Biodegradable Foams of Poly(lactic acid)/Starch. II. Cellular Structure and Water Resistance

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ABSTRACT: Biodegradable foams were prepared with poly(lactic acid) and starch by extrusion. The compression modulus of the foams was negatively related to the foam bulk density. The foam consists of both open- and close-cell structures. The presence of PLA significantly improved the water resistance of the foam, and significantly improved the foam recovery capacity, especially in high-moisture conditions. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3058–3062, 2007

Key words: poly(lactic acid)/starch; foam; extrusion; bulk density; water resistance; foam cell structure

INTRODUCTION

Thermoplastic foams are materials composed of a cellular core structure created by the expansion of a blowing agent. Starch is a good candidate for the promised biodegradable foams.[1] The foam structure and performance are influenced by many factors, including starch type, amylose/amylopectin ratio, derivatization, additives, and extrusion parameters (i.e., temperature setting, screw speed, and screw configuration).[2–4] However, these foams generally absorb moisture and consequently their properties and performance are reduced when these foams are used as a packaging material in high relative-humidity conditions. It is possible to convert starch from being hydrophilic to hydrophobic by chemical modification, but would add cost, for example, by acetylating native starch.[5] Simply blending starch with an affordable hydrophobic synthetic polymer is an alternative.[6–8] In a variety of commercially available polymers, poly(lactic acid) (PLA) is the only commercialized biodegradable polymer that is mainly derived from sugar-based biomass, and is considered a good candidate for water resistance because of its hydrophobic nature.[5] By blending starch with PLA, the resulting foams retain the important bio-degradability characteristic and have improved mechanical properties and water resistance. The extruded starch-based foams are promising for packaging and space-filling applications.

Guan and Hanna[5] incorporated 5, 10, and 15% PLA into acetylated corn starch to improve foam water resistance. In these cases, the highest PLA loading level was 15%.[5,9] However, the role of large PLA content, for example, higher than 20% in biodegradable foams has not been well established yet. This current work focuses on the investigation of the starch-based foam's morphological, mechanical, and water-resistance properties, with a view to establishing a properties-structure relationship as affected by a whole range PLA/starch ratio for foams extruded with water as a physical blowing agent and talc as a nucleation agent.

EXPERIMENTAL

Materials

The PLA used in this study was supplied by Shimadzu. (Tokyo, Japan). It had a weight-average molecular weight of 120 kDa, and was polymerized mainly from L-lactic acid. Cornstarch, containing 75% amylopectin and 25% amylose, was purchased from Cargill, Inc. (Minneapolis, MN). A commercial type of talc (<10 μm) from Aldrich Chemical Company (Milwaukee, WI) was used as a nucleation agent.

Foam preparation

Chips of PLA were ground by a laboratory mill (model 4 Laboratory Mill, Thomas-Wiley, Philadelphia,

PA) into about 2-mm fine powders before blending with cornstarch. Cornstarch was dried in a mechanical oven at 135°C for 2 h according to AACC Method 44-15A, to ensure the subsequent water incorporation was accurate. The PLA and cornstarch were premixed at various weight ratios, together with 15% water and 2% talc, with a stand mixer (Ultra Power Kitchen Aid, St. Joseph, MI) at room temperature for 10 min, and then kept in sealed plastic bags overnight to equilibrate the moisture.

Foam extrusion was carried out by a counter-rotating, twin-screw laboratory extruder (Leistritz Micro-18, American Leistriz Extruder, Sommerville, NJ) with a screw diameter of 18 mm, a screw operating-zone length of 30D, one feeding zone, and five heating zones. The temperature profile settings (30, 40, 80, 150, 185, and 195°C from inlet to die exit); 3.0-mm die size, 200-rpm screw speed, and 10 g/min feed rate were set for the extrusion. The extruded foams were allowed to cool to room temperature and then were cut into 20-mm lengthy cylinders. The collected samples were conditioned at 25°C and 50% RH for one week and then ready for characterizations.

