Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 7759–7762
DOI: 10.1021/ma1010028

Substrate Heterogeneity Induced Instability and Slip in Polymer Thin Films: Dewetting on Silanized Surfaces with Variable Grafting Density

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Received May 5, 2010; Revised Manuscript Received August 15, 2010

ABSTRACT: We employ dewetting behavior of thin polystyrene films to investigate the stability and slippage on the silanized Si wafers with different grafting density of silane brush. PS films are stable on our nonsilanized substrate, but an increase in the grafting density increases the contact angle from zero, causing the appearance and growth of holes. A clear signature of slippage (hole radius $\sim$ time$^{2/3}$) is obtained at low grafting density and low contact angles, which changes to no-slip behavior (hole radius $\sim$ time) on a uniform high density brush. It is also found that the molecular weight of PS does not influence the slippage implying that the slippage observed is caused neither by the entanglement of polymer chains, nor by high nonwettability of the substrate, but by the substrate heterogeneity or physicochemical roughness imparted by the incomplete, low density brush with intervening adsorbed PS chains.

1. Introduction

The dewetting of thin liquid films on a solid substrate is a common phenomenon of fundamental scientific interest, which also critically impacts various technological processes involving coatings. Dewetting experiments can link molecular and interfacial interactions with some macroscopically observable parameters like dewetting velocity and shape of the rim. The kinetics of hole-growth[1−6] is thus a facile and interesting probe for the interfacial properties, such as wettability and slip. When a polymeric liquid moves on a solid substrate, the tangential velocity at the solid/liquid interface is not always zero. The slippage is characterized by the slippage length, *b*, defined as the distance from the wall at which the velocity extrapolates to zero. The properties of the solid substrate play an important role in determining the interfacial frication, which changes the dewetting kinetics of the thin liquid films. In particular, slippage can greatly influence the flow and dewetting kinetics of ultrathin (< 10 nm) films. Previous studies show that many parameters, such as contact angle,[7,8] roughness or topographic structure of the surface,[9−11] and adsorbed chains at the solid/liquid interface,[12−14] govern slippage of liquid molecules at the solid−liquid interface. Increased contact angle or nonwettability indicates weaker liquid−solid interactions which tend to promote slip. Increased entanglement of chains in the higher-molecular-weight melts and strong chain−substrate interactions causing chain adsorption are other factors implicated in slippage. The latter produces slip by producing an incompatible interface between the substrate confined chains and the free chains.

We employed the kinetics of hole-growth to investigate the slippage of PS on the silanized Si wafers with variable grafting density of the silane layer. On the Si wafers used without the silane layer, it was found that the PS films were stable and the dewetting process was not observed in the annealing process at temperatures well above the glass transition. However, on the silanized Si wafers, PS showed nonzero contact angle and thus, the formation of holes in the PS film could occur by nucleation and growth. The interaction between the PS film and the Si substrate could be modulated by grafting different density silane layers on the Si wafer. We could thus systematically probe the influence of grafting density and contact angle on the slippage of polymer melt by characterizing the kinetics of hole-growth. Somewhat paradoxically, we find signature of a molecular weight independent slippage at low grafting densities where the contact angle is also small! Slippage decreases with increased grafting density and vanishes for complete silane coverage of the substrate.

2. Experimental Section

The system under investigation is a polymeric melt layer of polystyrene (PS, $M_w = 2500$ g/mol, and $M_w = 44\,000$ g/mol; $M_w/M_n < 1.1$) on the silanized Si wafer with different grafting density of the silane brush. Thin polystyrene films were prepared by spin-coating its toluene solution onto the Si wafers, which had been silanized (trimethylchlorosilane) prior to their use by the standard procedures[15,16] of treatment with trimethylchlorosilane dissolved in chloroform. Trimethylchlorosilane distributes uniformly on the silicon wafer, but its grafting density could be tuned by changing the concentration of the chloroform solution and the reaction time. The grafting density is calculated by the following equation:[17] $\gamma_1 P + \gamma_2(1 - P) = \gamma_3$, where γ_1 is the surface tension of trimethylchlorosilane; γ_2 and γ_3 are the surface energies of the silicon wafer and the silanized Si wafer, respectively and P is the grafting density. Contact angles of two different liquids (water and glycerin) on the grafted and bare solid substrates were measured by drop shape analysis at room temperature. These were used to calculate the surface energies of the solid substrates by the method of harmonic mean. The film thickness was measured by ellipsometry. The residual solvent was removed by storing the films in a vacuum oven for 24 h at room temperature, and then the samples were heated to a temperature well above the glass transition temperature of PS under the air. The surface morphology was continuously observed by optical microscopy (OM) in the reflection mode with a CCD camera attachment. The samples were quenched to room temperature and imaged using a commercial atomic force microscopy (AFM) operating in the tapping mode.

