Thin Film Slot Coating in a Rarefied Low Viscosity Gas

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Abstract

A key limitation of the slot coating process when attempting to coat very thin films is due to air entrainment. We show in this research that by replacing the air with a low viscosity gas and reducing the pressure it is possible to significantly reduce the thickness of coated films of an acceptable quality. This is likely to be of interest to manufacturers developing roll-to-roll systems producing, for example, flexible solar cells or batteries.

Introduction

The current drive to exploit cost effective solar cell manufacture includes developing methods for coating ultra-thin films onto flexible substrates. Films incorporating donor material in one layer and electron acceptor material in an adjacent layer are typically sandwiched between a transparent electrode and a reflecting electrode. These inner layers need to be of the order of 100nm to 500nm thick and comprise semi-conductive polymers capable of being dissolved in a variety of solvents. Manufacture up to fairly recently has focused on batch processing within a vacuum chamber using printing techniques. This is inherently expensive. There is accordingly much current interest in driving down the cost to the order of €0.5 per watt through exploiting roll-to-roll coating methods. Of the many coating processes available, slot coating is deemed to be the most appropriate as not only capable of achieving low laydowns but being metered, the wet thickness is well controlled.

A second important requirement is to extend the life of OPVs (organic photovoltaics) as much as possible. It is well established that this can be achieved by coating in an oxygen-free atmosphere.

The classic experimental work of Lee, Liu and Liu [1992] when studying conventional slot-over-roll coating showed that it is possible to achieve minimum film thickness down to the order of 100 to 160µm for speeds ranging from 3 to 35 cm/s (1.8 to 21 m/min) using silicone oil of viscosity 50mPa.s as test fluid, a slot gap of 0.25mm and a slot-to-web gap of 200µm – Figure 1. Lower wet thicknesses down to 30µm are possible using fluids of viscosity of the order of 10mPa.s for a coating speed of the order of 6cm/s (3.6m/min) using this method.

A major advance in achieving thinner films was made some years ago by dispensing with the backing roll leading to what is known as tensioned-web-slot coating. It is thus now possible to achieve films as thin as 0.5 µm but only at very low speeds, typically less than

10 m/min. Although, this is good progress in adapting slot coating to modern needs, increasing the speed is the next step in the development

In any coating process, the key limit to reducing the wet thickness to a desired low value for a given coating speed, or alternatively allowing higher speeds while achieving a low wet thickness is when air is entrained as a very thin film. This air film, when observed in a direction normal to the substrate is "saw tooth" shape – see Figure 2 for where a web plunges into a liquid pool as representative of where solid, air and liquid first meet in a coating process. The entrained air film breaks up to form minute bubbles at the apex of each trailing "vee" to adversely affect coating quality.

