Biodegradable Foams of Poly(lactic acid)/Starch. I. Extrusion Condition and Cellular Size Distribution

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ABSTRACT: Biodegradable foams derived from poly(lactic acid) (PLA) and starch were prepared by extrution using water as a blowing agent and talc as nucleation agent. Foam cellular size and size distribution was significantly affected by extrusion conditions (i.e., extruder temperature profiles, die diameters, and screw speed), and material compositions, (i.e., water concentration, PLA/starch ratio, and nucleation agent concentration). Foam with a relatively fine cellular size and uniform cellular size distribution was obtained under optimized conditions of PLA/starch ratio at 40/60, 15% water, 195°C temperature before the die, 3-mm die nozzle diameter, 200-rpm screw speed, and 2% talc. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 857–862, 2007

Key words: poly(lactic acid); starch; foam; extrusion; nucleation agent; water blowing agent; gelatinization

INTRODUCTION

Thermoplastic foams have been widely used in impact and sound insulation, packaging, gaskets, buoyancy devices, cushions, sports, and leisure.[1,2] Extrusion has been conventionally used in the last few decades for manufacturing low-density foam materials with physical blowing agents, by using a variety of polymers including polystyrene, unplasticized PVC, polyethylene, polypropylene, and, recently, starch/poly(lactic acid) (PLA).[3] Because of limited petroleum resources and environmental issues, biodegradable polymeric foam products are being developed from renewable materials.[4] Starch has been considered to be a major material for disposable foam production.[3,5,6] Starch foams, however, have limited applications due to starch–water solubility and low mechanical strength.[7,8] Biodegradable PLA, as an alternative to petroleum-based polymers, was blended with starch to improve the mechanical properties and water resistance of the foams.[3] Water has been used a blowing agent as well as a plasti-cizer for starch-based foams, such as breakfast cereals and insulation foams.[9] Water is an environmentally friendly solvent and is inexpensive. Starch-based foams usually have a more open-cell structure than expanded polystyrene based foams. The open-cell structure of the starch foam is caused by a sudden increase in water vapor pressure and water vapor pressure diffusion immediately after leaving the extrusion. Radial expansion and water resistance of the starch foam are improved by blending with hydrophobic polymers.[7,8,10] Limited information on PLA/starch foams has been available, mainly due to the limitation of PLA availability and poor compatibility between PLA and starch.

The present work aims to prepare PLA/starch foam by using water as a physical blowing agent and talc as a nucleation agent, to study foam cell size distribution as affected by extrusion temperatures, screw speed, and die size.

EXPERIMENTAL

Materials

The PLA was obtained from Shimadzu (Tokyo, Japan). It had a weight-average molecular weight of 120 kDa, and was polymerized mainly from L-lactic acid, with a glass transition temperature (T_g) of 60.0°C, crystallization temperature of 125.2°C, and melting temperature of 172.0°C; crystallinity of PLA was about 36.8%.[11] Cornstarch, containing 75% amylopectin and 25% amylose, was purchased from Cargill (Minneapolis, MN). Talc (< 10 μm) was supplied from Aldrich Chemical Company (Milwaukee, WI).

Foam preparation

Chips of PLA were ground by a laboratory mill (model 4 Laboratory Mill, Thomas-Wiley, Philadelphia, PA) into about 2-mm fine powder before blending with starch. Cornstarch was dried in an oven at 135°C for 2 h, according to AACC Method 44-15A, to minimize moisture and accuracy of subsequent water incorporation. The PLA/starch, at 40/60 ratio by weight, was premixed at various water concentrations (0, 11.9, 15, 20, 25, and 40 wt %) with a stand mixer (Ultra Power Kitchen Aid, St. Joseph, MI) at room temperature for 10 min.

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 center distance of 15 mm, a screw operating-zone length of 30D, one feeding zone, and five heating zones. The temperature before the die was set at 180, 185, 190, and 195°C, die size was 2.3, 3.0, and 4.0 mm, and screw speed was 100, 200, and 300 rpm. Within these parameter ranges, extrusion conditions were determined depending on each experimental design.

