Web tension optimization of slot die coated PEDOT: PSS based on resistance characteristics

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Abstract

Poly (3,4-ethylenedioxythiophene)-poly (styrene-sulfonate) (PEDOT:PSS) was coated on flexible polyethylene terephthalate (PET) substrate using slot die on a roll-to-roll (R2R) system under different web tensions. The electrical resistance, the standard deviation of the recorded resistance and surface roughness of the coating under different tensions were analyzed. Based on these data an optimum tension was determined for operation of the R2R system for slot die coating. A new image processing based method was adopted to quantitatively measure the proportion of peaks to the valley like features seen in the SEM images of the coatings. Based on this a relation between resistance and the surface texture has been observed.

***Keywords*: PEDOT: PSS pattern, roll-to-roll processing, resistance optimization, Slot die coating, tension control, image processing.**

1. INTRODUCTION

Slot die process is a technique to mass produce coatings on flexible substrates. It has found application in a variety of industries such as printing, laminating, printed electronics etc. Its application in printed electronics is comparatively recent. The Equipment used in this work is shown in Fig. 1(a). It is known as the roll-to-roll (R2R) system or the web handling system. Purpose of the R2R system is to transport the substrate (web) through the slot die coating system at constant velocity while maintaining a constant tension on the web. The schematic representation of the R2R system is shown in Fig. 1(b). It can be seen that the web is un-wound at the un-winder in span-1, it travels through the lateral control system followed by the slot die coater and Infra-red (IR) dryer in span-2 and finally re-wound in span-3. All the while the web tension is tightly controlled. From the process perspective, the control of web tension has always been regarded as the most important aspect of R2R system based production.

The key aspect of this technique is that it can coat a flexible substrate continuously in the form of stripes in the direction of substrate motion. The width and spacing between these stripes is determined by the die that is inserted into the slot die coating apparatus shown in Fig. 2. Another advantage of this method is that the thickness of the coating can be controlled almost perfectly by adjusting the concentration of the ink, the flow rate of the ink and web velocity.

In this paper PEDOT: PSS ink has been used, which is often used as a transparent conductive electrode. Solar cells have already been produced by slot die technique [1, 2, and 3]. All the R2R based fabrication techniques for solar cells including slot die have been summarized in [4]. The study of the effect of web tension on coating silver ink on poly ethylene terephthalate (PET) using an offset printer has been studied in [5]. Also the relation between web tension roughness and thickness of the coating has been studied, and a Meta model relating the roughness and thickness with tension velocity and viscosity of ink was developed. [6-12] describe the R2R system in detail, with [11] giving some tension control guidelines. Resistivity of conductive coating on flexible substrate subjected to stress has been analyzed in [13].