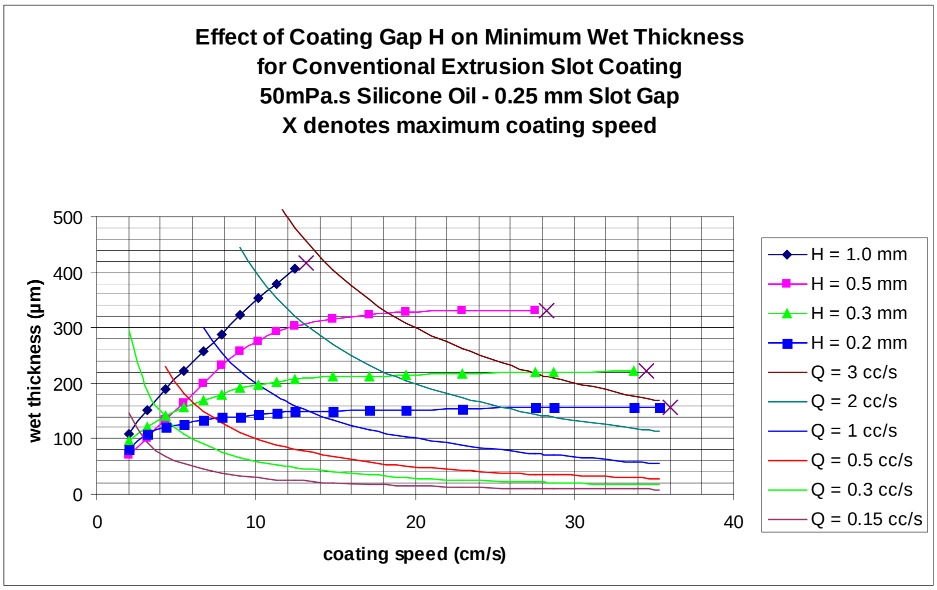

Fig.1

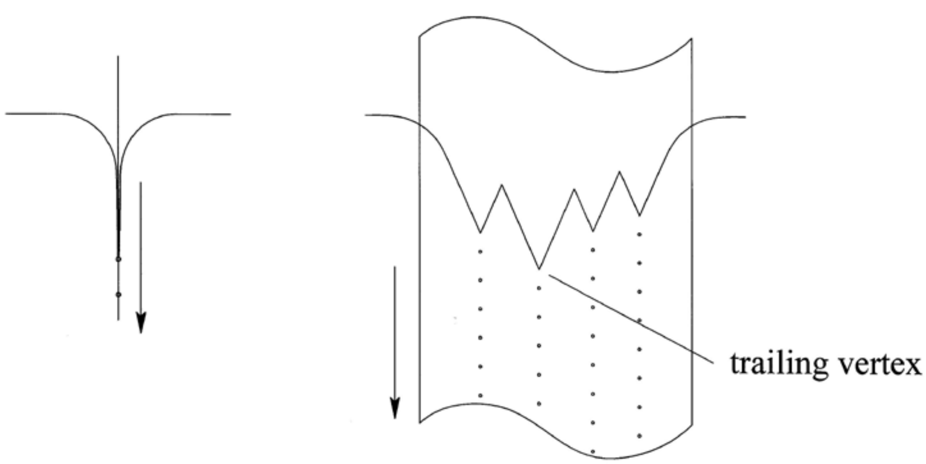

Fig.2

Benkreira and Ikin [2010] showed, using a simple dip coating process, that replacing air with a suitable gas and reducing the pressure significantly postponed the onset of gas entrainment to higher speeds – Figure 3. They proposed that the viscosity of the gas played an important role in determining the onset of gas entrainment as considering that the gas becomes entrained as a thin film within a “vee”. The coupling force between the gas and liquid consequently increases with gas viscosity leading to more gas being dragged down by the web.

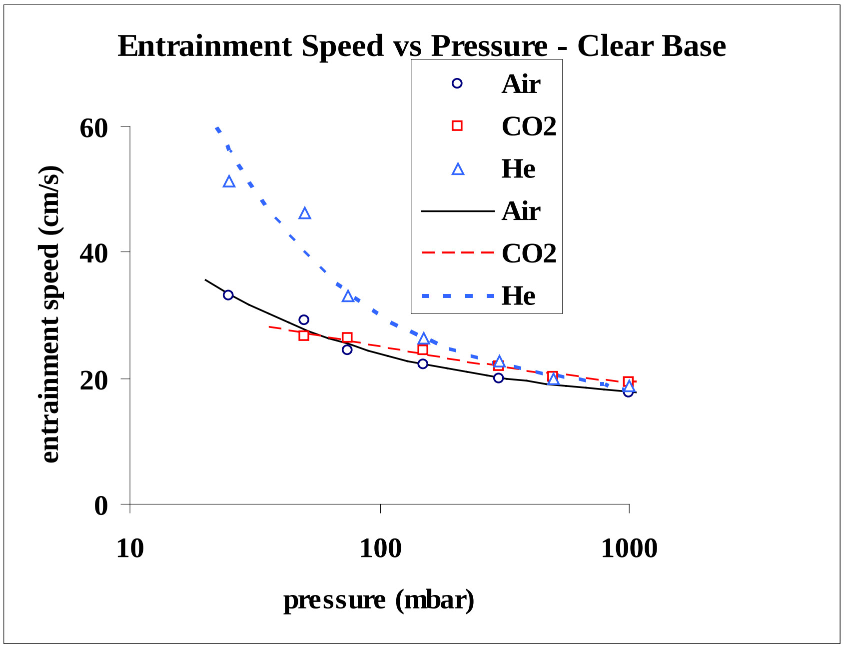

Fig.3

The bulk viscosities of the three gases when measured using an apparatus where the gap between the moving solid surfaces is of the order of millimeters remain fairly constant with pressure down to about 1mbar – Starling and Woodhall [1961] and are typically as shown in Table 1. This, however, fails to explain why helium at low pressure yields a significantly higher entrainment speed than CO_2 or air on reducing the pressure.

