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SLOT COATING MINIMUM FILM THICKNESS IN AIR AND IN RAREFIED HELIUM

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ABSTRACT

This study assesses experimentally the role of gas viscosity in controlling the minimum film thickness in slot coating in both the slot over roll and tensioned web modes. The minimum film thickness here is defined with respect to the onset of air entrainment rather than rivulets, the reason being that rivulets are an extreme form of instabilities occurring at much higher speeds. The gas viscosity effects are simulated experimentally by encasing the coaters in a sealed gas chamber in which various gases can be admitted. An appropriate choice of two gases was used to compare performances: air at atmospheric pressure and helium at sub-ambient pressure (25mbar), which we establish has a significantly lower "thin film" viscosity than atmospheric air. A capacitance sensor was used to continuously measure the film thickness on the web, which was ramped up in speed at a fixed acceleration whilst visualizations of the film stability were recorded through a viewing port in the chamber. The data collected show clearly that by coating in rarefied helium rather that atmospheric air we can reduce the minimum film thickness or air/gas entrainment low-flow limit. We attribute this widening of the stable coating window to the enhancement of dynamic wetting that results when the thin film gas viscosity is reduced. These results have evident practical significance for slot coating, the coating method of choice in many new technological applications, but it is their fundamental merit which is new and one that should be followed with further data and theoretical underpinning.

Keywords: *Coating flows; Slot coating; Low flow limit; Dynamic wetting; Air entrainment, Ribbing, Rivulets, Gas viscosity.*

1. INTRODUCTION

This paper is concerned with the technological calls to develop roll to roll liquid film coating processes in the new energy technologies of organic photovoltaics, organic electronic devices, polymer electrolyte membrane fuel cells, optical films for liquid crystal display and other high value thin film products to replace the more expensive vacuum coating based batch processes. Slot coating, which was originally invented by Beguin (1954) for the continuous production of photographic films, is currently believed to be best suited to achieve this (Galagan et al, 2011, Schmitt et al, 2013) as it can provide strict specifications in the

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gauge of the liquid films being coated as well as enabling coating in stripes and multilayer modes in a clean and controlled manner without any waste of coating fluids. The problem however is that it cannot coat sufficiently thin layers at speed without defects. The current targets for this technological challenge are low viscosity coating solutions (<100mPa.s), a wet film thickness in the range 0.5-10μm and a minimum speed of 10m/min (Søndergaard et al, 2012). Under such thin liquid film conditions, flow instabilities will occur above a critical coating speed, causing the film to be marred with defects, some subtle, such as uniform ribs across the film or entrained tiny air bubbles and others more pronounced such as lanes of no flow (rivulets) across the film (Gutoff and Cohen, 2006). All these instabilities are undesirable as they limit the performance of the products. Understanding how these instabilities arise and how they can be prevented or postponed to higher coating speeds in slot coating is the subject of this paper. It is important to note at the outset that unlike self-metered coating flows such as roll or blade coating for example, where the instabilities are associated with dynamic wetting failure at the dynamic wetting line or ribbing on the downstream meniscus, with pre-metered coating flows, the upstream meniscus can also be destabilized particularly as it approaches the feed slot corner (Fig.1). Unable to pin itself, the static contact line becomes the trigger for instabilities leading to defects that resemble classical (downstream meniscus) ribbing and (dynamic wetting failure) air entrainment. Thus the confusion in the terminology used to describe defects and the difficulty in describing the mechanisms that lead to these (Ding et al, 2016)

As illustrated in Fig. 1, slot coating is a pre-metered liquid coating flow which delivers through a gap h_g a set volumetric flow rate of liquid per unit width q to a web moving at speed v_w thus forming on the web a liquid film of thickness $h_w=q/v_w$. There are two configurations of slot coating: slot over roll coating (SRC) where the web passes around a backing roller at a preset gap and tensioned web slot coating (TWSC) where the web deforms due to being partially pressed towards the die by its tension. The difference between these is that in one (SRC), the liquid flows through a set gap between two rigid boundaries and in the other (TWSC), the liquid flows through a deforming gap between a rigid boundary and the tensioned web. Clearly, when the applied load is large and the coating fluid viscosity small, TWSC will allow lower flow rates to pass through than SRC and thus will deliver thinner films. SRC can be operated with a vacuum box upstream (Lee et al, 1992) to reduce somewhat the contribution of pressure to flow but this is practically not feasible with TWSC. SRC can be operated with a vacuum box upstream (Lee et al, 1992) as the bead pressure is low (sub-ambient at low capillary numbers). This reduces the minimum film thickness further to what is considered as the actual *low* flow limit of industrial situations. Also unlike with TWSC, there is a risk of the roll and the die surfaces clashing with SRC when attempting to operate at very low coating gaps to achieve very thin films. Normally, the lowest practicable gap in SRC will be not less than 25μm.

As mentioned earlier, in both SRC and TWSC, as with all coating flows, there will be flow instabilities. For pre-metered coating flows such as SRC and TWSC, this translates into a limited range of flow rates [q_{max}, q_{min}] that can be used at a given speed to produce a stable uniform coated film. Outside these conditions or coating window, the film becomes marred with various defects, the most prominent being at the lower limit, droplets on the web rather than a film or a film with rivulets and at the higher limit, dripping or flooding when the excess liquid slips out at the upstream end of the die (Durst and Wagner, 1997). The range of flow rates that can be accommodated is a good feature of slot coating as it enables a range of film thicknesses to be produced over a range of speeds. What is of most interest, however, is the flow limit q_{min}, which at a given coating speed, determines the minimum film thickness

$h_{w,min}$ on the moving web. This limit is also known as the high-speed limit when the flow rate is set and the speed increased or the wide gap-limit when both the flow rate and speed are set and the gap increased beyond a critical size. In terms of flow defects, the flow limit q_{min} is defined as the condition when one of two situations occurs (i) the downstream meniscus of the 2D continuous film issuing from the slot coater ceases to bridge the gap between the die and the substrate or (ii) the upstream meniscus invades the feed slot. In both situations, the coating bead breaks into a striped film or rivulets. Invasion of the feed slot by the upstream meniscus can be avoided if a small vacuum is applied upstream (Beguin, 1954) and in such a situation, feasible only with SRC because of the smaller bead pressures in comparison with TWSC, higher speeds of operation can be achieved and the *low*-flow limit is attained.. The low flow limit can be predicted fairly simply at low capillary numbers using the capillary model of Ruschak (1976) which consists essentially of two equations. The first equation is a balance of the forces acting on the coating bead that will sustain a minimum 2D film flow. As the flow in a slot die is composed of a drag flow minus a pressure flow, the rivulets low flow limit with SRC dictates that the flow rate out of the die is minimised when the pressure drop is maximised. This will occur as a first approximation (if we ignore viscous effect upstream in the bead) when the pressure gradient $\Delta p_{d,m}$ at the downstream meniscus forming the film is maximised by adopting the smallest radius of curvature, $r_{d,m}$, an arc of a circle delimited by the gap hg and the minimum film thickness attainable $h_{w,min,\mathrm{SRC}}$. This is expressed by:

$$\Delta p_{d,m} = \sigma / r_{d,m} \quad with \quad r_{d,m} = (h_g - h_{w,min,SRC})/2 \tag{1}$$

