



## The effects of concentrations of ZnO nanoparticles on dewetting suppression of PS thin films

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### Abstract

Thin polymer films are widely used in industry, such as protective coating, lubricant and electrical insulator, because of their specific properties. However, thin film in nanoscale tends to separate from substrate; this phenomenon is called Dewetting. In this research, a solution of polystyrenes with a concentration of 0.3 wt% in toluene, providing ~ 21 nm polymeric film, was prepared. Zinc-oxide nanoparticles were added in a polystyrene solution as a Dewetting inhibitor. The concentrations of zinc-oxide were varied from 0 – 1.0 wt%. Thin films were cast by a spin casting machine. After annealing at 90°C in a vacuum oven for various times, the film morphologies were studied by using optical, scanning electron, and atomic force microscopes. The surface energies of the films were calculated by contact angle measurement. We found that the addition of zinc-oxide nanoparticles at 0.3 wt% is an appropriate concentration to inhibit Dewetting in PS films which have a molecular weight of 35,000 g·mol<sup>-1</sup>.

## 1. Introduction

Dewetting behavior of thin films occurs by thermal fluctuations at the interface between air and film. After inducing by thermal or application, the continuous thin polymer film transfers to numerous droplets of polymer. When the relative surface and interface interactions favor minimization of the film's surface area, the phenomenon is initiated [1]. Dewetting behavior of thin polymer films will terminate significant properties of polymer which are required, such as resistivity [2]. Thus, the stability of polymer thin films is important for manufacturing and the performance of devices; for example, in organic electronics, photoresists, coatings, and adhesives [3-4]. As a result, many researchers have investigated the strategy to inhibit the dewetting behaviour. Improving the interaction between film-substrate by modification structure of polymer film or increasing entanglement in polymer film are the examples to avoid this problem [5].

In 2000, a group of researchers from The National Institute of Standards and Technology (NIST), Maryland found that the addition of C60 fullerene nanoparticles to the polymer solution can inhibit dewetting in thin polystyrene (PS) and polybutadiene (PB) films [6]. It was a remarkable exploration because this investigation contrasted with the basic knowledge that impure particles tend to promote dewetting in thin polymer films. The segregation of nanoparticles to the substrate which alters the interfacial interactions between the polymer-substrate and pins the contact lines of growing holes is a strategy to suppress dewetting [7,8]. In recent years, various inorganic nanoparticles have been used as additives to inhibit dewetting behaviour; such as silicon dioxide (SiO<sub>2</sub>) [9] and titanium dioxide (TiO<sub>2</sub>) [10].

Photocatalysis property, easy synthesis and low-cost growing method are the reasons promoting zinc oxide (ZnO) nanoparticles as a well-known inorganic nanoparticle in materials science [11]. Moreover, ZnO also has excellent chemical stability, nontoxicity,

and good electrical, optical, and piezoelectric properties.

Therefore, in this research, we are interested in using ZnO nanoparticles to improve the stability of thin polystyrene film. There are many factors associated with dewetting inhibition by adding nanoparticles technique. Concentration of nanoparticles also plays an important role in determining stability [12]. The correlation between nanoparticle's concentration, thickness, and molecular weight of polymer has been studied.

## 2. Experimental

Polystyrene (PS, MW = 35,000 g·mol<sup>-1</sup>) and zinc oxide nanoparticles (ZnO, diameter ≤ 20 nm) used as polymer matrix and additive were commercial grade. Concentration of mixed PS-ZnO solution was 0.3 wt% in toluene to control the thickness of about 21 nm. The ZnO suspensions were mixed with PS solution at the concentrations of 0, 0.1, 0.3, 0.5, 0.7 and 1.0 wt% which produced pure PS, PS-ZnO0.1, PS-ZnO0.3, PS-ZnO0.5, PS-ZnO0.7 and PS-ZnO1.0 composite film, respectively. Silicon wafers (1 cm x 1 cm) were used as a substrate. All Si substrates were cleaned by soaking in piranha acid at about 80°C for 1 h. After being rinsed with deionized water several times and dried by pressurized nitrogen gas, all Si surfaces showed a clean surface when observed with an optical microscope. Thin films of PS-ZnO in each condition were prepared by spin coating. Ultrasonicator bath was used to homogenize the mixtures. The spinning rate was kept constant at 1000 rpm for 10 s. After spin casting these solutions spread on Si wafers, all as-cast films were clean and continuously covered on the Si substrate. All spun-cast films were left overnight before annealing the films to initiate the Dewetting process.