Properties measurement

Foam cellular size and size distribution were analyzed from microstructure pictures taken by scanning electron microscopy (SEM; Hitachi *S*-3500*N*, Hitachi Science Systems, Japan). Extruded foams were cut into 3-mm thick slices perpendicular to the longitudinal axis, and were mounted on SEM stubs with conductive carbon paint.

Thermal transitions of native starch with various water concentrations were characterized by differential scanning calorimetry (DSC) (Perkin–Elmer Pyris 1, Norwalk, CT). The starch/water samples in stainless steel pans were hermetically sealed and equilibrated overnight before scanning from 20 to 200°C, at a scanning rate of 10°C/min under nitrogen flow protection.

The extruded cylindered foams were cut into 20-mm bars, and the weighted foams' dimensions were measured by a digital caliper (Absolute digimatic, Mitutoyo, Kawasaki, Japan). Then the bulk density was determined by dividing weight by its volume. At least 20 replicates were made.

RESULTS AND DISCUSSION
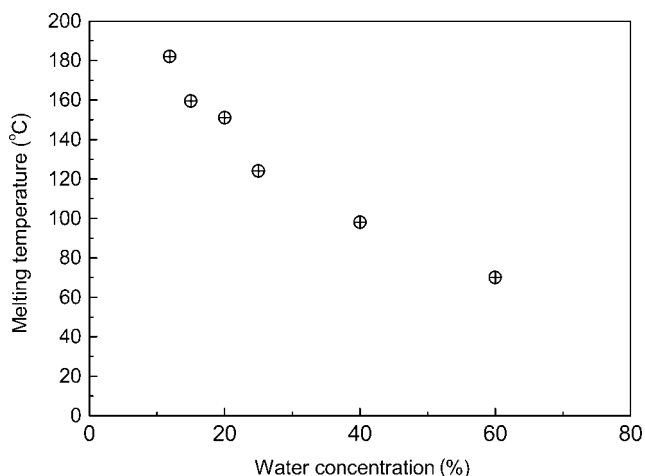
Water as a blowing agent

For the experiment to study the influence of water as a blowing agent on foam formation, the extrusion condition was fixed at 185°C, 200-rpm screw speed, 3.0-mm die size, and 0% talc nucleation agent. Water apparently plays a key role in starch-based foam

expansion (Fig. 1). Foam expansion ratio is defined as $(D/d)^2$, where D is the diameter of expanded foam after cooling to room temperature and d is the diameter of die nozzle. At 0% water content the $(D/d)^2$ was 1.68, which is attributed to a sudden pressure drop at the die. The foam expansion at 11.9% water is believed to be the result of inherited moisture of starch. The biggest expansion ratio, 53.7, was achieved at moisture content of 15%; the expansion ratio was dramatically reduced to 26.8 at 20% water, and leveled off at about 18.5 at 25% water content. In a previous paper, Blanche and Sun[12] discussed the melting temperature of starch and its relations to extrudate properties. They found that the temperature difference between the melting temperature of raw starch and the starch melt temperature behind the extruder die related negatively to the foam bulk density and positively to the starch expansion. At a large temperature difference, starch molecular mobility could be increased and favor amylase–lipid complex formation. However, the result obtained by Blanche and Sun can not be fully applied to the PLA/starch foam system because PLA has a melting temperature around 175°C, and PLA has, as compared to starch, very different melting viscosity and mechanical strength.

The melting temperature of starch in the presence of water is shown in Figure 2. The melting temperature of starch declined with an increase of water content, because water functioned as a plasticizer for starch. This reverse effect on foam expansion may be related to the low viscosity of the blend at higher water concentrations and thereafter to a low melt strength, which favors the loss of water and foam cell collapse.
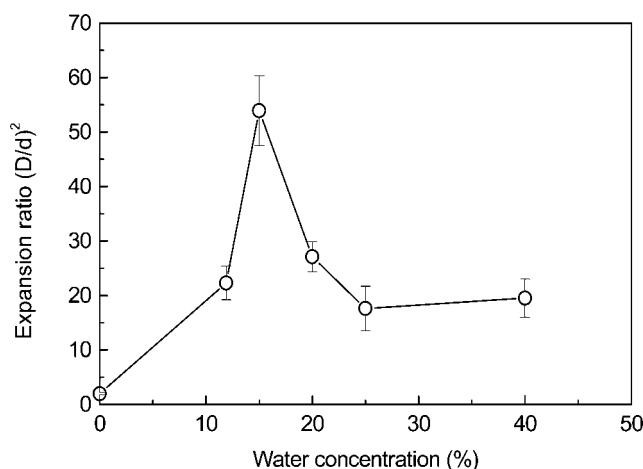
Figure 1 Effect of water concentration on expansion ratio of PLA/starch blends at extrusion conditions of 185°C, 200 rpm screw speed, 3.0 mm die nozzle, and without talc as nucleation agent.

