Controllable Growth of Gradient Porous Structures

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Cocontinuous phase structures of immiscible polymers can be developed under appropriate melt-blending conditions. Because of the presence of interfacial tension, such cocontinuous structures start to coarsen when heated to a temperature higher than the melting/softening temperature of both phases. In this study, a method for controllable growth of gradient porous structures utilizing variable coarsening rates in a gradient temperature field was investigated. The phase structure coarsens at a higher rate in higher temperature regions but at a slower rate in lower temperature regions, resulting in the generation of a gradient phase morphology. Subsequent dissolution of one phase in the binary blend yields a gradient porous structure made of the remaining polymer component. A polystyrene/poly(lactic acid) (PLA) blend was used as a model system. By designing proper thermal boundary conditions and introducing different thermal gradients during annealing, different types of gradient porous structures of PLA were created.

Introduction

Nature is an excellent producer of multifunctional porous materials, for example, wood, plant seeds, egg shell, bone, skin, and so on. These natural porous materials typically have a gradient porous structure (GPS), meaning that the porosity is not uniform. Rather, it is distributed in space so as to maximize the overall performance of the structure. Often, the pore size continuously varies from the skin to the core, as in bone and in egg shell.1 In bone, regions of dense “cortical” bone neighbor regions of low-density “trabecular” bone. With pores sizes decreasing from the core to the skin, bone is able to maintain a highly permeable core and yet provide an outer wall structural integrity. The increase of stiffness and strength with the reduction in pore size is understandable from both experimental and theoretical perspectives. This has been the main thrust for the recent development of microcellular polymers2–4 for lightweight structural applications. Similarly, the avian egg shell utilizes a GPS to achieve desired mechanical performance and in the meantime a necessary permeability. From inside to outside, the pore size varies from several hundred microns to a couple of microns.15 These graded pores serve for the exchange of matter between the outside and inside of the eggshell while having enough strength to prevent the shell from cracking caused by collision or impact.

The above known techniques for creating GPSs, however, typically have a low resolution, prohibiting the creation of fine GPSs, and are limited to simple part geometries and shapes. In particular, the centrifugal methods are mostly suitable for cylindrical part shapes. The feeding materials in most of these processes are also limited to powders, either in dry form or in suspension. Creation of a continuously varying and spatially controlled gradient in porosity with interconnected open pores represents an additional challenge for these processing steps. In this study, a new method for controllable generation of polymeric gradient porous structures was investigated, utilizing the unique thermal flow behavior of immiscible polymer blends. By controllable variation of the temperature distribution in the blend, a spatially varied and controllable gradient in phase structure is created. After dissolution of one of the two phases, the desired porous structure of the remaining polymer is obtained. Furthermore, with this approach, continuous porous structures with interconnected open pores can be generated with appropriate selection of polymers and processing conditions.
Experimental Section

Materials. The materials used in this study were two polymers, poly(lactic acid) (PLA) and polystyrene (PS). The PLA polymer was in an extrusion grade, 4032D from Natureworks LLC. It is a semicrystalline polymer, with a glass transition temperature at 60 °C and a melting temperature at 170 °C, as measured by differential scanning calorimetry (DSC). The PS polymer is of an atactic grade, from Dow Chemical, with a glass transition temperature at approximately 108 °C, measured by DSC. Both polymers have a thermal degradation temperature above 300 °C in the nitrogen environment, judged by thermal gravimetric analysis (TGA). The number average molecular weights for the two polymers were estimated from melt viscosities; they are 330000 g/mol and 590000 g/mol, for PLA and PS, respectively. Both polymers were obtained in a pellet form from the suppliers.

Blending. The PLA/PS mixture (50% by 50% in weight) was blended in a Brabender Intelli-Torque Rheometer. The torque rheometer head was mounted with Sigma blades capable of tumbling and distributive mixing. A compounding temperature of 200 °C and a mixing speed of 60 rpm were used during the blending process. A mixing time of 10 min was employed to ensure a uniform chamber temperature prior to blending. The achievement of homogeneous blend morphology inside the chamber was established by the development of a constant blending torque. A homogeneous PLA/PS blend was obtained at the end of 10 min. The as-mixed blend was immediately scraped out of the chamber in molten state and quenched in tap water.