The second equation expresses the variation of the film thickness $h_{w,min,SRC}$ with operating conditions. Following the approach of Landau and Levich (1942) in dip coating adapted to SRC, this gives $h_{w,min,SRC}$ as a function of radius of curvature $r_{d,m}$ and capillary number $Ca = \mu v_w / \sigma$, μ and σ being the viscosity and surface tension of the coating fluid respectively:

$$h_{w,min,SRC} = 1.34 r_{d,m} Ca^{2/3} \tag{2}$$

Combining Eq. (1)-(2) gives the minimum dimensionless film thickness attainable at the low flow limit as:

$$H_{w,min,SRC} = h_{w,min,SRC}/h_g = 1 \Big/ \left[1 + 1.49 Ca^{-\frac{2}{3}}\right] \cong 0.67 Ca^{2/3} \ when\ Ca \ll 1 \tag{3}$$

This analysis showing the dimensionless film thickness to increase with increasing Ca is valid only for Ca<<1 when viscous and inertia effect are considered negligible. A variation of this simple model was developed by Higgins and Scriven (1980) who considered the contribution to flow of all sections of the die using a lubrication type analysis. Using a more intricate approach that solves the full Navier-Stokes equations numerically, Carvalho and Kheshgi (2000) showed that the visco-capillary model predictions hold well up to Ca~0.25 but the film thickness then starts to decrease with increasing Ca when inertia effects are significant. Carvalho and Kheshgi (2000) provided data for a wide range of Ca in support of their predictions. Such a model indicates that with SRC, $H_{w,min,SRC}$ depends on Ca only and with it being directly proportional to die gap, h_g, the actual film thickness formed in the very low Ca region can be very thin indeed. Both the speed and the die gap, however, will then also have to be very low. Typically, for a low practicable coating gap of 50μm, the above equations indicate that a water based coating solution of 100mPa.s will yield a film thickness of 13.5μm at a speed of 10m/min. To achieve a film thickness of 5μm at the same speed one would have to use a coating gap of 18.5μm and a high risk of die-to-roll clash.

In TWSC the flow is different from SRC in that we have an elasto-hydrodynamically controlled gap between the fixed die face and the tensioned web over it. The pressure of the liquid exiting out of the feed slot, the geometries of the die lips and the web tension, stiffness and wrap angle will all have a controlling effect on film thickness, flow limits and related instabilities (bead break-up when the dynamic wetting line invades the feed slot and weeping when it reaches the upstream end of the die lip) and the onset of ribbing and of vortices in the flow which are also undesirable instabilities. These flow parameters and stability constraints make for a complex elasto-hydrodynamic analysis that need to be coupled with mathematical statements to describe the onset of instabilities. Necessarily, the solution of such a model will require a numerical method (Lin et al, 2007; Park, 2008; Nam and Carvalho, 2010). Fortuitously, it is found that the minimum film thickness or low flow limit, which is deemed to occur just before bead break-up when the upstream dynamic wetting line invades the feed slot can be related in a similar way to Eq. (3) but through replacing Ca by the web tension number $N_T = \mu v_w / T$ effectively replacing fluid surface tension σ by web tension T:

$$H_{w,min,TWSC} = h_{w,min,TWSC}/r_d = \alpha {N_T}^{\beta} \tag{4}$$

Here r_d is the radius of the downstream die lip. Although Eq. (4) resembles Eq. (3), it is important to stress that the low flow limit breakup mechanism in TWSC is not the same mechanism that occurs in the low flow limit in fixed gap slot coating (SRC). The breakup in TWSC is associated with the invasion of the upstream meniscus. The low flow limit in SRC is associated with the invasion of the downstream meniscus, as explained earlier. Nam and Carvalho (2010), who provide a comprehensive study and a practical guide to the design and operation of TWSC, show the coefficient α in Eq. (4) to depend strongly on the geometry of the die lip but the exponent β to vary only between 0.4 and 0.7. Clearly, unlike SRC which operates with a set gap, TWSC by its elasto-hydrodynamic nature will yield film thicknesses in the lower range, typically 5-10 μm at speeds higher than 10m/min.

The low flow limit constitutes a well predicted and experimentally verified criterion to assess theoretically the lowest film thickness that can possibly be attained in slot coating with vacuum applied upstream. In this paper, as will be shown later, the entire coating set-up is encased in a controlled pressure chamber. The use of a vacuum upstream is thus not possible. In such an operation without vacuum, the minimum stable film thickness that can be attained in SRC will be just before the bead is invaded by the upstream meniscus causing the gas phase to be entrained either as large pockets or as fine bubbles. As shown in Figure 2, the low flow limit measured by Lee et al. (1992), is well above that predicted from the visco-capillary model. This explains why the use of vacuum in SRC is so important in practice. Of course, and as explained earlier, with TWSC the use of a vacuum upstream will not be effective unless it can be manipulated so as to change the essence of dynamic wetting and prevent wetting failure and the onset of gas entrainment (very fine bubbles). This is precisely the objective of this work as will become clear later.

Ribbing is a type of instability commonly observed in coating flows. As mentioned earlier, in its classical definition, ribbing originates from small disturbances on the film forming meniscus causing waves to form as a result of large positive pressure gradients not being overcome by stabilising surface tension forces. Ribbing in slot coating may be overcome by a judicious design of the die-web gap profile to prevent large pressure drops from developing in the downstream region as shown by Nam and Carvalho (2010). Essentially, the gap, whether in SRC or TWSC, should be configured such that it does not develop from a converging profile into a diverging profile, typical of roll coating flows, which are prone to ribbing instabilities (Pearson, 1960; Pitts and Greiller, 1961). This however makes for a complex die design. Defects described as ribbing but said to be originating from instabilities on the upstream meniscus as it approaches the feed slot and pins itself at the corner point of the feed slot have also been reported (Lee et al, 1992; Yang et al, 2004 and Lin et al, 2007; Bhamidipati, 2014).