Figure 2 Native cornstarch melting temperature with various water concentrations, determined by DSC.

Water used as a physical blowing agent brings unique advantages to the starch-based foam. First, water is a good plasticizer for starch, to reduce the T_g and improve processability. Also, during a typical thermal process, (i.e., extrusion) starch granules undergo gelatinization in the presence of water, which is a physiochemical phenomenon involving swelling and loss of crystallinity of the granules.

Hence, water as a blowing agent affects two processes: participating in starch gelatinization and in volume expansion at the die to generate cellular structure. Especially at higher water concentrations, starch becomes fully gelatinized. Because PLA is hydrophobic, all of the available water is absorbed by the starch for gelatinization. The foaming process consisted of three steps: foam cell nucleation, cell growth, and cell coalescence.[13] Foam structure was developed after exiting the die, and foam expansion occurred rapidly because of a sudden pressure drop at the die, and meanwhile, most water evaporated. Water vapor could easily rupture the cell walls because starch in melted form has poor strength.[13] The mechanism of cell growth was governed by the mechanical properties of the polymer matrix, water vapor diffusion rate, and water content at a given processing condition. The final foam cell size was closely related to the amount of water vapor used for the cell growth. The water vapor inside the cells started condensing to liquid phase at 100°C, creating vacuum in the cells. The specific volume of saturated water vapor is 1873 cm³/g at 100°C.[14] At this point, if the foam structure was not stiff enough, it would tend to collapse, and then the volume expansion ratio decreased. Heat was lost through the surface of the foam to ambient during cooling. Therefore, the temperature on the foam surface should be the lowest along the cross section of the foam. As the foam surface structure became stable below the T_g, the

foam cellular structure and volume can be determined by the solidification of the polymer. If the foam cell is open structure, there would be no further foam expansion.
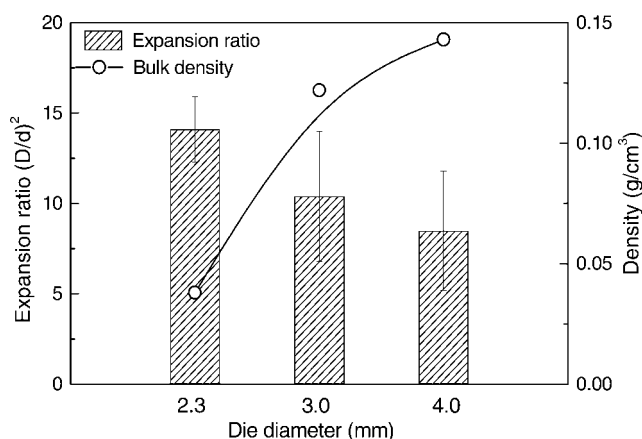
Effect of extrusion parameters

Die size

Die diameter, that governs the accumulated pressure before the die, is closely related to the foam structure formation. To evaluate the influence of die diameter on foam formation, three different die sizes were used: 2.3, 3.0, and 4.0 mm in diameter. The extrusion temperature before the die was set at 195°C and screw speed was set at 200 rpm. The PLA/starch ratio was 40/60 with 15% water and 2% talc content. The foam expansion ratio decreased as die size increased (Fig. 3), whereas bulk density increased as die size increased. The largest expansion ratio (13.8) was achieved at die size 2.3 mm while the bulk density was around 0.032 g/cm³ in this case.

