Statistical analysis for the manufacturing of multi-strip patterns by roll-to-roll single slot-die systems

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Roll-to-roll (R2R) slot-die coating systems are mostly devoted to the mass manufacture of printed electronics. This study examined the correlation among the operating conditions, thickness, and width of the patterned strip fabricated by the R2R slot-die system. A full factorial experiment was conducted to screen for effective parameters. The velocity of a moving substrate was found to be the most dominant parameter affecting the thickness and width of the patterned strips. The flow ratio of the supply to the slot-die, and gap between substrate and slot-die did not affect the width of the strip, but affected the thickness; therefore, the flow ratio and gap can be employed for the independent patterning of thickness against width. In addition, it was proposed to determine the R2R process conditions, such as gap, velocity, and flow ratio for the desired thickness and width of the patterned strips.

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1. Introduction

The roll-to-roll (R2R) printing methodology using gravure, inkjet, and slot-die printing technologies has been adapted for the manufacturing of printed electronic devices such as printed sensors, RFID tag, rectifier, OPV, EMI filter, artificial skins, etc. [1–8]. Mass production is desirable to open additional markets for “ambient intelligence” by R2R printed electronics for reducing the product cost [9].

Slot-die is one of the most promising technologies for the manufacturing of printed electronics which are multi-layered and flexible, and the ability of the slot-die method to produce pre-metered, thin, uniform, and large-area printing has made it the target of recent research [10]. Blankenburg proposed upscaling the process for thin polymer solar cells (OPV) using a laboratory R2R slot-die printing machine [11]. Krebs proposed polymer solar cell modules manufactured by full R2R processing (comprising flexography, slot-die, and rotary screen printing), which have a best power conversion efficiency of 2.75%. He also proposed the use of slot-die printing and screen printing for an indium tin oxide (ITO)-free flexible polymer solar cell with an efficiency of 1.4% [12,13].

Galagan analyzed the effect of process conditions on the performance of polymer solar cells that were adjusted for slot-die R2R printing [14].

In the slot-die printing, the thickness of printed pattern is determined in advance of the experiment by adjusting the flow rate of the solution that supplied to the slot-die according to the operating velocity of the moving substrate. It is known that the velocity of the moving substrate, the capillary number, and the viscosity of solution determine the thickness. However, the determination of the thickness is valid only by the applying of slot-die for whole coating or single strip printing due to its limitation of 2-dimensional mathematical model [15].

When the slot-die is applied in a multi-strip printing rather than to the whole area coating or single-strip printing, it is important to control the width of the patterned strip as well as the thickness precisely. In multi-layered printed circuits, printing errors with regard to the width of the strip can generate shortcircuits or electricity leakages.

There have been several studies on the influence of the process conditions of the slot-die, including the velocity, the thickness of the coated layer, the flow rate of the solution supplied to the slot-die, and the viscosity of the solution. Romero analyzed the mechanism of the limit of minimum thickness at given conditions of substrate velocity, capillary, and inertial forces in the flow [10,16]. Lin carried out theoretically two-dimensional numerical estimations on the operating windows of the slot die [17]. Chang investigated the minimum wet thickness of the slot-die coating in
experimental studies [18]. All of these results were carried out in a two-dimensional plane which consists of thickness-axis and time-axis, under the typical assumption of no variation in the width of the slot-die coated pattern. However, the width of the patterned strip is also subject to the operating conditions, which affects the quality of registration in multilayered patterning [13,14]. Accordingly, it is important to analyze the correlation between the process parameters and the coated thickness and width of the multi-strip. However, there has been no research with regard to variations in the width of the slot-die patterned multi-strip with changes in process conditions. In the current study, the effects of the operation parameters on the thickness and the width of the strips were analyzed. Using the full factorial design of experiment, the effects of operating conditions were examined in the range of experimental inputs. Analysis of Variance (ANOVA) tool was employed for statistical analysis of the major parameters. In addition, a mandatory strategy was proposed for fabricating multi-strip with the desired thickness and width by single slot-die system. These results can be used to tune the operating conditions for the patterning of multi-strip by the R2R slot-die systems (Fig. 1).

2. Mathematical modeling

The typical cross sectional view of slot-die lip during the coating process is depicted as shown in Fig. 2. At the downstream, the maximum pressure difference is calculated as Eq. (1) in given conditions of surface tension and gap between slot-die lip and substrate by the visco-capillary model [19].

\[ \Delta P_{\text{max}} = \frac{2\sigma}{H_0 - t} \]  

(1)

where \( \sigma \) is surface tension, \( H_0 \) is gap between slot-die lip and substrate, \( t \) is thickness of coated layer.

