

Roll-to-roll large-format slot die coating of photosensitive resin for UV embossing

Z. W. Zhong · X. C. Shan · S. J. Wong

Received: 17 February 2011 / Accepted: 26 August 2011 / Published online: 30 October 2011
© Springer-Verlag 2011

Abstract Roll-to-roll large-format coating and UV embossing processes aim to revolutionise the manufacturing of functional films, with the ability to process a large-area at one time, resulting in high throughput and cost reduction. In this article, we present the experimental results obtained during the process development for roll-to-roll large-format coating and UV embossing. We have investigated key areas of the processes with the aim of improving them in the long term through the understanding of the key factors associated with them and their effects on the processes. The areas investigated are the UV-curable liquid resin, the roll-to-roll film substrate, the coating process and quality, and the UV embossing process and quality. The emphasis is placed on the investigation of the coating process and quality. The results show that the roll-to-roll coating and embossing processes are capable of producing micro-scale structures and functional devices over a large area at one time. They are complex processes with many factors playing important roles.

1 Introduction

For the fabrication of structures on the micro to nano scale, continuous development of photolithography could lead to significant cost increases, while scanning beam lithography

requires many hours to pattern a small area such as 1 cm² (Gates et al. 2005). Using conventional fabrication techniques to manufacture nano scale features will eventually lead to massive cost increases and low throughput levels (Sotomayor Torres et al. 2003). Therefore, new techniques must be developed to meet the increasing demand and lower the manufacture cost so as to make the products more commercially viable (Gates et al. 2005).

New techniques based on moulding and embossing, have emerged as promising alternatives, and nanoimprint lithography, an embossing-based technique, is such a promising technique for low cost, high throughput and high resolution patterning (Ahn and Guo 2008, 2009; Chou et al. 1995; Guo 2004, 2007; Schiff 2008; Zhong et al. 2010). To make embossing-based techniques commercially viable, their throughput levels must be increased. Planar embossing processes have limitations, and utilising flat moulds is inappropriate for large area pattern fabrication, as the cost of large-scale flat moulds is very high and there are uniformity and releasing problems in large-scale flat moulding processes (Ahn et al. 2006).

Roll-to-roll embossing applies the continuous roll-to-roll process in order to drastically increase the patterning speed and thus increase throughput. There is much on-going research to develop roll-to-roll embossing and increase its range of applications (Ahn and Guo 2008, 2009; Kololuoma et al. 2004; Krebs 2009; Mäkelä et al. 2007; Nagato et al. 2010; Velten et al. 2008; Yeo et al. 2010). By fulfilling the aims of lower cost and higher throughput, roll-to-roll embossing is targeted to be a commercially viable method for fabricating of micro and nano scale structures.

Slot die coating is a method whereby a ribbon of coating fluid flows between the coating device and the coated surface, and was first invented by Beguin (1954) for

Z. W. Zhong (✉) · S. J. Wong
School of Mechanical and Aerospace Engineering,
Nanyang Technological University, 50 Nanyang Avenue,
Singapore 639798, Singapore
e-mail: mzwzhong@ntu.edu.sg

X. C. Shan
Singapore Institute of Manufacturing Technology,
71 Nanyang Drive, Singapore 638075, Singapore

manufacturing of photographic film to overcome many disadvantages and limitations of other coating methods such as dipping, applicator roll, and doctor blade. A slot die coating system consists of five main components: slot die, slot die positioner, backup roller, fluid delivery system, and substrate (Lippert 2006; Miller 2009). The advantages of slot die coating include increased production speeds, good coat weight control, cross-web distribution control, and improved waste management (Cohen 1992; Miller 2009).

This work focuses on the investigations of the key factors associated with the slot die coating process. Various experiments were carried out using a prototyped roll-to-roll large-format-coating and UV embossing machine to investigate the liquid photosensitive resin, the film substrate, the coating process, and the UV embossing process.