Air entrainment is a fundamental instability of coating flows. It will always occur above a critical speed when the dynamic wetting line fails to remain straight and breaks into a jagged shape comprising vees, allowing tiny air bubbles to be entrained in the trailing vertices of the vees as observed originally by Deryagin and Levi (1964). This was established later by Ruschak and Blake (1979) resulting in the concept of the maximum speed of wetting. Until recently, it was understood that the factors controlling air entrainment speed in coating flows with no hydrodynamic assistance were the viscosity of the coating solution (Burnley and Kennedy, 1976; Gutoff and Kendrick, 1982) and its ability to dissolve air (Jochem and van der Light, 1987), the entry angle of the substrate into the flow field (Cohu and Benkreira, 1998) and the roughness of the substrate (Buonoplane et al, 1986; Clarke, 2002; Benkreira 2004). Of all these factors, only a reduction of viscosity can significantly postpone air entrainment speed to higher values in accordance with the correlation due to Gutoff and Kendrick (1982):

$$v_{ae} = 0.05\mu^{-0.67} \tag{5}$$

Recently, Benkreira and Khan (2008) and Benkreira and Ikin (2010) demonstrated in a series of dip coating experiments in an environment comprising gas other than air that the viscosity of the very thin gas film entrained by the moving substrate also played a critical role. Using helium at very low pressures (~25mPa), they measured gas entrainment speeds that were much higher (as much as 3 times larger) than the air entrainment speed under atmospheric pressure. The mechanism they proposed for this assistance of wetting was the reduction in viscous coupling force exerted on the surrounding liquid due to the fact that the thin film viscosity of the rarified helium is substantially lower than that for air. [We will explain in the Experimental Method section what is meant by thin film viscosity and how it should be measured]. There is not as yet a model that explains this experimental finding but Shikhmurzaev (1997) shows in his fresh interface formation theory of wetting that as the gas-to-liquid viscosity ratio decreases, the contact-line speed corresponding to the onset of gas entrainment increases rapidly. Vandre et al. (2014) also have shown using a hydrodynamic model of dynamic wetting failure that decreasing the air viscosity relative to the viscosity of a coating liquid lessens the impact of the air stresses, allowing for steady wetting at higher Recently, Sprittles (2015) gave further theoretical insight into this gas viscosity effect.

We suggest that as in dip coating, the resistance to gas entrainment in slot coating will also be enhanced if a gas with a low thin film viscosity is used. Such enhanced wetting would result in widening the coating window to higher speeds leading to films that are thinner than when air is used. This is precisely the hypothesis of this paper which we propose to verify by carrying out comparative coating experiments of SRC and TWSC under air at atmospheric pressure and rarefied helium. A further motivation for the work is that coating in helium meets a prime requirement to enable manufacture of OPVs and similar oxidizing devices in an oxygen-free environment.

2. EXPERIMENTAL METHOD

The equipment broadly comprised a miniature slot coater, a web transport system and fluid handling system all housed within a sealed gas chamber. This enabled studying the effects of replacing air with helium maintained at low pressure and consequently presenting a much reduced thin film gas viscosity. Motorised or solenoid operated mechanisms were also mounted within the chamber where capable of operating for short periods in a vacuum. The chamber was fitted with observation windows to enable visualization and detection of the practical low flow limit as defined by the onset of gas entrainment or ribbing.

The Slot over Roll Coater: The 50 mm wide coater was constructed of Perspex and comprised a slot of internal width 425μm and length 4.2 mm, the upstream and downstream land-lengths being both 1.5 mm. Fig. 3 shows the positioning of the coater relative to a 100 mm diameter precision steel backing roller and the web winding rig. The backing roller was machined with microgrooves in order to minimize the tendency for air (or gas) becoming entrained between the web and roller. Fig. 4 shows how the slot coater was assembled on a cradle, which pivoted about bearings mounted on the upper translator. 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 coating 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. Fluid flow to the slot coater was enabled by switching on a solenoid valve.

The Tensioned Web Slot Coater (TWSC): This coater was mounted as for the slot over roll mode using the pivoting cradle and translator shown in Fig. 4 with the web caused to pass downwards directly over the slot exit as shown in Fig. 5. The upstream and downstream land lengths were now 1.5 mm and 0.2 mm respectively. The web tension was 4.3N, the free upstream and downstream spans 7.5 cm and 10.2 cm respectively and the web deflection was 2 mm. The coating fluid 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 web prior to start-up by developing a remotely controlled method for withdrawing the head away from the web by means of pulling the swing frame against the back stop using a cord wrapped about the motorized bobbin.

The Coating Fluid: Silicone oil (Basildon Chemicals) of viscosity 50 mPa.s and surface tension 17.9 mN/m measured at 23°C in an Anton Paar rheometer and an FTA 188 video tensiometer respectively was used as the coating fluid in view of its low partial pressure (typically << 1 mbar). This enabled the gas pressure to be significantly reduced without risk of evaporation. The rheometry data over a range of shear rates showed the coating liquid to be Newtonian.

It should be noted that limiting this work to the use of one fluid does not diminish its validity as in our earlier research (Benkreira and Khan, 2008; Benkreira and Ikin, 2010), we systematically measured the effect of coating viscosity on air entrainment. Also, the choice of silicone oil of this particular viscosity of 50 mPa.s was dictated by the need to validate our coating data in air against prior work performed by Lee et al (1992) using a similar slot coater. Lower viscosity coatings will produce in tensioned web slot coating thinner films, of the order of 1 micron, but these would be difficult to measure precisely. The stability of such thin films would also be difficult to ascertain with precision. Our approach is thus limited to much higher coating thickness (of the order of 100 microns for SRC and 10 microns for TWSC) than ultimately sought within industry; the aim of the research being to confirm our reasoning on the role of gas film viscosity drawn from our previous work by collecting data as precisely as possible.

The Web: This was a transparent smooth polyester base, 5cm wide, the roughness being less than 0.5 μm as measured using a Taylor Hobson series Talysurf 4. Wettability was measured by tracking to an accuracy of ±1° the contact angle of a drop of the coating fluid on the web using an FTA 188 video tensiometer. The angles measured changed from 105° when the drop first hits the web to 43° and 23° after 0.2s and 1s respectively and reached an equilibrium value of 19.5° after 10s.

The Measurement of Film Thickness and Flow Defects: In previous investigations of slot coating, the wet film thicknesses were measured indirectly by measuring flow rates and web speeds. Here, the attempt to measure flow rate using a specially designed capillary and micro-manometer worked well when operating at atmospheric pressure but failed when at low sub-atmospheric pressure due to the coating liquid being drawn further into the connecting tubes and trapping gas pockets. It was therefore necessary to use a direct technique to measure wet thickness at any instant, here a capacitance sensor supplied by Physik Instrumente GmbH. The sensor 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.

