European Polymer Journal 48 (2012) 779–788

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Impact of crystallinity of poly(lactide) on helium and oxygen barrier properties

Alain Guinault [a,b], Cyrille Sollogoub [a,b], Violette Ducruet [c], Sandra Domenek [d,*]

[a] Cnam, P-2AM, 292 rue saint Martin, F-75003 Paris, France
[b] Arts et Métiers Paris Tech, PIMM, 151 boulevard de l'hôpital, F-75013 Paris, France
[c] INRA, UMR 1145 Ingénierie Procédés Aliments, F-91730 Massy, France
[d] AgroParisTech, UMR 1145 Ingénierie Procédés Aliments, F-91730 Massy, France

ARTICLE INFO

Article history:
Received 23 November 2011
Received in revised form 6 January 2012
Accepted 23 January 2012
Available online 1 February 2012

Keywords:
Poly(lactide)
Poly(lactic acid)
Oxygen permeability
Gas barrier properties
Crystallinity
Rigid amorphous fraction

ABSTRACT

The helium and oxygen gas barrier properties of poly(lactide) were investigated as a function of stereochemistry and crystallinity degree. Poly(L-lactide) and poly(D,L-lactide) films were obtained by extrusion and thermally cold crystallized in either α'- or α-crystalline form with increasing crystallinity degree. Annealing of the films at low temperatures yielded to α'-crystals as well as the creation of a rigid amorphous fraction in the amorphous phase. Unexpectedly, the quantity of the rigid amorphous fraction was highest in poly(L-lactide) crystallized under α'-form. Unexpectedly, the gas permeability increased with increasing quantity of α'-crystals in poly(L-lactide) and remained constant with increasing quantity of α'-crystals in poly(D,L-lactide). A gain in gas barrier properties was obtained upon crystallization at higher temperatures yielding α-crystals. The analysis of the oxygen transport parameters, in particular the diffusion and the solubility coefficient showed that the diffusion was accelerated upon crystallization, while the solubility coefficient decreased in an expected manner which led to conclude that it remained constant in the amorphous phase. The acceleration of the diffusion seems to be correlated to the occurrence of the rigid amorphous fraction, which holds larger free volume. To conclude, for optimization of poly(lactide) gas barrier properties by focussing on the decrease of the diffusion coefficient it can be suggested to work with poly(D,L-lactide) and to aim a crystallization in α-form avoiding the formation of a rigid amorphous fraction.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

A novel class of biobased and/or biodegradable polymers is now emerging driven by growing environmental awareness. Poly(lactide), PLA, is actually one of the most used bioplastics, although market penetration is still lacking far behind petrochemical materials. Initially used for biomedical applications, the polymer gathers however several interesting technological properties for commodity applications, such as ease of processing, good clarity, and acceptable mechanical properties. Its oxygen barrier properties are rather moderated, and can be classified between poly(ethylene terephthalate) and poly(styrene) [1,2].

PLA is a semicrystalline polymer and with this respect increasing crystallinity for obtaining better barrier properties seems to be a good way for optimization. Following the hypothesis of Michaels and Bixler [3] proposed on the basis of their pioneering work on polyethylene, crystalline structures are impenetrable for small, permeating molecules, constituting an excluded volume within the material. The transport of permeates is therefore limited in the amorphous phase, in which they need to adopt a tortuous path. The tortuous path being prolonged, the permeation is delayed by a decrease of the macroscopically observed diffusion coefficient. Furthermore, the creation of crystalline structures decreases the amount of amorphous phase which is available

---

* Corresponding author. Address: AgroParisTech, 1 rue des Olympiades, F-91744 Massy Cedex, France. Tel.: +33 (0) 1 69 93 50 68.
E-mail address: sandra.domenek@agroparistech.fr (S. Domenek).

0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.eurpolymj.2012.01.014

for penetrant sorption. Hence, crystallinity acts on both parameters determining permeability, diffusion and solubility coefficient.

Kanehashi et al. [4] published recently a review using a very large number of literature data on the relationship between crystallinity degree and gas barrier properties of common semicrystalline and liquid crystalline polymers including PLA. They showed that in a large number of cases, correlation between crystallinity degree and gas permeability is poor. To give two examples contained in Ref. [4], in the case of semicrystalline syndiotactic poly(styrene) no effect on oxygen permeability is observed upon increasing crystallinity degree. In the case of poly(ethylene terephthalate) large scatter of data did not allow for concluding on an effect of the crystallinity degree.

