EXTRUSION FOAMING OF POLY(LACTIC ACID) WITH THERMALLY EXPANDABLE MICROSPHERES

Katalin Litauszki, Budapest University of Technology and Economics, Hungary
Akos Kmetty, Budapest University of Technology and Economics, MTA–BME Research Group for Composite Science and Technology, Műegyetem rkp. 3., H-1111 Budapest, Hungary

Abstract

This paper shows the production of biopolymer foam structures via extrusion and presents the effects of poly(lactic acid) D-lactide content with the use of different dosages of thermally expandable microspheres. The raw materials were characterized with various methods, including elongational viscosity, FTIR, thermogravimetry and differential scanning calorimetry. The resulting foamed products were characterized by scanning electron microscopy, differential scanning calorimetry, cell-population density and density measurements. We produced closed celled foam structures. The lowest foam density was achieved using 8 wt% of syntactic foaming agent and the resulted foam density was 0.35 g/cm³. The average size of the cells is in the order of 100 μm.

Introduction

Factors that influence cell structure during chemical foaming include the solubility and diffusion of the effective gases in the polymer melt [1, 2], the viscosity and melt strength of the polymer [3-5], and the step of cell nucleation and growth [6, 7]. In contrast to chemical foaming agents, there is a foaming agent type that allows the foam structure to be formed by mixing glass beads or polymer microspheres with the polymer matrix. The resulting foam structure is called a syntactic foam. Syntactic foams also belong to the family of porous structural materials. These foams are ideally closed cellular porous structural materials in which porosity is provided by cavities embedded in the matrix material with more or less regular and uniformly arranged spherical shells [8, 9].

The development of biopolymer foams produced by thermally expandable microspheres (TEMs) is an interesting foaming method. This foaming agent is typically a microsphere with a diameter of 5 to 50 μm in the non-expanded state. Its structure consists of an outer polymer shell that surrounds the inner core, generally aliphatic hydrocarbons. During the expansion phase, the diameter of the beads increases up to 60 times [10].

This syntactic foaming agent can also be considered a special type of foaming agent, which makes the effect of cell nucleation, effective gas solubility and concentration changes negligible during the foaming process, in contrast to chemical foaming [11]. Thus the differences observed can be originated from the expansion and stabilization phase of the foaming process, in which the rheological properties of the polymer are dominant [2].

Materials and Methods

Three types of poly(lactic acid) (PLA) were used as matrix. They are extrusion grade manufactured by NatureWorks LLC and only differ in their D-lactide content. Ingeo 4032D has 1.4%, Ingeo 2003D has 4.3% and Ingeo 4060D has 12% D-lactide [12]. All of the granules had a solid density of 1,24 g/cm³. The elongational viscosity of the granules was measured with a Ceast SR50 capillary rheometer at 190 °C, with the use of the Cogswell method [13]; the results are shown in Figure 1.
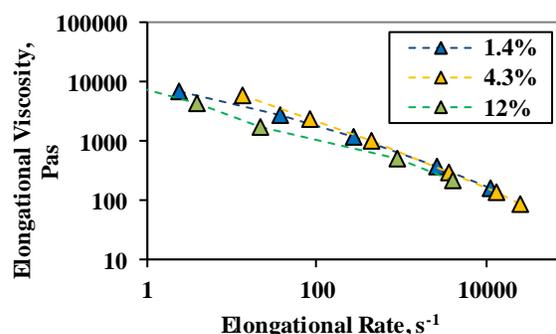

Figure 1. Elongational viscosity of PLA resins at 190 °C.

The DSC measurements of the reference extrudate and foam structures were carried out with a TA Instrument Q2000 device, in a heat-cool-heat cycle. The temperature range was 0-200 °C, the heating and cooling rate was 5 °C/min and the measuring atmosphere was nitrogen (20 ml/min). The degree of crystallinity was 40.6% (4032D), 28.4% (2003D), and 0% (4060D).

