



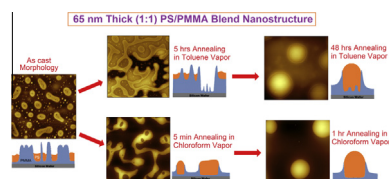
# Self-organized morphological evolution and dewetting in solvent vapor annealing of spin coated polymer blend nanostructures



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## GRAPHICAL ABSTRACT



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## ABSTRACT

**Hypothesis:** Dewetting pathways, kinetics and morphologies of thin films of phase separating polymer blends are governed by the relative mobilities of the two components.

**Experiments:** We characterize the morphological transformations of the nanostructures of a PS/PMMA blend by annealing in toluene and chloroform vapors. Toluene leads to faster reorganization of PS, whereas chloroform engenders the opposite effect.

**Findings:** Spin coating produces a very rough PMMA rich layer that completely wets the substrate and forms a plethora of slender columns protruding through the continuous PS rich layer on top. The nanostructures were stable under long thermal annealing but in the vapor annealing, phase separation and dewetting occurred readily to form the equilibrium structures of dewetted droplets of PS on top of PMMA which also climbed around the PS droplets to form rims. Toluene and chloroform annealing required around 50 h and 1 h respectively to attain the equilibrium. Substantial differences are observed in the intermediate morphologies (heights of nanostructures, roughness and size). PMMA columns remained embedded in the dewetted PS droplets, whereas a high mobility of PMMA in chloroform allowed its rapid evacuation during dewetting to produce an intermediate swiss-cheese like morphology of PS domains.

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**Abbreviations:** PS, Polystyrene; PMMA, Poly (methyl methacrylate);  $\chi$ , Flory–Huggins interaction parameter;  $\chi_{p-s}$ , polymer–solvent interaction parameter;  $\delta$ , Hildebrand solubility parameter;  $V_S$ , molar volume of the solvents;  $R$ , the universal gas constant;  $T$ , temperature;  $\delta_s$ , solubility parameter of the solvent;  $\delta_p$ , solubility parameter of the polymer;  $T_g$ , glass transition temperature;  $\rho_T$ , density of toluene;  $\rho_C$ , density of chloroform;  $A_{\text{eff}}$ , effective Hamaker constant;  $\gamma_{\text{PS}}$ , surface energy of PS;  $\gamma_{\text{PMMA}}$ , surface energy of PMMA;  $\gamma_{\text{PMMA-PS}}$ , PMMA/PS interfacial tension;  $H_R$ , rim height;  $\text{PS}_{\text{area}\%}$ , percentage area covered by PS.

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## 1. Introduction

Polymer blend thin films have been studied the last few decades as they have a plethora of potential applications in organic light emitting diodes [1,2], antireflection coatings [3], photovoltaic devices [4–6], semiconductors for organic thin film transistors [7], etc. In all these applications phase separation of polymer blend thin films have been utilized for the fabrication of wide variety of structured surfaces. When two immiscible polymers are used for the preparation of blend thin films via spin coating, phase separation occurs because of low entropy of mixing of the two dissimilar poly-

mer chains, different solubility of the polymers in the solvent, and enhanced concentrations of the components during the rapid evaporation of the solvent [8]. Phase separation and dewetting occurring during the spin coating of the polymer blend thin films already produce a variety of structures depending on the composition and molecular weight of the constituent polymers, properties of solvent, film thickness, the nature of the substrate, and spin coating condition (spin speed, acceleration, and atmosphere) [8–18]. However, due to rapid evaporation of the solvents during spin coating and relatively slow kinetics of phase separation/dewetting, the resulting structures are far from equilibrium [19]. Thus, further annealing of the film after spin coating is necessary to induce the polymer mobility allowing progress of the arrested nanostructures to the equilibrium configurations. It is known that the competition between wetting/dewetting during thermal annealing of a blend film produces a variety of useful structures such as bilayer [20], foam-like or bicontinuous morphologies [21], or layer inversion of the constituent polymers [19]. Interestingly, even thin films of miscible PMMA/SAN blend that are smooth after spin coating can undergo substrate induced phase separation by thermal annealing [22–25]. The situation with immiscible blend films is more complex, such as in the annealing of PS/PMMA blend structures obtained by spin coating [21,26,27,28,29]. However, in these studies, the focus was on understanding the evolution of thermally annealed post-spin coated relatively low molecular weight structures [21,26,27,28,29] where the annealing temperature was well above the glass transition temperature of both the constituent polymers.

Recently Li and co-workers have shown the phase separation and dewetting of initially smooth miscible PMMA/SAN blend films by solvent vapor annealing using acetic acid, which is a selective solvent for PMMA and 1,2-dichloroethane, which is a common solvent [30,31]. Bi and Yeow annealed immiscible PS/P2VP blend film in the chloroform vapor and demonstrated dewetting in the blend thin film triggered by nucleation mechanism [32].