Also, Landau and Levich [20] suggested the pressure drop along the meniscus of downstream as follows:

\[ \Delta P_{\text{max}} = 1.34 \frac{\text{Ca}}{t} \]  

(2)

where \( \text{Ca} \) is capillary number.

The capillary number is defined as

\[ \text{Ca} = \frac{\mu V}{\sigma} \]  

(3)

where \( \mu \) is viscosity, \( V \) is the velocity of a moving substrate.

The minimum thickness of the coated layer using the slot-die printing system can be determined as the following equation by combining Eqs. (1)–(3):

\[ t_{\text{min}} = \frac{H_0}{1 + 1.49\left(\frac{\mu V}{\sigma}\right)^{2/3}} \]  

(4)

Eq. (4) physically means the minimum thickness of coated layer, which do not break up the meniscus between slot die and substrate. In Fig. 3 effects of operating parameters on the minimum thickness were depicted as a function of velocity, viscosity, and gap. The operating condition was velocity of 7 m/min, viscosity of 4 mPa s, and surface tension of 20 dyn/cm. In both Fig. 3(a) and (b), the minimum thickness was proportional to the gap between slot-die and substrate. Also velocity and viscosity were proportional to the minimum thickness. Besides, the effect of velocity and viscosity on the thickness was increased as the size of gap raised.

In experiment, however, the thickness of coated layer could be larger than minimum thickness due to the flow rate of feeding solution, which was not considered in Eq. (4). In addition, from the experimental studies by Lee and Liu [21] the minimum thickness can be achieved only using negative pressure in the vacuum box of Fig. 2. It is known that without the negative pressure the thickness is greater than the minimum thickness of Eq. (4). Normally ambient printing condition is required for the wide applicability in the R2R printing process. In the general R2R printing condition of no vacuum box, therefore the minimum thickness of printed layer is greater than the results of Eq. (4).

Applying the law of conservation of mass to the slot-die nozzle in Fig. 2, it yields the following equation:

\[ \frac{d}{dt} \int V(x) dx = f_r - \left[ nwt V \right] \]  

(5)

where \( V(x) \) is mass in control volume, \( f_r \) is flow rate of supplying solution, \( n \) is number of strips, \( w \) is width of strip, \( t \) is thickness of strip, \( V \) is operating velocity.

At the steady-state Eq. (5) can be written as

\[ f_r = nwt V \]  

(6)

Combining and rearranging Eqs. (4) and (6) give

\[ w = \frac{f_r}{nVH_0} \left[ 1 + 1.49\left(\frac{\mu V}{\sigma}\right)^{2/3} \right] \]  

(7)

Eq. (7) is the width of the strip for minimum thickness of coated layer by the slot-die. As it was mentioned before, the thickness in experiment could be higher than Eq. (4) of minimum thickness due to no consideration of flow ratio. So, Eq. (7) of the width should also be affected by the variation of coated thickness. Therefore, experimental studies were performed to investigate the effects of operating parameters including flow ratio, velocity, and gap on the thickness and width of printed patterns.
3. Methods and materials

3.1. Printing materials

Polyvinylcarbazole (PVK) was purchased from TCI (Tokyo Chemical Industry, Japan). The solution for the experiment was formulated using the precursor of PVK and 0.55 wt% 1,2-dichloroethane, which acted as a solvent. The viscosity of the formulated solution was 3.8 mPa s at 16.5 °C and the surface tension was 20 dyn/cm.

Primer-treated PET (polyethylene terephthalate) substrate was purchased from TOYOBO (Japan). The substrate properties were as follows: thickness of 100 µm, width of 200 mm, Young’s modulus of 167 MPa, and coefficient of thermal expansion of 15.63 × 10⁻⁶ °C⁻¹ m⁻¹.

3.2. Printing methods

The experimental studies were carried out in ambient conditions using R2R slot-die systems composed of unwinding, infeeding, slot-die printing, hot air drying, cooling, outfeeding, rewinding, and pumping units as shown in Fig. 4. Process parameters such as the operating velocity, the tension of the substrate, the gap between the slot-die lip and the substrate, and the flow ratio of the supply solution were controlled in real-time during the experiments. The R2R slot-die systems and the pumping systems were manufactured by SAM (Sung-An Machinery, Republic of Korea), and ISMATEC (model: ISM901B, USA), respectively as shown in Fig. 5(a) and (b). Inside the slot-die, a shim plate with a thickness of 100 µm was installed. For the patterning of two strips, the shim plate had two blanks with a width of 50 mm each and spacing between them of 50 mm. An interferometer (model: NS-E1000, NanoSystem, Korea) was used for the measurement of the strip pattern, as shown in Fig. 6.