2 Experiments

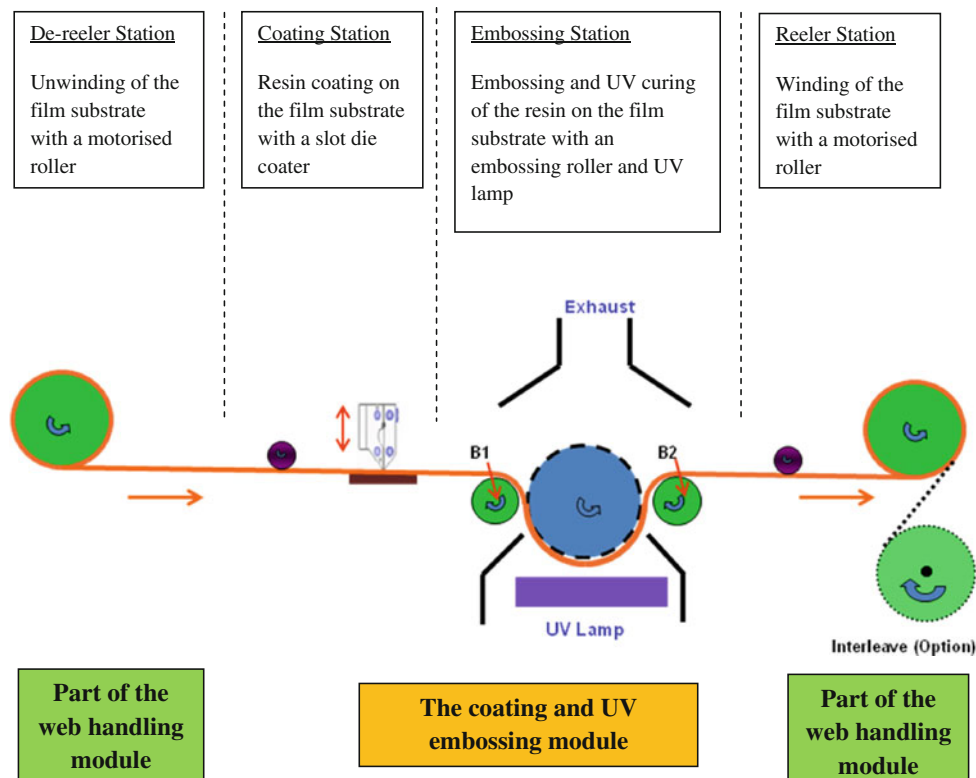
We target to develop roll-to-roll large-area ultraviolet (UV) embossing processes for fabricating micro features on flexible plastic films. Critical challenges in such processes include precision coating of UV-curable liquid resin and curing the resin for micro-structuring at a low temperature and a low pressure. The prototyped roll-to-roll large-format-coating and embossing machine used in this work is shown in Fig. 1. The components are arranged into two

main modules based on their functions. They are a web handling module, and a coating and embossing module.

The coating and embossing module is located at the centre of the machine and contains all the components required for the photosensitive resin coating on the flexible film substrate, the embossing, and the curing through UV light exposure. The key components in this model include a slot die coater, an embossing roller, and a UV lamp. The system can process 500-mm web-width flexible films, and the coating width of the slot die is 250 mm. By using different flexible moulds, various structures can be fabricated by roll-to-roll UV embossing.

As also shown in Fig. 1, the web handling module is located at the two ends of the machine, drives the flexible film substrate, controls its web-speed, and provides tension to the film substrate in the coating and embossing processes. It consists of a de-reeler station and a reeler station. A raw film roll is installed on a motorised roller at the de-reeler station, which feeds the raw film substrate into the coating and embossing module. After the coating, embossing and curing processes are completed, another motorised roller at the reeler station receives the film substrate containing the embossed features, and rolls it back into a roll so that it can be removed later by the machine operator. The web-speed of the film substrate is determined by the rotational speed of the reeler roller.

Fig. 1 Schematic diagram of the coating and embossing module and the web handling module



The UV-curable liquid resins (Epoxy Technology—EPO-TEK® OG134 and OG172) were mixed with different volume ratios to achieve different viscosities. Two mixtures, resin A (mixture of OG134 and OG172 in the ratio of 4:1) and resin B (mixture of OG134 and OG172 in the ratio of 2:1), were mainly investigated in this work.

Two types of film substrates were also investigated: untreated PET (polyethylene terephthalate) film, and treated PET film. The PET film thickness selected is 125 µm. The “treated PET film” is pre-treated on its both sides with a primer treatment for promoting adhesion of coated layers. Thus, this film has a structure of primer, base film and primer. The film is highly transparent with good ink adhesion properties.

The viscosity values of the UV-curable liquid resins were measured using a rotational cylinder type rheometer. To evaluate the wettability of the UV-curable liquid resins on the film substrates, the static contact angles of the liquid resin droplets on the two types of the PET film substrates were measured. In addition, the static contact angles of deionised water droplets on the two types of PET film substrates were also measured.

Several factors of the coating process using the slot die coater affect the quality of the coating produced. They are the pneumatic pressure applied to the liquid resin in the cylindrical reservoir through a vertical plunger, the web-speed which is the linear speed of the film substrate passing under the slot die coater, the viscosity of the liquid resin, and the slot-die-coater height, which is the vertical distance between the slot die coater’s lip and the film substrate. They were varied and their effects on the coating quality were investigated.

The slot die coater shown in Fig. 2 is located in the coating station of the coating and embossing module. It has a 250-mm coating lip width with a 0.1-mm slot gap, and has a simple triangular shaped cavity manifold design. The slot die coater utilises a shim in between the two halves of the slot die coater to maintain the 0.1-mm slot gap throughout the 250-mm coating lip width shown in Fig. 3,

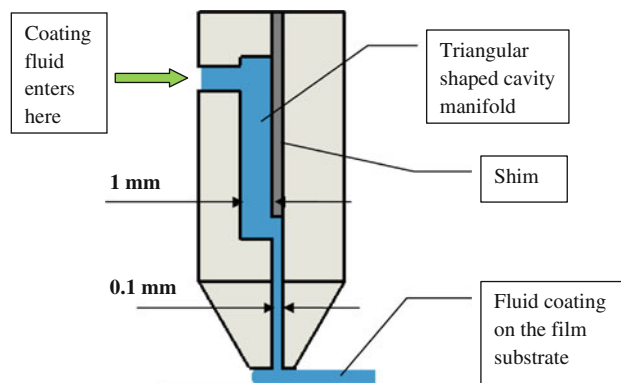


Fig. 3 Sectional side view of the slot die coater (drawing not to scale)

which shows a sectional side view of the flow of the coating fluid through the slot die coater. It has a flexible lip design to fine-tune the cross-web distribution of the coating fluid exiting the slot die. The flexible lip is adjusted using a series of bolts, which apply pressures to one side of the flexible lip and allow the user to fine-tune the slot gap.