The relationship between PLA crystallinity degree and gas barrier properties has been subject of a few studies yet [2,5–8]. Comparing the literature data, there are differences in observed behavior for PLA. Sawada et al. [5] observed for poly(D,L-lactide) (4/96), PDLLA, constant oxygen permeability up to roughly 40% of crystallinity degree and afterwards small decrease. Drieskens et al. [6] showed, still for PDLLA (4/96), decrease in permeability with increasing crystallinity degree, where slope was somewhat steeper for high crystallinity degrees. Colomines et al. [2] observed increase in oxygen permeability with increasing crystallinity for a poly(L-lactide) (PLLA) sample. Dedensification of the amorphous phase [2,6] was suggested for explanation of the observed trends which do not obey the excluded volume hypothesis of Michaels and Bixler [3]. Sawada [5] suggests a continuous space around crystalline regions, due to the stress imposed on macromolecular chains on the interface with the amorphous phases.

On a molecular scale, transport of gaseous molecules in polymers proceeds by jumps which are infrequent in the case of glassy materials. In fact, molecules spend most of the time "rattling" in a microvoid. Jumps occur in the case that a passage of one microvoid to another in the polymer structure is opened by chain movements [9,10]. Therefore, transport relies on macromolecular chain dynamics which are restricted in the glassy state yielding infrequent jumps from one position to another. Gas molecules can therefore be regarded as a probe for polymer microstructure.

PLA microstructure has been already widely studied, where PLLA has received far more attention due to its longer history and importance in the biomedical field. PLA crystallizes in different polymorphic forms, the main polymorph obtained by thermal crystallization is the α-form, described in 2003 [11]. An important feature with respect to transport is the small density difference between the crystals of PLLA (1.26 by computing [11], 1.290 by experiment [12]) and the amorphous phase (1.24 by experiment [12]). Kawai et al. [13] described in 2007 the α'-form, which is a distorted α-form obtained by thermal crystallization below 90 °C. The α-form is yielded at crystallization temperatures higher than 120 °C, between both temperatures, mixtures are obtained [14]. With regards to the amorphous phase, PLA has been described with the help of the three-phase model [15–19], considering besides the crystalline phase two fractions of the amorphous phase, the mobile amorphous fraction (MAF) and the rigid amorphous fraction (RAF). The latter does not relax at the glass transition temperature, because molecules are partially trapped in the crystalline lamellae [20]. In addition, some authors show a confinement effect on the mobile amorphous phase between crystalline lamellae, which develops during crystallization [21–24]. The confined MAF shows a glass transition temperature which is shifted to higher temperatures compared to a fully amorphous sample.

The structure/function relationship between PLA microstructure and transport properties and the role of the crystallinity degree are not understood today. Scarce experimental results are not always coherent. The aim of the present study is thus to go further in the investigation of the action of the crystallinity of PLA on transport properties. In this aim two different PLA grades differing in stereochemistry were probed. Thermal crystallization was carried out with both grades controlling the crystalline form and yielding increasing crystallinity degree with either α'- or α-crystallites. The transport properties were investigated with the help of helium and oxygen, two molecules differing in their molecular volume.

2. Material and methods

2.1. Sample preparation

Poly(L-lactide) (PLLA) Biomer L9000 was purchased from Biomer Biopolyesters (Germany). Following the producer its D-lactic acid units content is less than 1%. Poly(D,L-lactide) (PDLLA) INGEO 2002D was purchased from NatureWorks LLC (USA) and has a percentage of D-lactic acid units of 4.3% [25].

PLLA and PDLLA pellets were dried under low pressure (10^4 Pa) for 8 h at 80 °C and subsequently extruded by single screw extrusion with a 30 mm diameter extruder (with a 33 L/D (length on diameter) barrel) and a three sections screw without mixing elements. The extruder screw speed was set to 40 rpm. The temperature profile of the barrel for the six zones was 180–185–190–195–200–200 °C. The temperature of the mixer device (4 Sulzer SMX®) and the die was defined at 200 °C. A flat die of 200 mm width and a chill roll equipment were used to manufacture films of approximately 300 μm thickness. The roll temperature was fixed at 20 °C. Two extrusion campaigns were carried out for both grades of PLA.

In order to obtain samples with defined crystallinity the extruded film was themocompressed from the glassy state at 5×10^4 Pa with the help of a thermal press (Darragon, France) at defined temperature for defined time. For that, the film samples were sandwiched between two Teflon sheets and two stainless steel plates. After pressing, the sandwich was quickly opened and films were quenched to room temperature at a cold surface. Films were stored at room temperature.

The crystalline morphology of the film samples was observed by using an optical transmission microscope (Nachet, France) under polarized light. The samples were prepared by using a microtome (Leica, France) to yield thin samples of 5–10 μm thickness.

The crystalline structure of the films samples was investigated by wide-angle X-ray scattering (WAXS) by means

Download English Version:

https://daneshyari.com/en/article/1400610

Download Persian Version:

https://daneshyari.com/article/1400610

Daneshyari.com