The effects of temperature on surface morphology with varied ZnO concentrations were studied by annealing PS-ZnO films in a vacuum chamber. Dewetting behavior was initiated when heating in the oven at 90°C for different periods of time. Optical microscopy (Olympus, CX31) was used to study overall surface topographies of thin films. Scanning electron microscope (FEI, Quanta 250) was used to investigate local surface topographies. The films were scratched with a small needle and the depth profiles scanned and the thicknesses of thin films were explored by atomic force microscope (Bruker, SPA400). Dewetting

areas were calculated from topographic image. Surface energies of as-cast films were calculated by using the contact angles between film and water, film and diiodomethane and using the Owens and Wendt's method [13].

## 3. Results and discussion

After spin casting, all films were clean covering Si substrate. The samples were left at room temperature overnight. Two liquids, DI-water and diiodomethane were dropped on polymer surface and the contact angles between water-films and diiodomethane-films were considered. Then the surface energies of PS-ZnO films with varied concentration were calculated. By using Owens and Wendt's method, the surface energies were considered, as shown in Figure 1. The graph represents no significant difference in the energies of the films. These quite similar values clarify that addition of ZnO nanoparticles does not affect the surface energy of PS film. Therefore, ZnO nanoparticles do not change the thermodynamic properties of mixed polymer film.

From AFM analysis, the thicknesses of PS-ZnO films spin casted from the solution 0.3 wt% in toluene is  $20.90 \pm 1.8$  nm (~21 nm). The stability of thin films with varied ZnO concentrations was considered. All as-cast films showed a homogeneous and continuous surface. Annealing the films at 90°C induces the dewetting process. After heating for 1 h, some small holes are formed on the surface of pure PS film while mix films showed a smooth coating. The results confirm that the addition of a small amount of ZnO nanoparticles can suppress dewetting behavior, as a previous study has shown [14]. However, the effects of the concentration of ZnO inhibitors can be identified when the samples are annealed up to 18 h. Figure 2 represents OM images of pure PS, PS-ZnO0.1, PS-ZnO0.3, PS-ZnO0.5 and PS-ZnO0.7 films after annealing. For pure PS film, as shown in Figure 2(a), holes are expanded and holes' borders get closer to each other, representing the intermediate stage of the dewetting process [15]. Likewise, the PS-ZnO composite films are also destroyed. As shown in Figure 2(b), holes' diameters of PS-ZnO0.1 are about 20 μm which are greater than others films; however, the number of holes is fewer. An inhibition of Dewetting behavior is clearly shown in PS-ZnO0.3 film, as shown in Figure 2(c). The film is still smooth and flat covering Si substrate and

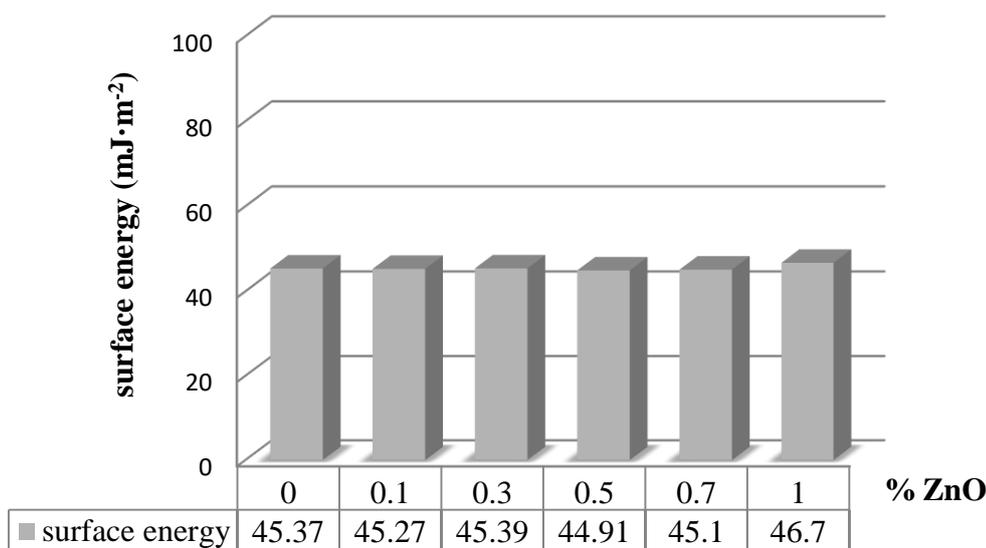
only a few holes occur on the film. Conversely, increasing the concentration of ZnO nanoparticles up to 0.5 and 0.7 wt%, numerous small holes are detected; as shown in Figures 2(d) and 2(e).