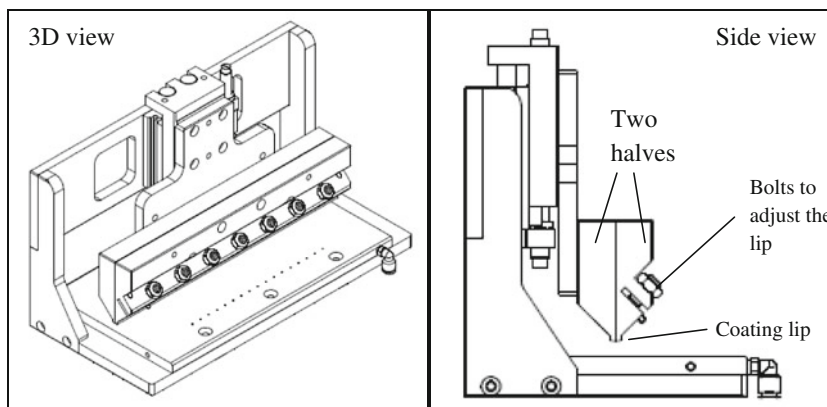
The coating fluid flows to the slot die coater from a cylindrical reservoir. A pneumatic pressure is tapped from the compressed air supply and controlled by an inline air pressure regulator. The pressure is applied to the coating fluid via a vertical plunger in the reservoir. The slot-die-coater height (the vertical distance between the coater’s lip and the film substrate) is adjusted with the aid of a dial gauge built into the coater.

The web-speed of the film substrate is determined by the rotational speed of the reeler roller, which is controlled by the controller of the roller motor. The web-speed can be read from a digital LCD, which displays the speed value obtained from a rotary encoder mounted on the roller that contacts the film substrate.

In this work, the following experiments were carried out:

1. The pneumatic pressure applied to the liquid resin reservoir was varied, and its effect on the coating

Fig. 2 The slot die coater used



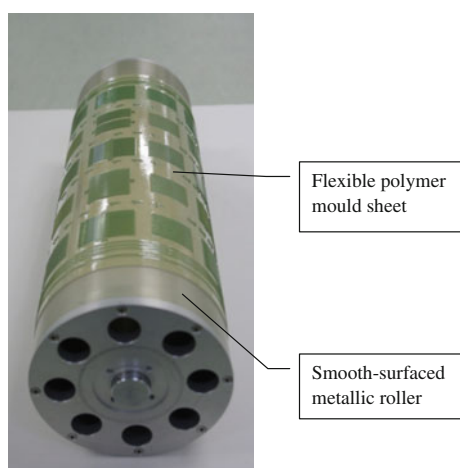


Fig. 4 A flexible polymer mould mounted on a metal roller

quality was investigated. The web-speed used in this experiment was 0.5 m/min.

- At a constant pneumatic pressure applied to the liquid resin reservoir, the web-speed was varied and its effect on the coating quality was investigated.
- Using resins A and B, the above two experiments were conducted and the effects of the liquid resins with different viscosity values on the coating quality were investigated.
- The slot-die-coater height was varied, with the other parameters being constant, and its effect on the coating quality was investigated.
- Continuous coating was performed for a length of 2 m. The cross-web and down-web uniformity of the coating was then measured to evaluate the performance of the slot die coater.

The coating thickness uniformity was measured after the liquid resin coating was cured through UV light exposure when it passed through the embossing station. The film substrate was then cut into breadth-wise strips and the coating thickness values were measured using a digital micrometer.

The embossing process used a flexible polymer mould, which was attached on a metal roller as shown in Fig. 4, via a double side adhesive tape, which is a method often used in flexo-printing. The mould contained micro-scale patterns to be embossed onto the resin coating on the film substrate. The UV lamp was located directly under the embossing roller. This configuration allows simultaneous embossing and curing of the liquid resin coating, increasing the production speed. After embossing, 3D surfaces of the embossed patterns and their corresponding mould patterns were generated using a contact profilometer. These 3D surfaces were then compared to determine the quality and fidelity of the embossed patterns.