Characterization

Compression of foams was carried out by an Instron testing machine (model 4465, Canton, MA) at room temperature. The 20-mm foam samples were mounted to the grip plates with grip distance of 40 mm. The samples were compressed longitudinally to half way at a crosshead rate of 30 mm/min, and then released. At least 10 replicates were tested, and average values were recorded.

Microstructure was observed by using scanning electron microscopy (SEM; Hitachi *S*-3500*N*, Hitachi Science Systems, Ibaraki, Japan). Extruded foams were cut into 3-mm-thick slices perpendicular to the longitudinal axis and mounted on SEM stubs with conductive carbon paint.

The dimensions of the foam samples were measured with a digital caliper (Absolute digimatic, Mitutoyo, Kawasaki, Japan). The weighed foam samples were used to calculate the bulk density. At least 20 replicates were made.

Water resistance of the foam samples was determined by immersing dried foam samples into distilled water for certain time intervals, and then samples were dried and weighed again to record the weight difference and to obtain starch loss due to solubilization by water.

RESULTS AND DISCUSSION

Cell structure and compression modulus

PLA plays a key role in the production, foam structure, and mechanical and physical properties of starch based foams. For simplicity, foam structure can be divided into two classes[10]: open-cell foams, in which the various cells interconnected; and closed-cell foams, in which cells are not connected to each other. Foams usually are hybrids and contain both open and closed cells. Based on assumption that the black ''holes'' are assigned to be the open cell [see arrow in Fig. 1(C)], the SEM pictures in Figure 1 clearly show that the foams had both open and closed cellular structures. It is noteworthy that the cell structure tends toward closed structure as the starch ratio of the matrix is reduced, where the cell wall mainly consisted of PLA phase. The method used can not precisely predict open/close cells, but is a good method for a roughly estimation.

A typical stress-stain curve of PLA/starch foams under compression is shown in Figure 2. It has a linear elasticity at low stresses, within a corresponding strain of ∼12%, followed by a long collapse plateau. A regime of densification was followed by a sharp stress increase. The linear elastic deformation depends on whether the cells are open or closed. The Young's modulus, *E*, is determined by the initial slope of the stress-strain curve. This Hookean behavior provides a clear indication that complete recovery from compression is possible within the elastic limit.[11] During compression, the plateau for the combined PLA/starch foams, is associated with collapse
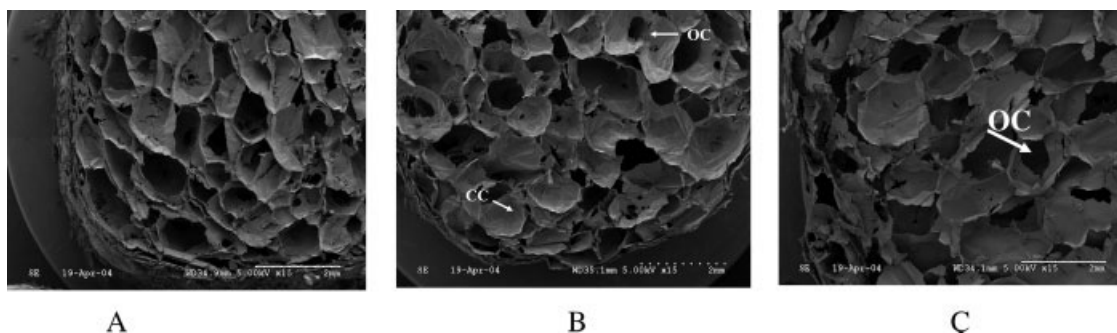

