Capillary velocity of liquids between heterogeneous surfaces.

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Introduction.

Capillary forces and capillary flows are well known and have been studied in detail[1]. Most of the research in this field has been conducted on vertical capillaries and less on horizontal ones, assuming that the surface within in the capillary is uniform.

Hypothetically, the capillary velocity in an endless horizontal capillary will asymptotically approach to a speed of 0 m/sec, but never reach an equilibrium. This velocity depends on several factors, like interactions between the liquid and solid surface, viscosity of the liquid and shear rate. In real life, capillary flows mostly are desirable and essential for a variety of physical phenomenon. However in some exceptional situations, it is advantageous to reduce and control capillary flows for example for the slot die coating process. Therefore the capillary velocity between heterogeneous (hydrophobic and hydrophilic) surfaces was explored

Horizontal Capillary effects .

Slot die coating operation (Figure 1) is a suitable method to apply thin functional layers on flexible substrates. An example of such an application is illustrated (Figure 2) by means of a flexible organic solar cell. Stripe coating is an interesting technology to pattern functional layers during the coating process. However it was noticed that due to the low viscosity of the coating solution, in combination with relative low coating speeds, the lateral capillary velocity is an important factor which affects the width of the coated stripes. This is troublesome, especially when several layers have to be stacked with a high accuracy to form an organic solar cell. Reduction and controlling the lateral capillary velocity is therefore crucial. This can be achieved by means of hardware modifications of the slot die for example by using a so called notched die lip. Drawback of such a modification is that each slot die has dedicated pattern. Therefore it was interesting to research patterned modification of the surface of the die lip by means of applying self-assembling monolayers (SAM). It was expected that hydrophobic SAM layers would be able to reduce

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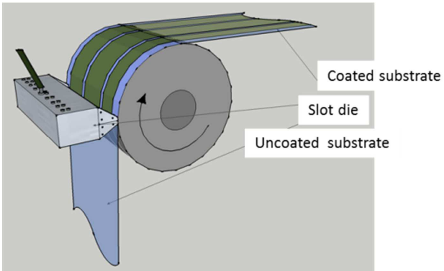


Figure 1. Slot die coating using of stripe coating.

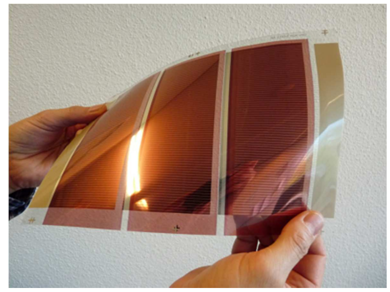


Figure 2. Flexible organic solar cell all functional layers solution processed.

the lateral capillary velocity. The die lip should then be locally hydrophobized . The capillary velocity would be then determined by two heterogeneous surfaces.

Ji Won Suk[1] used the following model to calculate the capillary pressure between heterogeneous surfaces for a horizontal capillary.

$$P = \frac{\gamma}{h}\left(\cos\theta_1 + \cos\theta_2 - \frac{2h}{w_0}\right) \qquad (1)$$

In which: P is the pressure in the liquid[Pa], γ Surface energy of the liquid[N/m , θ_1 Contact angle top surface [o], θ_2 Contact angle bottom surface [o], h Distance between plates[m] and w_0 the Channel width [m].

The capillary pressure can estimated by means of this model and subsequent the value can be used to estimate the volume flow rate, in the capillary a by means of the Hagen-Poiseuille equation(2). The calculated value will estimate the initial flow rate. In time the flow rate will decrease due to for example the friction between the liquid and the capillary walls.

$$Q = \frac{\pi R_h^4 P}{8 \mu L_0} \qquad (2)$$

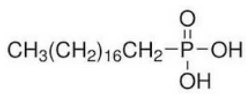
In which: Q is the Volume flow rate[m3/s], Rh the Hydraulic radius[m], P the Pressure in the liquid [Pa], µ the Liquid viscosity[Pa.s] and Lo the Channel length[m].

Experimental.

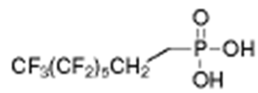
Self-assembling monolayers (SAM) layers are usually a suitable method to modify the energy level of surfaces, in this case the die lip. Besides the requirement to be hydrophobic and thin, the SAM layer needs to form a strong bond with the stainless steel.