Pressure drop at the die is the key factor for foam formation, and the drop over the length of the die can be described as[15]:

$$-\Delta P = \frac{2mL}{r_0} \left[\frac{q\left(3 + \frac{1}{n}\right)}{\pi r_0^3} \right]^n \tag{1}$$

where ΔP is the pressure difference (P_a) between the die inlet and outlet, m is the characteristic constant of non-Newtonian fluid over a temperature range (NS^n/m^2), L is the length of die nozzle (m), r_0 is radius of the nozzle (m), q is the volumetric flow rate of the polymer/water melt (m^3/s), and n is the dimensionless characteristic constant of non-Newtonian fluid over a temperature range. Equation (1) predicts that a smaller die size generates a larger pressure drop if other parameters are fixed. The pressure

Figure 3 Effect of die nozzle diameters on PLA/starch (40/60) foam expansion ratio, at extrusion conditions of 185°C, 200 rpm screw speed, 2% talc, and 15% water.
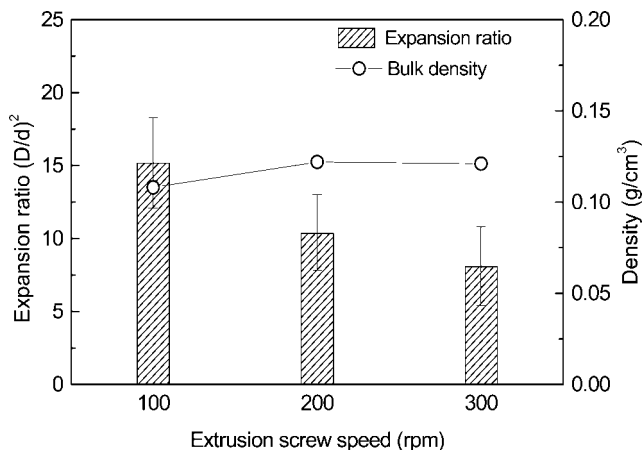
Figure 4 Effect of screw speed on PLA/starch (40/60) foam expansion ratio and bulk density at extrusion conditions of 185°C, 3.0 mm die size, 2% talc, and 15% water.

drop rate theoretically becomes infinitely large when the die nozzle diameter approaches zero, which favors foam nucleation along the die nozzle length. That is why the larger expansion ratio and lower bulk density was obtained by using a smaller die size (Fig. 3).

Screw speed

Screw speed determines the residence time of the PLA/starch melt in the extruder, and is directly associated with the mixing quality of the melt. As seen in Figure 4, lower screw speed gave the foam larger expansion ratio. Screw speed did not significantly affect the bulk density of the foam. This indicates that good mixing quality is necessary for water to be dispersed in the PLA/starch system and to give talc more chances to form nucleation. However, reduced screw speed limits the production of foam, and a longer residence time would increase the degree of PLA hydrolysis.

Temperature before the die

Foaming temperature was controlled by changing the temperature before the die (T_{die}). The T_{die} used in this study (180, 185, 190, and 195°C) was all higher than PLA's melting temperature. In this experiment, screw speed was set at 200 rpm and die size was 3.0 mm. The PLA/starch ratio was 40/60 with 15% water concentration and 2% talc content. The expansion ratio was positively related to foaming temperature (T_{die}) (Fig. 5). Though a high T_{die} favors foam expansion, PLA became hydrolyzed in the presence of water at elevated temperature, especially above melting point. Hence, improving foam expansion by increasing T_{die}, for instance to 200°C, would be at the risk of PLA decomposition. During

extrusion, starch and PLA undergo a melting process, which would cause a loss of the crystalline structure. Hence, both starch and PLA are under high shear–high temperature conditions, resulting in molecular fragmentation and formation of amylase–lipid complexes if lipid appeared in the starch. At an elevated temperature, the melt strength of PLA and its extensional viscosity decreased significantly. The decreased viscosity accelerated the water vapor diffusion rate through the foam cell walls; thus, the vapor quickly diffuses out of the cells into the environment and the volume of foam constraint.

