

# A Facile Route To Create Surface Porous Polymer Films via Phase Separation for Antireflection Applications

Cheng-Yu Kuo, Yen-Yi Chen, and Shih-Yuan Lu\*

Department of Chemical Engineering, National Tsing-Hua University, Hsin-Chu 30013, Taiwan, Republic of China

**ABSTRACT** A facile route was developed to create surface porous polystyrene/poly(vinylpyrrolidone) (PS/PVP) films, via phase separation in a dip-coating process, for antireflection applications. The film thickness, pore size, and pore depth of the product films can be effectively adjusted with the concentration of the PS/PVP (volume ratio of 7:3) solution and withdrawal speed. At an optimal concentration of 0.6 wt % and withdrawal speed of 19 cm/min, the product films had an average thickness of 125 nm, a pore size of 156 nm, and a pore depth of 20 nm, giving a percent transmittance increase of 3–4 % over the bare glass. Further removal of the PVP phase, which was concentrated at the pore bottom, with water etching deepened the pore depth to 37 nm, thus boosting the percent transmittance for another 0.5 %.

**KEYWORDS:** surface porous • antireflection • dip coating • phase separation

## INTRODUCTION

Porous polymer films have attracted much research attention in recent years because of their potential applications in a wide range of areas such as photonic crystals (1), cell cultivation (2), growth templates (3), and antireflection layers (4). To prepare these porous polymer films, a number of methods have been developed from which three major approaches may be identified: water droplet template (4, 5), phase separation with possible selective phase removal (6), and self-assembly of block copolymers (7). In the water droplet template systems, water droplets condense onto the polymer solution surface because of the cooling effect induced by evaporation of the solvent. The condensed water droplets pack into a hexagonal array and sink into the solidifying polymer film. Porous polymer films result when the water evaporates, leaving behind the void space. This process has been studied in depth with respect to several critical operating conditions, including the polymer solution concentration (5d), humidity level (5c), hydrophilicity of the substrate (5a), moisture flow (4), and solvent density (5b). In contrast to the water droplet template process, in which a high humidity or controlled water addition is required, immiscible polymer blends or nonsolvent-containing homopolymer solutions would undergo phase separation when a critical polymer or nonsolvent concentration is reached, respectively, during solvent evaporation. Porous polymer films are obtained when one phase of the phase-separated blends is removed with selective solvent etching (6a, 6d) or when the nonsolvent evaporates from the nonsolvent-containing phase (6b, 6c). For the

third approach, voids are generated from the packing of block copolymer micelles (7a) or the selective block removal of self-assembled diblock copolymers (7b).

Most of the above-mentioned methods created films with a spin-coating procedure, which suffers from the drawbacks of inefficient use of raw materials and limitations to flat substrates. In this article, we reported a facile dip-coating process for the production of surface porous polymer films for antireflection applications. As compared with spin-coating processes, dip-coating processes possess the apparent advantages of making efficient use of raw materials, being workable for curved substrates, and being able to create double-sided coatings in one step if so desired. To create the surface pores necessary to reduce the effective refractive index of the films for antireflection purposes, two immiscible polymers, hydrophobic polystyrene (PS) and hydrophilic poly(vinylpyrrolidone) (PVP) at a volume ratio of 7:3, were dissolved in a neutral solvent, chloroform, for the dip-coating operation. These two polymers phase-separated during the withdrawal step because of solvent evaporation. Interestingly, shallow surface pores formed from the phase separation, with the PVP phase concentrated at the bottom of the pores and the PS phase serving as the continuous phase. The present dip-coating process created surface pores without the need for selective phase etching, as is often required for phase-separation-based approaches, and the use of costly block copolymers. Furthermore, the present dip-coating process worked at a low relative humidity of 40 %, without the need for a high-humidity environment or the controlled addition of water, as is required for the water droplet template approach. This advantage makes the present process applicable in practical manufacturing.

The film thickness, pore size, and pore depth of the product films can be effectively adjusted with the concentration of the PS/PVP solution and withdrawal speed, to meet

\* Corresponding author. Fax: +886-3-571-5408. E-mail: sylu@mx.nthu.edu.tw.

