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Polymer film deposition from a receding solution meniscus: The effect of laminar forced air convection

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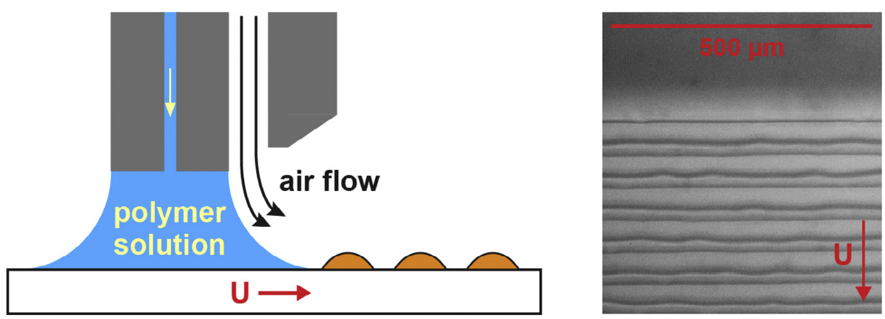
HIGHLIGHTS

- The solution deposition of polymer films is studied.
- The effects of air convection and coating speed are elucidated.
- A coating instability is observed for low air flow rates and small substrate speeds.

GRAPHICAL ABSTRACT



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ABSTRACT

When the meniscus of a polymer solution with a volatile solvent recedes over a wettable substrate, a polymer layer is deposited onto it. Even for chemically homogeneous and topographically flat substrates and constant coating speeds, the layer can exhibit quasi-periodic line patterns extending parallel to the contact line of the liquid meniscus. In this manuscript, we study such unstable solution deposition processes by means of well-controlled, systematic experiments and numerical simulations. The presence of laminar forced air convection gives rise to a linear increase in the average layer thickness with air flow rate. Initially, the line patterns increase in width and height with increasing air flow rate. However, beyond a certain critical value the coating instability is suppressed.

1. Introduction

Applying a thin film of non-volatile solute on a solid substrate by means of a solvent-based coating process in the presence of evaporation has received considerable interest in the past years. Le Berre et al. (2009) used a receding meniscus to deposit a phospholipid film with a controlled thickness. They identified the existence of two different regimes of coating. For a high substrate speed U_{sub}, the thickness of the dried film h_{dry} follows the classical Landau-Levich scaling (Landau and Levich, 1942) $h_{dry} \sim U_{sub}^{2/3}$, since the evaporation rate is insufficient to directly dry the film. For a low substrate speed, a cross-over occurs and h_{dry} is found to decrease with increasing U_{sub}. In this so-called 'evaporative' regime, the dry deposit directly emerges from the contact line. Based on the mass balances for the solvent and solute, Le Berre et al. (2009) deduced that in this regime the thickness scales as $h_{dry} \sim U_{sub}^{-1}$. The same exponent of -1 was found by a number of authors (Faustini et al., 2010; Jing et al., 2010; Rogowski and Darhuber, 2010; Vital et al., 2017).

Even on a flat, smooth and chemically homogeneous surface, a coating process can result in a non-uniform deposit. Masuda et al. (2004) placed a substrate vertically in a colloidal suspension and evaporated the solvent at a controlled temperature. The

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colloidal particles deposited in the form of regularly spaced lines oriented parallel to the contact line of the liquid meniscus. The width and spacing of the lines could be modulated by controlling the temperature of the solution. Similar experiments were conducted by Abkarian et al. (2004) and Ghosh et al. (2007) found analogous patterns while dip-coating a colloidal suspension with a low substrate withdrawal rate. They reported a disordered particle deposit in case of a high substrate speed. The deformation and rupture of the liquid meniscus, leading to the line formation, were monitored in situ by Mino et al. (2015) and Nadir Kaplan et al. (2015).

Bodiguel et al. (2009, 2010) measured the pinning force, induced by the solute deposit to pin the contact line. Noguera-Marín et al. (2014) studied the effect of the wetting properties of the substrate and found that the pinning of the contact line is enhanced by contact angle hysteresis of the substrate. Later, the same authors also varied the pH of the colloidal suspension, in order to alter the particle interactions and thus the importance of collective diffusion effects (Noguera-Marín et al., 2016). Similar experiments were conducted by Hsueh et al. (2013). Lee et al. (2009) varied the diameter of the colloidal particles and related the distance between two deposit lines to the particle size using a geometrical model. A similar correlation between the line width and spacing was found by Watanabe et al. (2009).