3.3. Selection of factors and levels

Three factors (velocity of moving substrate, gap between slot-die lip and substrate, and flow ratio of supplying solution into slot-die) were selected in this study. Two levels were determined for each factor in the experiment. For example the velocity of a moving substrate (factor A) is within 7 m/min and 9 m/min, the gap between slot-die lip and substrate (factor B) is within 350 µm and 425 µm, and flow ratio of solution supplying into slot-die (factor C) is in the range of 8 cm³/min and 9.6 cm³/min. The notation of (+) means high value of the level, and (−) means low value of the level. The operation conditions and notations of factor of R2R slot-die printing were summarized in Table 1.

3.4. Statistical method [22]

For the statistical analysis, the 2^n full factorial design was employed with combination of 8 treatments using the two levels of three R2R parameters. The combination was outlined as shown in Table 2. The third column of treatment represents the experimental condition of level of each factor, e.g. ‘c’ is low level of A and B, and high level of C. The fourth column of replication represents the number of measurement of each output.

The main effect of factor can be determined by

\[ X_A = \frac{T_1 - T_0}{2^{n-1} r} \]

where \( X_i \) is main effect of i-factor, \( n \) is number of factor, \( r \) is number of replication, and \( T_i \) is sum of all case of i-level of factor, e.g., \( T_1 = T_{100} + T_{101} + T_{110} + T_{111} \).

The interaction can is calculated by

\[ X_{A \times B} = \frac{(T_{11} + T_{00}) - (T_{01} + T_{10})}{2^{n-1} r} \]

\[ X_{A \times C} = \frac{(T_{11} + T_{00}) - (T_{01} + T_{10})}{2^{n-1} r} \]

\[ X_{B \times C} = \frac{(T_{11} + T_{00}) - (T_{01} + T_{10})}{2^{n-1} r} \]

Fig. 3. Numerical simulation of effect of operating conditions on minimum thickness: (a) effect of velocity and gap on minimum thickness and (b) effect of viscosity and gap on minimum thickness.

Fig. 4. Schematic of slot-die patterning system.
Total sum of square (SS_T), sum of square of effect (SS_i), and sum of squared error (SS_E) are calculated by the following equations:

\[
SS_T = \sum_{i=0}^{r} \sum_{j=0}^{c} \sum_{k=0}^{b} y_{ijk}^2 - \left[ \frac{\sum_i^r \sum_j^c \sum_k^b y_{ijk}}{2^{n-2}} \right]^2
\]

SS_i = r2^n-2X_i

SS_E = SS_T - \sum SS_i

where X_i is effect of i-factor, n is number of effect.

Total degree of freedom (\(\phi_T\)), degree of freedom of main factor (\(\phi_i\)), interaction (\(\phi_{ij}+\phi_{i,j,k}\)), and error (\(\phi_E\)) are calculated by

\[
\phi_T = 2^n - 1
\]

\[
\phi_i = (l) - 1
\]

\[
\phi_{ij} = \phi_i + \phi_j
\]

\[
\phi_{i,j,k} = \phi_{i,j} + \phi_k
\]

\[
\phi_E = \phi_T - \sum \phi_i
\]

where i, j, k are factors, l is number of level of i-factor.

Mean square (MS_i), F statistic (F_i), and F critical value (F_{crit}) are calculated by the following equations:

\[
MS_i = \frac{SS_i}{\phi_i}
\]

\[
F_i = \frac{MS_i}{MS_E}
\]

\[
F_{crit} = \frac{F_{crit}}{F_i}
\]
\[ F_r = \frac{M_{S_r}}{M_S} \]  
(15)

\[ F_{cri} = F(\phi_1, \phi_2; \alpha) \]  
(16)

where \( M_{S_r} \) is mean square of error, \( \alpha \) is significance level.

4. Results and discussion

4.1. Experimental results

The experimental results of measured thickness and width of printed strips in treatment combinations are summarized in Table 3. For the reliability of the experiment, 5 samples were measured and averaged. Then, the experimental results were verified using the dimensionless number, \( T \), which was suggested as follows:

\[ T = \frac{100 \text{wt}}{f_{ii}} \]  
(17)

where \( w \) is width (cm), \( t \) is thickness (cm), \( f_{ii} \) is supplying volume per unit length (cm³/m).