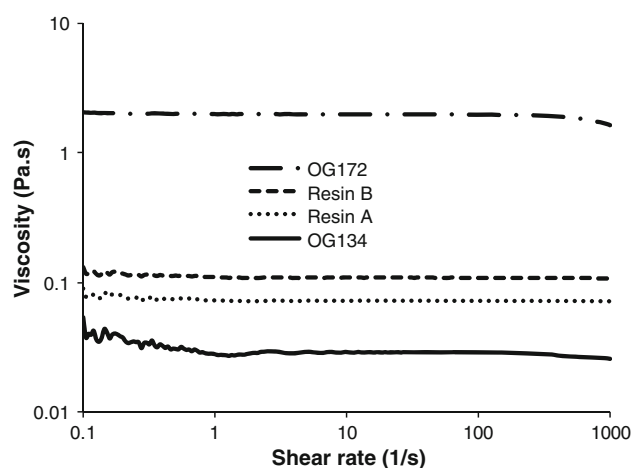


Fig. 5 The rheology curves of the UV-curable liquid resins

3 Results and discussions

Figure 5 shows the rheology curves of the UV-curable liquid resins. The curves for all the liquid resins investigated indicate that the viscosity values are relatively constant and independent of the shear rate. The liquid resins behave as Newtonian fluids whereby their viscosity values are constant. This means that the liquid resins do not suffer from shear thickening whereby the viscosity increases with the shear rate, and do not suffer from shear thinning whereby the viscosity decreases with the shear rate.

Figure 6 shows a series of images showing the shape change of the liquid resin droplet over time. The images were captured with the aid of image capturing and computer software, at various time intervals after the liquid resin droplet came into contact with the PET film substrate. In these images, the liquid resin droplet is observed to be spreading with a corresponding drop of its contact angle as time increases. More importantly, these images allow the contact angle of the liquid resin droplet to be measured accurately at the corresponding time point.

Figure 7 shows the variations of the contact angles, over time after contact, of resins A and B on the untreated and treated PET films investigated. Table 1 shows the contact angle values of deionised water on the untreated and treated PET films. Figure 7 clearly indicates that the contact angles of resins A and B are functions of time, and decrease as time increases because of solvent evaporation during the contact angle experiments.

In addition, there is a difference of the contact angle behaviours between deionized water and resins on the untreated and treated PET films investigated. Based on the contact angle measurements of the liquid resins on the films (Fig. 7), it can be seen that the untreated PET film offers slightly better wettability compared to the treated

Fig. 6 Captured images showing the shape change of the liquid resin droplet over time

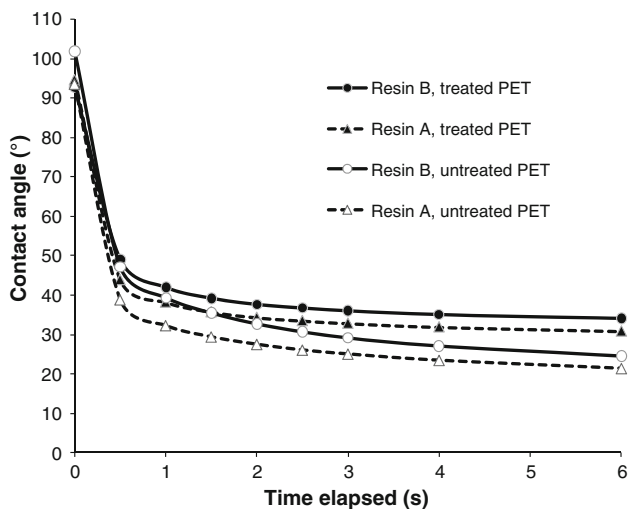
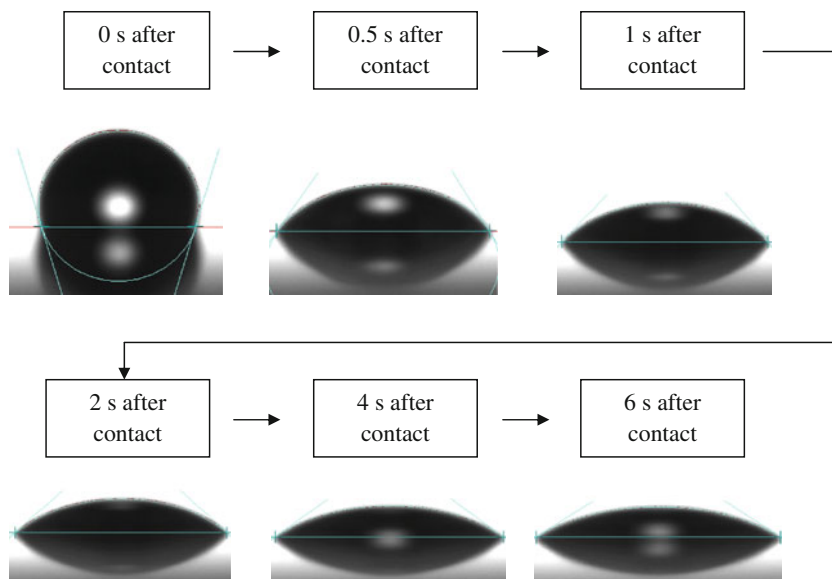


Fig. 7 The variations of the contact angles, over time after contact, of resins A and B on the untreated and treated PET films investigated

