



# Sacrificial mica substrates influence the slip boundary condition of dewetting polymer films



S. Mostafa Sabzevari<sup>a</sup>, Joshua D. McGraw<sup>b</sup>, Karin Jacobs<sup>b</sup>, Paula Wood–Adams<sup>a,\*</sup>

<sup>a</sup> Department of Mechanical and Industrial Engineering, Concordia University, Montreal, Canada

<sup>b</sup> Experimental Physics, Saarland University, D-66041 Saarbrücken, Germany

## ARTICLE INFO

### Article history:

Received 21 May 2015

Received in revised form

14 August 2015

Accepted 19 August 2015

Available online 22 August 2015

### Keywords:

Thin films

Dewetting

Slip

Preparation effects

## ABSTRACT

In the experimental study of thin polymer films, a two-stage sample preparation scheme is commonly used: the polymer film is cast first onto mica, and then the film is transferred to another substrate via a water bath. We present evidence of polymer chain conformational or compositional changes arising from the annealing history of the film on mica. Flow dynamics and rim morphology of dewetting holes in monodisperse polystyrene films on hydrophobized silicon wafers are examined using optical and atomic force microscopy. A significant difference in flow dynamics and rim morphology of holes is observed. The difference depends on whether the interface of the film that was previously in contact with mica remains the interface that touches the hydrophobized substrate from which the film dewets. In this case the difference is consistent with a reduced slip boundary condition, and the reduction depends on pre-annealing to be observed. Furthermore, the slip length disparity is sensitive to the molecular weight distribution of the dewetting films. The disparity of boundary conditions is attributed to long-lasting compositional or conformational arrangements arising from surface segregation and/or surface ordering of chains or their segments.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Thin polymer films are extensively studied due to their ubiquitous industrial applications, from microelectronic fabrication to coatings and adhesives. The interest comes as well from the fact that polymer physics may be significantly affected by chain confinement at an interface in which case surface properties are different from those of the bulk [1,2]. As the ratio of the surface to bulk increases, confinement may induce apparent variations in bulk properties such as the glass transition temperature [3–5] or the viscosity [6]. Other important physical aspects of polymer chains that can change with confinement include free volume [7], chain conformation [8,9], chain stiffness, and entanglement density [1,10,11]. The causes of these changes may include chain end surface localization [12–14], chain ordering [15], and entropic– or enthalpic–driven surface segregation [16–22]. Hydrodynamic transport properties can thus in principle be greatly affected by the properties of a polymer melt inherited from its confining interface [23,24]. As we show here, pre-annealed polymer films show

differing slip boundary conditions after transfer to hydrophobic substrates, depending on whether the pre-transfer solid/liquid or liquid/vapour interface is probed.

While many of the thin polymer film properties discussed above appear in equilibrium, experimental observations are often conflated with effects arising from the film preparation [25–27]. Two examples include: i) the presence of residual stresses due to spin coating [1,28]; and ii) the formation of irreversibly adsorbed brushes to the substrate, a process which is also time dependent [25–27]. Both of these examples can affect the entanglement network near the substrate [29–31], which in turn controls much of the macroscopic behavior observed in experiments [32]. In this regard, the effect of annealing and more importantly annealing time is still an open question. The extent of change in surface and thin film properties listed above is therefore a complicated function of all changes owing to confinement effects and preparation history. Having a thorough understanding of all these effects when examining surface properties is thus, though a considerable challenge, essential.

Surface effects induced by the use of sacrificial substrates in the preparation of thin polymer films have not yet to our knowledge been explored. As in this study, the investigation of thin polymer

\* Corresponding author.

E-mail address: [paula.wood-adams@concordia.ca](mailto:paula.wood-adams@concordia.ca) (P. Wood–Adams).

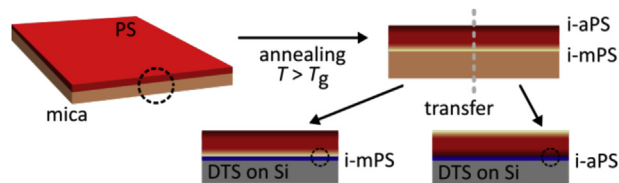
films often includes a two-step film casting procedure using such a sacrificial mica sheet: the polymer film is first spin coated onto a freshly cleaved sheet of mica, which offers a complete wetting condition [33] for polystyrene. The film is then transferred to the desired substrate by floating onto a clean water bath [5,34–37]. Films may as well be pre-annealed on mica. This two-step procedure is typically used when: i) the polymer solution is ejected from the hydrophobized substrate [34,35], precluding the formation of a film; ii) direct deposition of the solution dissolves an underlying coating [36,37]; or, iii) the study of free-standing films is undertaken [5,10,38]. It is of crucial importance to understand whether these preliminary steps influence final properties in any way [1].

One way to investigate this possibility is to use the dewetting experiment that has long been used to study flow dynamics and surface behavior of polymer melts [39]. In dewetting experiments, the rim morphology of the dewetting front (or dewetting hole) reflects physical characteristics of the polymer/solid interface represented by the slip length [40]. The linear Navier slip length is defined as the ratio of bulk viscosity to the friction coefficient at the slip plane [41]. Any compositional or structural change of the molecular layer in the immediate vicinity of the slip plane thus has the potential to be reflected in slip properties and consequently in the rim morphology.