Applying Eq. (17) to Table 3, then the dimensionless number \( T \) was calculated as 2.06, 1.79, 2.88, 2.73, 3.51, 4.44, 4.27, and 5.72 in descending power. The differences in \( T \) were initiated by both measuring limitation and uneven thickness at side. The thickness of coated layer was measured by interferometer at each edge of strip so that the transferred mass increased in both ends, during the coating, cross directional meniscus occurred at each side of strip so that the transferred mass increased in both ends, which resulted in uneven thickness. However, we could assume that the trend of thickness in cross direction is regular, and it is comparable within experimental ranges.

4.2. Statistical results

In the beginning of ANOVA test, all factors were included for the test. And their effect, sum of square, degree of freedom, mean square, and \( F \)-value were calculated using Eqs. (8)–(15). The significant factors can be determined by comparing \( F \)-statistic \( (F_i) \) and \( F \)-critical value \( (F_{cri}) \). The \( F_{cri} \) works as a threshold to evaluate the significance among the factors. If \( F_i \) is larger than \( F_{cri} \), the \( i \)-factor is determined as a dominant one for the output. The \( F_{cri} \) for ANOVA test which included all factors is \( F(1,101) = 39.86 \) calculated by Eq. (16). And \( F_i \) calculated by Eq. (15) is summarized in the sixth column of Tables 4 and 5. The effect of respective factors and interactions were calculated by Eqs. (8) and (9) in the second column of Tables 4 and 5.

In case of thickness, dominant factors are velocity \((A)\), gap \((B)\), and flow ratio \((C)\). Also the interaction of velocity \( \times \) flow rate \((A \times C)\) is significant for thickness. However, the interactions of velocity \( \times \) gap \((A \times B)\) and gap \( \times \) flow ratio \((B \times C)\) are not dominant for the thickness. The trends of thickness also can be estimated by Eq. (4) that thickness is proportional to the gap and the velocity. But the effect of flow ratio cannot be estimated by Eq. (4), otherwise the statistical analysis gives an experimental verification of flow ratio as it is proportional to the thickness. The effects of every factor on the thickness are positive. Velocity \((A)\) is most effective factor and flow ratio \((C)\), gap \((B)\), velocity \( \times \) flow ratio \((A \times C)\), velocity \( \times \) gap \((A \times B)\), gap \( \times \) flow ratio \((B \times C)\) are effective factors in descending series on thickness.

In regard to the width, the statistic of \( F_A \) is outstanding among the factors but it is hard to estimate that of the dominance due to a meager margin of \( F_A \) comparing \( F_{cri} \). Therefore, ANOVA test for width should be conducted repeatedly with pooled trivial factors into the error; \( F_i \) less than 1 is pooled so that the recalculated results are summarized in Table 6. \( F_{cri} \) is 8.52 with pooling of the trivial factor in Table 6. Only factor \( A \) (velocity) is larger than \( F_{cri} \); therefore factor \( A \) (velocity) is dominant for the width of strip. And other factors \((B, C)\) or interactions are not significant for the width. In contrast to the thickness, the effects of every factor on width are negative except velocity \( \times \) flow ratio \((A \times C)\).

Furthermore, the factor \( A \) (velocity) is unique dominant factor for the width with negative relationship. But on the other hand, the factors \( A \) (velocity), \( B \) (gap), \( C \) (flow ratio), and \( A \times C \) (velocity \( \times \) flow ratio) are dominant for the thickness with positive relationship. These relationships between dominant factors and output (thickness and width) can be used for fabrication of multi-strip patterns with desired thickness and width. First, the

Table 3

<table>
<thead>
<tr>
<th>Treatment combination no.</th>
<th>Factors</th>
<th>Average of thickness (µm)</th>
<th>Average of width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (m/min)</td>
<td>B (µm)</td>
<td>C (cm³/m)</td>
</tr>
<tr>
<td>1</td>
<td>+</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>–</td>
<td>–</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>+</td>
<td>–</td>
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</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>–</td>
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<td>5</td>
<td>–</td>
<td>–</td>
<td>+</td>
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<td>6</td>
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<td>7</td>
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<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Table 4

Result of ANOVA test for thickness with all factors.

