



Research Article

Thermal stability of zinc oxide - polystyrene composite thin film

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Abstract

Thin polymer films need to be stable on solid substrates while processing application to preserve their properties. Increasing temperature causes polymer thin films lost their stability. From classical knowledge, the existence of impurity in polymer thin film usually induces dewetting behavior. However, addition of small amount of nano-fillers enhanced thermal stability of polymer thin film. In this research, thermal stability of composite film was investigated by adding zinc oxide nanoparticle into polystyrene thin film. The concentrations of zinc oxide nanoparticles were 0, 0.1, 0.2, 0.5 and 1.0 wt% in polystyrene (MW = 35,000 g/mol). After annealing the composite films at 90 °C for various times, the film morphology was studied by using optical microscope. Contact angle and surface energy of films were calculated by using contact angle measurement. Dewetting area was observed and considered to compare the percentages of each samples. From these results, we found that addition of zinc oxide nanoparticles can retard dewetting behavior of polystyrene film and increasing amount of nanoparticles increases thermal stability of composite films.

Keywords: dewetting, nanoparticles, thin film

Introduction

Polymer thin film is a famous material used in various technological applications such as dielectric coatings, optical coatings, lithography resisting, electronic packaging, and surfaces lubricating because of a remarkable insulation property of polymer. The thin film need to be stable on the substrate in technology application. However, because of the difference of chemical structure between polymer film and metal oxide substrate, polymer film trend to separate from the substrate which is called dewetting behavior. The first step of dewetting process, early stage, occurs when small holes are created. Subsequently, the small holes are expanded and merged which each others showing ribbon structure, intermediated state. Finally, ribbon structure is disconnected and the film presents a number of droplets which is called completely dewet.

Many researches have been investigated how to retard dewetting action of polymer thin films, for example, modification of polymeric structure and/or substrate surface (Henn et al., 1996; Choi and Zhang, 2006) addition of polymer additive (Carroll et al., 2006; Akhrass et al., 2008), and addition of nanoparticles (Barnes et al., 2000; Barnes et al., 2001).

All techniques preventing dewetting behaviour base on two general principles, thermodynamic and kinetic (Xue & Han, 2012). The aim of thermodynamic strategy is change a surface energy. Increasing an interfacial interaction between film and substrate, a stability of polymer thin film is improved. On the other hand, kinetic strategy purposes to reduce a mobility of polymer chains which can promote the wettability also.

In this research, thermal stability of zinc oxide - polystyrene composite thin film is investigated. All films with the thickness ~23 nm are annealed under various heat treatment conditions. The thermal stability of all films is investigated. Topographies are examined by optical microscopy (OM). Percent dewetting areas are calculated by measuring dewetting area from optical micrograph and using commercial image analysis software. The surface energy is calculated by using contact angles and the Owens-Wendt-Kaelble equation (Erbil, 2006).

Materials and methods

Polystyrene (PS, MW = 35,000 g/mol) and zinc oxide nanoparticles (ZnO, diameter \leq 20 nm) were used as polymer matrix and additive. Concentration of PS and ZnO solution was 0.3 wt% in toluene to control the thickness of about 23 nm. The ZnO suspensions were mixed with PS solution at the concentrations of 0, 0.1, 0.2, 0.5 and 1.0 wt% which produced pure PS, PS-ZnO0.1, PS-ZnO0.2, PS-ZnO0.5 and PS-ZnO1.0 composite film, respectively.

Cleaned silicon substrates of the films were prepared by soaking in a 7:3 v/v solution of conc. H_2SO_4 and 30% H_2O_2 at about 80 °C for 1 h. The substrates were rinsed with deionized water for several times and were dried by pressurized nitrogen gas. All substrates showed the clean surface when observed with optical microscope. All thin films were prepared by spin coating. The solutions provided film thicknesses about 23 nm (Pangpaiboon et al., 2015). The spinning rate was kept constant at 1000 rpm for 10 s. Three samples were prepared for each condition.