From the results, increasing the amount of additives from 0.1 to 0.3 wt% can decrease dewetting behavior. Obviously, the dewetting areas of PS-ZnO0.1 and PS-ZnO0.3 are less than of pure PS. On the contrary, when concentrations of additives rise up to 0.5 and 0.7 wt%, the films exhibit higher number of holes which refers to the higher values of dewetting area.

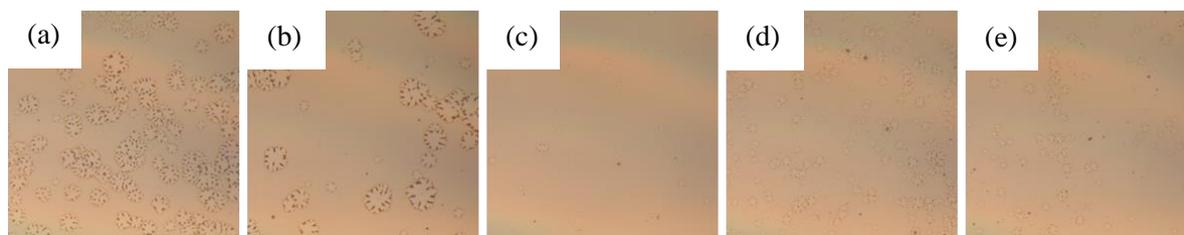
Consequently, the addition of ZnO nanoparticles at 0.3 wt% is a suitable concentration to inhibit the dewetting process in the PS films which have a molecular weight and thickness of 35,000 g·mol<sup>-1</sup> and 21 nm, respectively. To confirm this conclusion, all films were heated at 90°C up to 72 h. PS-ZnO0.3 indicated that the number and size of holes slightly

increased, as shown in Figure 3(a). On the other hand, Figure 3(b), PS-ZnO0.5 represents the expanded holes and the films rise to intermediate stage of dewetting behavior. Accordingly, the addition of ZnO nanoparticles up to 0.5 wt% increases the number of holes in annealed films. At these concentrations, the stabilities of adhesion between film-substrate drop.

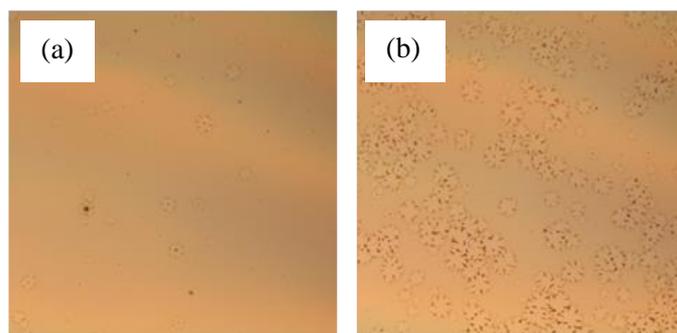
Because the thicknesses of PS and PS-ZnO films are very thin, about 21 nm, the rim's holes of the films are small and narrow. It is not clear to verify topography at the local area by OM; therefore, we used SEM to characterize the surfaces thoroughly. Annealing the films for 72 h, SEM images of PS and PS-ZnO0.3 films are shown in Figures 4(a) and 4(b), respectively. The topographies of topical area confirm that PS film is filled by small holes, while PS-ZnO0.3 film shows fewer holes and less dewetting area.