PET film, as the corresponding contact angle is slightly lower. A lower contact angle would indicate higher solid surface energy and chemical affinity or good wetting. This is not an expected result as the treated PET film was expected to offer better adhesion. We believe that the reason for this is that there probably are some chemical interactions between the PET films and the resins investigated in this work, which cause this unexpected phenomenon. However, there are not chemical interactions between the PET films and deionized water. Therefore, it can be seen from Table 1 that the contact angles of deionised water on the treated PET film are lower than those on the untreated PET film. This means that the

Table 1 Contact angle values of deionised water on the untreated and treated PET films investigated

No.	Contact angle on untreated film (°)	Contact angle on treated film (°)
1	76.31	66.30
2	76.84	66.39
3	77.97	67.30
4	77.45	66.42
5	76.89	67.88
6	76.21	66.25
7	76.02	66.67
8	77.08	66.32
9	77.64	66.19
10	77.07	66.87
Average contact angle (°)		66.66

treated PET film offers better wettability for deionised water on it, compared to the untreated PET film.

Considering potential optical applications of the embossed patterns, the clarity of the PET film to be used is very important. The untreated PET film has a slightly hazy appearance, while the treated PET film has excellent optical transparency. Therefore, the treated PET film was eventually selected for the experiments carried out for the investigations of the coating process and the embossing process in this work.

Figures 8 and 9 show the thickness variations and the average coating thickness versus web-speed, with a constant pneumatic pressure applied to the liquid resin reservoir when resins A and B were used, respectively. The figures contain the thickness values obtained at different

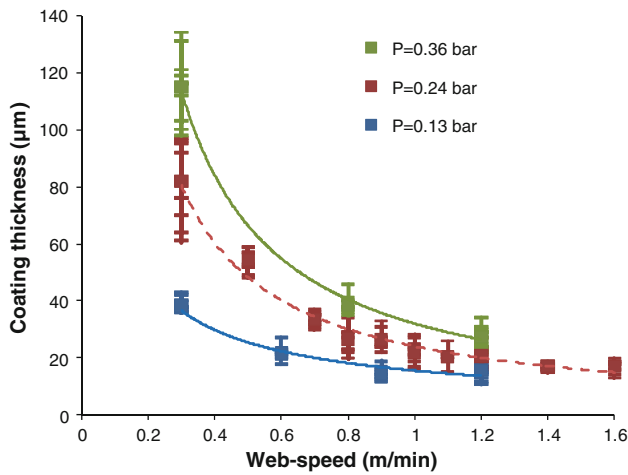


Fig. 8 Thickness variations and the average coating thickness versus web-speed, with a constant pneumatic pressure applied to the liquid resin reservoir when resin A was used

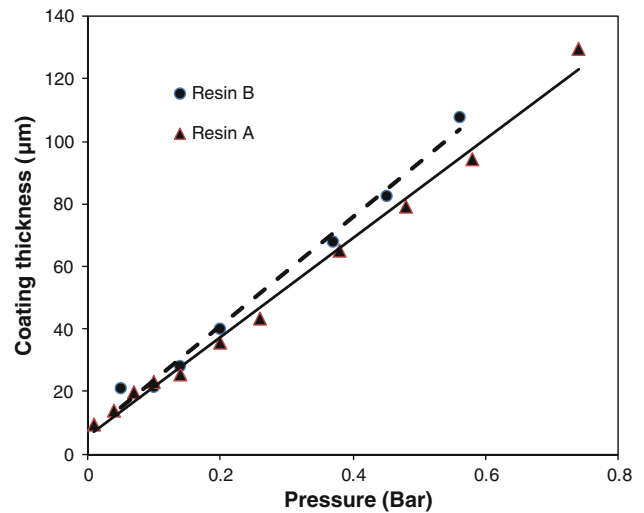


Fig. 10 The average coating thickness versus the pneumatic pressure (web-speed = 0.5 m/min)

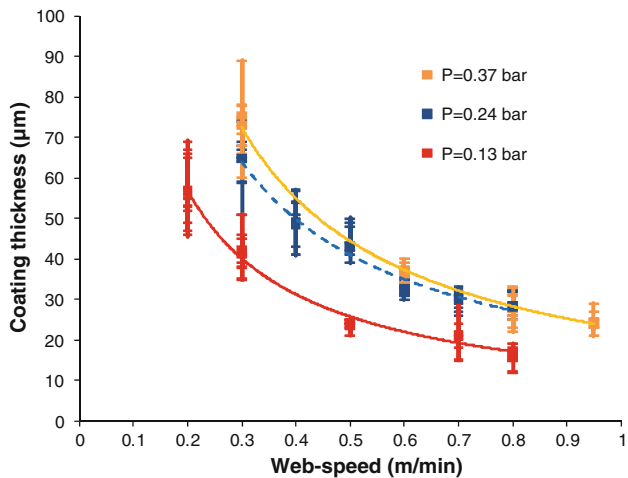


Fig. 9 Thickness variations and the average coating thickness versus web-speed, with a constant pneumatic pressure applied to the liquid resin reservoir when resin B was used

but constant pneumatic pressures. There is a decrease in the coating thickness when the web-speed is increased with a constant pressure applied to the liquid resin reservoir. This trend is evident in all the experiments carried out using resins A and B at the pneumatic pressures. The results are reasonable for slot die coating, as the thickness of the fluid coating can be controlled by regulating the pneumatic pressure and the web-speed. The results also suggest that there is a minimum achievable coating thickness, after which any increase in the web-speed or decrease in the pneumatic pressure will not allow for the formation of an acceptable fluid coating with a lower thickness.