Figure 1 Typical foam structure of poly(lactic acid)/starch (A) PLA/starch (40/60); (B) PLA/starch (30/70); (C) PLA/starch (20/80), (inserted OC denotes Closed-cell).
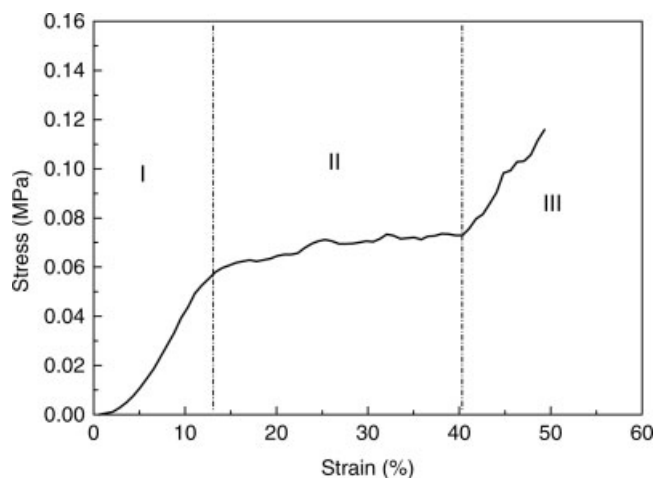
Figure 2 Typical stress-strain curve of PLA/starch foams under compression.

of the cells by means of elastic buckling of the elastomeric foams, with the formation of plastic hinges that yield, and by brittle crushing of the brittle fractions. When the cells are almost completely collapsed, opposing cell walls touch, and the strain further compresses the solid cell walls themselves, giving a final region of rapidly stress increase.[12]

It is widely accepted that the physical properties of a given foam depend on many factors.[13] A possible functional dependency would be:[14]

$$Y = f(\rho, CC, CS, PM, GE, etc) \tag{1}$$

where Y can be any physical property, ρ is the foam density, CC is the chemical composition, CS is the cellular structure, PM is the polymer morphology related to foam size and its distribution, and GE is the kind of gas enclosed.

Foam structure and properties are significantly influenced by processing conditions, such as extrusion temperature profile, screw speed, die nozzle diameter.[2–4] Mechanical properties of foams largely depend on their bulk density. The theory predicts scaling laws between the mechanical properties, such as Young's modulus and the relative density of the foam, as:[12]

$$\frac{E_f}{E_s} \propto \left(\frac{\rho_f}{\rho_s}\right)^m \tag{2}$$

where E_f is the Young's modulus of the foam, E_s is the Young's modulus of the matrix (solid cell walls), and ρ_f and ρ_s are densities of the foam and the matrix, respectively. From eq. (2), an increase in density (ρ_f) increases the Young's modulus of the foam. The power law depends upon whether the foams are open-cell or close-cell. For open-cell foam, $m = 2$, and for close-cell foam, $m = 3$. The uni-axial com-

pression modulus as a function of foam relative bulk density is described in Figure 3. The slope of the plot is around 2.2 ($r^2 = 0.95$), indicating that the foams are mainly open-cell structures. Although the exponent constant of the data fitting by power law was found near the specific exponent 2 as an open-cell structure, the SEM cell structure (Fig. 1) at small starch ratios shows predominantly closed-cell structure. As the starch ratio increases, the portion of open-cells increases. Even though no obvious evidence is seen from Figure 3, the nucleation and cell-growth mechanism, as discussed in Part I, may contribute to the difference. Water was preferred as a blowing agent and was distributed in the starch phase. At fixed water content, as starch content increased in the foam matrix, the water availability in the starch phase decreased; hence the plasticizer function of the water decreased, rendering the starch much more brittle. Consequently the starch was easily ruptured by water vapor during expansion, resulting in more opened cells.