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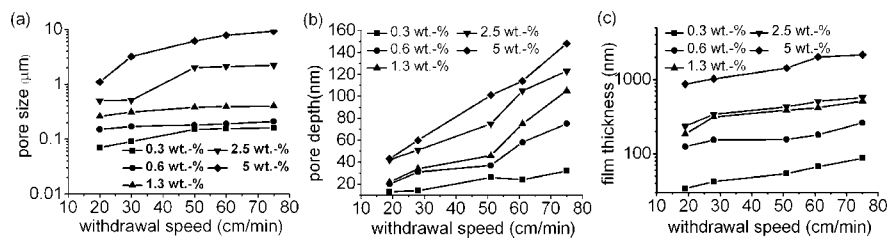


FIGURE 1. (a) Pore size, (b) pore depth, and (c) film thickness as a function of the withdrawal speed, with the concentration of the polymer solution as the variable parameter.

the basic requirements of an antireflection film such as a film thickness of a quarter of the visible wavelengths for the destructive interference of reflected lights, reduced effective refractive indices intermediate of those of the air and substrate to suppress reflections, and the lack of structural features of characteristic size comparable to or larger than the visible wavelengths to avoid visible light scattering (6a).

## EXPERIMENTAL SECTION

PS (MW of  $2.5 \times 10^5$ ) and PVP (MW of  $5.8 \times 10^4$ ) were dissolved in chloroform separately at concentrations of 0.3, 0.6, 1.3, 2.5, and 5 wt % and then mixed together at a volume ratio of 7:3 (PS/PVP). The slide glass ( $7.3 \times 1.3$  cm) was cleaned by immersion in a piranha solution ( $\text{H}_2\text{O}_4/\text{H}_2\text{O}_2$  of 3:1 in volume) for 20 min, followed by rinsing with deionized water and drying under a nitrogen flow. The cleaned slide glass was hydrophilic and was made hydrophobic by further immersion in a hexane solution containing 6% (w/w) trimethylchlorosilane for 1 h, followed by rinsing with hexane and drying under a nitrogen flow. The treated slide glass was vertically immersed into the PS/PVP mixture solution and then withdrawn at a controlled speed (19, 28, 51, 61, and 75 cm/min) in a dip coater. The relative humidity of the operation environment was maintained at a relatively low level of around 40% by operations in air-conditioned space. The morphology and pore size of the resulting films were observed with an optical microscope (Olympus BH2-UWA) in transmission mode and a field emission scanning electron microscope (JEOL JSM-6700) operated at 3 kV. The transmittance spectra of the films were recorded using a CCD array spectrometer with a resolution of 0.5 nm. The pore depths and film thicknesses of the product films were measured with an atomic force microscope (Digital Instrument Inc. Nanoscope E) in contact mode and an  $\alpha$ -step surface profiler, respectively.

## RESULTS AND DISCUSSION

The concentration of the polymer solution and withdrawal speed are two processing parameters that can be easily adjusted in a dip-coating process. We studied the effects of these two processing parameters on the structural parameters of the product films to find optimal operation conditions for the production of films suitable for antireflection applications. Figure 1 shows how the concentration and withdrawal speed affected the thickness, pore size, and pore depth of the product films. A general trend was observed from Figure 1. The thickness, pore size, and pore depth all increased with increasing concentration and withdrawal speed. For film thicknesses, it has been theoretically studied that the film thickness increases with increasing capillary number of the system (8). Here, the capillary number is defined as  $\mu U/\sigma$ , in which  $\mu$ ,  $\sigma$ , and  $U$  denote the dynamic viscosity and surface tension of the solution and withdrawal

speed, respectively. For the present work, the surface tensions of the polymer solutions remained close to that of the solvent, chloroform, of 27 mN/m, only decreasing slightly with increasing concentration from 26.2 mN/m of 0.3 wt % to 25.5 mN/m of 5 wt %. The viscosity, however, increased quite pronouncedly with increasing concentration from  $7.13 \times 10^{-4}$  Pa  $\cdot$  s of 0.30 wt % to  $1.01 \times 10^{-2}$  Pa  $\cdot$  s of 5 wt %. Consequently, the capillary number and thus the film thickness increased with increasing concentration and withdrawal speed.

