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Controllable Growth of Gradient Structures for Biomedical Applications

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ABSTRACT Co-continuous phase structures of immiscible polymers can be developed under appropriate melt-blending conditions. Because of the presence of interfacial tension, such co-continuous structures start to coarsen when heated to a temperature higher than the melting/softening temperature of both phases. In this article, a systemic study of controllable growth of gradient porous structures utilizing variable coarsening rates in either a gradient temperature field or a gradient shear field is presented. Based on experimental results, the gradient of shear viscosity is identified as the mechanism for generating variable coarsening rates inside a co-continuous blend. By controllable variation of the shear viscosity distribution in a 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. A poly (lactic acid) (PLA)/polystyrene (PS) 50/50 wt% blend was used as a model system. By designing proper thermal and/or dynamic boundary conditions and introducing different thermal/shear rate gradients during annealing, several gradient porous structures of PLA were created.

INTRODUCTION
Nature is an excellent producer of multifunctional porous materials, e.g., wood, plant seeds, egg shell, bone, skin, etc. 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 pore 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 polymers [2]–[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 100 nm to a couple of microns.[1],[5] 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 natural materials exemplify the unique capabilities of GPSs, particularly the ability to integrate different functions, often contradictory, and achieve an optimized design. The incorporation of GPSs in synthetic materials may lead to the creation of new functional materials for many innovative applications. In fact, a number of authors have already discussed the potential use of gradient porous structures for selective applications, including porous bearing,[1] tissue engineering scaffolds,[6],[7] medical implants,[8]–[10] graded membranes for enhanced filtration,[11]–[13] graded porous beams for structural applications,[14] and functional coating materials.[15] However, very few techniques have been reported on the fabrication of synthetic materials with GPSs. Kinemuchi et al.[16] disclosed a centrifugal sintering process for creating grading porous ceramics. The grading porosity is caused by enhanced sintering using centrifugal force, which increases linearly along the radius of rotation. Centrifugal forces were also used in casting processes with powder-liquid suspensions. In particular, Biesheuvel and coworkers[11],[17],[18] incorporated centrifugal forces in ceramic suspension casting and created a graded porosity along the radius of rotation. Harley et al.[7] used a similar technique to cast collagen suspension in acetic acid under spinning conditions and formed a graded porosity along the spinning radius. Compared with centrifugal processing, layered approaches received more attentions.[6],[8],[10],[13]–[15] Placement of layers with different porosity can be carried out by coating/deposition processes[13]–[15] or by layered stereolithographic methods.[8] The materials used in these processes can be powders with variable sizes,[10],[13] fibers with different diameters and spacing,[6] or other layered materials with variable pore sizes.

The above known techniques for creating GPSs, however, typically have a low resolution,

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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 article, a systemic study of controllable growth of gradient porous structures utilizing variable coarsening rates in either a gradient temperature field or a gradient shear field was presented. Based on experimental results, the gradient of shear viscosity was identified as the mechanism for generating variable coarsening. By controllable variation of the shear viscosity 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

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.

Annealing with temperature gradient
In this exploratory study, a specific thermal boundary condition was used to generate a temperature gradient during annealing, as shown in Figure 1. In this case, a temperature difference is imposed between an upper and a lower platens, between which a polymer blend is annealed. This annealing experiment was conducted on a hydraulic press with heated platens. 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 in order to minimize the lateral out-squeeze.
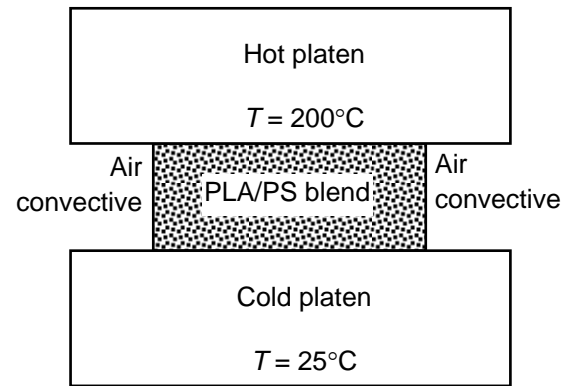

**Figure 1.** *Thermal boundary conditions for creation of 1-D thermal gradients.*

Annealing with shear gradient
A parallel-plate rotational rheometer (Model: AR2000EX, TA Instruments), running at small-strain oscillation mode, was used in this study to form a shear rate gradient inside the PLA/PS blend. The shear rate varied from zero, at the center, to the maximum, at the edge of the disc; the value of shear rate followed a linear relationship with the radial distance. This made the shear rate gradient directly proportional to the imposed angular frequency at 100 rad/s. A uniform processing temperature, 200°C, was used in this experiment. The gap distance between the two plates was set at 1 mm. After the annealing process, the sample was cooled down to the room temperature with a cooling rate of 10°C/min.

