

# Periodic porous stripe patterning in a polymer blend film induced by phase separation during spin-casting

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## **Introduction**

Preparation of porous material using phase separation has attracted attention due to its application versatility [1]. The phase separation of immiscible polymers induced by evaporating solvents (ex. solvent casting) has been extensively studied for fabricating such porous materials. It has been known that the morphologies created by the phase separation in the thin film are changed with the processing schemes such as drops coating, dip coating, and spin coating. This study shows that a periodic striping pattern with micro-scale pore size could be created on the surface of the thin films by spin-casting a polystyrene (PS) and polyethylene glycol (PEG) blend solution. The effects of the drying rate, rotation speed of spin coating, and molecular weight of polymer on the formation of the periodic porous striping pattern are discussed.

## **Results and discussion**

A single phase solution of PS ( $M_w=222,000$ ) and PEG 200 ( $M_w=200$ ) at a ratio of 70/30 in a 90 wt% benzene solvent was cast on a glass slide and immediately spin-coated at the 3000 rotation speed. SEM micrographs were taken at the edge of the coated film. Figure 1 shows SEM micrographs of the surface of the resulting PS/PEG films. As shown in Figure 1 (b), a periodic porous stripe pattern, which consists of lines of fine pores in single micron sizes (Figure 1 (a)) and the solid regions (Figure 1 (c)), was

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prepared.

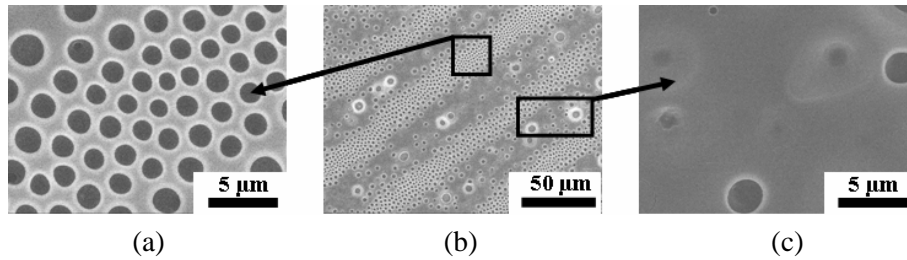


Figure 1. SEM micrographs of PS/PEG 200 (70/30) (w/w) film made from 90 wt % benzene solution: (a) the porous region, (b) the periodic porous stripe pattern, (c) the solid region.

The formation mechanism of the periodic porous striping patterns was speculated as follows: the formation of the periodic porous striping patterns consists of the two steps. The first step is the formation of the periodic hill-and-valley pattern on the film surface. At the initial stage of the spin casting, the solution flows on to the substrate in a radial direction due to the centrifugal force. Solvent evaporates from the surface and induces a temperature gradient between the surface and the bottom of the cast solution. The formation of the hill-and-valley pattern is caused by the regular surface undulations created by convection rolls [2, 3]. In the second step, solvent evaporation induces phase separation twice in the PS/PEG/solvent ternary solution [4]. The first phase separation occurs with the precipitation of PEG droplets from the solution. Due to the solvent-evaporation-induced convection as well as the higher drying rate on the hills, the PEG-rich domains (droplets) flowed preferentially to hills. The secondary phase separation then occurred in the PEG droplet, which formed solvent-rich and PEG-rich domains. Further solvent evaporation created a cavity in a PEG droplet

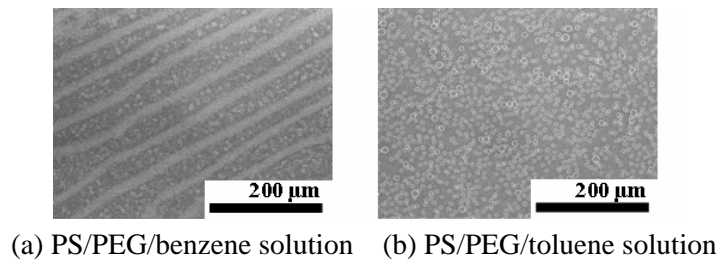


Figure 2 SEM micrographs of PS/PEG 200 (70/30) (w/w) film made from 90 wt % (a) benzene solution and (b) toluene solution.