Another feature of the experimental technique used here was to record film thickness and images of the instabilities (air/gas entrainment and ribbing) while the web speed was ramped up at a preset acceleration rather than in discreet steps. Ramp-up time was typically 20 seconds, during which the capacitance sensor output was recorded on one of two channels of a Pico-scope coupled to a computer. The second channel was used to record the output from a laser tachometer monitoring holes in a disk mounted at the end of a web transport roller to thus yield the web speed profile. CCD cameras were used to record images of the instantaneous web speed as displayed by an oscilloscope monitoring the laser tachometer output, a view of the coater as observed through a chamber side port and a view of the coating uniformity. A multiplexer was set up to enable 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 for the SRC mode 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. Visualisation of the coating quality for the TWSC mode was obtained with a camera directed normal to the web and opposite the slot exit using illumination at grazing incidence from one side of the web supplied from a lamp with a parabolic back reflector. 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 Gas Used (Helium) & Its "Thin Film Viscosity": Helium was chosen firstly because it has at sub-atmospheric pressures a lower thin film viscosity than air, and secondly it meets the prime requirement to enable manufacture in an oxygen-free environment. Thin film viscosity is used here to contrast it with bulk viscosity and refers to the viscosity of the gas film entrained during dynamic wetting. The film thickness is typically less than 2 µm - as measured by Muës et al (1989) using laser-doppler velocimetry. Bulk viscosities are typically measured using a gap of the order of millimeters (Starling and Woodhall, 1961) and found not to differ very much for air and helium (181 µPa compared with 199 µPa at 20˚C and 1 atm.) The thin film viscosity, on the other hand, needs to be measured using a gap representing the entrained film. For the case of helium at 25 mbars, the gap is then less than the mean free path - namely 11.4 µm (Benkreira and Ikin, 2010). A specialised technique for measuring the effective viscosity is thus required. Andrews and Harris (1995) have developed such a set-up, comprising two micro-machined plates spaced apart by 2 µm, one plate oscillating in a direction normal to the other spring-loaded plate. The relative motion is measured capacitively to determine the phase difference and from this, using a theoretical relationship, the gas viscosity responsible for damping. Using this technique, they were able to develop a master curve for a range of gases relating relative viscosity to d/λ, d being the gap and λ the mean free path of the gas and hence pressure. 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 and helium varies with pressure – see Fig. 6. It will now be seen that the effective thin film viscosity of helium at low pressures is very significantly lower than for air at atmospheric pressure.

3. RESULTS AND DISCUSSION

As both the slot over roll and tensioned web slot coaters used here were miniature design devices enclosed in a chamber, a first necessary step was to exploit the methods described to validate against previous data.

For slot over roll coating, we tested the accuracy of our experimental technique against the classic data of Lee et al (1992) obtained with no vacuum applied upstream. These workers carried out a comprehensive experimental programme using a steel roller of diameter 20 cm, a die with a slot 0.25 mm wide, 4 silicone oils of viscosities 10, 50, 350 and 1000 mPa.s and four slot-to-web coating gaps (200, 300, 500 and 1000 µm). The flow rates and film thicknesses were obtained by measuring the coated film scraped off the roller using a squeegee. Their criterion for minimum stable film thickness corresponds to the well-established method of Gutoff and Kendrick (1987) whereby, for a fixed flow rate, the coating speed was increased after initially achieving uniform defect-free coating until air entrainment or ribbing appeared. The data presented earlier in Figure 2 is reproduced from Figure 6 in their paper and shows how the minimum wet thickness firstly increases with speed and then levels off to a constant value provided the gap is sufficiently low. It should be noted that in addition to using similar if not identical fluid to ourselves, the coating speeds are within the same range as studied in our work.

We replicated Lee et al (1992) coating conditions that led to the lowest film thickness at the highest Ca, i.e. with their lowest gap of 200 μm and compared the minimum film thicknesses obtained in air at atmospheric pressure and helium at 25mbar. As shown in Fig.7, under atmospheric air we were able to reproduce their results. With helium maintained at 25 mbar pressure, we observed typically a 17% reduction in the minimum achievable wet thickness when using the slot over roll configuration. Although this may appear to be a marginal gain, the fact that the minimum stable film thickness has now been shifted to a lower value shows that our hypothesis holds true. However when we compare these minimum film thicknesses with the low flow limit predicted by the visco-capillary model, we find they are significantly higher suggesting that the use of a standard low vacuum upstream is the best option in practice as it prevents the upstream meniscus from invading the feed slot. Although encasing an SRC device in a high vacuum chamber filled with He helps wetting, it does not prevent the upstream meniscus from invading the feed slot.

Turning now to tensioned web slot coating, we carried out similar comparative experiments and were able, as shown in Fig.8, to measure more than a 25% reduction in the minimum achievable wet thickness or typically a two fold increase in the maximum coating speed for a given minimum achievable wet thickness. This is a significant gain which can be explained as follows. It should be remembered that in normal TWSC, the application of a low vacuum upstream is ineffective because the pressure in the coating bead is above atmospheric to counter the force imposed by the tensioned web over the die face. Under such a pressure field, the upstream meniscus in TWSC will be far upstream of the feed slot. As the web speed is increased, the dynamic wetting assistance of a reduced gas viscosity results in lower shear stress within the gas film (Vandre et al. [2014]) and less tendency to penetrate forward to result in gas entrainment. So in practice, our results show that the limit then becomes that due to ribbing caused by instability of the downstream meniscus.

Thus, although the range of the data obtained is limited due to the nature of the experimental set-up, we have established that as in dip coating, replacing air with helium at low pressures causes a delay in air/gas entrainment leading to higher operating speeds and lower film thickness. In the case of tensioned web coating, which is the only technique capable of achieving the very thin films required, we could double the maximum speed of operation.

What will be interesting is to carry out similar experiments but at much lower vacuum to establish the extent to which further enhancement can be achieved. This would require a more sophisticated set-up with stronger vacuum pumping than our simple preliminary method. There are however theoretical pointers to consider so as not to assume the expectation of an ever continuous wetting enhancement with reduced pressure. For example, according to Teletzke et al (1982) there is a critical gas capillary number $Ca_g^* = \mu_g v_w^* / \sigma_g$ that must be exceeded in order to entrain a thin gas film - namely to break dynamic wetting. Thus, assuming Ca_g^* to remain constant, we would expect that as the gas viscosity μ_g approaches zero as pressure is reduced then, v_w^* the critical web speed at which the gas is entrained will apparently increase to infinity. Our previous results in dip coating (Benkreira and Ikin, 2010) in fact show that Ca_g^* reduces monotonically with pressure in such a way as to dictate a finite maximum gas entrainment speed as gas viscosity approaches zero. Reasons for this finite limit would include other dissipative effects and the fact that a gas can no longer be considered as a viscous fluid and the whole concept of viscosity becomes questionable as pressure approaches zero (Knudsen flow).

As stated above, ribbing is known to occur at the downstream meniscus where there is a positive pressure gradient. What is of interest is that Yang at al.[2004] discovered another form of ribbing associated with a concave upstream meniscus using SRC operating at Ca < 0.1. Further work is therefore also needed to gain understanding as to the mechanisms involved for explaining these two instabilities with the aid of visualizing the shape and movement of the menisci viewed from one side of the coaters. A sound theoretical basis can then be established for explaining these effects in these interesting and widely used coating flows in order to quantify the extent to which we can lower this wetting low flow limit.