Surface topographies of polymer thin films were studied by using optical microscopy (OM). The technique was used to investigate large area surface with the magnification of 50X - 1000X. The effects of temperature on surface morphology were studied by annealing all films in vacuum chamber, inducing dewetting behavior. The samples were heated in the oven at 90 °C for different periods of time. Dewetting area was measured by using commercial image analysis software. The contact angle between film-water and film-diiodomethane were measured by contact angle measurement. In addition, the surface energies of as-cast films were calculated by using Owens and Wendt's method (Erbil, 2006).

Results and discussion

Thermal stabilities of PS-ZnO composite thin films are investigated by annealing pure PS and composite films at 90 °C in vacuum chamber. All as-cast films (concentrations of 0, 0.1, 0.2, 0.5 and 1.0 wt %) are continuous film spreading cover the Si substrate. Figure 1 (a) illustrates surface topography from optical microscope of as-cast pure PS film. The homogeneous pure PS film becomes completely dewet after annealing for 5 min, as shown in Figure 1 (b). The film is destroyed and demonstrates a number of polymer droplets.

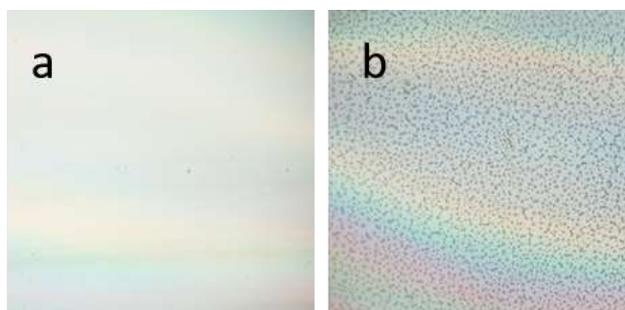


Figure 1. Optical micrographs illustrate (a) as-cast pure PS film and (b) pure PS film after annealing at 90 °C for 5 min. Magnification of the images are 1000 x.

Effects of ZnO nanoparticles on thermal stability of thin PS films are illustrated, as shown in Figure 2. The composite films present dewetting behavior after annealing at 90 °C for 5 and 15 min. At this condition, PS-ZnO film with concentration of nanoparticles 0.1 wt%, PS-ZnO0.1, transfers to absolutely dewetting films as same as pure PS film (not shown). The mix films with concentration of ZnO 0.2 wt% shows merging by several holes which represents intermediated stage of dewetting behavior, as shown in Figure 2 (a). The early stage of dewetting behavior is presented in PS-ZnO0.5 film, Figure 2 (b), indicating that the various small holes are formed while annealing. Percent dewetting areas of PS-ZnO0.2 and PS-ZnO0.5 films are ~48.89% and ~11.26%, respectively. Accordingly, it seems like addition small amount of nanoparticles can delay hole expansion. As same as 0.2 and 0.5 wt% ZnO films, addition ZnO nanoparticle 1.0 wt% retards dewetting behavior, as shown in Figure 2 (c). No hole is discovered and the film remains continuous over the substrate.

The PS-ZnO films undergo the dewetting process when annealing time increases to 15 min, Figure 2 (d-e). The PS-ZnO0.2 film reaches the final stage of dewetting, showing countless droplets of polymer. Furthermore, increasing annealing time results in expansion and merging of the holes in PS-ZnO0.5 film. Percent dewetting area of the film increases to ~16.72%. However, PS-ZnO0.5 film still continuously covers the substrate. It is obvious that adding small amount of ZnO nanoparticles interrupt the dewetting process in the PS film even at a very low concentration of 0.2 wt.%. The results also reveal that increasing ZnO nanoparticles concentration significantly improves the stability of the PS thin film. Addition ZnO nanoparticle only 1.0 wt% can suppress dewetting behavior. The existence of ZnO nanoparticle in PS films is expected to retard movability of PS chain by pinning effect. Each nanoparticle presses on polymer chain, therefore the polymer movement is limited. This mechanism effects to delay hole creation and also hole growth (Sharma et al., 2001).

