



Chemical foaming extrusion of poly(lactic acid) with chain-extendors: Physical and morphological characterizations

J.M. Julien ^{a,b,c}, J.-C. Quantin ^{c,*}, J.-C. Bénézet ^c, A. Bergeret ^c, M.F. Lacrampe ^{a,b}, P. Krawczak ^{a,b}

^a Univ. Lille Nord de France, 59000 Lille, France

^b Ecole des Mines de Douai, Department of Polymers and Composites Technology & Mechanical Engineering, 941 Rue Charles Bourseul, BP 10838, 59508 Douai, France

^c Ecole des Mines d'Alès, Centre C2MA, 6 Avenue de Clavières, 30319 Alès Cedex, France

ARTICLE INFO

Article history:

Received 27 January 2015

Received in revised form 5 March 2015

Accepted 7 March 2015

Available online 17 March 2015

Keywords:

Poly(lactic acid)

Extrusion foaming

Chemical foaming agent

Epoxide based chain-extender

Cell morphology

ABSTRACT

The effects of an epoxide-based chain-extender (CE) on the properties of poly(lactic acid) (PLA) foams obtained by chemical foaming extrusion using 4 wt.% of chemical foaming agent (CFA) were studied. PLA/CE blends with different weight ratios of CE were initially processed using a co-rotating twin-screw extruder. PLA/CE foams were then produced using a single-screw extruder. Various PLA/CE foams characterizations, including solution viscosity, thermal properties (DSC, TGA), cellular structure (void fraction, cell size, open cell content), mechanical and dynamic rheological behaviors, were investigated. Results show that the addition of CE enhances the viscosimetric average molecular weight and rheological properties (viscosity and storage modulus) of PLA, but it has no significant effects on the thermal properties of PLA, except the occurring of a cold crystallization. The CE incorporation also led to a decrease in the void fraction of cellular PLA, in the cell size and in the open cell content and to an increase in the cell density. Furthermore, the tensile mechanical properties such as yield stress and elongation at break of cellular materials increased with the addition of CE.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

One way to overcome the issues related to the management of waste plastic parts, to the oil price fluctuations and to the gradual depletion of fossil resources is to use biodegradable polymers derived from renewable resources, called bio-based and biodegradable polymers. Poly(lactic acid) (PLA) is one of the most promising polyesters for this purpose [1]. Therefore, it generates a huge scientific and industrial literature [2–5], especially because its mechanical properties are equivalent or even higher to those of traditional polymers [6]. It is synthesized from L- and D-lactic acid, which are themselves produced from

the fermentation of dextrose provided by starch hydrolysis (starch can be extracted from corn, wheat, potatoe or sugar cane for example), either by ring-opening polymerization or by condensation polymerization depending on the targeted molecular weight [2,7,8]. In non-medical industries, PLA is mainly used in packaging applications [9] because of its biodegradability [10]. The biocompatibility and bioresorbability of PLA make it also particularly well-suited in the biomedical industries for high added value products [4,7,11] such as bone plates, bone screws, drug delivery and tissue repair systems [12–15]. Moreover, PLA can be processed by traditional plastic processing techniques for the production of films, fibers, extruded or injection molded parts or foams [7,16]. For this latter case, obtaining PLA-based foam products is of major industrial interest, in order to reduce carbon footprint and

* Corresponding author. Tel.: +33 4 66 78 53 46; fax: +33 4 66 78 53 65.
E-mail address: jean-christophe.quantin@mines-ales.fr (J.-C. Quantin).

environmental impact by plastic parts lightening at equivalent end-use performances.

