Nanocellular and needle-like structures in poly(L-lactic acid) using spherulite templates and supercritical carbon dioxide

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Supporting Information

DSC measurements were carried out by Q20TA instruments in the temperature range from 10 to 190 °C at a heating rate of 10 °C/min. The degree of crystallinity (χ_c) for each foamed specimen was calculated from the following equation:

$$\chi_c(\%) = (\Delta H_m - \Delta H_c) / \Delta H_m^0 \times 100_{(1)}$$

where ΔH_m^0 is the heat of fusion for perfectly crystalline PLLA (93 J/g), ΔH_m is the heat of fusion for PLLA during a DSC heating run, and ΔH_c is the heat of crystallization for PLLA during a DSC heating run.

The cell diameter (D) was determined by using the "Diameter (mean)" option of image analysis software (Image-Pro Plus). This function calculated the average length of 90 diameters passing through cell's centroid, and the angle between neighboring diameters was 2 degree. The average length represented the diameter of a cell. About 700-1000 cells were used to calculate the average cell diameter.



Fig. S1 Schematic diagram of the measurement of the diameter in an asymmetric cell.

We used the SEM to characterize the spherulite structure. Two different average spherulite diameter, D_u and D_f , represented the average spherulite size of PLLA unfoamed and foamed after the saturation step, respectively. D_u and D_f were measured from the SEM images of crystalline morphology and foam morphology, respectively. For a single asymmetric spherulite, the measuring method of spherulite diameter was similar to that of cell diameter. The average length of 90 diameters passing through spherulite's centroid was regarded as the spherulite diameter. About 30-40 spherulites were used to calculate the average spherulite diameter. The border of the spherulite in SEM images of foam morphology was considered to be located at the position where the terminal of the radial needle-like cells reached.

The cell density (N_0) , that is, the number of cells per cubic centimeter of nonporous sample before conditioning with CO₂, was determined using the following equations:

$$N_0 = N_f / (1 - V_f), N_f = (nM^2/A)^{3/2}, V_f = \pi N_f D^3/6$$
 (2)

where $N_{\rm f}$ is the number of cells per cubic centimeter of foamed sample, $V_{\rm f}$ the void volume fraction, *n* the number of cells on the SEM image, *M* the magnification factor, *A* the area of the micrograph (in cm²), and *D* the average cell diameter.

The spherulite density (N_u) for the unfoamed PLLA was calculated from the following equation:

$$N_u = (nM^2/A)^{3/2} \, (3)$$

where N_u is the number of spherulites per cubic centimeter of unfoamed PLLA, *n* the number of spherulites on the SEM image, *M* the magnification factor, and *A* the area of the micrograph (in cm²).

The volume expansion ratio ($\Phi_{\rm f}$) of the PLLA foams was calculated according to Equation (3):

$$\Phi_f = \rho_0 / \rho_{(4)}$$

where ρ_0 and ρ are the mass densities of PLLA before and after foaming, respectively.

The volume expansion ratio (Φ_s) of the PLLA spherulites was determined using Equation (4):

$$\Phi_s = \left(\frac{D_f}{D_u}\right)^3 (5)$$

where $D_{\rm f}$ and $D_{\rm u}$ are the spherulite diameters of foamed and unfoamed PLLA, respectively.