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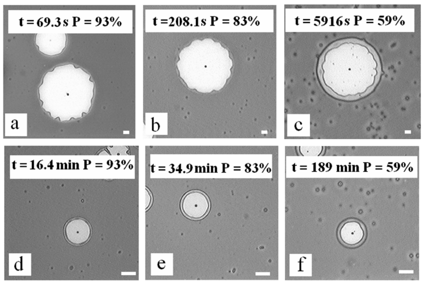

Figure 1. Series of OM images on the silanized Si wafer with different grafting density: (a−c) PS M_w = 2500 g/mol, the hole radius in parts a−c is about 45 μm; (d−f) PS M_w = 44 000 g/mol, the hole radius in parts d−f is about 7.5 μm. The holes tracked are marked by blue dots in the center. The scale of bar is 10 um. *P* is the grafting density.

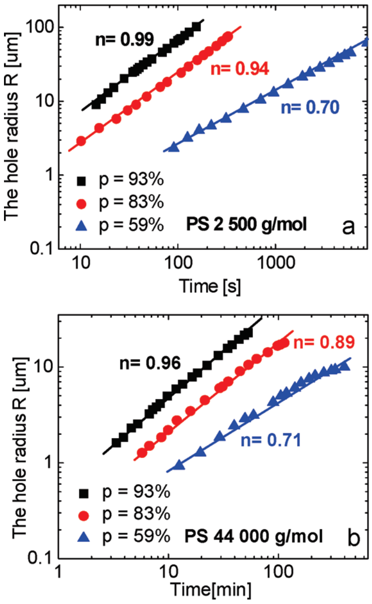

Figure 2. Kinetics of hole growth on the silanized Si wafer with different grafting density. (a) The film thickness of PS film (M_w = 2 500 g/mol) is 60 ± 2 nm; the annealing temperature is 120 °C. (b) The film thickness of PS film (M_w = 44 000 g/mol) is 66 ± 2 nm; the annealing temperature is 150 °C. *P* is the grafting density. The error bar of the exponent, *n*, is smaller than 5%.

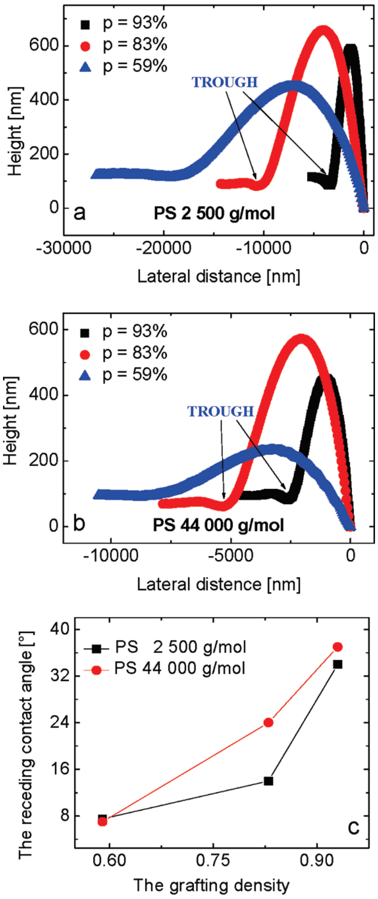

Figure 3. Profile images of the rim: (a) PS film (M_w = 2500 g/mol, the film thickness *h* = 60 ± 2 nm); (b) PS film (M_w = 44 000 g/mol, the film thickness *h* = 66 ± 2 nm); (c) plot of the receding contact angle and the grafting density.