Molecules which are usually necessary to form a SAM layer generally consists of two parts, the reactive head group and the functional tail. The head groups react with the surface and the hydrophobic tails align towards the opposite side. For this study the following precursors to form SAM layer were used[3]:

- Octadecylphosphonic acid(OPA) is a SAM with a phosphonic head group. Attached to this head group is a tail of 18 carbon atoms.
- 1H,1H,2H,2H-Perfluorooctanephosphonic acid(FOPA) has the same head group as the OPA molecule, but instead of 18 carbon atoms, the tail consists of only 8 carbon atoms which are fluorinated.



OPA



FOPA

In order to be able to measure the capillary flow velocity, a capillary was constructed with on top a horizontal glass plate on top and a stainless steel plate at the bottom . Except for the reference capillary , the stainless steel plate consist of a hydrophilic and hydrophobic area(Figure 3). The capillary velocity was measured through the glass with a camera. The stainless steel sample and glass were taped (thickness 45 µm) against each other to form a 90µm capillary (Figure 4).

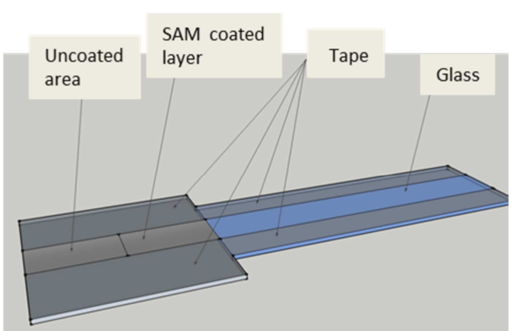


Figure 3. Connection of the steel and glass plate.

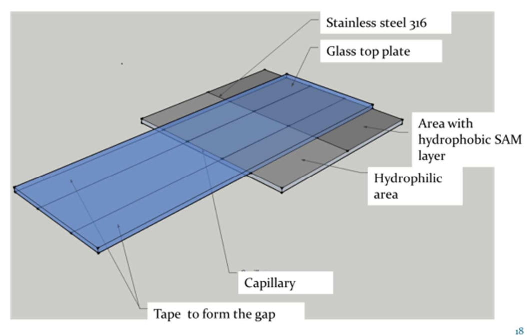


Figure 4. schematic drawing of the capillary test set-up

The experiment itself was performed by applying a droplet(with known volume) of the desired liquid to the glass surface, and subsequent the liquid was drawn into the capillary. This process was recorded through the glass . The relative speed reduction of the sample with a hydrophobic SAM layer was calculated in this way using the reference samples as a baseline .

Results and discussion .

Basic properties of the tested liquids are listed in Table 1. The velocity measurements show (Table 2) that a velocity reduction of at least 70% could be achieved . The results further show that the FOPA adds an additional 5% velocity reduction compared to the OPA.

Although the properties of the liquids deviate substantially it is surprising that the effect on the relative velocity reduction is more or less the same. The reason for this will be studied into more detail.

Liquid	Surface tension (mN/m)	Viscosity (cP) at 20C
Water	70	1.0
Toluene	28	0.56
Pedot::PSS	34	10

Table 1. properties of liquids.

Liquid.	Surface treatment.	Average capillary velocity(mm/sec).	St.dev.	Relative velocity reduction(%)
Water	None	1,59	0,17	
	OPA	0,42	0,01	74
	FOPA	0,31	0,03	80
Toluene	None	4,68	1,18	
	OPA	0,79	0,08	83
	FOPA	0,60	0,01	87
Pedot:PSS	None	0,25	0,02	
	OPA	0,07	0,003	70
	FOPA	0,06	0,002	75

Table 2. Capillary velocity reduction of water, toluene and Pedot:PSS between heterogeneous surfaces.

Summary and Conclusion.

The results of the experiments show, that hydrophobic SAM layers could be applied to a stainless steel effectively . Due to this, the lateral capillary velocity between the hydrophobic and hydrophilic plates could be reduced significantly. Next phase of the research is to conform the results in a R2R slot die coating process.

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