Water resistance

Hydrophilic starch absorbs moisture rapidly in high-humidity conditions, and eventually loses functions due to too much water. Especially, starch-based foam used for packaging as a cushion or heat insulation may completely lose its function after exposing to high humidity condition. Incorporation of hydrophobic PLA significantly improved the water resistance of the bulk foam.[15] At constant PLA/starch ratio (40/60), starch loss into water from the foam increased dramatically during the initial hours, and then leveled off at about 17 to 20% (Fig. 4). Foams
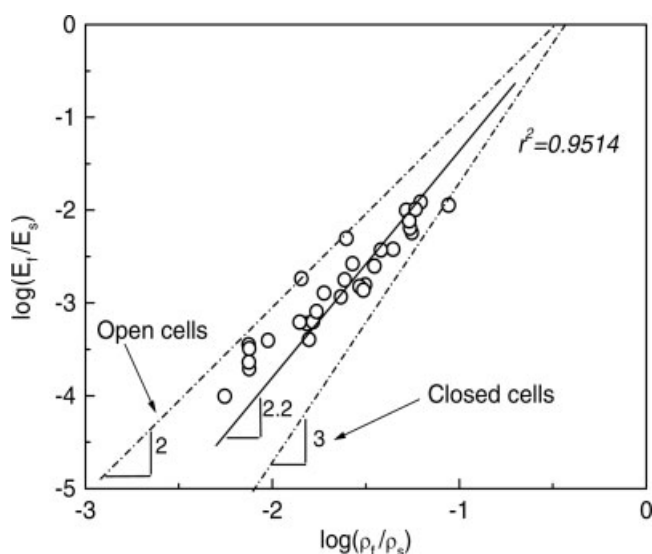

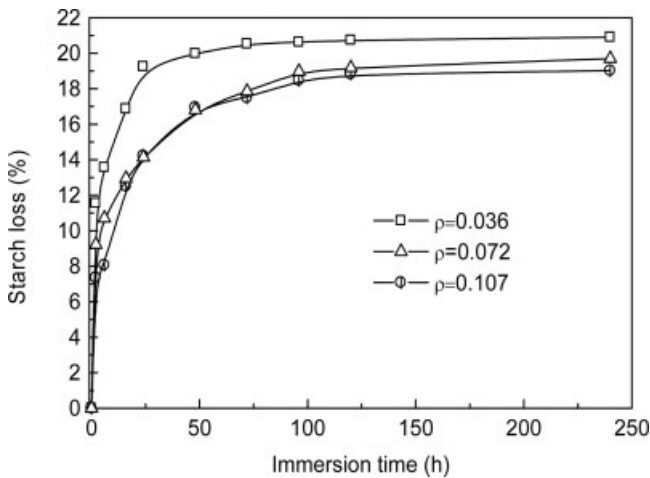**Figure 3** The relationship between compression modulus and foam bulk density.

Figure 4 Starch loss from PLA/starch (40/60) foams as affected by foam density and soaking time.

with lower density had slightly greater starch loss because a larger contact area between starch and water resulted from cell expansion. Starch loss increased when foam density was ≤0.036.

Starch loss was also significantly affected by PLA/starch ratio (Fig. 5). The foam with 60% starch had starch loss of 19.7% after 240 h of immersion. At the same immersion time, starch loss of the foam with 80% starch was almost 60%. The foam with 100% starch was completely collapsed, and starch was dissolved in water, after 2 h of immersion.

As previously mentioned, density is a factor slightly influencing starch loss. The four samples showed in Figure 5 had densities of 0.072 (40/60), 0.065 (30/70), 0.051 (20/80), and 0.038 g/cm^3 (0/100). The total starch losses of these foams were believed to be the cooperative contribution of PLA/starch ratios and foam density variations. Ke and Sun reported that the continuous PLA phase was interrupted when starch
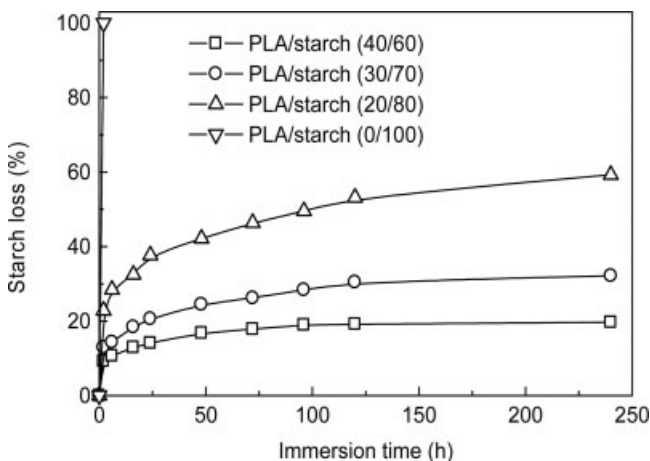
content reached 45% or more in the matrix.[16] For the foam samples in this study, PLA was not able to form its continuous network, but it may have encapsulated some starch granules and therefore, improved water resistance. The encapsulation was obviously weakened by the significant increase of starch content, and so more starch granules were exposed to water, especially for open-cell foam materials. In addition, the open-cellular structure provided direct tunnels for water to diffuse in, and then the dissolved starch easily leached out of the foam.