For antireflection applications, the film should have a thickness of a quarter of the visible wavelengths, 100–175 nm, to enhance destructive interferences of the reflected lights and a lack of structural features of characteristic size comparable to or larger than the visible wavelengths to avoid visible light scattering. With these two requirements in mind, one can readily identify a suitable polymer concentration of 0.6 wt % from Figure 1. At this concentration, the film thickness can be controlled to within 100–175 nm with slower withdrawal speeds (19, 28, and 51 cm/min). The average pore sizes obtained at this concentration were 156, 180, and 184 nm for withdrawal speeds of 19, 28, and 51 cm/min, respectively. On the other hand, the corresponding average pore depths increased from 20 to 31 to 37 nm when the withdrawal speed increased from 19 to 28 to 51 cm/min. Basically, smaller pore sizes are beneficial for suppressing visible light scattering, while deeper pores give smaller effective refractive indices favoring antireflection. Consequently, the effects of the pore size and pore depth competed with each other for the present case with increasing withdrawal speed. Films produced from all three withdrawal speeds at a concentration of 0.6 wt %, when coated on glass, showed better transmittance than the bare glass, with that from the speed of 19 cm/min giving the best transmittance, 3–4% over the bare glass. Films from all other processing conditions investigated in this work did not improve on the transmittance of glass. In fact, films with large pore sizes even appeared white because of the severe light scattering, and films with large thicknesses turned opaque from the intensive light absorption.

Parts a–c of Figure 2 show the optical images of polymer films produced using a polymer solution of 5 wt % at withdrawal speeds of 5, 19, and 61 cm/min, respectively. The circles appearing on the images are, in fact, shallow surface pores. The inset of Figure 2a is an AFM image of the film obtained at a withdrawal speed of 5 cm/min, showing a typical surface pore structure. The film morphology changed

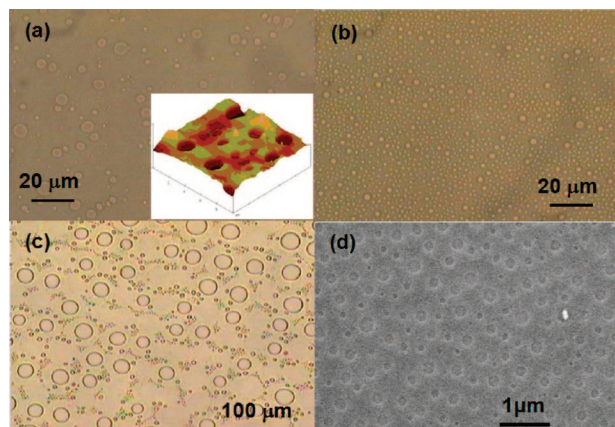


FIGURE 2. Optical images of the polymer films produced from polymer solutions of 5 wt % with withdrawal speeds of (a) 5, (b) 19, and (c) 61 cm/min. (d) SEM image of the polymer film produced from a polymer solution of 0.6 wt % with a withdrawal speed of 19 cm/min. The inset of part a is the corresponding AFM image of the film, showing the surface pores of submicron to micron meter size.

quite drastically with the withdrawal speed at a concentration of 5 wt %. Sparsely distributed surface pores were found for a withdrawal speed of 5 cm/min (Figure 2a). The surface pores became densely populated with a relatively more uniform pore size distribution when the withdrawal speed was increased to 19 cm/min (Figure 2b). The pore size distribution, however, turned bimodal, with the larger pores surrounded by much smaller pores, when the withdrawal speed was further increased to 61 cm/min (Figure 2c).

The drastic morphology difference in surface pores achieved with the withdrawal speed adjustment may be roughly explained based on the competition between drying and phase separation during solvent evaporation at different withdrawal speeds. At a low withdrawal speed, the formed liquid film was thin and dried quickly, leaving not enough time for the polymers to proceed with a complete phase separation for surface pore generation. Consequently, sparsely distributed surface pores resulted. As the withdrawal speed was increased, the liquid film became thicker and it took a longer time to dry the film, giving enough time for the phase separation to go to completion for generation of densely populated surface pores. In fact, once these surface pores were created from phase separation, they would also start to proceed with coagulation growth. The surface pores of Figure 2b, although in a relatively more uniform distribution, were observed to have some larger pores. If the withdrawal speed was further increased, even thicker liquid films were produced and there existed even more time for pore formation and growth. The consequence of more intensive pore growth was evident from Figure 2c, exhibiting an apparent bimodal pore size distribution typical for simultaneous nucleation and coagulation growth.