Figure 10 shows the average coating thickness versus the pneumatic pressure applied to the liquid resin reservoir. There is a linear increase in coating thickness of resins A

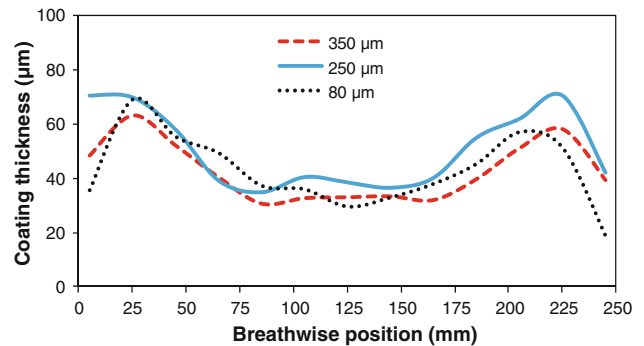


Fig. 11 Curves representing the cross-sectional profiles of the coatings produced at different slot-die-coater heights (resin A, pressure = 0.2 bar, web-speed = 0.5 m/min)

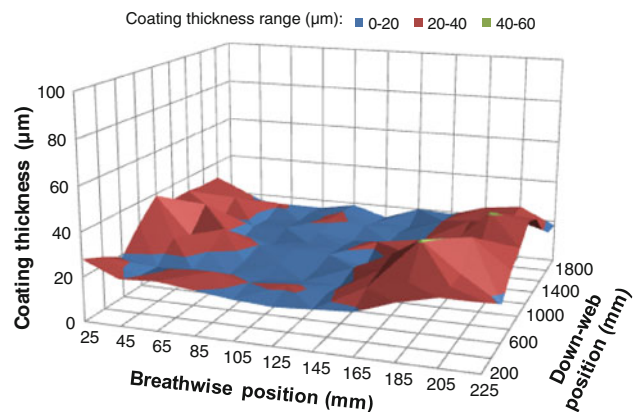


Fig. 12 3D view of a coating surface generated with the data obtained from cross-web and down-web uniformity measurements (resin A, pressure = 0.1 bar, web-speed = 0.66 m/min)

and B as the pressure applied to the liquid resin reservoir is increased. This result is also reasonable for slot die coating, as the thickness of the fluid coating can be controlled by