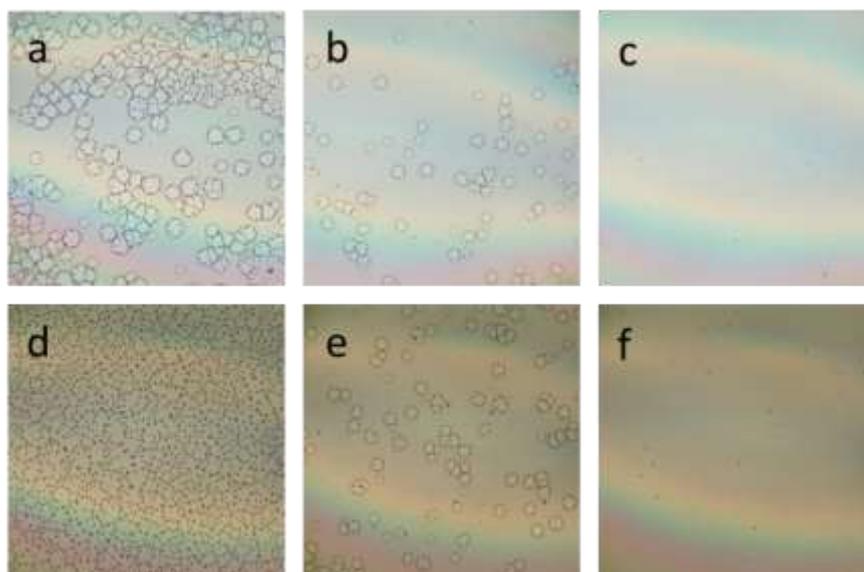


Figure 2. Optical micrographs illustrate dewetting pattern of (a, d) PS-ZnO0.2 film, (b, e) PS-ZnO0.5 film and (c, f) PS-ZnO1.0 film after annealing at 90 °C for 5 and 15 min, respectively. Magnification of the images are 1000x.

Contact angles of water and diiodomethane on pure PS, PS-ZnO0.1 and PS-ZnO0.2 film surfaces are measured, as shown in Table 1. Surface tensions are calculated by using equation of the Owens-Wendt-Kaelble approach. The tensions of each films are not significantly difference, both dispersive and polar component. Addition ZnO nanoparticles in PS films is not effect to the attractive force at the interface between film and substrate. Consequently, the results also confirm that the major mechanism suppressing dewetting behavior should be pinning contact line effect supporting to kinetic strategy (Xue & Han, 2012). The ZnO nanoparticle in PS films presses on polymer chain as pinning effect. The mobilities of composite polymer films are decreased and, finally, the dewetting action is retarded.

Table 1. Contact angles of water and diiodomethane on different surfaces and their solid surface tension components calculated by using simultaneous equation of the Owens-Wendt-Kaelble approach.

films	θ water (degree)	θ diiodomethane (degree)	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)
Pure PS	83.5 ± 1.9	18.2 ± 3.1	47.47 ± 0.88	1.38 ± 0.41	48.85 ± 0.97
PS-ZnO0.1	83.4 ± 2.6	15.4 ± 2.0	48.20 ± 0.50	1.34 ± 0.50	49.54 ± 0.94
PS-ZnO0.2	80.7 ± 3.5	14.5 ± 0.6	48.42 ± 0.14	1.95 ± 0.99	50.37 ± 1.12

Conclusion

The presence of ZnO nanoparticles in PS films plays role as a dewetting inhibitor. Addition of 0.2 wt% nanoparticles improves thermal stability of PS films. Furthermore,



increasing nanoparticle concentrations, 0.5 and 1.0 wt%, also decreases the dewetting behavior. The surface tension of pure PS and composite films show no significantly difference; hence, the attractive force at the interface between all film and substrate are the same. The pinning contact line effect may be the major mechanisms improving film stability. However, for clearly understanding, the exact position of nanoparticles in PS matrix should study further.

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