RESULTS AND DISCUSSIONS
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 180°C and 200°C. Using the well-known Cox-Merz rule[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.[20],[21] Second, the annealing 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.[22],[23] From Figure 2, it is seen that the zero-shear viscosity for both PLA and PS is sensitive to temperature changes. This strong dependency on temperature indicates that the phase size coarsening

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rate can be effectively varied by applying a relatively small temperature gradient during annealing and this prediction matches the experimental observation presented in Figure 3.
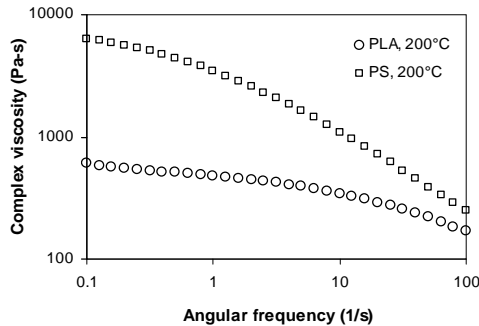
(a)
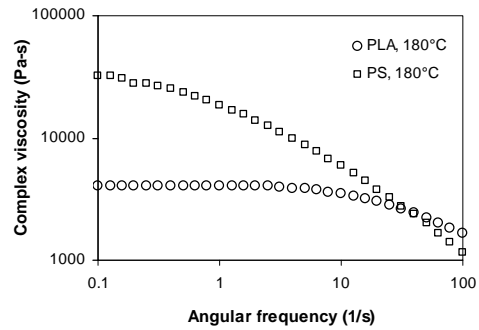
(b)

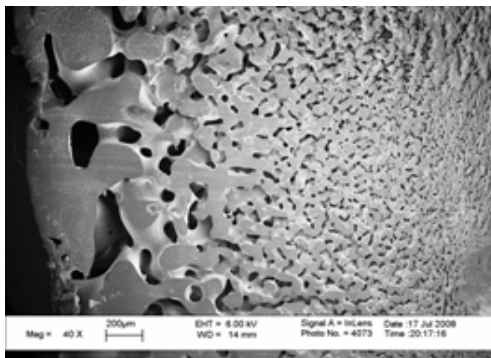*Figure 2. Complex viscosity of PLA and PS at different temperatures: (a) 200°C and (b) 180°C.*
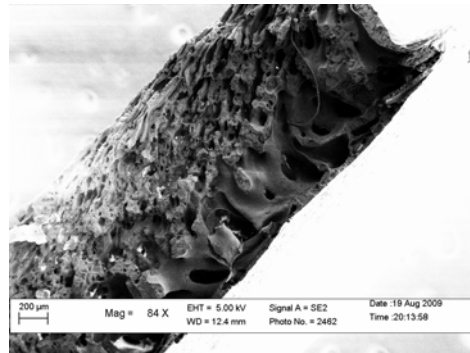

Figure 3. Gradient porous structure from 1-D thermal gradient.

Similarly, viscosity gradient can be generated at the existence of a shear rate gradient. In this study, a parallel-plate rotational rheometer was used to apply a shear rate gradient in the radial direction at 200°C. Based on the assumption that the viscosity at the annealing step determines the coarsening rate, this variable shear field induced viscosity gradient
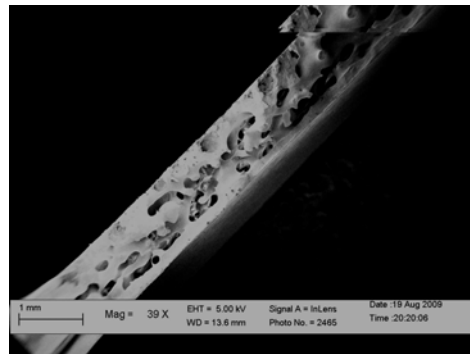
should result in an axisymmetric gradient porous structure, which is supported by SEM images in Figure 4.
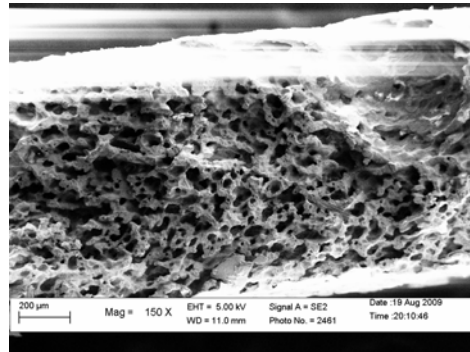
(a)

(b)

(c)

Figure 4. Gradient shear field induced gradient porous structure prepared at 200°C and 100 rad/s: (a) at the disc center; (b) in middle; (c) at the edge.

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