4. CONCLUSIONS

These experiments in slot coating, while limited to much higher coating thicknesses than ultimately sought within industry, confirms our reasoning drawn from our previous work on the role of gas film viscosity on dynamic wetting. We have demonstrated that it is possible to reduce the minimum achievable wet thickness by replacing air at atmospheric pressure with helium at low pressures. The work should therefore be of interest to industry involved in developing systems for manufacturing OPVs within an oxygen-free atmosphere. The enhancement is particularly significant with tensioned web slot coating as the upstream meniscus invasion is delayed with improved wetting. With slot over roll coating, the use of a small vacuum upstream is more effective at holding the upstream meniscus.

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.

The work, being wholly experimental, invites further study aimed at establishing a sound theoretical model for this effect, which we explain as resulting from less viscous coupling between the moving web and surrounding liquid and a consequential reduction in the force on the gas film enhancing its stability against entrainment.

5. ACKNOWLEDGEMENTS

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6. NOTATIONS

Ca	Capillary number with respect to the liquid phase $[= \mu v_w^* / \sigma]$
Ca_g^*	Capillary number with respect to the gas phase $[= \mu_g v_w^* / \sigma_g]$
h_g	Slot-web coating gap
h_w	Coating film thickness on the web
H_w	Dimensionless film thickness $[= h_w / h_g$
q	Coating flow rate delivered by the slot
p	Pressure
r	Radius of curvature
t	Time
T	Web tension
v_w	Web speed

v_{ae}	Air entrainment velocity
θ_c	Contact angle
λ	Mean fee path of the gas
μ	Viscosity of the coating liquid
μ_g	Viscosity of the gas when constrained to form a thin film
σ	Surface tension of the coating liquid
σ_g	Surface tension of the gas when constrained to form a thin film

7. REFERENCES

Andrews, M.K. and Harris, P.D., 1995. Damping and gas viscosity measurements using a microstructure. Sensors and Actuators, A Physical A 49 (1-2):103-108.

Beguin, A. E., 1954. Method of coating strip material. US Patent No. 2,681,294

Benkreira, H., 2004. The effect of web roughness on air entrainment in dip coating. Chemical Engineering Science 59, 2745-2751.

Benkreira, H., Ikin, J.B., 2010. Dynamic wetting and gas viscosity effects. Chemical Engineering Science 65, 1790–1796.

Benkreira, H., Khan, M.I., 2008. Air entrainment in dip coating under reduced air pressures. Chemical Engineering Science 63, 448–459.

Bhamidipati, K.L 2011. Detection and Elination of Defects during Manufacture of High-Temperature Polymer Electrolyte Membranes. PhD Thesis, Georgia Institute of Technology.

Blake, T.D., Ruschak, K.J., 1979. A maximum speed of wetting. Nature, 282, 489

Buonoplane, R. A., Gutoff, E. B., Rimore, M. M.T., 1986. Effect of plunging tape surface properties on air entrainment velocity. AIChE Journal 32, 682-686.

Burley, R., Kennedy, B. S., 1976. An experimental study of air entrainment at a solid-liquid gas interface. Chemical Engineering Science 31, 533-540.

Carvalho, M.S., Kheshgi, H.S., 2000. Low-flow limit in slot coating: theory and experiments. AIChE Journal 46, 1907-1917.

Clarke, A., 2002. Coating on a rough substrate. AIChE Journal 48, 2149-2156. 682-686

Cohu, O., Benkreira, H., 1998. Air entrainment in angled dip coating. Chemical Engineering Science 53, 533–540.

Deryagin, B.V., Levi, S.M., 1964. Film Coating Theory. Focal Press, London.

Durst, F., Wagner, H., 1997. Liquid Film Coating, Chapter 11a, Editors Peter M. Schweizer, and S.F. Kistler Chapman and Hall, UK.

Ding, X., Liu, J., Harris, T.A.L., 2016. A review of the operating limits in slot die coating processes. AIChE Journal DOI 10.1002/aic.15268.

Galagan, Y., de Vries, G. I., Langen, A.P., Andriessen, R., Verhees, W.J.H., Veenstra, S.C., Kroon, J.M., 2011. Technology development for roll-to-roll production of organic photovoltaics. Chemical Engineering and Processing 50, 454–461.

Gutoff, E.B., Cohen E.D. Coating and Drying Defects, John Wiley & Sons, Inc., Hoboken, New Jersey, (2006).

Gutoff, E.B., Kendrick, C.E., 1982. Dynamic contact angles. AIChE Journal 28, 459–466.

Higgins, B.G., Scriven, L.E., 1980. Capillary pressure and viscous pressure drop set bounds on coating bead operability. Chemical Engineering Science 35, 673–682

Jochem, C.M.G, van der Light, J.W.C., 1987. Method and arrangement for coating a fibre. USP 4,704,307.

Landau, L., Levich, B., 1942. Acta Physicochim URSS 17, 42

Lee, K.-Y., Liu, L.-D., Liu, T-J., 1992. Minimum wet thickness in extrusion slot coating. Chemical Engineering Science 47, 1703–1713.

Lin, F-H., Liu, C-M., Liu, T-J., Wu, P-Y., 2007. Experimental study on tensioned-web slot coating. Polymer Engineering and Science 47 (6), 841-851.

Mues, W., Hens, J., Boiy, L., 1989. Observation of a dynamic wetting process using laser-doppler velocimetry. AIChE Journal 35 (99), 1521-1526.

Nam, J., Carvalho, M.S., 2010. Flow in tensioned-web-over-slot die coating: Effect of die lip design. Chemical Engineering Science 65, 3957–3971.

Park, E., 2008. Physics of coating tensioned web over slot die. PhD Thesis, University of Minnesota.

Pearson, J.R.A., 1960. The stability of viscous flows under rollers and spreaders, Journal of Fluid Mechanics, 7, 481–500.

Pitts, E., Greiller, J., 1961. The flow of thin liquid films between rollers. Journal of Fluid Mechanics 11, 33–50.

Ruschak, K.J., 1976. Limiting flow in a pre-metered coating device. Chemical Engineering Science 31, 1057–1060.

Schmitt, M., Baunach, M., Wengeler, L., Peters, K., Junges, P., Scharfer, P., Schabel, W., 2013. Slot-die processing of lithium-ion battery electrodes—Coating window Characterization. Chemical Engineering and Processing 68, 32– 37.

Shikhmurzaev, Y.D., 1997. Moving contact lines in liquid / liquid / solid systems. Journal of Fluid Mechanics, 334, 211-249.

Søndergaard, R., Hösel, M., Angmo, D., Larsen-Olsen, T.T., Krebs, F.C., 2012. Roll to roll fabrication of polymer solar cells. Materials Today, 36 (15), 36-49.

Sprittles, J.E., 2015. Air entrainment in dynamic wetting: Knudsen effects and the influence of ambient air pressure. Journal of Fluid Mechanics, 769, 444-48.

Starling, S.G., Woodhall, A.J., 1961. Physics. Longmans, UK, pp 215-216.