Compression and foam recovery

In general, foams undergo deformation under compression. Upon removal of the external forces, the foam starts to partly recover, depending on the characteristics of elastic–plastic deformation of the foam. Figure 6 exhibits the recovery of PLA/starch foams at various ratios and three relative-humidity conditions. The foam samples dried at 135°C for 2 h, then immediately undergoing mechanical compression testing, showed no recovery at all, and all inside structure fractured into pieces, regardless of starch/PLA ratios. The foam samples conditioned at 50% relative humidity for one week at room temperature and then tested yielded up to 73% recovery after 1 h of force removal. The recovery was reduced with the reduction in starch content. As mentioned before, water can be a good plasticizer for starch, and PLA could reduce water diffusion into the starch phase. After immersing the foams in distilled water at room temperature for one week, however, foams with PLA showed instant recovery to their original shape after one minute of force removal regardless of PLA/starch ratio. After soaking in water, the
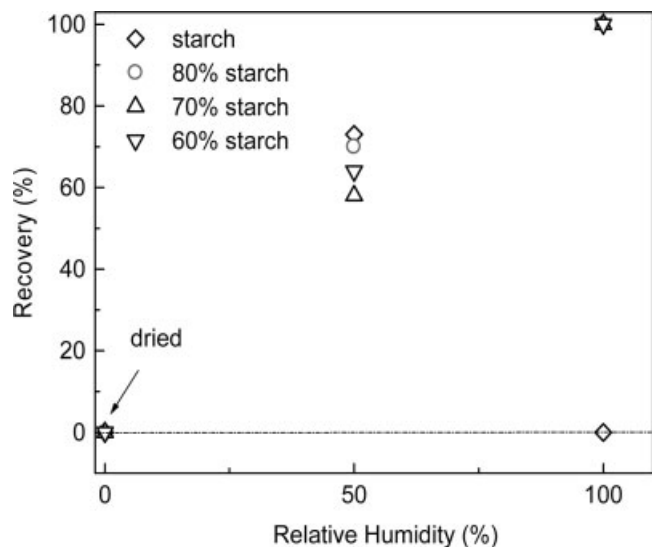

Figure 5 Starch loss from PLA/starch foams as affected by PLA/starch ratio and water soaking time.

Figure 6 Compression and recovery of PLA/starch foam at three different humidity conditions.

foam with 100% starch completely collapsed and dispersed in water.

Water and PLA content influence the foam recovery. Moisture in the samples containing starch acts as a plasticizer, giving materials a large elastic response. Without moisture, the materials exhibit brittle plastic deformation. Unlike 100% starch foam, the addition of PLA provided the foam skeleton to endure deformation under compression and keeps the starch from dissolving in water.

CONCLUSIONS

The foam derived from PLA and starch had both open- and close-cell structures. The compression modulus of the PLA/starch foams is closely related to the foam cell structure and bulk density, exhibiting a power law relationship. Adding PLA significantly improved the water resistance of the foams, and dramatically improved the foams' recovery ability, especially in high-humidity conditions.

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