Another factor that contributes to the cell size expansion is the bubble surface tension. To a first order approximation, the surface tension contribution to the equilibrium cell size for a spherical bubble is given by eq. (2) for a given foaming pressure[16]:

$$(D_c)_{surface} \propto \frac{4\gamma_{bp}(T)}{\Delta P} \tag{2}$$

$$\left(\frac{D_{c2}}{D_{c1}}\right)_{surface} = \frac{\gamma_{bp}(T_2)}{\gamma_{bp}(T_1)} \tag{3}$$

where D_c is the average cell size (μm), γ_{bp} is the surface energy of the polymer/bubble interface (N/m), ΔP is the pressure difference between the gas in the cluster and the ambient nucleation pressure (P_a), and T is the absolute temperature (K). Because $(\partial\gamma_{bp}/\partial T)_p$ is proportional to the entropy, it follows from the second law of thermodynamics that the surface tension must decrease with an increasing temperature. Equation (3) implies that the surface tension effects tend to decrease the equilibrium cell size when the foaming temperatures increase.
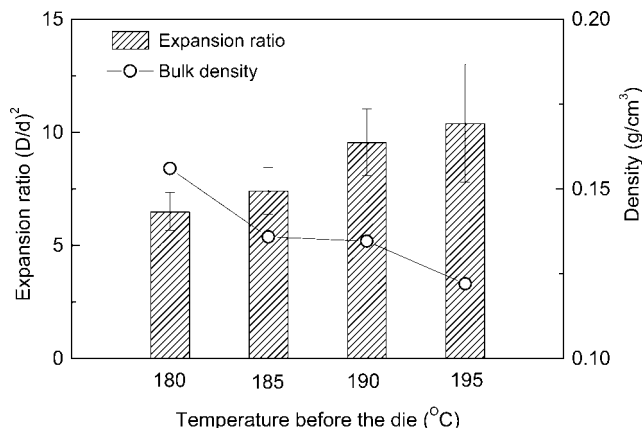
Figure 5 Effect of extrusion temperature on PLA/starch (40/60) foam expansion and bulk density under extrusion conditions of 200 rpm screw speed, 3.0 mm die size, 2% talc, and 15% water.

Nucleation and cell size distribution

At lower water concentrations, the nongelatinized or partly gelatinized starch itself acts as a nucleation agent in the PLA/starch system, inducing the foam formation. The nucleation function was reduced at higher water concentrations, at which the starch crystalline structure melted and dispersed evenly in the PLA matrix. Water vapor randomly distributed in the system, especially at the interface between starch and the PLA melt phase. Occasionally in the area where a high concentration of water vapor accumulates, starch in these areas became saturated with water. In such area, larger cell size and broader size distribution were observed.
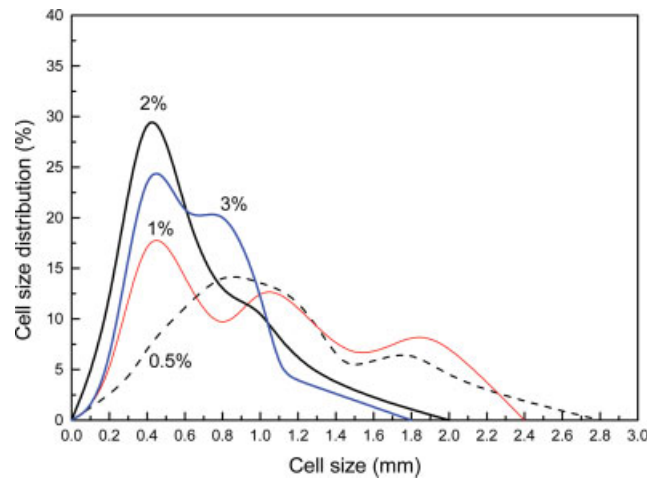
The foam structure was dramatically affected by solid inorganic fillers that acted as nucleation agents. With 0.5% talc the expansion ratio of the foam was dramatically reduced by almost 50% (Fig. 6). The expansion ratio was further reduced with talc concentration. At 3% talc, the foam expansion was 11.2, < 25% of the expansion ratio of the foam without talc. In contrast, the bulk density remained the same and increased slightly at a talc concentration of 3%.

With a reduction in the expansion ratio by talc, the foam cellular structure was also changed dramatically. Compared with foams without talc, the texture of the foam with talc became uniform and fine (Fig. 7). Cell size distribution became narrower as talc content increased from 0.5 to 2.0 wt %. Majority cell size (MCS) was also reduced. For example, the MCS was between 0.6 and 1.2 mm for the foam with 0.5% talc, whereas the MCS was about 0.4 mm with 2% talc. At 3% talc, the cell size becomes larger and distribution becomes broader again.