In the present work we investigate surface effects arising from the two-step film casting procedure as a common practice in many polymer thin film studies. Specifically, we show that annealing a polymer film on mica results in a difference between the air/polymer interface relative to the air/mica interface (termed i-aPS and i-mPS in the following). The difference between i-aPS and i-mPS is elucidated through the study of the solid/liquid boundary condition of the film after transfer to a hydrophobic substrate. A schematic representation of the sample preparation protocol is shown in Fig. 1. Mechanisms contributing to the observed differences may include short-chain surface segregation and ordering of polymer chains (or their segments) that can cause conformational or compositional heterogeneities along the film thickness, and importantly, near the solid–liquid interface after transfer. The investigations were undertaken by observing, with optical microscopy, the growth of nucleated holes in polymer films with undisturbed thicknesses  $150 < h_0 < 200$  nm. Quantitative information about the slip boundary condition was obtained by recording the profiles of the rims formed ahead of the dewetting fronts with atomic force microscopy (AFM).

## 2. Experimental

We used polystyrene (PS, purchased from Polymer Source Inc.) with number-averaged molecular weights  $M_n = 10, 27, 51, 130$  and  $465$  kg/mol and polydispersity indices below 1.05; we refer to these as the monodisperse polymers, and use, for example, the shorthand



**Fig. 1.** Schematic of the sample preparation undertaken in this study. A polystyrene (PS) film is spin coated onto a mica substrate. Annealing above the polymer glass transition temperature,  $T_g$ , results in differences between the air/PS interface (i-aPS) and the mica/PS interface (i-mPS). After placing these interfaces in contact with a hydrophobic substrate (DTS schematically indicated, native  $\text{SiO}_2$  layer not shown), it is possible to detect differences between i-aPS and i-mPS through dewetting of the polymer film.

notation PS(465k). These monodisperse polymers were dissolved in toluene with various concentrations in order to obtain undisturbed film thicknesses  $150 < h_0 < 200$  nm when spin coated onto freshly cleaved mica. Bidisperse solutions of PS(465k), with weight fraction  $\phi$ , and PS(27k), with weight fraction  $1-\phi$ , in toluene were also prepared. Total polymer mass fractions in the toluene solutions were chosen in order to obtain the same range of film thicknesses as for the monodisperse films. These film thicknesses were at least 8 times the unperturbed polymer size (radius of gyration) of the polymers used here [42].

PS films on mica were cut into several smaller pieces, roughly  $7 \text{ mm} \times 7 \text{ mm}$ , using a scalpel blade. In cases where the comparison between as-cast and pre-annealed films were made, half of the pieces examined were floated and transferred to hydrophobic substrates (see below) and the remainder were pre-annealed. Films were pre-annealed in air using a Linkam heating stage at 95, 110, 130 and  $150^\circ\text{C}$  for 1 h for molecular weights 10, 51, 130 and 465 kg/mol. Bidisperse films were all pre-annealed at  $150^\circ\text{C}$  for 1 h. All raw data (i.e. optical or atomic force microscopy) compared to each other in a given figure has the same preparation history on mica, aside from the pre-annealing procedure, and comes from the same film on mica. Although we do not systematically study the dependence of annealing time or temperature on a given sample, we note that the protocols used are similar to what is often used in polymer thin film studies focused on annealing effects [26,27,30,31].

All films were floated onto the surface of an ultra-clean water bath (TKA-GenPure,  $18.2 \text{ M}\Omega \text{ cm}$ , total organic carbon content  $< 5$  ppb) and picked up using hydrophobized Si wafers (Si-Mat Silicon Materials, (100) crystal orientation). Silicon wafers were hydrophobized in two ways. The first was to use dodecyltrichlorosilane (DTS, Sigma–Aldrich) self-assembled monolayers (SAMs), with the details of the silanization procedure found in Ref. [43]. Monodisperse films were dewetted from these SAMs. Second, we used a fluoropolymer AF 2400 (Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxido-co-tetrafluoro-ethylene], Sigma–Aldrich) which was used for the dewetting of bidisperse films. General conclusions drawn in this study are not affected by the choice of the substrate, and we note that similar effects as reported in Figs. 2 and 3 have also been observed using monodisperse 173 kg/mol poly(methyl-methacrylate) dewetting from DTS.

We selectively picked up the floating films from the top or bottom surface as schematically depicted in Fig. 1. In films picked up from the top surface, the polymer/air interface is placed onto the DTS. When the film is picked up from the bottom surface, its polymer/water interface – previously in contact with mica – is placed onto the DTS. Therefore, we categorize polymer films on DTS according to their previous contact with air (denoted as i-aPS) or mica (denoted as i-mPS). Before picking up the polymer/air interface, the hydrophobized substrate was first inserted into the water. This allows us to ensure that the substrate contact with water, as occurs in case of the polymer/mica interface, is not the source of any potential discrepancy in results.

Samples were heated to above the glass transition temperature,  $T_g \leq 100^\circ\text{C}$ , to start dewetting by nucleation and growth of holes. Optical microscopy (Leitz) and atomic force microscopy AFM (Multimode) were used to capture the flow dynamics and morphology of the dewetting rim. In all experiments on as-cast and annealed samples, dewetting was captured only for holes nucleated with at least 10 min delay after the dewetting temperature was reached. This can be considered as additional pre-annealing on the dewetting substrate. The pre-annealing is vital to ensure that dewetting is least affected by spin coating-induced frozen-in stresses, which are likely the highest in case of as-cast films [44].

Download English Version:

<https://daneshyari.com/en/article/5179989>

Download Persian Version:

<https://daneshyari.com/article/5179989>

[Daneshyari.com](https://daneshyari.com)