



# Development of polylactide bead foams with double crystal melting peaks



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## ARTICLE INFO

### Article history:

Received 18 February 2015

Received in revised form

18 May 2015

Accepted 28 May 2015

Available online 30 May 2015

### Keywords:

Poly lactide

Crystallization

Foaming

## ABSTRACT

In this study, we report the development of polylactide (PLA) bead foams with a double crystal melting peak structure. PLA bead foams with 3- to 30-fold expansion ratios and average cell sizes ranged from 350 nm to 15  $\mu$ m were prepared. We found that the PLA's foam structure was significantly affected by the amount of perfected crystals (that is, crystals with a high melting temperature) generated during CO<sub>2</sub> saturation. The structure was also affected by crystals with a low melting temperature that formed during foaming and cooling. Various CO<sub>2</sub> pressures further influenced the crystallization kinetics of the crystals with a high melting temperature during the saturation. At various pressures, different crystallization kinetics also significantly affected the PLA foam's cell morphology and its uniformity. At a high saturation pressure, the increased content of dissolved CO<sub>2</sub> in the PLA promoted the cell nucleation rate through the increased degree of thermodynamic instability. On the other hand, at high pressures, small-sized perfect crystals were induced as high-melting peak crystals. Thus, the heterogeneous cell nucleation around these crystals was further improved, which also caused the generation of a more uniform foam structure. Moreover, this study introduces this bead foam technology as an innovative new way to produce nanocellular foam products.

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## 1. Introduction

Poly lactide (PLA) is a thermoplastic aliphatic polyester polymer derived from renewable resources such as cornstarch and sugar-cane. Unlike petroleum-based polymers, it is environmentally-friendly and biodegradable [1–4]. Recently, it has received increased attention as a potential substitute for polystyrene (PS) products [5–8]. For example, expanded PS (EPS) bead foams are now being widely used in applications such as packaging, cushioning, construction, and thermal and sound insulation. But their weak bead-to-bead sintering property and their non-biodegradable nature, means that broken EPS beads threaten the environment. In this context, PLA bead foams can provide a suitable and green

substitute for these EPS products [9–11]. As well, the use of green physical blowing agents, such as gaseous or supercritical CO<sub>2</sub>/N<sub>2</sub> has been well established in the manufacture of foam product [9,12,13]. Therefore, the concerns about ozone depletion, global warming potential, blowing agent toxicity and flammability, which accompany traditional hydrocarbon and hydrochlorofluorocarbon blowing agents, are eliminated [9,10,14]. For example, PLA can be saturated with supercritical CO<sub>2</sub> or N<sub>2</sub> under a high pressure at a given temperature. Then, a rapid pressure drop can be induced to generate a thermodynamic instability, which creates a foam structure within the PLA matrix in various foaming processes [12,13,15–17].

Although few companies currently produce expanded PLA (EPLA) bead foams, the bead sintering needed to manufacture three-dimensional final foam products still remains a serious challenge [18–23]. Currently, EPLA bead foams are costly to manufacture, and the bead-to-bead sintering is weak, as in the

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case of the EPS. Therefore, expensive and non-biodegradable adhesives or coatings are being used for bead-to-bead bonding. Despite the promise of EPLA bead foams, their weak bead-to-bead sintering, the high cost of the adhesive/coating and their environmental drawbacks have become a serious impediment to their promotion within the industry and commercial usage [21–23]. In this work, we have developed a new technology that removes the environmental challenges and the expensive practices associated with bead sintering. We have created a double crystal melting peak in the EPLA bead foams, by using low melting temperature peak crystals that melt during the sintering stage (i.e., molding). This causes sintering of the beads while the crystals with a high melting temperature maintain the beads' integrity. This concept has been used for the existing expanded polypropylene (EPP) bead foaming technology [24–27] but has not been used for other materials, especially for the EPLA bead foams. Specifically, crystals with a high melting temperature form during the isothermal saturation step in the batch-based bead foaming process [24–26], through crystal perfection [28,29]. In the steam-chest molding process (that is, the process used to produce three-dimensional foam products), sintering among the beads occurs when the steam temperature is between the high and low melting peaks. Consequently, the low-melting temperature crystals will melt and contribute to good bead sintering whereas the high-melting temperature crystals will stay unmelted, and will maintain the overall cell structure and the foam bead shape [24,26]. Although this double crystal melting peak technology cannot be applied in amorphous foams such as EPS, PLA has the potential of having this structure, despite its very slow crystallization kinetics. To create two-peak crystal characteristics in PLA foams, the fabrication steps will be different from those associated with existing PLA foaming technologies [18–23].