Gas	Bulk viscosity at 20˚C and 1 atmos.
air	181 µP
carbon dioxide	149 µP
helium	199 µP

Table 1

The mean free paths for these gases, on reducing the pressure down to 25 mbar, for example, are 3.8µm for air, 2.5µm for CO_2 and 11.4 µm for helium. However, the work of Muës, Hens and Boiy [1989] showed from measurements using a laser-doppler velocimetry technique that the thicknesses of entrained air films are typically less than

2 μm. The entrained gas can thus be constrained to less than the mean free path. It is therefore critically important to take viscosity data where the measuring technique reasonably well simulates these conditions.

A literature search revealed that Andrews and Harris [1995] had in fact set up a microstructure as shown in Figure 4. This comprised two micro-machined plates set apart by 2 μm. One of the plates was driven so as to oscillate in a direction normal to the other spring-loaded plate. The relative motion was measured capacitively to determine the phase difference and from this, using a theoretical relationship, the gas viscosity responsible for damping. They showed on plotting the measured viscosity of dry air, nitrogen, argon, carbon dioxide, oxygen and hydrogen expressed as a fraction of the fully developed value against pressure expressed as d/λ, that the data collapse onto a master curve. Here d is the gap and λ is the mean fee path. Assuming that helium also falls on the master curve and assigning published values for λ at 20°C and atmospheric pressure and the value of d as set by Andrews and Harris [1995], it is possible to predict how the thin film viscosity of dry air, carbon dioxide and helium varies with pressure – see Figure 5. It will now be seen that the effective viscosity of helium is very significantly lower than for air and CO_2. This now yields a plausible explanation for the behaviour shown in Figure 3 for dip coating.

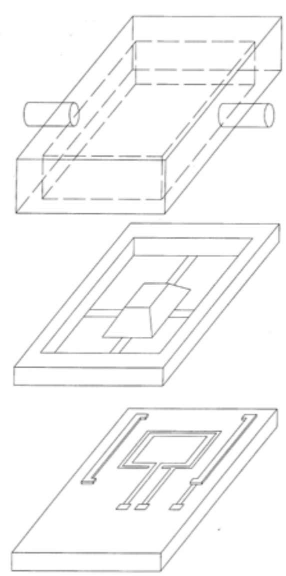

Fig. 4

Based on this evidence, it seemed reasonable to conjecture that replacing air with helium at low pressure for typical slot coating processes would also advantageously postpone gas entrainment to higher speeds when coating a layer of given wet thickness, or alternatively allow thinner defect free coatings at a given coating speed. This was deemed to be of potential interest to manufacturers developing OPVs. A further motivation for the work was that coating in helium meets a prime requirement to enable manufacture in an oxygen-free environment. The following describes the experiments run to validate our hypothesis for firstly the conventional slot-over-roll process and secondly for the tensioned web slot coating process.

Experimental Investigation – Slot-over-Roll Coating

A 50 mm wide slot coater was mounted in a vacuum chamber, within which a web winding rig was set up. Figure 6 shows the case study incorporating a 100 mm diameter precision steel backing roller. The roller was machined with microgrooves in order to minimize the tendency for air becoming entrained between the web and roller. Silicone oil of viscosity 50mPa.s measured at 23°C was used as coating fluid in view of its low partial pressure thus enabling the gas pressure to be significantly reduced without risk of evaporation.

