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Effect of chain extender and water-quenching on the properties of poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) foams for its production by extrusion foaming

Heura Ventura [a], Ester Laguna-Gutiérrez [b], Miguel Angel Rodriguez-Perez [b], Mònica Ardanuy [a,*]

[a] Departament d'Enginyeria Tèxtil i Paperera, Universitat Politècnica de Catalunya (UPC), C/Colom 11, 08222 Terrassa, Barcelona, Spain
[b] Cellular Materials Laboratory (CellMat Lab), Condensed Matter Physics Department, Universidad de Valladolid (UVa), Paseo Belén 4, Facultad de Ciencias, 47011 Valladolid, Spain

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ABSTRACT

Bacterial polyesters such as polyhydroxyalkanoates (PHAs) are of great interest for a large number of applications both because of their properties and because they come from renewable resources, despite having a higher cost than commodity polymers. Their foaming—although it presents some difficulties—could be an option to increase their competitiveness. In this work, two strategies have been studied to enhance the poly(3-hydoxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB) foamability by extrusion foaming. The effect of the cooling system (water-quenching or air-cooling), chain extender (CE) addition and chemical blowing agent (CBA) amount were evaluated. Density, cellular morphology, mechanical and thermal properties were studied. Optimal density reduction was achieved with use of CE and 3–4 wt.% of CBA masterbatch. The most effective strategy on density reduction was the addition of CE, while the water quenching had only a slight influence on the samples in which CE was not present. CE addition decreased the viscosity and the degradation rate of the polymer, thus leading to lighter foams with larger cells but with equal or even slightly better resistance to compressive and tensile stress, in general terms.

1. Introduction

PHAs are a family of microbial biodegradable bacterial biopolyesters [1–3] that are obtained from renewable resources, and are of interest for a wide range of applications from packaging to biomedical industries [2,3]. However, due to its current high price compared with other commodity polymers, PHAs' commercial use is currently limited to those applications in which the biodegradability or biocompatibility properties are capable of outbalancing the cost of the PHA resin.

A possible strategy to reduce the amount of polymer required for a certain application and therefore, the cost of the final good, is the weight reduction obtained from foaming the solid material leading to a foam with improved specific mechanical properties [4]. Nonetheless, the foaming of PHAs has some difficulties, since most PHAs are intrinsically difficult to foam because of a narrow processing window and a low melt strength, which leads to a tendency towards cell coalescence and collapse at high expansion [5].

* Corresponding author.
E-mail address: monica.ardanuy@upc.edu (M. Ardanuy).

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Among all the foaming techniques, one of the most widely used is extrusion foaming due to its low cost for the production of continuous foams and high productivity. With this technique, blowing agents can be physical (PBAs) or chemical (CBAs). PHAs have already been foamed with super critical CO_2 gas as PBA [6], with exothermic CBAs such as azodicarbonamide (ADA) [5,7], or with more eco-friendly endothermic CBAs mainly based on sodium bicarbonate and citric acid [5,8,9]. The use of PBAs requires extruders with PBA-pumping systems and, in some cases, screws with special profiles, thus meaning that special processing machinery is necessary. Due to that, this study focuses on the use of CBAs, which allows its foam-processing in conventional extruder machines.

The aforementioned endothermic CBAs, which release CO_2 gas, have been shown to achieve lower density-PHA foams than exothermic CBAs such as ADA, which release N_2 gas [5]. Nevertheless, the use of endothermic CBAs has some drawbacks. The thermal decomposition of sodium bicarbonate produces water in addition to CO_2, which can lead to an hydrolytic degradation of PHAs—an effect that is more noticeable at high processing temperatures [5,10–12] or large residence times [13] in which PHAs also suffer from thermal degradation. Both thermal and hydrolytic degradation of PHAs are caused by random chain scission, and hence, a decrease in the molecular weight is produced [10], which reduces not only the properties of the polymer but also its foamability. Therefore, both the CBA and the process itself adversely affect the resulting foam.

On the other hand, it is known that branched structures can enhance the melt strength and, therefore, the foamability of polymers. Epoxy-functionalised chain extenders (CEs) can be used to increase the molecular weight and melt viscosity, and also to improve the melt strength by means of chain branching and chain extension in other polymers [14]. The use of CEs for foamability improvement has already been proved in other biodegradable polyesters, such as PLA. In some cases, their addition increased the molecular weight, enhanced melt viscosity and improved the cellular structure by promoting the formation of a large amount of uniform small cells [15–18]. Furthermore, the use of CEs in PHAs has been reported to increase thermal stability, thus widening the processing window to improve sheet extrusion or foaming processes [19]. Nonetheless, to the authors' knowledge, only a few articles have focused on the influence of these CEs in the properties of PHAs; and even fewer have focused on the variation of cellular structure and mechanical properties of PHA foams due to CE addition.

Another proposal for improving PHA foamability when produced via extrusion foaming is water-quenching [5]. Wright and Frank [5] found an improvement in the cellular structure of extruded PHA SB-blown foams when water-quenching post-extrusion was performed, since foams presented better cellular homogeneity and higher cell density. This was explained based on controlling the crystallinity due to the fast cooling rate produced by the water-quenching. Nevertheless, these authors did not study the effect of the use of a chain extender and no analysis of the effects on the mechanical properties was performed.

From the large family of PHAs, poly(3-hydroxybutyrate) (PHB) and its copolymers such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) (P3HB4HB), or poly(3-hydroxybutyrate-*co*-hydroxyhexanoate) (PHBHHx) are the most widely studied. Regarding PHAs' foaming, the aforementioned research is mainly focused on PHBV and, in fewer cases, on PHBHHx. Nevertheless, to the authors' knowledge, none has focused on the PHB copolymer used in this study (P3HB4HB).

The aim of this study was to evaluate the combinations of the two strategies (water quenching and addition of chain extender) to enhance P3HB4HB extrusion foamability using an endothermic CBA, since their immediate application to the current processing technologies would be simple. The effects on the foamability of CBA content, chain extender addition and the cooling system were evaluated by means of cellular structure characterisation and analysis of the thermal and mechanical properties.

2. Experimental section

2.1. Materials

The poly(3-hydroxybutyrate-*co*-4-hydroxybutyrate) used for this research was Mirel P3001 (thermoforming grade, Metabolix Inc., USA). The chemical blowing agent (CBA) used was Hydrocerol BIH40E in masterbatch form (40 wt.% of CBA) from Clariant GmBH, Germany. Joncryl ADR-4368-C (FDA approved grade, kindly provided by BASF, Germany) was used as the chain extender (CE).

2.2. Samples preparation

Foamed samples were produced directly by extrusion foaming in a Collin Co-rotating Twin-screw Extruder ZK 25 T. P3HB4HB and CBA were previously dried at 50 °C for 16 h in a P-Selecta Vacuum Drying Oven VacioTem TV. A reverse extrusion profile was used, linearly decreasing from 170 °C in the hopper to 150 °C in the die. The screw-speed was fixed to 70 rpm. The feeding and mass flow rates at these conditions were estimated to be around 71 ± 3 g/min. The pressure measured at the die was in the range of 6.1 ± 3 MPa. At the exit of the die (with a circular profile of 4-mm diameter), 50–60 specimens of each sample (with a length of ~20–25 cm) were collected. Half of the specimens were water-quenched in a water bath at 23 ± 1 °C after few seconds (5–10 s) of their exit through the die (referred to as W). The other specimens were air-cooled at room temperature (referred to as A). Sample cooling was done under no stress. After cooling, all the specimens were kept in standard conditions of temperature and relative humidity (23 ± 2 °C, 50 ± 10% RH). Twelve different