Journal of Power Sources 239 (2013) 382–392

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Slot die coating of polybenzimiazole based membranes at the air engulfment limit

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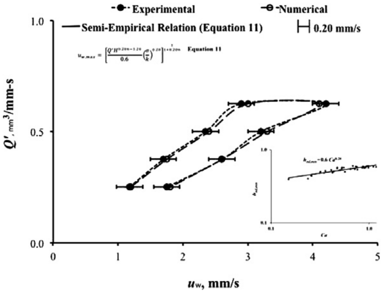
## HIGHLIGHTS

- Air engulfment in shear-thinning solutions is investigated.
- A semi-empirical model is derived to predict air engulfment velocity.
- Smaller coating gap or higher operating temperature enable larger coating speed.
- Air engulfment can be delayed by employing solutions with higher surface tension.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 14 December 2012
Received in revised form
21 March 2013
Accepted 22 March 2013
Available online 6 April 2013

*Keywords:*
Slot die
Shear-thinning
Coating window
Semi-empirical model
Air engulfment

## ABSTRACT

The objective of the current study is to analyze the slot die coating process of highly viscous (1–20 Pa s), shear-thinning solutions. The upper and lower coating boundaries are determined with respect to various non-dimensional parameters. Polyphosphoric acid doped polybenzamidazole (PPA/PBI) solutions are used as the test solutions. Simulations are performed using 2D, volume-of-fluid (VOF) model available in FLUENT 6.3.26 to predict the coating windows. The numerically predicted coating window compared within ±4% of the experimental data. Design of Experiments (DOE) is performed to understand the impact of operational and processing conditions on the coating windows. It is observed that the air engulfment could be delayed by using smaller coating gaps and higher processing temperatures, which would facilitate faster processing of thin films, an important attribute during industrial scale processing. One major contribution from the study is the development of a semi-empirical model, in which operational and processing parameters are supplied as inputs to predict the air engulfment velocity within ±10% accuracy.

## 1. Introduction

Slot die coating classified as a pre-metered coating technique, is successfully being used for manufacturing a broad range of thin films such as photographic films, papers [1], coatings on glass substrates [2], optical films for liquid crystal displays (LCD) [3], fuel cell membranes [4–6], etc. As shown in Fig. 1, in this method, a solution with a predetermined flow rate, ($Q_{in}$) is suspended from a slot die onto a substrate moving at speed ($u_w$). The coated film attains a constant thickness downstream of the die, which is called the wet thickness ($h$). One of the main advantages of slot die coating is that the coating thickness is pre-metered and controlled, meaning the final coating thickness is determined from the flow rate through the slot die and the substrate speed [7,8].

A limited range of operating conditions, for which high quality films are produced, exists for slot die coating as defined by the "coating window" as shown in Fig. 2. Outside the coating window, various types of defects such as dripping, air entrainment, and break lines will be formed [9–11]. Dripping corresponds to the top most boundary of the coating window and occurs when the flow

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http://dx.doi.org/10.1016/j.jpowsour.2013.03.132

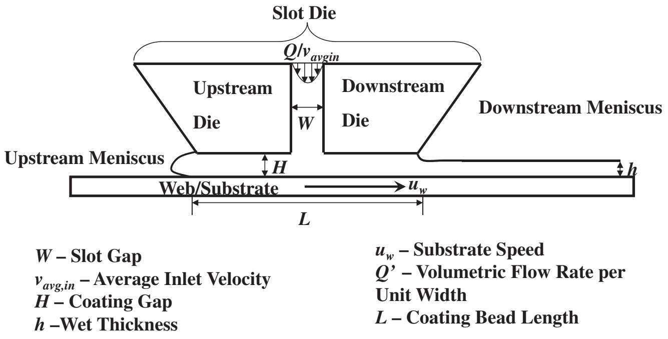

**Fig. 1.** Schematic of the slot die coating process from the point of fully developed flow between parallel plates [6].

rate is too high relative to the substrate speed causing the solution to collect behind the upstream die, and creep up the outer wall of the upstream die. When dripping occurs, the pre-metering characteristic of the slot die is lost since the thickness of the film can no longer be controlled. Because of the limitation posed by air entrainment on the coating speed, which is an important factor in improving the production rates of the thin film, it is considered as a major defect encountered during slot die coating, especially for high-viscosity solutions (i.e., solution having a capillary number, ($Ca$), $>0.1$) [11]. At higher substrate speeds, air bubbles get entrained between the substrate and the liquid film [12,13]. In some cases, the air bubble is restricted to only a fraction of the total film thickness, while in other cases; the bubble extends all the way to the top of the film resulting in a hole [6]. Extending the coating speed beyond the air entrainment value results in the formation of break lines [14,15]. It has been found that as the coating speed increases, the originally straight contact line breaks into "vee" structures (also termed as sawteeth), and the air bubbles eventually break up from the tip of these sawteeth [6,12,16]. Some researchers [17,18] employed vacuum at the upstream end to delay air entrainment, however, air entrainment in this study corresponds to the no-vacuum conditions as is the case with other studies [10,15,19,20].