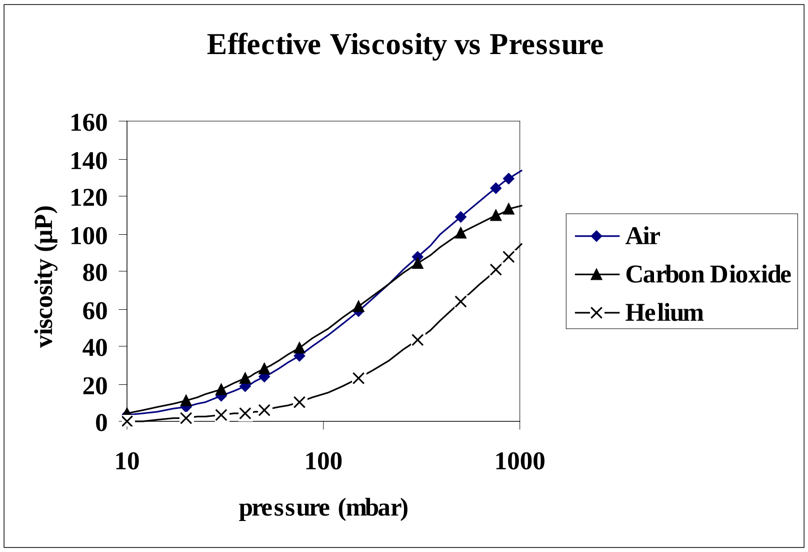

Fig.5

The fluid was supplied from a reservoir suspended at variable heights in order to achieve a range of flow rates. The height was remotely controlled from outside the chamber using a motorized bobbin. Oil flow to the slot coater was enabled by switching on a solenoid valve. The slot coater was constructed of Perspex and comprised a slot of width 425μm and length 4.2 mm, the upstream and downstream land-lengths being 0.2 mm and 1.5 mm respectively. The slot coater was mounted on a cradle as shown in Figure 7. The cradle pivoted about bearings mounted on an upper translator and its lower position was determined by a pin mounted on the lower translator. The upper and lower translators thus served to control slot inclination angle and the slot-to-web gap respectively. The slot-to-web gap was set to 0.2 mm.

The wet thickness for a given flow rate was monitored using a capacitive sensor supplied by Physik Instrumente GmbH. This was mounted opposite an ultra-flat earthed plate against which the back of the coated web passed. The sensitivity to oil film thickness was first calibrated by mounting the assembly on a cantilever suspended over a pool of oil in a dish. The assembly was lowered by means of a micrometer screw to allow oil to partially fill the gap between the reference plate and the sensor and signals recorded as a function of displacement.

When running a coating experiment, the sensor output was recorded on one of two channels of a Picoscope coupled to a computer while ramping the web speed up at a preset acceleration for typically 20 seconds. The second channel was used to record the web speed profile obtained using a laser tacho set up opposite holes in a disk mounted at the end of a web transport roller.