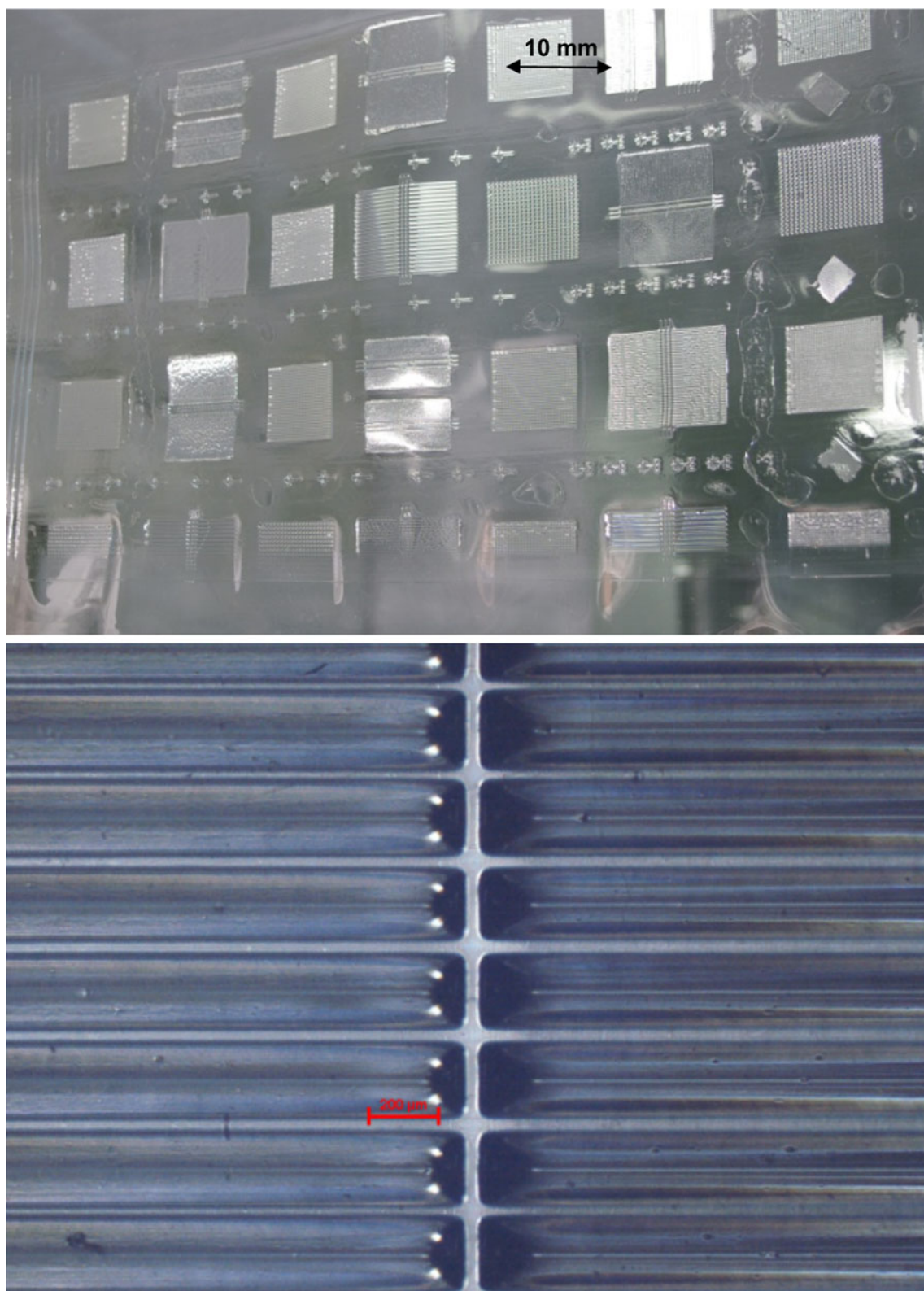


Fig. 13 Embossed patterns on the PET film substrate and the protrusive lines on the film

regulating the pneumatic pressure applied to the liquid resin reservoir and all the fluid going into the slot die is applied to the substrate surface without any wastage (Lippert 2006; Miller 2009).

The curves in Fig. 11 represent the cross-sectional thickness profiles of the coatings produced at different slot-die-coater heights. Adjustment of only the slot-die-coater height had a little effect on the achievable coating thickness. However, when the experiment was carrying out, it was observed that as the slot-die-coater height was increased, it took a longer time for cross-web distribution of the liquid resin to stabilise and form a uniform fluid coating. When the slot-die-coater height was set at 350 μm , the time taken for the fluid coating to stabilise was long, resulting in wastage of the liquid resin. Therefore, the decision was made not to further increase the height for testing.

Closer inspection found that the slot die coater lip was not straight but instead was slightly concaved. This meant that the edges of the slot die coater were slightly closer to the substrate compared to the central region. The slot-die-coater height was inconsistent along the width of the slot die coater. According to Lippert (Lippert 2006), the face-to-web gap of the slot-die-coater affects the wiping shear generated, which is an important factor in the generation of a good coating. The concave nature of the slot-die-coater lip would result in a varying wiping shear along the width of the slot die coater.

Figure 12 is a 3D view of a coating surface generated with the data obtained from cross-web and down-web uniformity measurements. The figure shows the cross-web and down-web uniformity of the resin coating over a continuous 2-m down-web length of the film substrate. There was good down-web uniformity and cross-web uniformity over the central portion of the coating surface. There was more variance of the measured coating thickness at the edges. The edges of the coating surface were thicker compared to the central portion of the coating.

According to (Chan and Venkatraman 2006; Gutoff and Cohen 2006a, b), when the edges of a fluid coating are thinner and contain less fluid amounts, this could result in an increase in the coating thickness at the edges after curing, due to the surface tension effect. As the coating is thinner at the edges, the solvent evaporation is much faster at the edges of the film, because there are larger surface areas per unit volume of the fluid near the edges. A solvent usually has a lower surface tension compared to the resin. As a larger amount of the solvent evaporates, the edges start to have a higher surface tension compared to the central region of the resin, which causes the fluid resin to be transported from the central region to the edges. When this happens, the newly formed surface in the central region would have a lower surface tension due to the

exposure of the underlying resin which has a higher solvent concentration. This leads to even more fluid resin transported from the central region to the surrounding areas due to the surface tension gradient across the regions.

Figure 13 shows pictures of the embossed patterns on the PET film substrate and the protrusive lines on the film obtained via roll-to-roll UV embossing. Resin A was used and the coating thickness was about 20 μm . The embossed protrusive lines replicated the profiles of the channels precisely, with the width and pitch of 100 and 500 μm , respectively. The height of the embossed lines ranged from 11.5 to 12 μm , with a fidelity error $<5\%$ in the vertical direction. Patterns of channel/line = 500 $\mu\text{m}/500 \mu\text{m}$ with an aspect ratio (height to width) = 0.59 were also achieved and the fidelity error in the vertical direction was -7.5% .

4 Conclusions

UV-curable resins with different viscosity values have been investigated for roll-to-roll large-format coating and embossing, and coating thicknesses ranging from 10 to 130 μm have been achieved using a slot die coater. It has been found that the pneumatic pressure and the web-speed are key factors in determining the coating thickness. The roll-to-roll coating and embossing processes are capable of producing micro-scale structures and functional devices over a large area at one time. They are complex processes with many factors playing important roles. The need to produce features of micro sizes on a large area with high fidelity results in even higher demands on the machine and processes. Therefore, further improvements will have to be made in order for the roll-to-roll large-format coating and embossing processes to become commercially viable.