Teletzke, G.F., Davis, H.T. & Scriven, L.E. (1982) Wetting Hydrodynamics Paper 77b AIChE Annual Meeting, Chicago.

Vandre, E., Carvalho, M.S., Kumar, S. 2014 Characteristics of air entrainment during dynamic wetting failure along a planar substrate. J. Fluid Mech. 747 pp 119-140

Yang, C.K., Wong, D.S.H., Liu, T-J, 2004.The Effects of Polymer Additives on the Operating Windows of Slot Coating. Polymer Engineering and Science 44 (10), 1970-1976.

LIST AND CAPTIONS OF TABLES AND FIGURES

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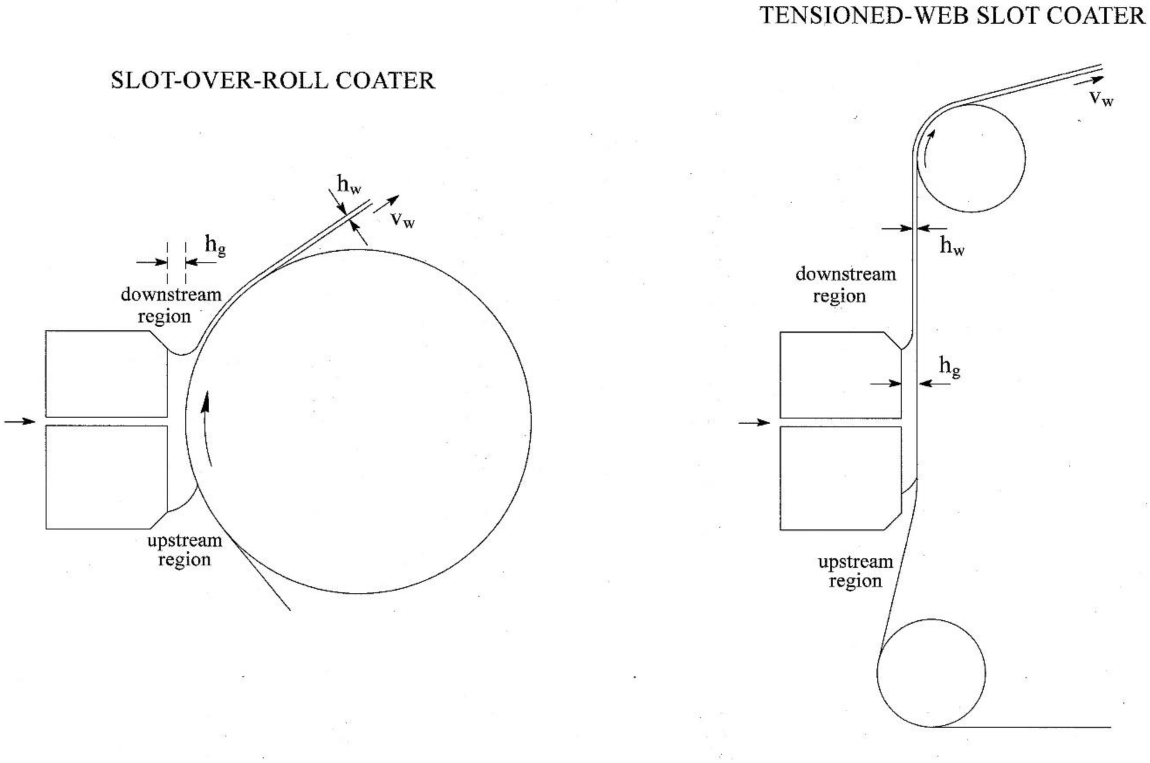
Fig.1: Slot coating flow domain or bead and its features.



SLOT-OVER-ROLL COATER

TENSIONED-WEB SLOT COATER

Fig.2: Minimum film thickness without vacuum and low flow limit using the visco-capillary model

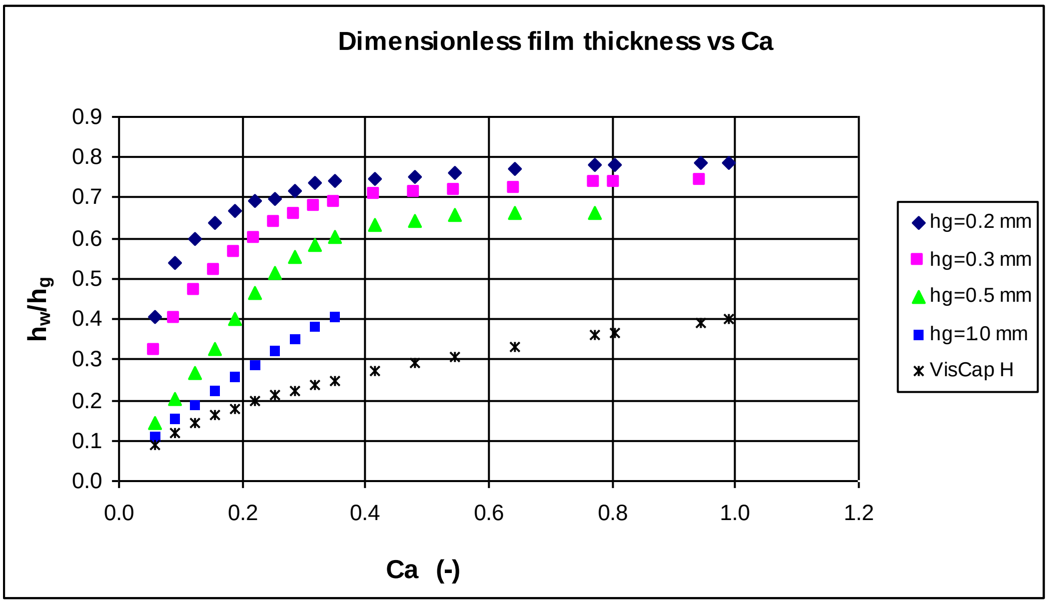


Fig.3: The slot coating over roll apparatus enclosed in a gas chamber.