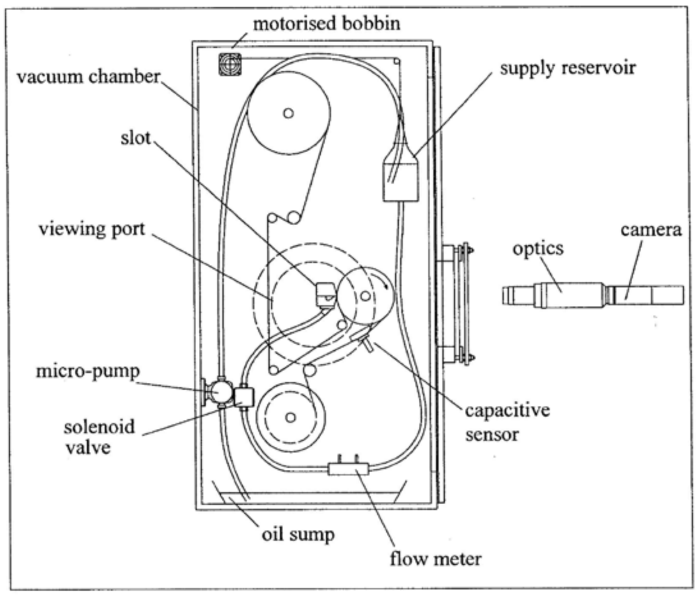

Fig.6

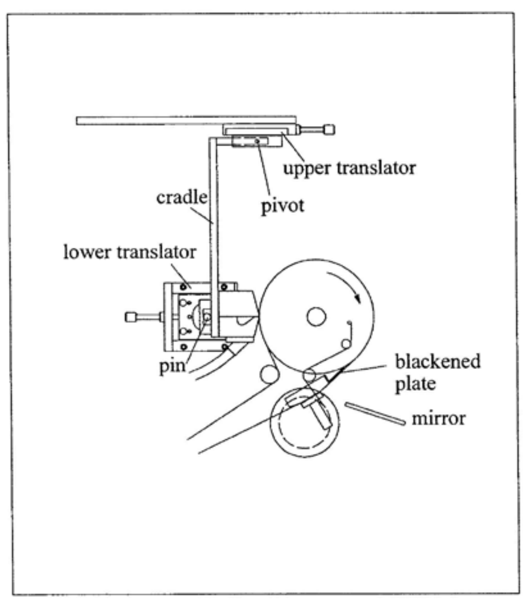

Fig.7

CCD cameras were used for recording images of the instantaneous web speed as displayed by an oscilloscope monitoring the laser tacho output, a view of the coater as observed through a chamber side port and the coating uniformity. A multiplexer was used for enabling all images to be displayed on the computer monitor and for recording a composite video file in memory.

A time lapse of typically 3 seconds was allowed before switching on the flow in order to prevent flooding of the sensor. The optimum observation of coating quality was either at a point on the backing roller diametrically opposite the slot exit or in front of a blackened plate positioned just behind the free span between the backing roller and the sensor – see Figure 7. The minimum achievable wet thickness was determined from the oil film thickness at the speed at which ribbing or entrainment was first observed on playing back the video sequences after allowing for the displacement between the coating and observation points measured along the web path.

The results shown in Figure 8 for where the coating was carried in air at atmospheric pressure agree well with those obtained by Lee, Liu and Liu [1992] using the same silicone oil for fluid. They also show that replacing the surrounding air with helium maintained at 25 mbar pressure results in typically a 17% reduction in the minimum achievable wet thickness when using the slot-over-roll configuration.

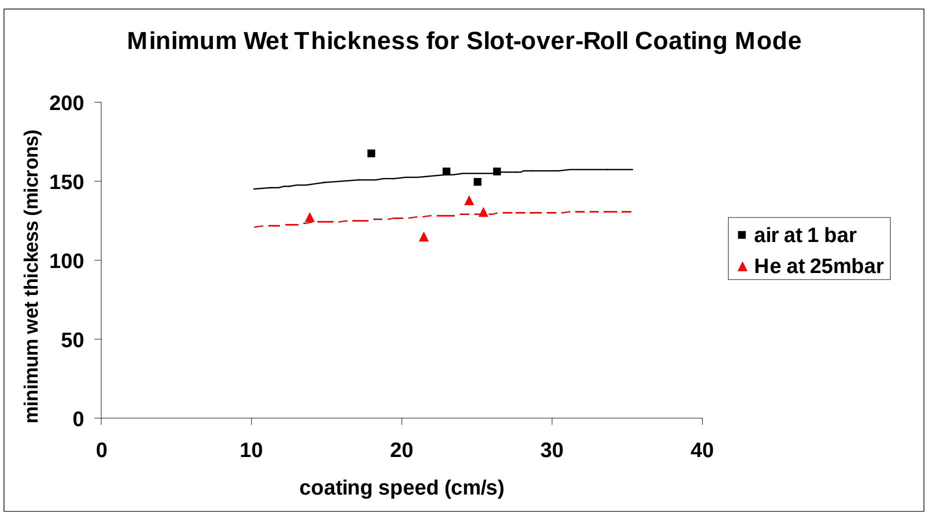

Fig. 8

Experimental Investigation – Tensioned Web Slot Coating

The coater was mounted as for the slot-over-roll mode and the web caused to pass downwards directly over the slot exit as shown in Figure 9. The upstream and downstream land-lengths were now 1.5 mm and 0.2 mm respectively owing to the reversal of web direction. The web tension was 4.3N, the free upstream and downstream spans 7.5 cm and 10.2 cm respectively and the web deflection 2 mm.