At a given flow rate, the range of the wet thickness of defect-free films is restricted by the air entrainment/break lines and dripping. Maximum wet thickness ($h_{\max}$) is achievable at the minimum substrate speed ($u_{\mathrm{w,min}}$), and the minimum wet thickness ($h_{\min}$) is obtained at the highest coating speed ($u_{\mathrm{w,max}}$). Lee et al. [21] found that in the slot die coating of the Newtonian solutions, the dimensionless minimum wet thickness ($h_{\mathrm{nd,min}} = h_{\min}/H$), increases as capillary number ($Ca = \mu u_{\mathrm{w,max}}/\sigma$) increases until a critical capillary number, $Ca^*$, is reached (Region I). Beyond $Ca^*$, the dimensionless minimum wet thickness was found to be only a function of coating gap and was independent of capillary number (Region II). Carvalho and Kheshgi [17] found that by increasing the capillary and Reynolds numbers beyond the values reported by Lee et al. [21], there was another region in which the dimensionless minimum wet thickness decreases with capillary number (Region III). Experiments performed by Chang et al. [15] show that the transition from Region I to Region II will occur around $Re = 1$, and the transition from Region II to Region III will occur around $Re = 20$. Furthermore, while moderate and high-viscosity fluids followed Regions I and II, low viscosity solutions followed Regions II and III [15]. Region I was primarily dominated by viscous and surface tension forces [22] and the transition from Region I to Region II had competing viscous and inertial forces. Region II was influenced predominantly by inertial forces. The inertial forces grew significantly from Region II to Region III, such that the fluid exiting the slot die resembled a jet impinging on a moving substrate.

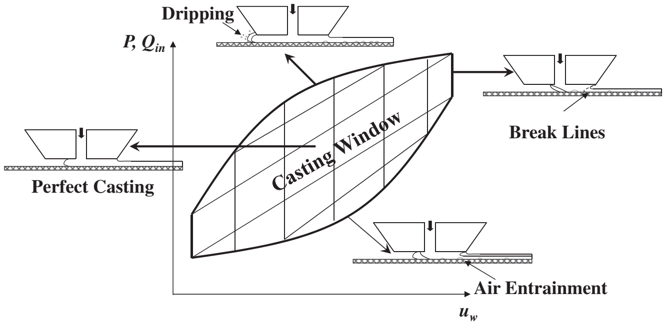

**Fig. 2.** Illustration of the coating window [6].

Gutoff and Kendrick [9] studied the effect of the non-Newtonian behavior of coating solutions on the coating window using polyvinylalcohol (PVA) solutions. They found that compared to the coating windows obtained using Newtonian solutions, the width of the coating window increased for non-Newtonian solutions. In the study, it was shown that the maximum coating speed increased by about an order for the non-Newtonian solution. Ning et al. [10] found that for an optimum polymer concentration in glycerin-water solutions, the maximum coating speeds can be achieved. On the other hand, experiments and simulations performed by Romero et al. [23] on high molecular weight polymers in dilute solutions showed that as the extensional viscosity of the coated liquid increases, the width of the coating window decreases. Existing literature regarding the effect of the surface tension on the coating window is inconclusive, due to the contradicting findings by various researchers. Gutoff and Kendrick [9] reported that surface tension does not play a significant role on the coating window and it only impacts the shape of the coating bead. According to Hamers et al. [24], solutions with lower surface tension assisted in widening the coating window, while studies performed by Tiu et al. [25] and Chu et al. [26] found the opposite trend; i.e., solutions with higher surface tension form more stable coating beads, extending the coating window.

To understand the effects of operational parameters like slot gap ($W$) and coating gap ($H$) on the size of the coating window, Lee et al. [21] conducted various experiments with the silicon oil solution. They found that a smaller coating gap and higher coating speeds will increase the coating windows and that the slot gap had negligible effect. Chang et al. [19] showed that for solutions with viscosities of 0.075 Pa s and 0.2 Pa s, smaller minimum wet thickness values were attainable if smaller coating gaps were used. However, they found that the effect of coating gap was insignificant for solution with viscosities lower than 0.003 Pa s.

Several theoretical and numerical studies have been conducted to understand the coating process. Ruschak [27] performed the first theoretical study to predict coating windows for pre-metered coating processes. Higgins and Scriven [28] extended the study to include viscous effects. Both studies assume the flow field to be steady and completely two-dimensional.

Saito & Scriven [29] and Carvalho & Kheshgi [17] used two-dimensional, finite element methods to analyze slot die coating of Newtonian solutions. Similar models were employed by Romero et al. [8,18,23,30] to predict the coating windows for Newtonian fluids, mildly viscoelastic fluids, and high molecular weight polymer fluids. In some of these studies [18,23,30], the slot die parallel-plate regions and the upstream regions are excluded from the computational domain, following the findings by Carvalho and Kheshgi that these regions (slot die parallel-plate regions and the upstream regions) have no impact on the operating conditions at low capillary and Reynolds numbers. These assumptions pertaining to the computational domain prevent extracting data on the