As discussed above, during spin coating, immiscible polymer blends develop into partially phase separated and dewetted nanostructures. Most of the previous studies have addressed the evolution of these structures by thermal annealing. In this study, we systematically investigate the phase separation, dewetting, and morphological evolution of spin coated PS/PMMA blend nanostructures by solvent vapor annealing using two different solvents, *i.e.* toluene and chloroform. The objective is to study the role of polymer mobility in the structure evolution in the blend thin films. Interestingly, even the long time thermal annealing in the immiscible high molecular weight PS/PMMA blends studied here is found to be ineffective owing to low mobilities (slow kinetics of phase separation and dewetting). The solvent vapor annealing not only greatly enhances the chain mobility, but can also alter the wettability of the structures rather profoundly by the introduction of a new component (solvent) which can for example, segregate at the substrate–polymer interface and introduce further destabilizing interactions [33]. The solvent vapors chosen here, toluene and chloroform, are both common solvents for PS and PMMA. The spin coating of the blend was performed in toluene solution. Thus, the use of toluene vapor for annealing indicates the direction in which the structures may have had the propensity to evolve if the toluene solvent had not evaporated completely.

The interaction or affinity between a polymer and its solvent is indicated by the Flory–Huggins interaction parameter (also known as  $\chi$  parameter). The polymer–solvent interaction parameter ( $\chi_{p-s}$ ) is related to the Hildebrand solubility parameters ( $\delta$ ; square root of the cohesive energy density, *i.e.*, energy of vaporization per unit volume) of the polymer and the solvent:

$$\chi_{p-s} = \frac{V_s}{RT} (\delta_s - \delta_p)^2 + 0.34 \quad (1)$$

where  $V_s$  is the molar volume of the solvents,  $R$  is the universal gas constant,  $T$  is the temperature, and  $\delta_s$  and  $\delta_p$  are the solubility parameters of the solvent and the polymer respectively [34,35]. The lower values of  $\chi$  imply higher interaction and mobility of the polymer chains. In our system  $\delta$  values for PS, PMMA, toluene, and chloroform are 18.6, 19.2, 18.2, and 19 MPa<sup>1/2</sup> respectively [34,36]. Thus, based on the values of  $\chi_{p-s}$ , PS has higher interaction and mobility in toluene compared to PMMA, whereas PMMA has higher interaction with chloroform during the respective solvent vapor annealing. Contrasting the behavior in the two solvents can thus help understand the role of PS and PMMA mobilities and solvent modification on the morphological transformations and spatial phase distributions. We show that both the kinetics and the morphologies of the phase separated intermediate nanostructures are very distinct in the two vapors.

## 2. Materials and methods

### 2.1. Materials

PS and PMMA of molecular weight (Mw) 280,000 g/mol and 350,000 g/mol with narrow molecular weight distribution were chosen for the studying of the influence of solvents on annealing of PS/PMMA blend. The polymers were obtained from Sigma Aldrich and were used without any further purification. The glass transition temperature ( $T_g$ ) of PS and PMMA are 100 °C and 105 °C respectively as provided by the supplier. Toluene (Merck, HPLC grade), chloroform (Merck, HPLC grade), cyclohexane (Merck, HPLC grade), acetic acid (Merck, HPLC grade) were purchased and used as received. Thoroughly cleaned silicon wafers (100, Wafer World, USA) with a native oxide layer were used as substrates.

### 2.2. Preparation of PS/PMMA blend thin films

The polymer blend solution was prepared by dissolving 1:1 wt/wt PS and PMMA in toluene so that the resulting concentration of the solution became 1%. The blend of PS/PMMA on silicon wafer substrates (size 15 mm × 15 mm) were prepared by spin coating ~200  $\mu$ l solution (filtered with 0.2  $\mu$ m PTFE microfilter) at 3000 rpm for 1 min. After spin coating, the samples were dried in the vacuum oven for 6 h at 60 °C (well below the glass transition temperature of both the polymers) in order to remove the residual toluene.

### 2.3. Annealing of PS/PMMA blend thin films

All the blend films were annealed at room temperature (~25 °C) in a closed sealed chamber (a covered glass desiccator) containing saturated vapor of toluene or chloroform. The chamber was filled with the vapor 2 h prior to annealing by placing a liquid source for the vapor. The blend film was placed at 1 cm above the level of the liquid solvent inside the chamber. After removing the blend films from the solvent vapor chamber, they were dried in the hot air oven at 60 °C for 1 h in order to remove any remnant solvent.

In order to compare the dewetting of PS/PMMA blend samples annealed in toluene or chloroform vapor with the thermal annealing, the spin coated blend samples were heated at 160 °C (well above the glass transition temperature of both the polymers) for 72 h in the vacuum oven.

### 2.4. Selective washing of blend samples

To distinguish between the PS and PMMA rich phases, the blends were washed with cyclohexane (selective solvent for PS) and acetic acid (selective solvent for PMMA) for 2 h.

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