Annealing with Temperature Gradients. In this exploratory study, three different types of thermal boundary conditions were used to generate three different types of temperature gradient during annealing, as shown in Figure 1. In the first case, a temperature difference is imposed between an upper and a lower platens, between which a polymer blend is annealed. In the second case, a temperature gradient is applied around a corner of a blend sample with a square cross-section. In the third case, a heated pin of a diameter of 1 mm is inserted into a room-temperature blend disk to create a radial temperature gradient. All these annealing experiments were conducted on a hydraulic press with heated platens. In all three cases, the hot platen was set to 200 °C and the cold platen was left at room temperature with tap water cooling. The free surfaces on the samples were exposed to natural air convection in the ambient environment. During annealing, some blend material was squeezed out in the lateral direction. Only a small amount of contact force was applied to minimize the lateral out-squeeze.

Characterizations. The rheological properties of the two polymers were characterized on a rotational rheometer (Model: AR2000EX, TA Instruments). The thermal properties were characterized on a DSC unit (Model: Q200, TA Instruments) and a TGA unit (Model: Q5000-IR, TA Instruments). After blending and controlled annealing, the sample was quenched in tap water. The polystyrene phase in the cooled blend was extracted with cyclohexane performed in a solvent bath for 7 days. The weight loss was measured to calculate the extent of continuity of the PS phase. The cross sections of the remaining porous samples were sputter-coated with gold and then imaged using scanning electron microscopy (SEM) on a Hitachi S-800 SEM unit.

Results and Discussion

The rotational rheometry was operated under the small-strain oscillatory shear mode with a strain amplitude of 0.01. Figure 2 shows the dependency of the complex viscosity of PLA and PS on the angular frequency at two different testing temperatures. Using the well-known Cox–Merz rule\(^\text{19}\) for shear viscosity, one can convert angular frequency equivalently to shear rate. From the resulting shear rate dependency, it is clearly seen that both polymers are highly pseudoplastic, with viscosity
decreasing with increase of shear rate. Two types of viscosity are important in the current study. First, the viscosities and their ratio at the processing shear rate during batch mixing are major factors affecting the phase structure of the blend. For example, the phase inversion can be related to the viscosity ratio (see Supporting Information for details).\(^{20,21}\) Second, the zero-shear viscosities determine the coarsening rate during annealing; in general, the phase size growth rate is inversely proportional to the equivalent viscosity of the blend (see Supporting Information for details).\(^{22,23}\) The batch mixing step was performed at a mixing speed of 60 rpm and a temperature of 200 °C. The shear rate at this mixing speed with a rotor diameter of 35.5 mm was estimated to be 95 s\(^{-1}\). The viscosity ratio of PLA over PS in this case is 0.7, calculated from the data in Figure 2. For a 50/50 wt % PLA/PS blend used in this study, this viscosity ratio would result in a cocontinuous phase morphology. Different from mixing under external forces, phase coarsening during annealing is a spontaneous process, driven by the interfacial tension. The deformation rate involved in annealing is typically much smaller than in mixing. Thus, the zero-shear viscosity is the relevant viscosity for predicting the phase coarsening process. From Figure 2, it is seen that the zero-shear viscosity for both PLA and PS is sensitive to temperature changes. When temperature changes from 200 to 180 °C, the zero-shear viscosity increased by a factor of 6.5 for PLA and a factor of 5 for PS. This strong dependency on temperature indicates that the phase size coarsening rate can be effectively varied by applying a relatively small temperature gradient during annealing.

Figure 3 compares the phase structures before and after isothermal annealing at 180 °C for 2 min. In both cases, the PS phase was solvent extracted, leaving a porous PLA structure. Before solvent extraction, the samples were smoothly cut with a sharp blade. This left a flat surface in the final porous structure, making it easier for phase size comparison. In both cases, a well-defined continuous porous PLA structure can be clearly seen in the SEM micrograph. Comparison of the sample weight before and after solvent dissolution showed that nearly 100% PS was extracted, suggesting the existence of a continuous PS phase in both cases. Therefore, the blend before and after annealing both had a cocontinuous phase structure. Aside from these findings, the comparison more importantly shows the significant effect of the annealing temperature. After annealing for only 2 min, the phase size grew much coarser, at least twice larger than the original phase size. Figure 4 shows a porous PLA structure formed after more extensive annealing at 180 °C for 30 min. The sample was brittle fractured after extraction of the PS phase. The phase size resulting from this prolonged annealing was more than 20 times larger than the original one. It is noteworthy to report that, at this large phase size, a well-defined continuous porous PLA structure still persisted.