Physical and chemical foaming agents [17–19] can be used for PLA. Physical foaming is achieved by gas injection (for example nitrogen) in the molten PLA. Chemical foaming is achieved by blending solid endothermic or exothermic chemical foaming additives (so-called CFA) with the polymer matrix. The result is the release of a gas and the growing of cells while the temperature increases leading to a reduction in density of about 50% [17–19]. This reduction depends on processing conditions such as screw speed, die geometry and processing temperature [20]. A previous study [1] assessed the optimization of the PLA chemical foaming conditions based on a maximal void fraction criterion. Using an endothermic chemical foaming agent, an homogeneous cell structure with low open cell content (27%) corresponding to a void fraction of 47% was obtained in optimized processing conditions. Nevertheless this study showed also that the low melt strength of the PLA [21,22] could be considered as a limiting factor to foaming. In order to overcome this drawback three ways of PLA modification were explored in literature: The first way consists in combining the effect of irradiation (electron beam or γ -ray) and of a crosslinking agent (such as a polyfunctional monomer, for example TAIC (triallyl isocyanurate which is commonly used)). The second one will compensate the degradation of the polymer induced by the first one [3,23–26]. The second way consists in adding melt strength enhancers with high molecular weights (acrylic, ...) in PLA. That will enhance the elongation viscosity of the melt, resulting from entanglements [27]. The third and last way reported in literature consists in adding a chain-extender combined with a crosslinking agent (peroxide or isocyanate) to induce chain scission, extension, crosslinking, or any combination of the three, depending on the chain extender amount, resulting in the variation of the gelation level of the material [28,29]. Di et al. [29] have modified a PLA ($\text{l-lactide} > 92\%$) by sequentially adding different ratios of 1,4-butane diol and 1,4-butane diisocyanate as chain-extenders using an internal mixer at 170 °C. The results show higher molecular weights and rheological properties (viscosity and moduli). The higher viscosity and elasticity of the modified PLA samples allowed the production of physical foams (using a mixture of CO_2 and N_2 as foaming agent) with a smaller cell size, a higher cell density and a lower density compared to the unmodified PLA. Other chain-extenders with di-functional ($f_n = 2$) compounds such as carboxylic acid, hydroxyl, amine, anhydride and epoxide lead to a lower enhancement in molecular weight compared with multi-functional compounds ($f_n \geq 3$). This is because di-functional compounds will only link two end groups, thereby leading to a linear polymer [30]. Thus, the use of chain-extenders with multi-functional compounds has become an attractive means to increase their efficiency. These products lead to a branched structure which can be useful in a polymer foaming process, because they allow the polymer to withstand the triaxial deformation that occurs during the cell growth. Among multi-functional chain-extenders, the multi-functional epoxide based chain-extenders have a very broad processing window, which

can be used in traditional extrusion or injection-molding equipments without vacuum or catalysts [4]. The reaction mechanisms of epoxide-based chain-extenders in reactive extrusion have been largely described in the literature [31–35]. But up to now, no study has been reported concerning the use of these components to assist chemical foaming extrusion of PLA matrices.

In this context, the present study focuses on the chemical foaming extrusion of modified PLA with an epoxide-based chain-extender. The effects of chain-extenders on the void fraction, the cell morphology (cell size, cell density, cell-wall thickness), the thermal and mechanical properties of PLA foams are investigated. The main objective is to perform cellular materials with better controlled characteristics (density, cell morphology and mechanical properties) by varying the amount of chain extender.

2. Experimental

2.1. Materials

A commercial grade of linear polylactic acid (PLA 7000D[®], NatureWorks[®] LLC, USA, containing 6.4% of *D*-lactide (determined by polarimetric analysis by Max Mousseron Institute of Biomolecules, UMR CNRS 5247, University of Montpellier 1, University of Montpellier 2, Faculty of Pharmacy, Montpellier, France) was used in this study, in combination with an endothermic chemical foaming agent (CFA, Hydrocerol[®] CT3108, Clariant Masterbatches, France) containing sodium bicarbonate and citric acid. The gas yield of the CFA is around 50 ml/g (supplier data). A CFA amount of 4 wt.% was incorporated into the PLA according to a previous work [1]. The chain-extender (so-called CE, CESA-Extend BLA0050109-ZN, Clariant Masterbatches, France) is a multi-functional epoxide-based chain-extender (Fig. 1), composed of a styrene-acrylic oligomer with a number-averaged molecular weight (M_n) around 6800 g/mol and a high number-average functionality ($f_n \sim 9$) (supplier data). This agent was especially designed by the supplier to increase the intrinsic viscosity and the molecular weight of the PLA. Various CE amounts up to 3 wt.% were used (0.5, 1.5, 2 and 3 wt.%). The nomenclature is PLAXC where X represents the weight percentage of CE (for example PLA1.5C for 1.5 wt.% of CE).

2.2. Materials processing

PLA pellets were dried under vacuum for 15 h at 50 °C to remove any moisture excess. The residual moisture content was about 500 ppm (measured by Karl Fischer titration). PLA, CE and CFA were dry-mixed before introduction into the hopper of the extruder. The two following processing steps were implemented for the elaboration of PLA/CE foams.

2.2.1. PLA/CE compounding

A dry blend of PLA/CE was compounded using a twin-screw intermeshing co-rotating extruder (BC21, CLEXTRAL, France) which screw diameter, centerline distance and L/D ratio are equal to 25 mm, 21 mm and 36

Download English Version:

<https://daneshyari.com/en/article/1400434>

Download Persian Version:

<https://daneshyari.com/article/1400434>

[Daneshyari.com](https://daneshyari.com)