Improving PLA crystallization kinetics will not only provide the potential of generating a double crystal melting peak structure, but will also enhance the poor foaming feature of PLA products significantly. Specifically, crystals formed during the saturation step (that is, crystals with a high melting temperature) can significantly affect the cell nucleation and expansion of the PLA bead foams. According to heterogeneous cell nucleation theory, cell nucleation can be promoted through the local stress variations [30,31] around the formed crystals [31–35]. On the other hand, the molecules connected through the crystals improve the PLA's low melt strength and consequently increase the PLA's ability to expand by minimizing the gas loss and cell coalescence [12,36]. It must also be noted that too high a crystallinity will also depress the foam's expansion ratio due to the increased stiffness [34,37,38].

In our work, for which a patent has been issued [39], we developed EPLA bead foams with a double crystal melting peak structure. A branched PLA with reasonably high crystallization kinetics [40,41] was selected. First, we characterized the generated double peaks in PLA using a regular and a high-pressure differential scanning calorimeter (DSC and HP-DSC). Subsequently, EPLA bead foams were produced with double crystal melting peaks. Then, the EPLA bead foams were characterized, and the dependency of bead foam properties on the high melting temperature crystals that were generated during CO<sub>2</sub> saturation, and the low melting temperature crystals that were formed during cooling while foaming occurred was investigated. Moreover, the DSC was used to analyze the bead foams' crystallization behavior. The effects of various CO<sub>2</sub> pressures on the crystallization kinetics of the crystals with a high melting temperature and thereby on the resultant PLA beads' foam properties were also investigated. In addition, this manufacturing method was introduced as a novel way to produce nanocellular foams.

## 2. Experimental

### 2.1. Materials

Long-chain branched (LCB) PLA was used in this study. This branched PLA was supplied directly from NatureWorks, and was produced from the melt extrusion of a linear PLA (Ingeo™ 8051D NatureWorks® LLC) with 0.7 wt% of an epoxy-based multi-functional chain extender (BASF Joncryl™ ADR 4368C). The PLA had a D-lactide content of 4.6 mol% and an average molecular weight of 280,110 g/mol with a polydispersity index of 2.5. For further foaming experiments, this branched PLA was also provided, directly from NatureWorks® LLC, with 0.5 wt% talc (Mistron Vapor-R grade, Luzenac America), and with 0.5 wt% talc and lubricant (a proprietary material). These branched samples were referred to as PLA, PLA-T, and PLA-TL, respectively. CO<sub>2</sub> with 99.98% purity was also supplied as the blowing agent from Linde Gas.

### 2.2. Procedure to form double peak crystals in PLA

Fig. 1a shows a schematic of the double crystal melting peak generation steps during a bead foaming process: that is, the evolution of the crystals with a high melting temperature during the isothermal saturation step and, subsequently, the evolution of the crystals with a low melting temperature during cooling/foaming. Fig. 1b shows the procedure of the simulation experiment within the DSC and the actual bead foaming process: (i) First, the generation of crystals with a high melting temperature via isothermal annealing/saturation, (ii) Second, the generation of crystals with a low melting temperature via cooling/foaming, and (iii) Third, the characterization of the peaks generated in the sample. It should be noted that the gas pressure in the first step was high in order to simulate the gas saturation process, and the pressure was decreased in the second step to simulate the foaming process. The third step was to investigate the double peak crystals that developed in the PLA bead foams. This action is described in detail in the following section.

### 2.3. Characterization of generated double-peak crystals in PLA through DSC and HP-DSC

The evolution of the double crystal melting peak in the PLA samples was investigated by varying the annealing temperature ( $T_a$ ) and the time ( $t_a$ ) using a DSC (DSC2000, TA Instruments) in a nitrogen atmosphere. The PLA samples were heated at a rate of 30 °C/min to various  $T_a$  (around the PLA's  $T_m$ ) [29] and were isothermally annealed at various  $t_a$ . The samples were then cooled at a rate of 20 °C/min to room temperature, during which the low melting temperature crystals formed. The double crystal melting peak behavior was subsequently analyzed by reheating the samples to 200 °C at a rate of 5 °C/min. In addition, the plasticizing effect of CO<sub>2</sub> (at 6 MPa) [29,42] on the generated double crystal melting peak was analyzed using an HP-DSC (NETZSCH DSC 204 HP). The annealing temperature ( $T_a$ ) and the annealing time ( $t_a$ ) terminologies were used exclusively for dealing with a non-high-pressure gas using a regular DSC. Otherwise, the saturation temperature ( $T_s$ ) and the saturation time ( $t_s$ ) were used to deal with a high-pressure gas, when the HP-DSC or foaming apparatus were used.

### 2.4. Preparation and characterization of foam samples

The PLA bead foams were prepared by saturating the pellets with gaseous and supercritical CO<sub>2</sub> in a small autoclave foaming chamber. After the samples were loaded and the chamber was vacuumed to remove moisture, it was pressurized with CO<sub>2</sub> using a

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