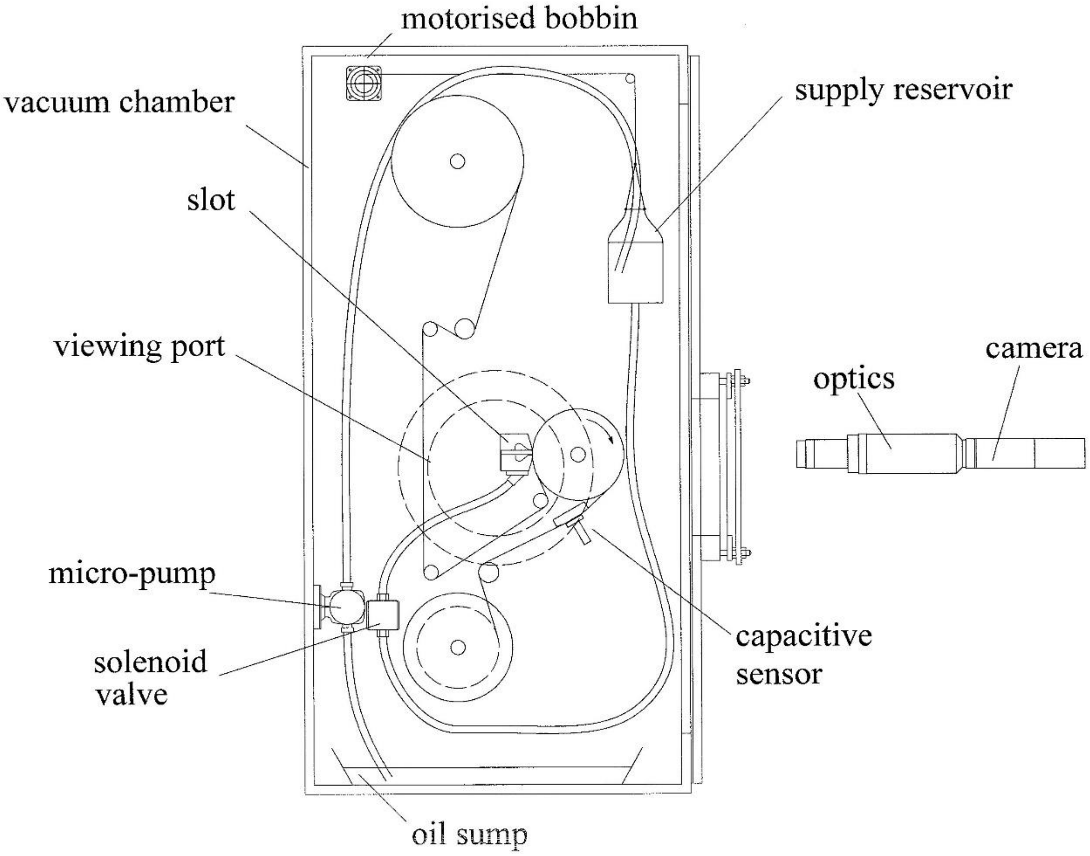


Fig.4: Mounting of the slot coater on a pivoting cradle and a translator.

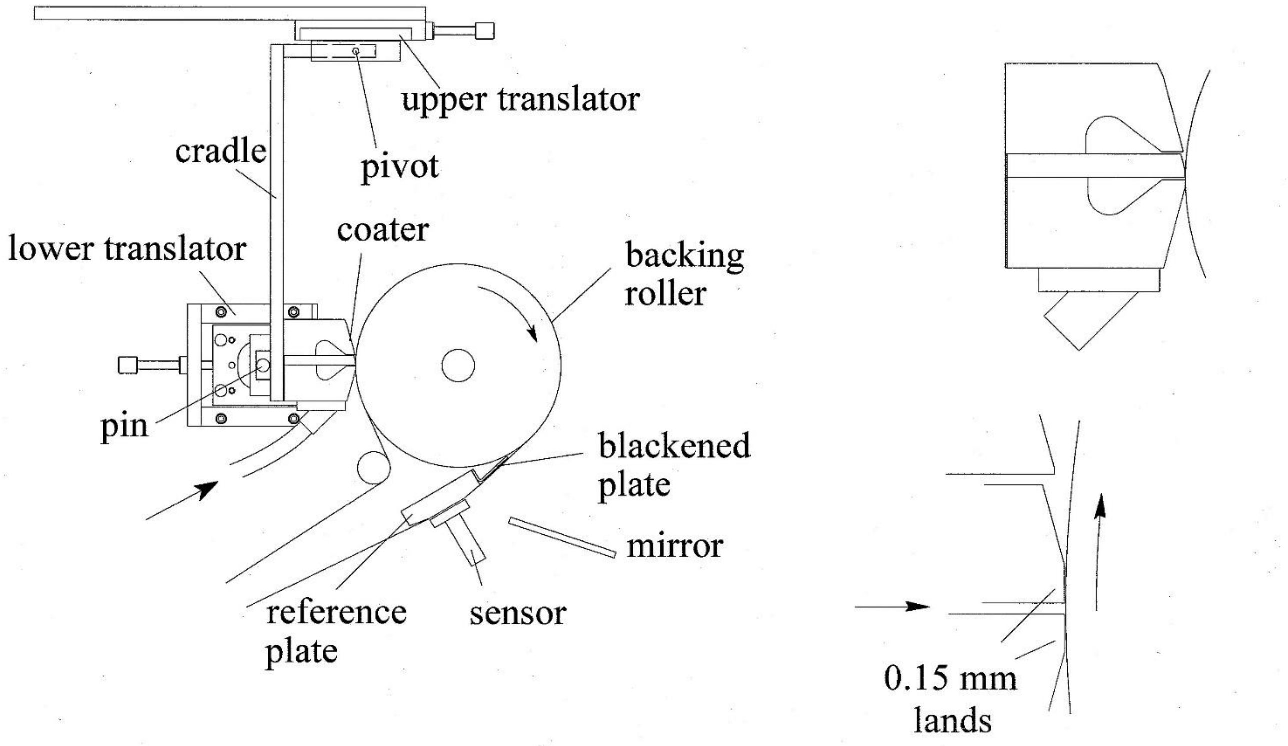


Fig.5: The web tensioned slot coating apparatus enclosed in a gas chamber.