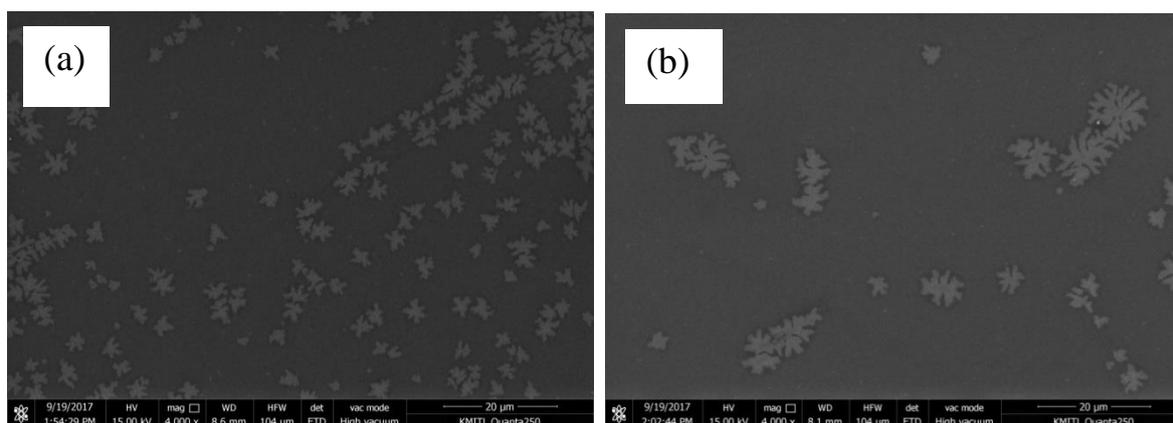
**Figure 1.** Surface energies of pure PS, PS-ZnO0.1, PS-ZnO0.3, PS-ZnO0.5, PS-ZnO0.7, and PS-ZnO1.0 composite films.



**Figure 2.** Optical micrographs of annealed films at 90°C 18 h of pure PS (a), PS-ZnO0.1 (b), PS-ZnO0.3 (c), PS-ZnO0.5 (d) and PS-ZnO0.7 (e) (1000x magnification).



**Figure 3.** Optical micrographs of annealed films at 90°C 72 h of PS-ZnO0.3 (a) and PS-ZnO0.5 (b) (1000x magnification).



**Figure 4.** SEM images of annealed films at 90°C 72 h of pure PS (a) and PS-ZnO0.3 (b).

There are two mechanisms that explain why the addition of nanoparticles in polymer thin film can retard Dewetting behavior [16]. The first mechanism is pinning contact line effect. In this mechanism the nanoparticles which stay in polymer matrix press the polymeric chains. Therefore, the mobility of polymer film is decreased, and Dewetting behavior is retarded. Another mechanism is that the nanoparticles in polymer matrix go down to the interface between polymer film and substrate and created a nanoparticle-rich layer. The roughness of the film-substrate interface is amplified and the interfacial interaction at the interface is improved. Finally, the stability of thin polymer film on substrate is enhanced. However, in 21 nm films, the size of ZnO nanoparticles is similar to the thickness of PS film; the ZnO-rich layer cannot be formed. Accordingly, the pinning line effect is a major mechanism improving the stability of PS-ZnO films.

From the results, we found that, although increasing concentration of ZnO nanoparticles to 0.3 wt% increases the stability of PS film, the addition of nanoparticles more than 0.3 wt% reduces

the efficiency to inhibit dewetting. The ZnO nanoparticles in PS thin film refer to the existence of small dust inside the film. Small amount of nanoparticles can improve film stability; however, higher amount of nanoparticle may induce dewetting. We conclude that the additive concentration is a key factor of the pinning contact line effect. An appropriate concentration depends on the thickness and molecular weight of the polymer matrix. Increasing concentration of additive above the suitable value will activate the dewetting process. The number of holes indicates the amount of nuclei which is formed by unnecessary particles. The excess nanoparticle is as an impurity in the film and will nucleate a hole, as shown in PS-ZnO0.5 and PS-ZnO0.7 films.

#### 4. Conclusions

The pure PS and PS-ZnO films were prepared by spin coating technique. Concentrations of ZnO additive were varied from 0 - 1.0 wt%. The addition of ZnO nanoparticles in PS films can actually

stabilize the film against dewetting, even though the surface energies of PS-ZnO composite films were not changed. Moreover, the concentration of a ZnO inhibitor played an important role in dewetting suppression. When the thickness of film and diameter of nanoparticle are relatively similar, the pinning contact line effect is a major cause of the stability. The suitable concentration of additive to inhibit dewetting is related to the thickness and molecular weight of PS film. An inordinate amount of nanoparticles results in increasing impurity in the film and reduces the stability improvement.

## 5. Acknowledgements

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