European Polymer Journal 91 (2017) 149–161

Contents lists available at ScienceDirect

European Polymer Journal

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

Gas transport and characterization of poly(3 hydroxybutyrate) films

Valentina Siracusa[a,*], Carlo Ingrao[a], Svetlana G. Karpova[b], Anatoly A. Olkhov[c,d], Alexey L. Iordanskii[c]

[a] Department of Chemical Science, University of Catania, Viale A. Doria 6, 95125 Catania (CT), Italy
[b] Emanuel Institute of Biochemical Physics, Kosygin Str. 4, Moscow 119991, Russian Federation
[c] Semenov Institute of Chemical Physics, Kosygin Str. 4, Moscow 119991, Russian Federation
[d] Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow 117997, Russian Federation

ARTICLE INFO

Keywords:
Poly(3-hydroxybutyrate) (PHB)
Polyesters
Biomaterials
Structure-property relations
Barrier
Gas permeation

ABSTRACT

Renewable biodegradable films of poly(3-hydroxybutyrate) (PHB) were produced via thermo-compression and casting method (specimens 1 and 2). On specimens 1, gas permeability coefficients with CO_2, O_2, N_2, and C_2H_4 gases were measured at 277 K, 288 K and 296 K. The physicochemical characteristics of PHB based on calorimetric, mechanical, and thermal examination were performed for both specimens. SEM and probe ESR technique showed the dramatic differences in their surface morphology and segmental motilities in polymer bulk. In the selected temperature range, the gas permeability ranking (P_i) for the thermo-compressed films is as follows: $P(CO_2) > P(O_2) > P(N_2) \approx P(C_2H_4)$. The gas diffusion coefficients were considered to be dependent on the gas critical volume, in accordance with the semi-logarithmic function, consistent with a free volume model. The activation energies of permeability, diffusivity and spin probe rotation, as well as the apparent heat of sorption equilibrium, forecast the values of PHB barrier characteristics in the range of foodstuffs stored temperatures.

1. Introduction

Currently, petrochemical polymers engage an essential segment in the area of barrier materials, especially as packaging materials [1]. Owing to the availability of resources, a low market cost, appropriate mechanical behaviour, and gas selectivity, they have been widely used as special materials in biomedicine, membrane separation, and packaging industry [2–4]. In spite of those advantages, petrochemical polymers used as packages, coating films, and containers cause a few intrinsic challenges. Among the latter, there are two principal tasks: (i) their industrial manufacturing is based upon non-renewable fossil resources, which have been progressively depleting, and (ii) after the lifetime and successive land filling, they are accumulated as non biodegradable wastes. These and other inconveniences bring about the search for eco-friendly packaging formulations, based on biodegradable polymers [5–8]. Biopolyesters, such as poly(α-hydroxyacides), namely polylactides (PLA), and poly(β-hydroxyacides), namely polyhydroxybutyrate (PHB) as the main homolog of the family, offer attractive alternatives as long as their characteristics can be tailored to packaging application.

Both families of the biopolyesters have been comprehensively explored along the years as thermoplastic and biodegradable systems with relevant mechanic characteristics and biocompatibility. The principal claims of PHB are that it is obtained from

---

[*] Corresponding author.
E-mail address: vsiracus@dmfci.unict.it (V. Siracusa).

http://dx.doi.org/10.1016/j.eurpolymj.2017.03.047
Received 23 August 2016; Received in revised form 8 March 2017; Accepted 23 March 2017

renewable resources and can be enzymatically degraded in many ecosystems, such as soil, sewage sludge and sea water [9]. Because of high crystallinity and low gas permeability as well as owing to biocompatibility, PHB was intensively explored as promising barrier packaging material in biomedicine and food industry [10–14].

Along with the positive features of PHB, there are some inconveniences related to its fragility, low ductility and relatively high cost. Optimization of mechanical characteristics is related with the control of crystallinity degree, which depends upon the thermo-mechanical history and the way of polymer processing (casting, molding, rolling, etc.). Besides the mechanical behaviour, for PHB as barrier material there is another important aspect related to gas transport characteristics, which determine direct its application in different packaging sectors, especially in food packaging area.