The presence of nucleation agent reduced the nucleation barrier to disordering the equilibrium status of the PLA/starch/water system. The cell nucle-
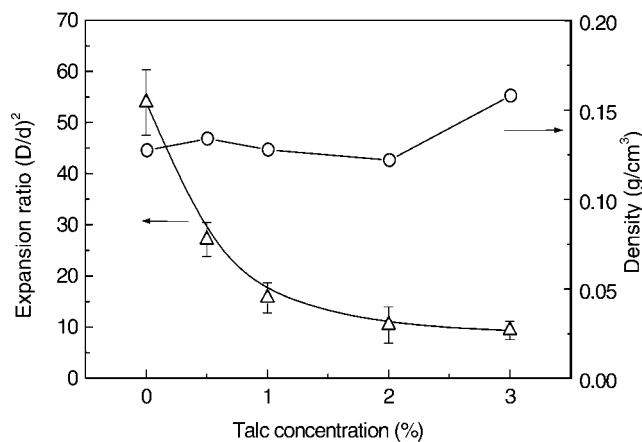
Figure 7 Effect of nucleation agent (talc) content on PLA/starch (40/60) foam size and cell-size distribution at extrusion conditions of 185°C, 200 rpm screw speed, 3.0 mm die nozzle size, and 15% water: (a) 0.5%; (b) 1%; (c) 2%; (d) 3%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ation rate can be predicted by the classical nucleation theory[17]:

$$N_{nucl} = f_0 C_0 \exp(-\Delta G_{nucl}/kT) \qquad (4)$$

$$\Delta G_{nucl} = 16\pi\gamma_{bp}^3 3\Delta P^2 \qquad (5)$$

where N_{nucl} is the nucleation rate; ΔP is the pressure drop of the gas/polymer system; f_0, C_0, and k are constants; ΔG is the nucleation barrier; and T the temperature. Combining eqs. (4) and (5), the nucleation rate is largely associated with the bubble surface tension at constant extrusion settings:

$$\ln N_{nucl} = A - B \cdot \gamma_{bp}^3 \qquad (6)$$

where A $\ln f_0 C_0$ and B $16\pi/3\kappa T \cdot \Delta P^2$. A nucleation agent could reduce surface tension of bubbles, which significantly increased the nucleation rate.

The relationship of nucleation rate with pressure drop (resulting from the various die diameters) and extrusion temperature, can also be reflected by the combination of eqs. (4) and (5) when other variables are assumed as constants. During pressure drop or increasing extrusion temperature, which instigate thermodynamic instability, some stable cells nucleate early, while the PLA/starch melt is still in the nozzle. The water vapor will diffuse to the nucleated cells to reduce the free energy of the system. As the water steam, which can be regarded as gas, diffuses to these cell regions with low gas concentration (where nucleation cannot occur) are generated adjacent to the stable nuclei by talc. As the melt pressure drops further, the system will either nucleate additional microcells or expand the existing cells.

Figure 6 Effect of nucleation agent (talc) content on PLA/starch (40/60) foam expansion ratio and density at extrusion conditions of 185°C, 200 rpm screw speed, 3.0 mm die nozzle size, and 15% water.

Because steam preferentially diffuses to the existing cells, the gas remaining between the existing cells is less than the critical amount needed to nucleate additional cells. But if the size of the gas region is less than the dimension between existing cells, then additional cells will tend to nucleate between existing cells.

The degree of foaming generally increases with increasing blowing agent content, which supplies more nucleation sites. But when the blowing agent was water, steam reduced the melt strength of the PLA/starch system so that it easily allowed the steam escape to outside of the foam.

CONCLUSIONS

Foams of PLA/starch were successfully prepared by using water as a blowing agent in the presence of talc, which acted as an effective nucleation agent. Water concentration, foaming temperature, nucleation agent concentration, screw speed, and die nozzle diameter were factors influencing foam forming, cell size, and cell distribution. Water was a good blowing agent for the PLA/starch system. Talc at 2% gave the PLA/starch foam fine foam cell size and uniform cell size distribution. Optimized extrusion conditions for the PLA/starch with 15% water and 2% talc were determined: 200 rpm screw speed, 3.0 mm die diameter, and 195°C temperature before the die.

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