3. Results and Discussion

The PS films on silanized Si wafer with three different grafting densities, 59%, 83%, and 93%, were heated to a temperature well above the glass transition temperature of PS. The dewetting process of PS film was continuously observed in real time under an in situ optical microscope. Figure 1 shows a series of OM images. From Figure 1 it is clear that the dewetting time increases with the decrease in the grafting density at the same hole radius. The dewetting velocity decreases with the decrease in the grafting density. Figure 2 shows the kinetics of the hole growth. The representative data in Figure 2 is obtained by tracking the dynamics of single holes, for example the holes marked by blue dots in the center in Figure 1. The data pooled from different holes on the same substrate showed that the error bar of the exponent, *n* is lower than 5% in every case. From Figure 2, it is found that in the case of the silanized Si wafer with the highest grafting density, the hole radius, *R*, almost keeps a linear relation with time, as expected for a nonslipping film. However, with the decrease in the grafting density, the hole radius displays a nonlinear growth, $R \sim t^n$, where the exponent, *n* decreases with the decrease in the grafting density. Theoretical predictions[2] for a nonslipping film indeed show a linear growth of hole, $R \sim t$; whereas the exponent declines to a minimum value of 2/3 ($R \sim t^{2/3}$) in case of strong slippage of the film on the substrate. The observed kinetics of the hole growth thus implies increased slippage with the decrease in the grafting density (Figure 2), which also corresponds to lower contact angles (Figure 3). Further, the same effect is observed at low and relatively higher molecular weights. These observations are interesting because an important signature of slippage is detected when the contact angle is low, but not for more strongly nonwettable surfaces at nearly complete silane coverage. On homogeneous smooth surfaces without chain entanglement, the contact angle is one of the main parameters influencing slippage. Previous studies[7,8] reported that the slippage effect increases with the increase in the contact angle. The increase in the contact angle implies a weaker molecular interaction of liquid and solid molecules, which decreases liquid−solid adhesion compared to cohesion in liquid. This factor tends to promote slippage at the solid/liquid interface. However, Figure 3 clearly shows that the receding contact angle, *θ*, of the polymer on silanized substrates increases with the increase in the grafting density. It may also be noted that although slippage enhances the growth kinetics, the lower velocity in Figure 2 for slipping films is a composite effect of two factors in that the lower contact angles for slipping films (Figure 3) produce an overall slower kinetics compared to the films with less slip. However the main signature of slippage is an exponent approaching 2/3 as in Figure 2. Besides, we also observe the shape of the rim. From Figure 3, it is found that on the “wet” side of the rim, where the profile connects to the undisturbed thin film, the rim shapes on the three different substrates deviate

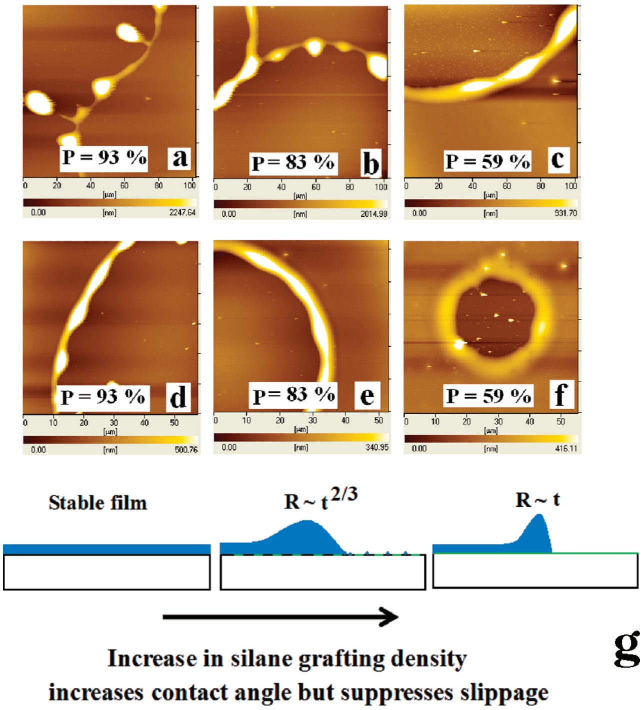

Figure 4. Series of the AFM images on the silanized Si wafer with different grafting density at the position of the holes: (a−c) PS M_w = 2500 g/mol; (d−f) PS M_w = 44 000 g/mol; (g) the schematic diagram.