The effect of the withdrawal speed on the surface pore morphology was much reduced for very dilute polymer solutions, less than 1.3 wt % for the present work. For example, for a concentration of 0.6 wt %, the surface pore morphology of the resulting film did not change much with increasing withdrawal speed. As an illustration, Figure 2d shows a typical film morphology for a withdrawal speed of

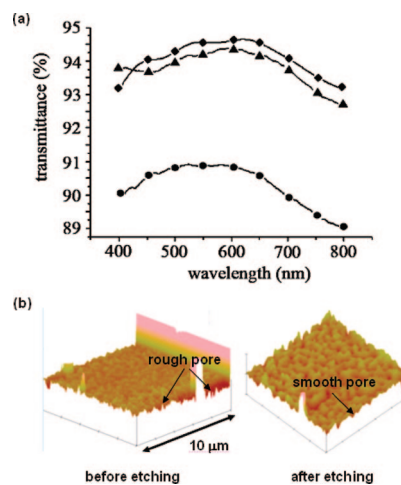


FIGURE 3. (a) Transmittance curves of the bare glass (●), glass coated with a PS/PVP film (▲), and glass coated with a PS/PVP film with the PVP phase removed (◆). (b) AFM images of the films before and after the PVP etching. The PVP/PS film was produced from a polymer solution of 0.6 wt % at a withdrawal speed of 19 cm/min.

19 cm/min. Basically, for dilute polymer solutions, the drying time would be long enough to avoid situations like those in Figure 2a and the pore density would not be large enough to experience severe coagulation growth like that presented in Fig. 2c. Consequently, the resulting surface pores would be moderately spaced and uniformly distributed as shown in Figure 2d.

Figure 3a shows the transmittance curves of three glass samples in the optical wavelength regime. The glass coated with a layer of the PS/PVP film, produced from a 0.6 wt % solution at 19 cm/min, showed better transmittances, 3–4 % more, than the bare glass, demonstrating the improvement in antireflection. To increase the porosity of the film for further reduction in the effective refractive index for better antireflection performance, we immersed the PS/PVP film in water to remove the exposed water-soluble PVP phase. After the water etching, the pore size of the film remained unchanged, but the pore depth was deepened from an average of 20 to 37 nm, implying that the PVP phase was concentrated at the bottom of the pores. The resulting transmittance, as shown in Figure 3a, was improved further by another 0.5 % in the optical regime. Figure 3b shows the AFM images of the films produced from a 0.6 wt % solution at 19 cm/min, before and after the PVP etching. The shallow surface pore structure can be observed from the edges of the graphs. After the PVP etching, the pore structure became more pronounced and the pore surface became smoother.

The transmittance improvement achieved by the films produced from the present dip-coating process was only moderate, as compared with films produced from more elaborate processes. First, the pore size of 100+ nm would still cause some extent of light scattering, limiting the transmittance improvement of the films. Second, the surface pores generated on the films were relatively shallow, as can be seen from a comparison of the average pore depth to the average film thickness (Figure 1b,c), and thus further limited the transmittance improvement. The surface pores, although deepened after the PVP etching, still remained shallow,

leading to limited increases in the film porosity and thus limited transmittance improvement with the PVP etching. The present work, however, demonstrated a facile process for the generation of surface porous films, based on which product performances can be continuously improved with further investigations.

## CONCLUSIONS

A facile dip-coating process was developed to prepare surface porous polymer films from the phase separation of two immiscible polymers, induced by solvent evaporation. With suitable adjustment of the solution concentration and withdrawal speed, the film thickness can be controlled to fall within a quarter of the optical wavelengths while maintaining the pore sizes to be much smaller than the optical wavelengths. Such surface porous films, showing good transmittance improvement when applied on glass, 3–4% over the bare glass, are good candidates for antireflection applications.

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