The 50mPa.s oil was metered to the coating head using a micro-pump supplied from a suspended reservoir. Special care was taken to prevent fluid migrating down the substrate prior to start-up by developing a remotely controlled method for withdrawing the head away from the substrate based on pulling the swing frame against the back stop using cord wrapped about the motorized bobbin. Experiments were limited by outbreaks in bubbles caused by cavitation within the pump and heat generated within the solenoid valve used for switching the flow on and off.

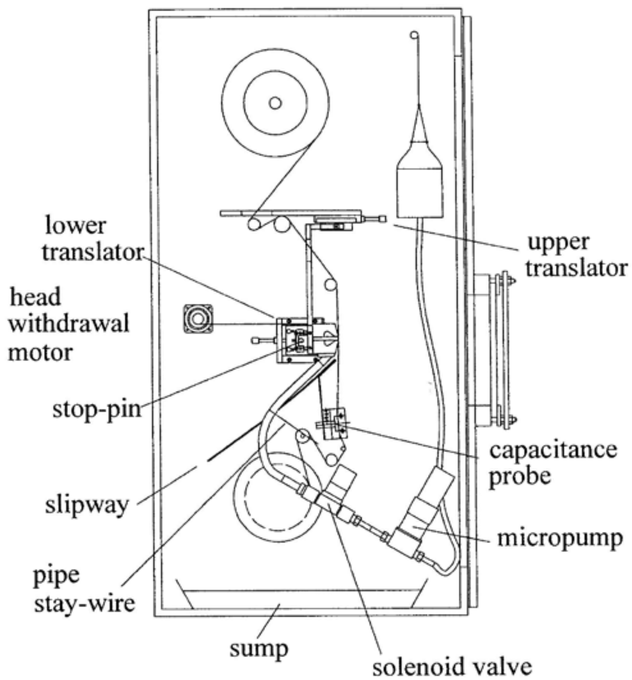

Fig.9

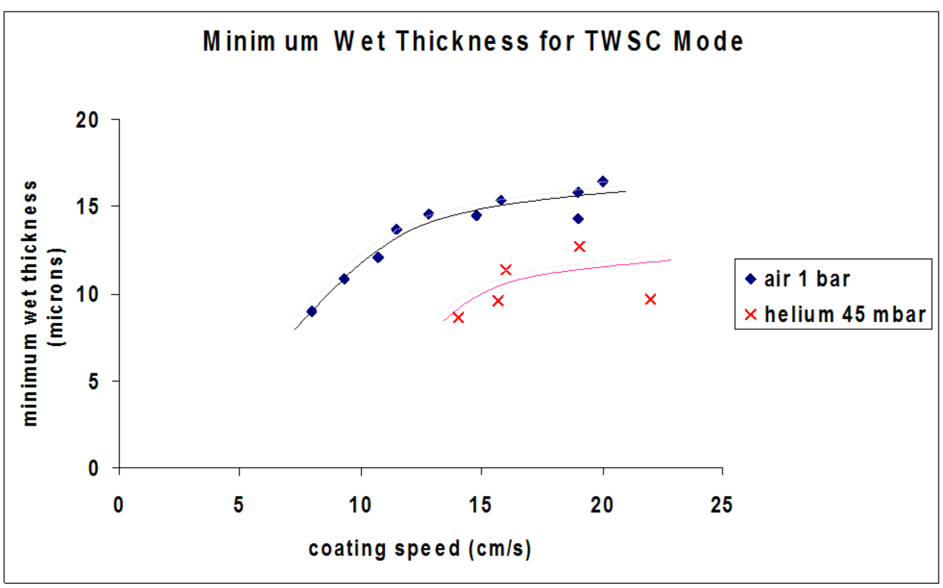

Fig 10

Figure 10 shows that in this case replacing the surrounding air with helium maintained at 50mbar allows a very significant reduction in the minimum achievable wet thickness at a given coating speed or typically a two fold increase in the maximum coating speed for a given minimum achievable wet thickness. The cause of the lower thickness limit when air was present was air entrainment whereas the cause of the limit when helium was present and maintained at low pressure was ribbing.