Patterned deposits have been observed with a large variety of material systems such as colloidal suspensions of gold (Ming et al., 2008; Nakanishi et al., 2011; Watanabe et al., 2012; Watanabe and Miyahara, 2013), silver (Sambandan et al., 2010; Watanabe and Miyahara, 2013), polymer (Abkarian et al., 2004; Ray et al., 2005; Ghosh et al., 2007; Han et al., 2011; Noguera-Marín et al., 2016; Zhang et al., 2016) or silica (Masuda et al., 2004; Lee et al., 2009; Bodiguel et al., 2010; Watanabe and Miyahara, 2013; Li et al., 2014; Noguera-Marín et al., 2014, 2016; Mino et al., 2015; Nadir Kaplan et al., 2015) nanoparticles, carbon nanotubes (Zeng et al., 2011; Xiao et al., 2012; Joo et al., 2014), nanofibrils (Gao and Han, 2013) and nanowhiskers (Xiao et al., 2012), protein molecules (Lin et al., 2010), virus capsules (Lin et al., 2010), silica and titania sol-gel films (Uchiyama et al., 2012; Uchiyama, 2015), phospholipid (Le Berre et al., 2009) and polymer solutions (Yabu and Shimomura, 2005; Lin and Granick, 2005; Hong et al., 2005, 2007a,b; Xu et al., 2006; Byun et al., 2008; Kim et al., 2008; Lin, 2010; Kwon et al., 2011a,b; Park et al., 2012; Chen et al., 2012; Hsueh et al., 2013; Men et al., 2014; Sun and Yang, 2015; Sun et al., 2017). Yabu and Shimomura (2005) studied the pattern formation process from a receding meniscus of a polymer solution. Depending on the initial concentration of the polymer, they found different deposition patterns, namely dot arrays, stripes parallel to the contact line and ladder structures. Park et al. (2012) created an array of polymer stripes over a distance of several cm by confining a polymer solution between the substrate and a roll, which was moving over the substrate. They demonstrated the possibility to control the size of the stripes by varying the speed of the roll. Kim et al. (2008) prepared a micropatterned film of a diblock copolymer. Upon thermally annealing this structure, they demonstrated the molecular alignment of the block-copolymer in a lamellar morphology in the coating direction.

The formation of non-uniform deposits has also been studied by numerical simulations (Nonomura et al., 2003; Lara-Cisneros et al., 2008; Doumenc and Guerrier, 2010, 2013; Frastia et al., 2012; Colosqui et al., 2013; Dey et al., 2016; Zigelman and Manor, 2016; Jung et al., 2017; Zigelman and Manor, 2018). Frastia et al. (2012) used a thin film model to study the solution deposition process in a receding meniscus. The contact line was allowed to recede either by evaporation or by dewetting of the partially wettable substrate. Unlike in a dip-coating process, there was no imposed (average) speed of the contact line. They found that the contact line receded by a periodic pinning-depinning cycle and identified various deposition patterns depending on the system parameters. Doumenc and Guerrier (2010) studied the drying of a polymer solution in a receding meniscus in a dip-coating geometry, i.e. with an imposed contact line speed. The evaporation rate was assumed to be limited by the diffusion of solvent vapor in the gas phase, while the hydrodynamics in the solution was described with a thin film model. Their model reproduced the evaporative regime and the Landau-Levich regime and obtained only homogeneous deposits. However, by including a solutal Marangoni stress (Doumenc and Guerrier, 2013; Dey et al., 2016), they obtained patterned deposits in the evaporative regime for certain ranges of the control parameters.

This manuscript focuses on the periodic pattern formation that occurs during deposition of a polymer solution from a receding meniscus in a horizontal die-coating geometry. The die-coating setup comprises an air nozzle to induce well-controlled, laminar gas-phase convection, which allows to increase the effective evaporation rate. Several authors had already employed forced air convection to introduce ‘dry’ air devoid of solvent vapor (Lee et al., 2009; Jing et al., 2010; Bodiguel et al., 2010; Zeng et al., 2011; Noguera-Marín et al., 2014, 2016), most likely to maintain the evaporation rate at a steady-state value for extended times. However, they did not study the influence of the gas phase convection itself on the pattern formation process. We conducted systematic experiments and numerical simulations to study the effect of the two main control parameters: the substrate speed and the air flow rate. Section 2 focuses on the experimental setup and procedures. Section 3 describes the details of the numerical model, which is similar to the one developed by Doumenc and Guerrier (2010, 2013) and Dey et al. (2016). The experimental and numerical results are discussed in Section 4.

2. Materials and methods

Fig. 1(a) shows a sketch of the experimental setup. A custom-made slot-die is placed at a height $H \approx 500\ \mu m$ above a horizontal glass substrate. The slot-die is mounted on several mechanical stages, that allow it to be tilted around three perpendicular axes of rotation. The substrate is placed horizontally on a sample holder, which is connected to a computer-controlled translation stage (Newport XMS 160). We use a Cartesian coordinate system for describing positions and orientations. The x-axis is oriented in the direction of substrate motion, the z-axis vertically upwards. Fig. 1(b) shows a bottom view of the slot-die. The slot-die consists of two metal parts, both with a width $w_{sd} = 1$ mm, that are fastened together. One of the parts contains a rectangular slot with dimensions $w_l = 0.1$ mm in the x-direction and $w_y = 1$ cm in the y-direction. The coating liquid is injected through this slot and is confined between the slot-die and the substrate by capillary pressure. The receding coating meniscus is monitored from below using a microscope, consisting of a long working distance objective (Mitutoyo, M Plan Apo 10X/0.28) and a CCD camera (AVT Pike F-145B). The optical axis of the microscope is oriented along the y-direction and extends into a cavity in the sample holder. A small mirror is connected to the objective with its surface normal oriented at an angle of 45° relative to the z-axis for looking upwards. A separate air nozzle can be connected to the slot-die on the side of the receding meniscus. This creates a rectangular slot with dimensions $w_a = 0.75$ mm in the x-direction, $w_y = 1$ cm in the y-direction and $L_z = 11$ mm in the z-direction. The exit of the air nozzle is placed 0.5 mm above the exit of the slot-die. A large volume syringe (Hamilton, product number 86020, 100 ml) placed on a syringe pump (KDS Gemini 88) is used to drive the flow of air