The gradient porous structures created from the nonisothermal annealing experiments, as described in Figure 1, with controlled thermal boundary conditions are shown in Figures 5–7. At each thermal boundary condition, the experiment was repeated for at least three times. The obtained morphology was found to be consistent from run to run. The structure shown in Figure 5 was obtained from the annealing experiment of a 6 mm thick blend plate between two parallel platens with an imposed temperature difference. Three different locations are indicated in Figure 5a, and the resulting cross-sectional structures along the direction perpendicular to the temperature gradient are given in Figure 5b–d. After an annealing time of 30 min, large pores with a size around 200 μm were formed on the hot platen side (left side in Figure 5), while the pore size on the cold platen side were left unchanged, with the same phase size around several microns as that in the as-mixed blend. In between the two platens, a gradient in phase size can be clearly seen. For this simple 1-D case, the distribution of pore size can be well correlated to the temperature distribution. The melting temperature of the PLA component is 170 °C, below which no coarsening effect would occur during annealing. The distance from the hot platen corresponding to this temperature can be analytically calculated to be 0.17H, where H is the plate thickness. In the current case, this distance would be 1 mm; that is, after a distance of 1 mm from the hot platen, no significant coarsening effect would be expected. This calculation, in general, agrees with the experimental observation in Figure 5. The structure in Figure 6 was obtained from the annealing condition described in Figure 1b. For this more complex case,
an analytical solution of temperature field would be difficult to obtain, but a 2-D distribution of phase size can be clearly seen in the experimental phase structure. The largest pores were present right at the corner, where the highest temperature, close to the hot platen temperature, was expected. Away from the corner, the pore size decreased along both edges with a relatively large gradient in pore size. This again can be qualitatively related to the unique temperature distribution in the vicinity of the corner in this annealing experiment. Similarly, the gradient structure shown in Figure 7 can be correlated with the unique temperature field resulting from the annealing setup in Figure 1c. The high-temperature pin attached to the hot platen gave rise to a negative temperature gradient in the radial direction. This, in turn, resulted in the decrease in the coarsening rate in the radial direction and, consequently, a radial gradient structure. The porosity and interconnectivity of pores in the above porous structures were evaluated by weighing the samples before and after solvent extraction of the sacrificial phase. The results showed that nearly 100% PS was removed after solvent extraction, indicating that interconnected pores were presented in the gradient porous structure.

Figure 5. Gradient porous structure from 1-D thermal gradient: (a) overall structure, (b) cross-sectional structure at location A, (C) cross-sectional structure at location B, and (d) cross-sectional structure at location C.

Figure 6. Pore gradient in two directions around an exterior corner.

Figure 7. Gradient of pore size toward a center hole.
Conclusions

This exploratory study demonstrated the feasibility of producing gradient porous structures via controllable nonisothermal annealing of immiscible polymer blends under designed thermal boundary conditions. With a model blend of PLA and PS, three types of gradient porous structure were created, each resulting from a unique temperature field incorporated in the annealing setup. The pore size resulting from these annealing experiments varied from several microns to several hundreds of microns, distributed in the space, and interconnected through a cocontinuous structure. The unique gradient in pore size in each case was correlated with the unique temperature field developed in each special annealing setup. A positive temperature gradient resulted in a growth of pore size in this direction. With further understanding of this novel process in a more quantitative manner involving parametric experiments and modeling of the thermal and two-phase flow problem, more complex porous structures with designed gradient in pore size can be produced.

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Supporting Information Available. An additional section on concept development for gradient porous structure is provided, with a figure illustrating gradient porous structures created from different thermal gradients: (a) thermal gradient in one direction, (b) thermal gradient in two directions, (c) converging thermal gradient in a 2-D square domain, (d) converging thermal gradient in an axisymmetric domain, (e) diverging thermal gradient in an axisymmetric domain, and (f) spatially distributed thermal gradient. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(2) Kumar, V. Cell. Polym. 1993, 12, 207–223.