References

- Ahn SH, Guo LJ (2008) High-speed roll-to-roll nanoimprint lithography on flexible plastic substrates. *Adv Mater* 20(11):2044–2049
- Ahn SH, Guo LJ (2009) Large-area roll-to-roll and roll-to-plate nanoimprint lithography: a step toward high-throughput application of continuous nanoimprinting. *ACS Nano* 3(8):2304–2310
- Ahn S, Cha J, Myung H, Kim S-M, Kang S (2006) Continuous ultraviolet roll nanoimprinting process for replicating large-scale nano- and micropatterns. *Appl Phys Lett* 89 (21). Article Number: 213101
- Beguín AE (1954) Method of coating strip material. US Patent 2,681,294, EASTMAN KODAK CO
- Chan C-M, Venkatraman S (2006) Coating rheology. In: Tracton AA (ed) *Coatings technology handbook*, 3rd edn. Taylor & Francis Group, LLC, Boca Raton, pp 2–1–2–14
- Chou SY, Krauss PR, Renstrom PJ (1995) Imprint of sub-25 nm vias and trenches in polymers. *Appl Phys Lett* 67(21):3114–3116

- Cohen ED (1992) Choosing the coating method. In: Cohen ED, Guttoff EB (eds) *Modern coating and drying technology*. VCH, New York, pp 1–22
- Gates BD, Xu QB, Stewart M, Ryan D, Willson CG, Whitesides GM (2005) New approaches to nanofabrication: molding, printing, and other techniques. *Chem Rev* 105(4):1171–1196
- Guo LJ (2004) Recent progress in nanoimprint technology and its applications. *J Phys D Appl Phys* 37(11):R123–R141
- Guo LJ (2007) Nanoimprint lithography: methods and material requirements. *Adv Mater* 19(4):495–513
- Guttoff EB, Cohen ED (2006a) Problems in slot, extrusion, slide, and curtain coating. In: Guttoff EB, Cohen ED (eds) *Coating and drying defects: troubleshooting operating problems*. Wiley-Interscience, Hoboken, pp 97–142
- Guttoff EB, Cohen ED (2006b) Surface tension driven defects. In: Guttoff EB, Cohen ED (eds) *Coating and drying defects: troubleshooting operating problems*. Wiley-Interscience, Hoboken, pp 157–168
- Kololuoma TK, Tuomikoski M, Makela T, Heilmann J, Haring T, Kallioinen J, Hagberg J, Kettunen I, Kopola HK (2004) Towards roll-to-roll fabrication of electronics, optics, and optoelectronics for smart and intelligent packaging. *Proc SPIE* 5363:77–85
- Krebs FC (2009) All solution roll-to-roll processed polymer solar cells free from indium-tin-oxide and vacuum coating steps. *Org Electron* 10(5):761–768
- Lippert H (2006) Slot die coating for low viscosity fluids. In: Tracton AA (ed) *Coatings technology handbook*, 3rd edn. Taylor & Francis Group, LLC, Boca Raton, pp 19–11–19–15
- Mäkelä T, Haatainen T, Majander P, Ahopelto J (2007) Continuous roll to roll nanoimprinting of inherently conducting polyaniline. *Microelectron Eng* 84(5–8):877–879
- Miller MD (2009) Slot die coating technology. <http://www.pstc.org/files/public/Miller09.pdf>. Accessed 7 Sep 2010
- Nagato K, Sugimoto S, Hamaguchi T, Nakao M (2010) Iterative roller imprint of multilayered nanostructures. *Microelectron Eng* 87(5–8):1543–1545
- Schift H (2008) Nanoimprint lithography: an old story in modern times? a review. *J Vacuum Sci Technol B: Microelectron Nanometer Struct* 26(2):458–480
- Sotomayor Torres CM, Zankovych S, Seekamp J, Kam AP, Clavijo Cedeño C, Hoffmann T, Ahopelto J, Reuther F, Pfeiffer K, Bleidiessel G, Gruetzner G, Maximov MV, Heidari B (2003) Nanoimprint lithography: an alternative nanofabrication approach. *Mater Sci Eng C* 23(1–2):23–31
- Velten T, Schuck H, Richter M, Klink G, Bock K, Malek CK, Roth S, Schoo H, Bolt PJ (2008) Microfluidics on foil: state of the art and new developments. *Proc Inst Mech Eng. Part B: J Eng Manufact* 222(1):107–116
- Yeo LP, Ng SH, Wang ZF, Xia HM, Wang ZP, Thang VS, Zhong ZW, de Rooij NF (2010) Investigation of hot roller embossing for microfluidic devices. *J Micromechan Microeng* 20(1). Article Number: 015017
- Zhong ZW, Shan XC, Yao YC (2010) Investigation of antiadhesive coatings for nanoimprinting lithography. *Mater Manuf Process* 25(7):658–664