<table>
<thead>
<tr>
<th>Source</th>
<th>Effect</th>
<th>Sum of square</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>676.415</td>
<td>228,769</td>
<td>1</td>
<td>228,769</td>
<td>454.88</td>
</tr>
<tr>
<td>B</td>
<td>309.055</td>
<td>47,757</td>
<td>1</td>
<td>47,757</td>
<td>94.96</td>
</tr>
<tr>
<td>C</td>
<td>313.375</td>
<td>49,102</td>
<td>1</td>
<td>49,102</td>
<td>97.63</td>
</tr>
<tr>
<td>A × B</td>
<td>51.345</td>
<td>5273</td>
<td>1</td>
<td>5273</td>
<td>10.49</td>
</tr>
<tr>
<td>A × C</td>
<td>116.0175</td>
<td>26,920</td>
<td>1</td>
<td>26,920</td>
<td>53.53</td>
</tr>
<tr>
<td>B × C</td>
<td>46.3775</td>
<td>4302</td>
<td>1</td>
<td>4302</td>
<td>8.55</td>
</tr>
<tr>
<td>Error</td>
<td>503</td>
<td>362,626</td>
<td>7</td>
<td>503</td>
<td></td>
</tr>
</tbody>
</table>

Table 5

Result of ANOVA test for width with all factors.

<table>
<thead>
<tr>
<th>Source</th>
<th>Effect</th>
<th>Sum of square</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>–18.65</td>
<td>173.91</td>
<td>1</td>
<td>173.91</td>
<td>35.05</td>
</tr>
<tr>
<td>B</td>
<td>–6.15</td>
<td>18.91</td>
<td>1</td>
<td>18.91</td>
<td>3.81</td>
</tr>
<tr>
<td>C</td>
<td>–3.35</td>
<td>5.61</td>
<td>1</td>
<td>5.61</td>
<td>1.13</td>
</tr>
<tr>
<td>A × B</td>
<td>–3.925</td>
<td>30.81</td>
<td>1</td>
<td>30.81</td>
<td>6.21</td>
</tr>
<tr>
<td>A × C</td>
<td>1.675</td>
<td>5.61</td>
<td>1</td>
<td>5.61</td>
<td>1.13</td>
</tr>
<tr>
<td>B × C</td>
<td>–1.575</td>
<td>4.96</td>
<td>1</td>
<td>4.96</td>
<td>1.0</td>
</tr>
<tr>
<td>Error</td>
<td>4.96</td>
<td>244.78</td>
<td>7</td>
<td>4.96</td>
<td></td>
</tr>
</tbody>
</table>

Table 6

Result of ANOVA test for width with reduced factors.

<table>
<thead>
<tr>
<th>Source</th>
<th>Effect</th>
<th>SS</th>
<th>Degree of freedom</th>
<th>MS</th>
<th>F value</th>
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<tbody>
<tr>
<td>A</td>
<td>–18.65</td>
<td>173.91</td>
<td>1</td>
<td>173.91</td>
<td>35.05</td>
</tr>
<tr>
<td>B</td>
<td>–6.15</td>
<td>18.91</td>
<td>1</td>
<td>18.91</td>
<td>3.81</td>
</tr>
<tr>
<td>C</td>
<td>–3.35</td>
<td>5.61</td>
<td>1</td>
<td>5.61</td>
<td>1.13</td>
</tr>
<tr>
<td>A × B</td>
<td>–3.925</td>
<td>30.81</td>
<td>1</td>
<td>30.81</td>
<td>6.21</td>
</tr>
<tr>
<td>A × C</td>
<td>1.675</td>
<td>5.61</td>
<td>1</td>
<td>5.61</td>
<td>1.13</td>
</tr>
<tr>
<td>B × C</td>
<td>9.92</td>
<td>244.78</td>
<td>7</td>
<td>4.96</td>
<td></td>
</tr>
</tbody>
</table>
operating velocity should be adjusted for the desired width of patterned strips because only velocity is dominant factor for the width. After that, gap and flow rate should be adjusted for desired thickness of strips.

5. Conclusion

This paper analyzed the effects of operating conditions such as velocity, flow ratio, and gap on the width and thickness of a patterned strip in the R2R slot-die patterning system. A full factorial experiment was applied for determining the dominant parameters, and the velocity was found to be the most effective parameter on both the thickness and width of the strip. The thickness was proportional to the velocity, but the width was inversely proportional to the velocity. The flow ratio and gap were irrelevant to the width, so these can be used as the control parameter for the independent patterning in the width and thickness. Based on these results, it is possible to determine the operating conditions necessary to achieve a desired thickness and width. These results are significant for the prevention of electric leakage or short circuits due to geometric printing defects in R2R slot-die printed circuits.

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References