The applied syntactic foaming agent was Tracel G 6800 MS (Tramaco GmbH), in granular form. Microspheres were distributed in a polymer matrix. We analyzed the foaming agent polymeric carrier by Attenuated total reflectance–Fourier transformation infrared spectroscopy (ATR-FTIR). The detected absorption peaks in the case of

1739, 1238 and 1020 cm^{-1} are related to the vinyl acetate groups. The detected 718 cm^{-1} peak is related to long - CO_2- chains building up polyethylene, the 2916 and 2851 cm^{-1} peaks are related to the asymmetric, symmetrical stretching of -CH_2-. The peaks at 1470 and 1360 cm^{-1} refer to the deformation of CH_2 and CH_3 groups [14]. Based on these results, the carrier polymer of the foaming agent is ethylene vinyl acetate (EVA).

The chemical composition of the core material and foaming agent in the shell were analyzed by Thermogravimetric analysis–Fourier-transform infrared spectrometry (TGA-FTIR). The TGA was a Q5000 manufactured by TA Instruments. The TGA device was connected to a Bruker Tensor 37 FTIR device. The peek between 1147 and 1270 cm^{-1} is due to the C-O-C stretching vibration. The 1726 cm^{-1} band shows the presence of the acrylate carbonyl group. The 1451 cm^{-1} band may be attributed to the bending oscillations of the CH bonds of the -CH_3 group. Two bands, 2994 and 2948 cm^{-1} can be assigned to -CH_3 and -CH_2- groups with CH bonding vibrations, which refer to methyl methacrylate copolymer [15]. The 2243 cm^{-1} band may be attributed to the $C \equiv N$, nitrile group, which is typical for acrylonitrile and methacrylonitrile content. The 1108 cm^{-1} band may be attributed to the oscillation of the $O = Si = O$ group, which refers to the content of silicon dioxide stabilizer for the production of expanding microspheres [10]. Based on the results, it can be stated that the shell structure of the expandable microspheres contains methyl methacrylate, acrylonitrile and or methacrylonitrile, as well as silicon dioxide. Intensity peaks of the encapsulated effective gas characterised by TGA-FTIR are 1380 cm^{-1} C-C, 1470 cm^{-1} C-H stretching, and 2960 cm^{-1} C-H stretching. Therefore, the detected gas is isopenthane [15].
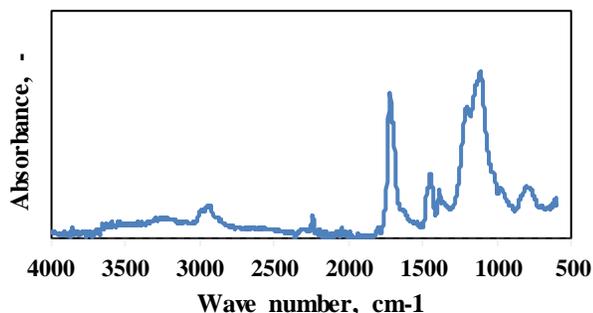

Figure 2. FTIR spectra of Tracel G 6800 shell material

Thermogravimetric measurement was carried out on the foaming agent to determine the ratio of the components; i.e., the amount of effective gas, the ratio of the polymeric carrier and expandable microspheres. The first step in weight loss, 18.6%, is the release of the effective gas (isopenthane) from the system. The second step in weight loss, 16% is the decomposition of the shell structure of TEMs (acrylonitrile/methyl methacrylate). In the third and most significant, step of weight loss, the carrier material (EVA), with a weight ratio of 36.8% disappears. The last mass loss step, involves the loss of the silica stabilizer (SiO_2) with a weight ratio of 25%. It takes place between 500 °C and 600 °C.

A twin-screw extruder was used (Teach-line ZK25T, Collin GmbH, screw diameter: 25 mm, L/D=24) to produce syntactic foams. The temperature profile of the extruder was: 155 °C, 160 °C, 175 °C, 190 °C, and 190 °C from the feeding section to the die. Screw speed was 10 rpm. The extrusion die was a rod shape type with a circular cross-section, and with a nominal diameter of 3 mm. Foaming agents were added to PLA before extrusion by dry mixing. The dosages of thermally expandable microspheres were 0%, 0.5%, 1%, 2%, 4%, 8 wt%. Before manufacturing, the PLA granules were dried at 80 °C for 6 hours in a WGL-45B type drying oven.

