrances namely external and internal hindrances. External hindrances are related to geometrical restrictions like the confinement between nanolayers [7,8] or the addition of additives such as fillers [9,10] or plasticizer [11]. On the other hand, internal hindrances are related to the materials itself, in other words its microstructural modifications such as spherulitic crystallization [12,13] or orientation/crystallization of the amorphous phase induced by drawing [5,14].

In the last decade, the growing interest for polylactide (PLA) as a promising substitute to petroleum issued polymers has led researchers to investigate how its macroscopic properties could be tailored by controlling its microstructure. Because of the strong dependence of PLA macroscopic properties on its microstructure [15] and molecular dynamics [16], the cooperativity of the alpha relaxation process has been particularly investigated when the relaxation dynamics of the amorphous phase are modified by orientation [17], crystallization [13], or even plasticization [11]. However, the impact of several microstructural modifications on the amorphous phase dynamics remains unknown. For example, as illustrated by several authors [18–20], given conditions for drawing or thermal crystallization may induce the development of an intermediate ordering structure called a mesophase which prefigures the crystallization. The observation of the mesophase is generally reported for semi-crystalline materials [18–22] for which crystals strongly impact the investigation of the molecular mobility. Consequently, no study deals with the impact alone of the mesophase on the molecular dynamics of the amorphous phase. One of the challenges to carry out such a study lies in obtaining a unique microstructure where the mesophase is only dispersed in the oriented amorphous phase, without the presence of crystals. In the current study, we propose to electrospin polylactide (PLA) fibers to create this specific microstructure. Electrospinning is a simple technique to implement in order to produce polymer fibers with diameters ranging from the micro-to the nanoscale [23–25]. The technique has emerged as a useful technique to produce micro- and nano-fibers that have found wide applications in fields such as tissue engineering [26], biomedical [27], filtration [28], or electronic [29]. Despite the simplicity of the technique, many factors influence the fiber morphology including the solution flow rate, the distance between the syringe and the collector, solution concentration and the spinning voltage among others. In addition, very complex processes are involved that influences the fiber structure including the very rapid solvent evaporation as well as the mechanical and electrical forces which induce an orientation of the macromolecular chains along the fiber axis [24]. For these reasons, electrospinning can lead to complicated internal microstructures and high contents of mesophase [30]. Zong et al. [31] initially reported that electrospun fibers of polylactide (PLA) exhibit highly oriented chains although they are non-crystalline. Recently Ma et al. [32] confirmed this result by showing that the electrospinning carried on free-end fibers of PLA leads to the formation of an original microstructure where the amorphous phase is oriented with evidence of a mesophase but without the formation of any crystals. In the current study, we report for the first time on the cooperativity lengths obtained for as-spun fibers of polylactide using Donth's approach. We use the electrospinning technique in order to avoid the effects related to the confinement of the amorphous phase by crystals, similar to what is observed during drawing. The process has been designed to prevent any formation of the crystalline phase during the fiber formation.

As is well known, the applications for neat PLA are usually compromised due to its inherent brittleness [33]. Thus, plasticizers are often added to PLA in order to improve its mechanical properties. Acetyl Tributyl Citrate (ATBC) considered here, is among the most widely used plasticizers [33,34]. In this study, we report for the first time the electrospinning of plasticized PLA. Here, the goal is to observe if the internal modifications related to the mesophase still exist when ATBC is added as a plasticizer. It will allow another aspect of the impact of microstructural modifications on the amorphous phase dynamics to be depicted from the combination of both internal/external hindrances. Two series of samples have been analyzed: as-spun plasticized fibers and bulk plasticized PLA. Finally it is of interest to determine if the plasticizer remains inside the fibers after the electrospinning process and thus still acts as a plasticizer for the polymer nanofibers.

2. Experimental

2.1. Materials

Semi-crystalline PLA pellets (grade 4042D) were provided by Natureworks. The content of L-lactide and D-lactide were about 96% and 4% respectively. The number-average and weight-average molecular weights were M_n = 116 kDa and M_w = 188 kDa respectively, as measured by Gel Permeation Chromatography. Acetyl tributyl citrate (ATBC, CAS Number 77-90-7) was purchased from sigma Aldrich (France). PLA and ATBC were dried at 80 °C under vacuum for 12 h. Blending was performed with an internal mixer (Haake Rhecord 9000) at 160 °C and 60 rpm for 15 min. After a subsequent drying step (4 h at 80 °C under vacuum) bulk samples were obtained. In order to perform WAXS, bulk samples were thermo-molded in films of 1 mm thickness. For each system, neat PLA were heated during 5 min between two hot plates, and then the obtained films were quickly quenched in cold water. The measure of density leads to a constant value equal to 1.25 g/mol independent of the plasticizer content.

2.2. Electrospinning set-up

The polymer solutions were prepared in mix solvent of chloroform and acetone (chloroform:acetone = 2:1 in volume), both purchased from sigma Aldrich (South Africa). Plasticized and non-plasticized PLA were dissolved in the mix solvent and stirred using a magnetic stir bar at room temperature until homogenization of the solution. The required amounts of polymer were figured out to give a concentration solution of 8 wt% in PLA. Then, the polymer solution was placed in a horizontally glass pipette with a capillary around 1 mm diameter. At 5 cm from the needle, a petri-dish covered by an aluminum foil took place as a collector. The needle and the collector were connected to a high-voltage power supply which can generate a voltage up to 50 kV. The electric field applied was 1 kV cm^{-1}. The flow rate was controlled by a pump at 0.04 mL min^{-1}. The electrospinning process took place under controlled atmospheric conditions at 25 ± 2 °C and 35 ± 4% relative humidity. The thickness of the final as-spun fibers mat was less than 1 mm.

2.3. Scanning electronic microscopy (SEM)

The morphology of as-spun PLA fibers was investigated by scanning electronic microscopy (LEO 1430VP) after being gold coated during 3 min. The diameter of as-spun fibers was measured with an image analyzer (AxioVision 40LE). For each sample, average fiber diameter and standard deviation were determined from more than 200 measurements of the random fibers.