significantly: the highest grafting density exhibits the steepest rim and the lower grafting density supports a shallow decline. On the Si wafer with the 93% and 83% grafting densities, an obvious “trough” can be observed on the wet side of the rim (see Figure 3); however, there is no trough in the case of the Si wafer with the 59% grafting density and the rim almost decay monotonically into the unperturbed polymer film, especially for high molecular weight PS (M_w = 44 000 g/mol). According to the above observations, we find that a decrease in the grafting density amplifies the asymmetry of the rim profiles. From previous works,[18,19] asymmetric rims are related to slippage. Both the disappearance of the “trough” on the wet side of the rim and the tendency toward asymmetry also imply that the decrease in grafting density amplifies the slippage of the PS film at the solid/liquid interface.

From Figure 2 and Figure 3, one can conclude that the molecular-weight-independent slippage effect decreases with the increase in the contact angle. Thus in this system, the contact angle is not the main factor governing the slippage effect. In order to investigate the reason further, Figure 4 shows the AFM images of the hole. Figure 4 shows that in the case of the high grafting density of silane, corresponding to a near complete coverage, the hole-floor or the dewetted zone remains devoid of polymer fragments. However in the cases of partial coverage with the decrease in the grafting density, small droplets or remnants of the polymer are observed in the dewetted area, especially in the case of the low molecular weight PS (M_w = 2500 g/mol). This is also indicative of stronger polymer−substrate interactions without the silane coverage. In our experiments, PS is stable on the Si wafer without the grafting silane layer implying a strong polymer−Si wafer interaction and chain adsorption. Thus, with the decrease in the silane grafting density, the interaction between PS and the solid substrate becomes stronger, and the PS chains become adsorbed at Si wafer/liquid interface areas that are devoid of grafted silane molecules (see Figure 4).[7,8,12−14] Figure 4g shows the schematic diagram. These adsorbed chains may be responsible for slippage, but the key factor that allows observing its effect is to make the film unstable to the growth of a hole by engineering a nonzero contact angle. The latter is produced by partial silanization. In the case of the low grafting density, PS chains in the dewetting rim can move on these anchored PS chains producing slippage. Thus, interestingly, a heterogeneous composite substrate, containing both PS adsorbed chains and grafting silane molecules produces both slippage and the thermodynamic condition necessary for nonwettability and hole-growth. Partial grafting or coverage of Si wafer with silane thus produces a two component substrate each of which brings a new functionality; silane playing a thermodynamic role in making dewetting possible and bare Si wafer sites controlling the kinetics of dewetting by promoting chain adsorption and slippage. Thus, controlling the extent of silanization appears to be a facile way to control the stability and kinetics of dewetting in thin polymer films all the way from a perfectly stable layer to a nonslipping film and in-between regimes of variable slippage. In conclusion, the slippage induced by the composite substrate shown here originates neither from the polymer rheology (chain entanglement) or high contact angle, but from the adsorbed chains.[7,8,12−14] However, adsorbed chains also promote the film stability, which is made unstable by partial silanization.

4. Summary

We investigated the dewetting kinetics of the PS films, which are stable on Si wafers but made unstable to dewetting on silanized Si wafers, on three different densities of the grafting silane brush. It is found that the hole radius grows as, $R \sim t^n$, where n is 1 on a completely silane-covered Si wafer, but decreases with the decrease of grafted density (and the receding contact angle). On relatively sparsely grafting substrates, n reaches a value of nearly 2/3, indicating a strong slip. The slippage, which grows stronger at lower contact angle, is found independent of molecular weight of the polymer, thus ruling out the nonwettability and chain entanglement as the causative factors for the slippage in this system. The results suggest an interesting scenario where the composite substrate plays a dual role---silane component promoting nonwettability and hole-growth and the adsorbed chains on the bare patches of the Si wafer promoting slippage by chain adsorption. Without some degree of silanization, the film remains thermodynamically stable, and at complete coverage by the silane brush slippage is suppressed owing to nonadsorption of chains despite a much higher contact angle. The strategy of using a multifunctional composite substrate may thus allow a far greater control over the stability and kinetics of thin polymer films.

Acknowledgment. This work is supported by the World Class University Grant No. *R*32-2008-000-20082-0 of the National Research Foundation of Korea.

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