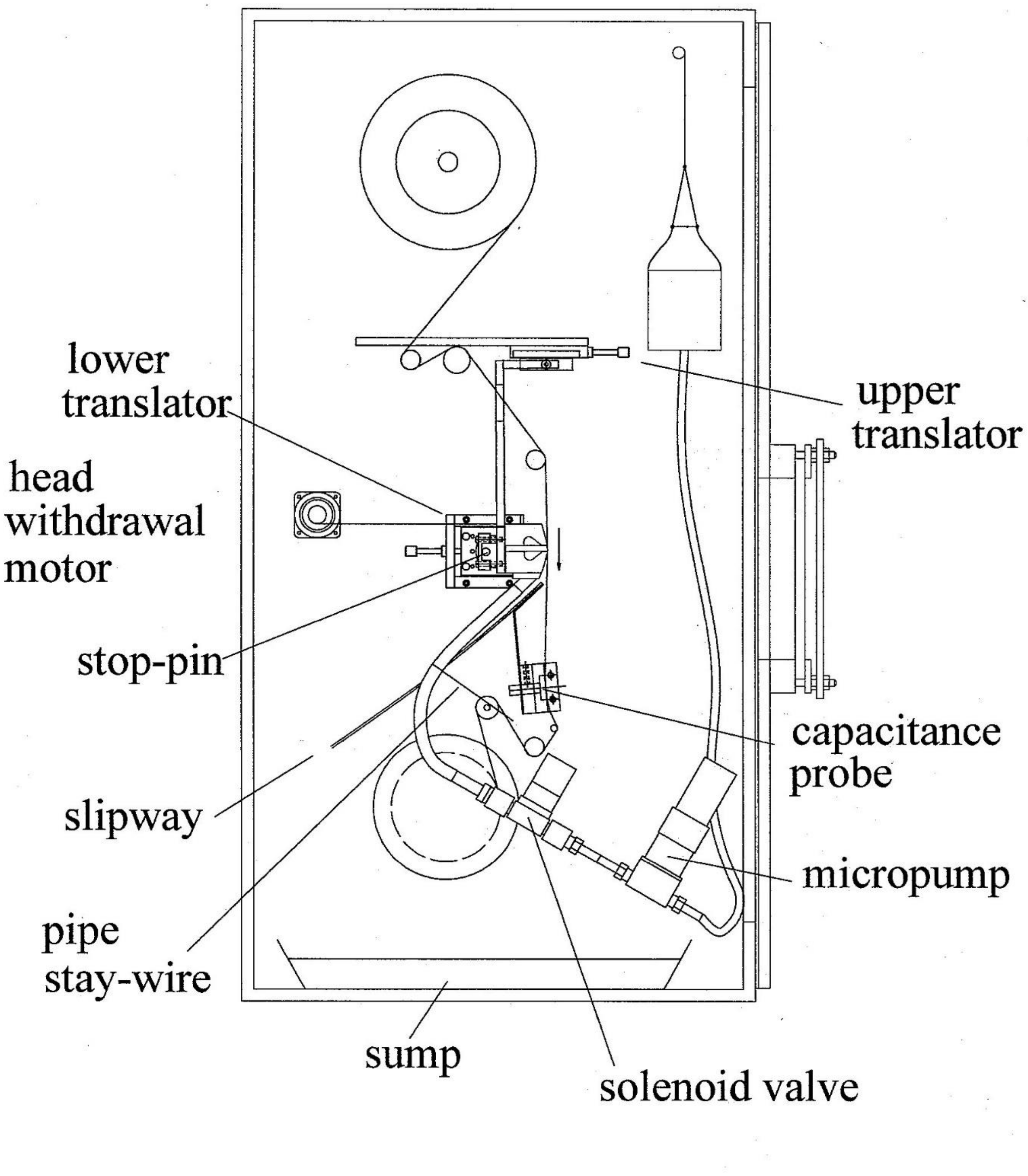


Fig.6: Mean free path and thin film viscosity of air and helium at sub-ambient pressures.

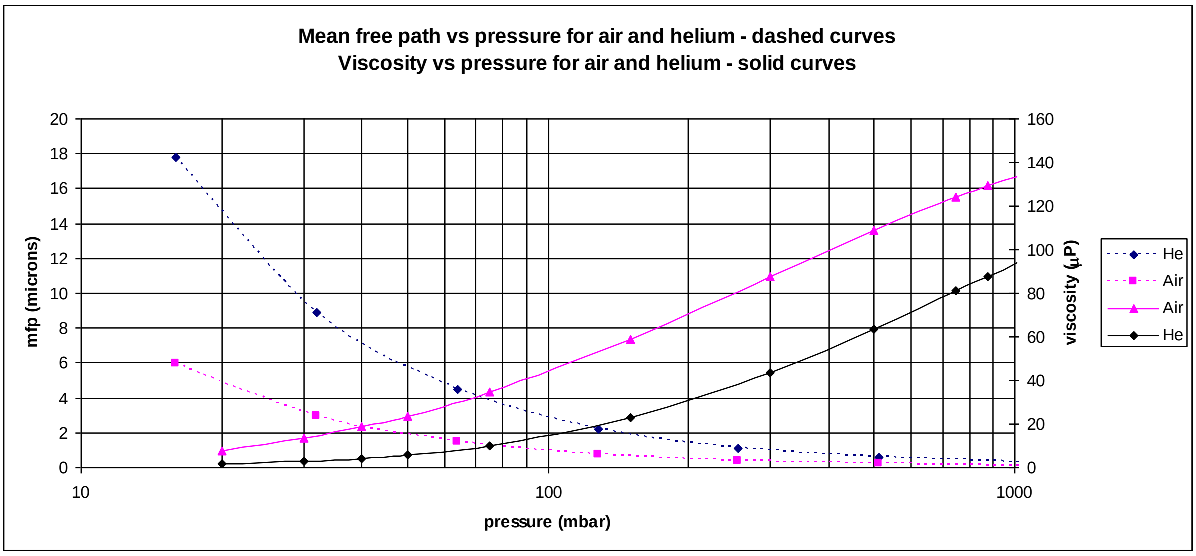


Fig.7: Minimum film thickness measured with slot over roll coating in air at atmospheric pressure and helium at 25mbar.

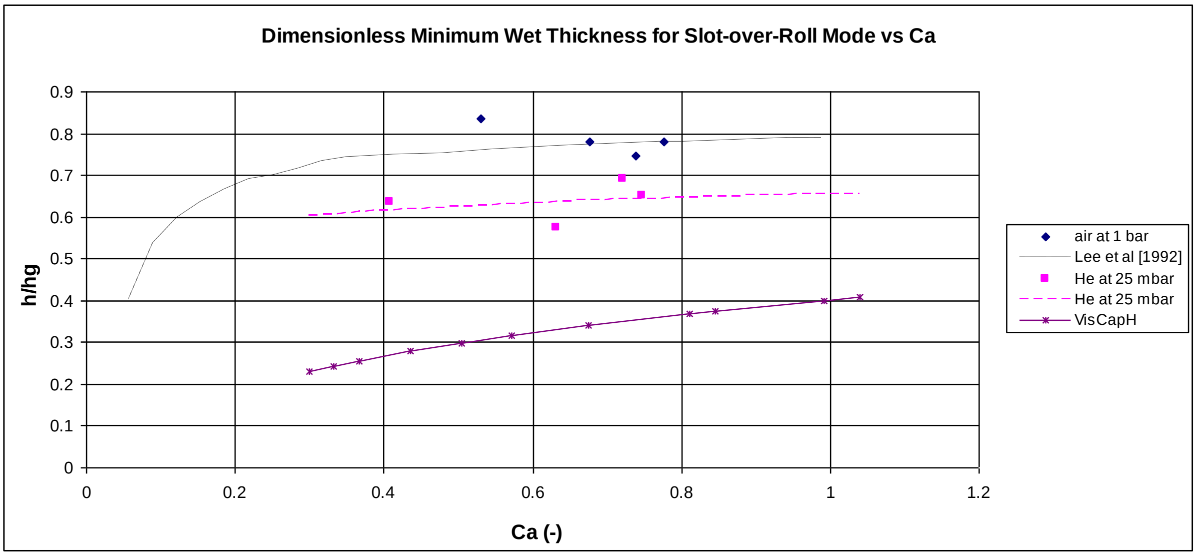


Fig.8: Minimum film thickness measured with tensioned web slot coating in air at atmospheric pressure and helium at 25mbar.