Conclusions

These preliminary experiments, while limited to much higher coating thickness than ultimately sought within industry, confirms our reasoning drawn from our previous work. It is thus possible to reduce the minimum achievable wet thickness or alternatively increase coating speed by replacing air at atmospheric pressure with helium when coating a flexible substrate using the slot-over-roll process and also when using the tensioned-web slot coating process. The work should therefore be of interest to industry involved in developing systems for manufacturing OPVs within an oxygen-free atmosphere.

In searching for a suitable gas, it is important that the thin film viscosity rather than the bulk viscosity be taken as the critical property. Any measurements of viscosity should thus be made using apparatus replicating the very thin films actually entrained at coating.

Further work is clearly needed to explore what can ultimately be achieved in driving down the wet thickness and increasing the coating speed in order to meet the commercial requirements for cost effective manufacture of OPVs. This includes resolving problems with bubble generation within the system supplying the coating head – possibly through reverting to gravity feed and varying the height of the reservoir by remote control. A reliable method is also required for accurately defining the thickness profiles of ultra-thin coatings on transparent substrates possibly using fluorescent dyes and optical methods for measuring the fluorescence.

References

1. Andrews, M.K. & Harris, P.D. *Damping and gas viscosity measurements using a microstructure* Sensors and Actuators **A49** pp 103 – 108 [1995]
2. Benkreira, H and Ikin, J.B. 'Dynamic wetting and gas viscosity effects.' Chem. Eng. Sci., **65**, 1790 [2010]
3. Carvolho, M.S. & Kheshgi, H.S. 'Low-flow Limit in Slot Coating: Theory and Experiments' AIChE Journal **46** (10) pp 1907-1917 [2000]
4. Chang, Y-R.; Chang, H-M.; Lin, C-F, Liu.; T-J. & Wu, P-Y. 'Three minimum wet thickness regions of slot die coating' Colloid and Interface Science **308** pp 222-230 [2007]
5. Chang, Y-R, Chang, H-M, Lin, C-F, Liu, T-J & Wu, P-Y. 'Three minimum wet thickness regions of slot die coating' – Colloid and Interface Science **308** pp 222-230 [2007]
6. Lee, K-Y., Liu, L-D. & Liu, T-J. 'Minimum wet thickness in extrusion slot coating.' Chem. Eng. Science, **47** (7) pp 1703-1713 [1992]

7. Lin, F-H.; Liu, C-M.; Liu, T-J. & Wu, P-Y. ‘Experimental Study on Tensioned-Web Slot Coating’ Polymer Eng. And Sci. **47** (6) pp 841-851 [2007]
8. Lin, F-H., Liu, C-M., Liu, T-J & Wu, P-Y. ‘A Macroscopic Mathematical Model for Tensioned-Web Slot Coating’ Polymer Engineering and Science **48** pp 307-315 [2008]
9. Muës, W., Hens, J. & Boiy, L. ‘Observation of a dynamic wetting process using laser-Doppler velocimetry.’ *AIChE*. **35** (9) pp 1521-1526 [1989]
10. Nam, J. & Carvalho, M.S. ‘Two-layer tensioned-web-over-slot die coating: Effect of die lip geometry.’ Chem. Eng. Science, **65** (13) pp 4014-4026 [2010]
11. Ning, C-Y, Tsai,C-C & Liu, T-J ‘The Effect of Polymer Additives on Extrusion Slot Coating’ – Chem. Eng. Sci. **51** (12) pp 3289-3297 [1996]
12. Romero, O.J., Scriven, L.E. & Carvolho, M.S. ‘Slot coating of mildly viscoelastic liquids’ Journal of Non-Newtonian Fluid Mechanics **138** pp 63-75 [2006]
13. Starling, S.G. & Woodhall,A.J. “Physics” pp 215-216 Longmans [1961]
14. Yang, C.K., Wong, D.S.H. & Liu, T-J. ‘The Effects of Polymer Additives on the Operating Windows of Slot Coating’ – Polymer Eng. & Sci. **44** (10) pp 1970-1976 [2004]