Foam characterization

Foam structures were characterized by scanning electron microscopy (SEM, Jeol JSM-6380LA, with an acceleration voltage of 10 kV). Prior to the test, the samples were sputter-coated with a gold/palladium alloy. The density of the foamed and non-foamed extruded samples was determined with the buoyant method in a distilled water measuring medium. Cell-population density was calculated based on the SEM images, according to equation (1):

$$N_c = \left(\frac{nM^2}{A} \right)^{\frac{3}{2}} \cdot ER \qquad (1)$$

where n [-] is the number of cells counted in the recorded image, A [mm^2] is the cross-sectional area of the sample, M [-] is the magnification factor and ER [-] is the expansion ratio [16].

Foam compressive strength tests were performed with a Zwick Z005 universal testing machine (in compression mode). A Mess & Regeltechnik KAP-TC type load cell was used (measuring range 0-5000 N, preload 1 N). The measurement speed applied was 2 mm/min.

Results

Fig. 3 shows the scanning electron microscopy image of the foamed samples in the case of 4060D (12% D-lactide content), with the use of different amounts of syntactic foaming agent. The resulted foam structures are homogeneous and closed-celled. Fig. 4 shows the density of foams as a function of the amount foaming agent added. In the case of chemical foaming, where the usual foam densities are around 0.5 g/cm^3 presented in the literature in the case of a non-modified PLA matrix [17, 18], we produced foams with a density of 0.35 g/cm^3. Depending on the dosage of the foaming agent, the density shows an exponentially decreasing tendency, which can be fitted with the following equation (4) in the case of PLA with 4,3% D-lactide (R^2=0.97):

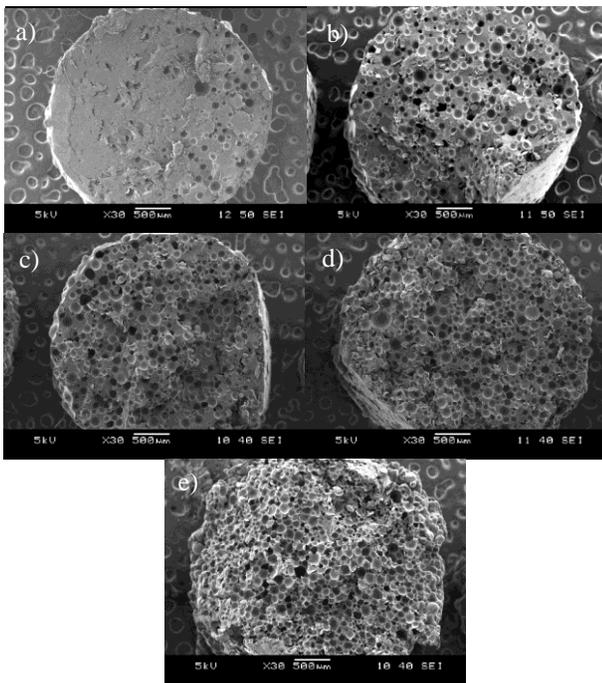$$y = 1.15e^{-0.157x} \tag{4}$$

Figure 3. The SEM images of samples produced with a syntactic foaming agent as a function of foaming agent content in the case of 12% D-lactide content PLA a) 0.5 wt%, b) 1 wt%, c) 2 wt%, d) 4 wt%, e) 8 wt%

The reason for the decreasing tendency of density is that the structure of the microspheres capable of expanding remained intact during the manufacturing process at 190 °C. A closed-celled foam structure was formed, and the beads introduced into the polymer matrix were able to function as cell nucleates.
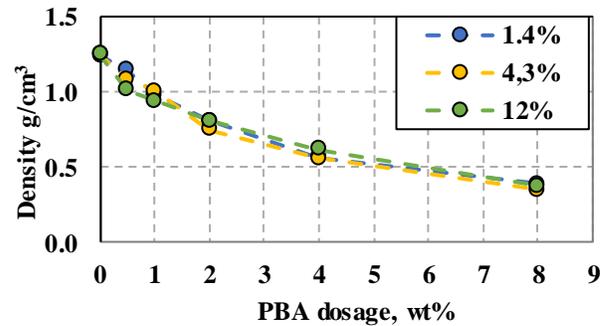

Figure 4. The density of samples produced with a syntactic foaming agent as a function of foaming agent content (190 °C)