In order to confirm the mechanism, we performed several experiments with different drying rates and rotation speeds. Figure 2 shows the comparison of the surface morphologies between PS/PEG films prepared from two different solvents, benzene and toluene. In the case of the toluene solution, the periodic striping pattern did not appear on the surface. The vapor pressure of toluene is lower than that of benzene. The lower vapor pressure made the drying rate lower and the convection roll weaker. The convection was established by thermo-capillary effect. The higher drying rate made the liquid surface cooler because of the latent heat removal. The larger temperature difference enhanced the hill-and-valley formation. The temperature gradient in the toluene solution was small due to the lower evaporation rate and thus the convection was suppressed in the toluene system as shown in Figure 2 (b).

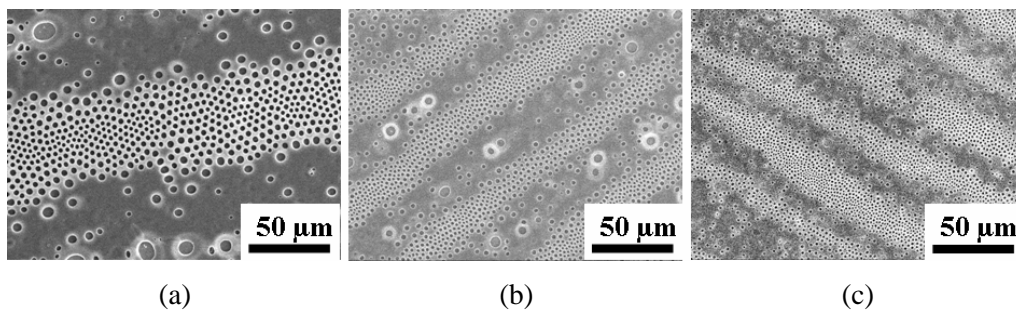


Figure 3 SEM micrographs of PS/PEG 200 (70/30) (w/w) film made from 90 wt % benzene solution; (a) 500, (b) 3000, (c) 8000 rpm.

Figure 3 shows SEM micrographs of the film surface made at three different rotation speeds (500, 3000, 8000 rpm). As shown in Figure 3, the width of the porous line decreased with the increase of rotation speed and the line boundary became unclear at 8000rpm (Figure 3 (c)). The rotation speed directly affected the thickness of the film. When the film became thinner due to the higher rotation speed, the decrease in film thickness tended to make the temperature in the solution uniform. Therefore, the convection roll was not enhanced and the width of the line was reduced.

To see the effect of the molecular weight on the pattern, two different molecular weights of PEG ( $M_w = 200$  and  $2000$ ) were individually blended with PS at a weight ratio 90/10 and used for preparing the film. In the experiments, the polymer concentration was set to 10 wt % and the rotation speed was kept

at 3000 rpm. Figure 4 shows SEM micrographs of the film surface

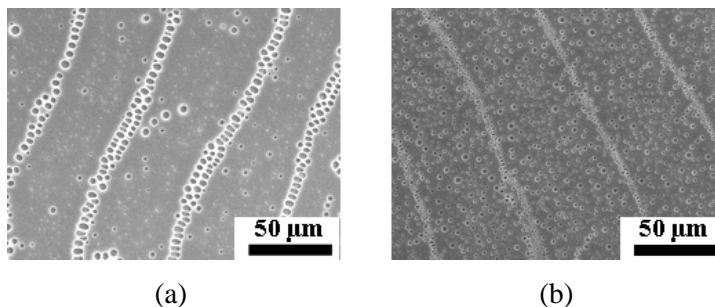


Figure 4 SEM micrographs of PS/PEG 200 (90/10) (w/w) film made from 90 wt % benzene solution; (a) PEG 200, (b) PEG 2000.

As shown in Figure 4, the pore size as well as the width of porous line was changed by the PEG molecular weight. Particularly, the density of pores between the porous stripe lines increased as shown in Figure 4 (b). The increase of molecular weight of PEG increased the viscosity in the system. High viscosity of solution suppressed the convection. As a result, there is not enough time for the PEG-domains (droplets) to move toward the hills. Moreover, the mobility of high molecular weight of the polymer is lower and it could be retarded by the higher polymer chain entanglement [5]. Those two effects suppressed the coalescence of the PEG-droplets after the first phase separation and stopped the convection before all PEG droplets moved to hills. Therefore, PEG-rich domains formed not only at hill but also at valley but the pore size was reduced by suppressing the coalescence as shown in Figure 4 (b).

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