To date, a limited number of publications have been developed to assess the issue of transport in PHB and its copolymers, and most of those describe water diffusion in biopolymers [15–17]. This situation is quite clear because, being PHB biodegradable, it is structurally sensitive to water molecules on chemical (bond cleavage) and morphological (physical age) levels. Conversely, experimental data on PHB permeability and diffusion of organic vapours and especially transport of gases are extremely poor. The exception is a few recent papers and comprehensive series of communications where the gas barrier characteristics of PHB are represented as auxiliary information for development of PLA-PHB blend packaging [18–24]. A somewhat large numbers of works on gas transport are devoted to the study of PLA, a polyester with structure and kinetic behaviour similar to PHB [22,23,25–27]. However, the use of the permeability PLA results for predicting the gas barrier features in PHB would not be quite correct, since in spite of the similarity of their molecular structures, there are real differences in the glass transition temperatures, crystallinity degree, and molecular stereo-regularity.

Thus, the study discussed in this paper was aimed at performing an in-depth analysis of the transport characteristics of PHB and foremost its permeability to several atmospheric gases. The presented results assess the PHB application as potential material for food packaging or biomedicine field. Besides, kinetic investigations will be accompanied by structural and physical chemical characteristics, combined with probe Electron Spin Resonance (ESR) spectroscopy technique to estimate segmental dynamic of PHB molecules [28].

2. Material and methods

2.1. Materials

The PHB was kindly presented by Biomer Co (Krailing, Germany), as lot 16F. The initial polymer was in the form of white powder with particle size of 5–7 µm, MW = $2.06 \cdot 10^5$ Da. Samples of PHB were prepared following the two procedures discussed below. In particular, PHB films (specimens 1) were prepared by thermo-compression molding using a manual hydraulic press with heated platens, manual thermostat control and maximum pressure of 25 MPa. First, the press was pre-heated at 150 °C and then the PHB powder was placed in a stainless steel frame with top and bottom covers (50 × 50 × 1.0 mm). Films were obtained at 12 MPa of pressure during 3 min at 172 °C. To prevent the molded film adhesion to the metal surface and promote sample detaching, the polyimide film (Kapton DuPont) was used.

Specimen 2 was dissolved in chloroform (5% wt/v) under stirring at 70 °C. Then it was cast from chloroform solution (5 wt.% PHB) on glass plate under slow evaporation (for 24 h) at room temperature. The obtained films were dried in vacuum to constant weight and then stored at least 2 weeks at room temperature.

The stable nitroxide radical, 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO), was absorbed from the gas phase in the special glass set. The concentration of the TEMPO in PHB was $3.7 \cdot 10^{17}$ spin cm^{-3} (PHB).

For greater rank of detail, Fig. 1 was reported to show the chemical formula of both the PHB and TEMPO.

2.2. Polymer preparations

Samples of PHB were prepared following the two procedures presented below. In particular, PHB films (specimens 1) were prepared by thermo-compression molding using a manual hydraulic press with heated platens, manual thermostat control and maximum pressure of 25 MPa. First, the press was pre-heated at 150 °C and then the PHB powder was placed in a stainless steel frame

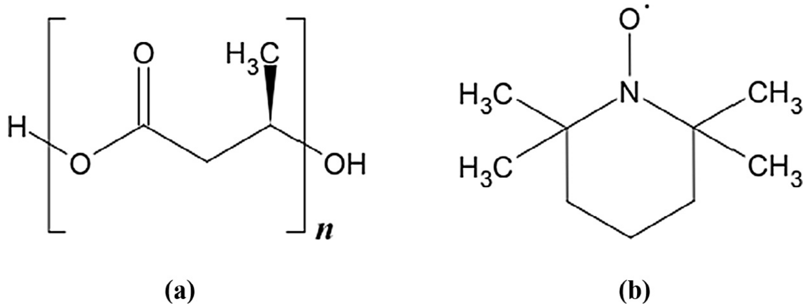

Fig. 1. Chemical formula of both PHB (a) and 2,2,6,6-tetramethyl-1-piperidinyloxyl (b) (TEMPO).