With regard to cell-population density (Fig 5.), unlike chemical foaming, syntactic foaming exhibits a linear tendency (R^2 greater than 0.97) in all of the PLAs. The highest cell-population density was in the order of 10^8 cells/cm^3 at the dosage level of 8 wt%. Another factor of density reduction is cell growth, which was characterized by the average cell size (Fig 6.) and cell size distribution (Fig. 7.). The average size of the cells is in the order of 100 µm and the standard deviation of cell size is between 28 and 52 µm. The maximum cell size is 200 µm. Thus, the microspheres were able to grow sufficiently to form a foam and to form a homogeneous cellular structure.
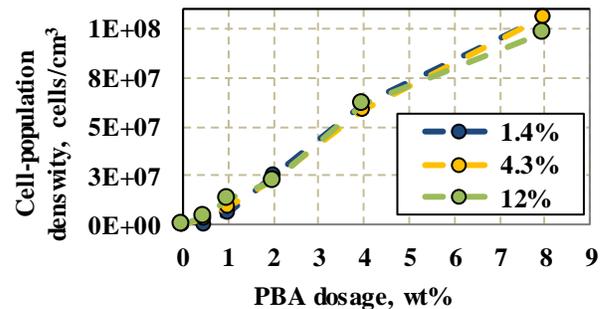

Figure 5. The cell-population density of samples as a function of foaming agent content
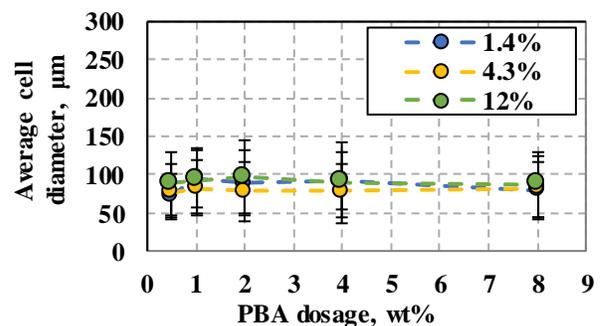

Figure 6. The average cell size of samples as a function of foaming agent content

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The degree of crystallinity was with the use of 8 w% of thermally expandable microspheres 5.5% (4032D_8%_6800), 0% (2003D_8%_6800), and 0% (4060D_8%_6800), therefor the samples have negligible percentage of crystalline fraction after extrusion. We did not find any significant difference that can be attributed to the different D-lactide content of PLAs in terms of the expansion step of the foaming process. Foam samples were tested mechanically (Fig 8.). The relative compressive strength of the foamed samples as a function of foaming agent content a decreasing tendency.
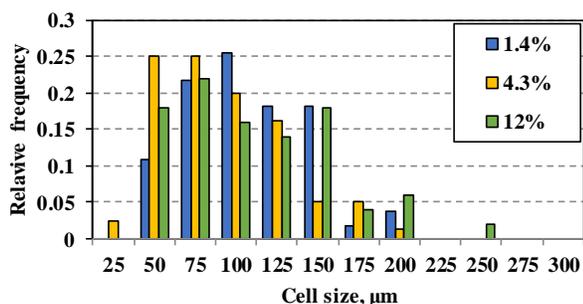

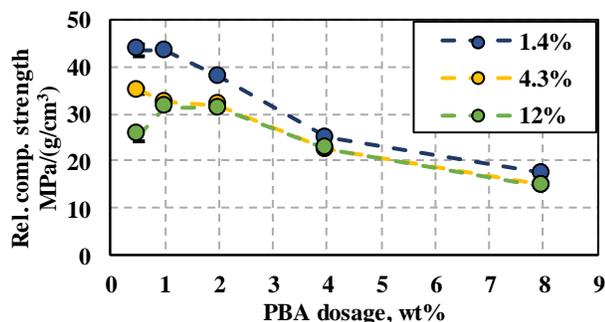Figure 7. The cell size distribution of the foamed sample (2 wt% of syntactic foaming agent)

Figure 8. Relative compressive strength of the foamed samples as a function of foaming agent content

Conclusions

We produced closed-celled foam structures. The lowest foam density was achieved with 8 wt% of syntactic foaming agent and the resulted foam density was 0.35 g/cm^3. The average size of the cells was in the order of 100 μm. Depending on the dosage of the syntactic foaming agent, the density showed an exponentially decreasing tendency, to which the following equation can be fitted in case of PLA with 4,3% D-lactide: $y = 1.15e^{-0.157x}$ (R^2=0.97). We did not find any effect of different D-lactide content of PLAs on the expansion step of the syntactic foaming process.

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Aknowledgements