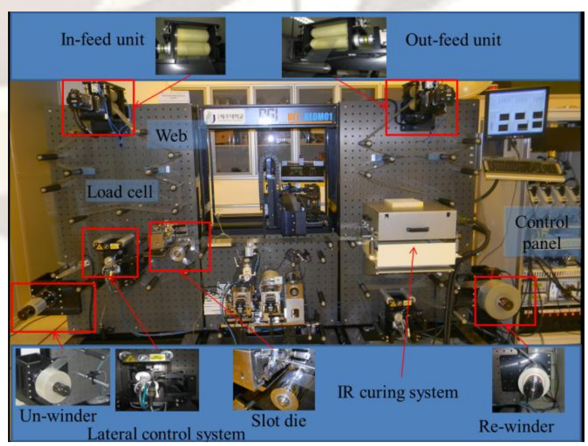

Figure 1(a) R2R system

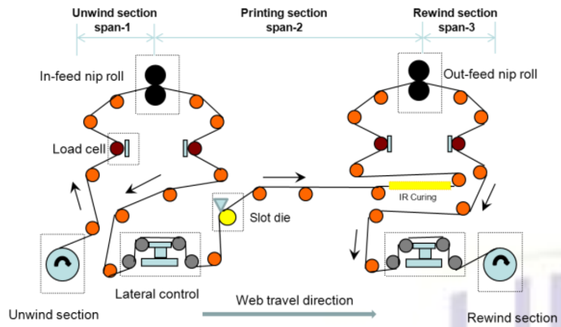

Figure 1(b) Schematic representation of slot die coating system

In material science image processing techniques have been applied to automatically identify and quantify features that are of interest seen under optical microscope or SEM images [14]. It is also useful when image quality has to be improved for distinguishing the features of the image better [15]. Some of the ideas of image thresholding are discussed in [14,16].

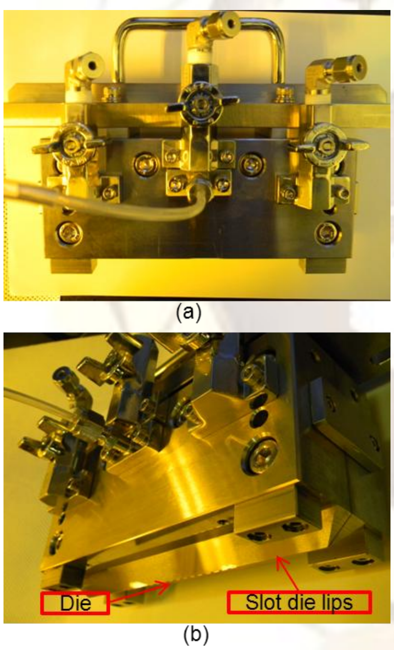

Figure 2(a) Front view of slot die; (b) View of slot die lips and the tip of the die

In this paper the sheet resistance of PEDOT: PSS coating has been studied with respect to change in web tension during processing. Similar study in offset printing has revealed that the change of web tension has a significant effect on the interaction between the web and the ink [5]. There is a need for a study that relates web tension to sheet resistance in slot die coating, as sheet resistance is the ultimate performance measure of a conductive coating/electrode in a printed device not thickness or roughness. This paper addresses this need by printing the conductive polymer PEDOT: PSS on a PET substrate using slot die coating with the web being maintained at various tensions. During this study image processing techniques have been used to enhance the insight into the electrical properties of the conductive coating.

2. MATERIALS AND METHODS

2.1. Formulation of PEDOT:PSS ink

Formulation of PEDOT: PSS ink was done by using 3:2 ratio of PEDOT:PSS diluted with isopropyl alcohol and continuously shaken for 5 h using a mechanical shaker. The obtained solution was kept undisturbed for half a day and the clear solution is separated by decantation and then filtered using polymeric filter to achieve homogeneous dispersion. The viscosity and conductivity of formulated ink were found to be 125 *mPa.s* and 7.00 *mS/cm* respectively.

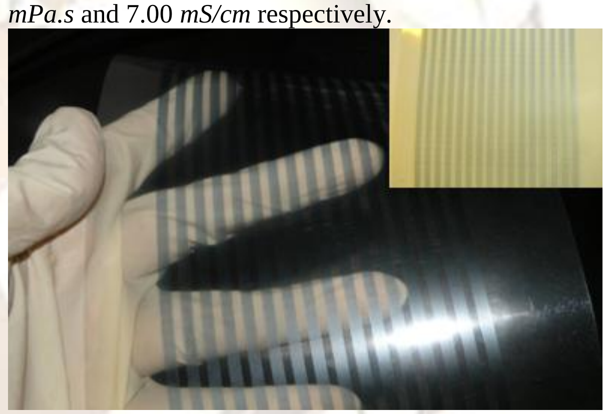

Figure 3 Photograph of PEDOT: PSS coated on PET substrate using slot die process.

2.2 Web Handling System and Slot Die

The web handling system along with the slot die is shown in Fig. 1. R2R system transports the PET substrate from the un-wind section to the re-wind section through the slot die. The width and thickness of the PET substrate are 120 mm and 0.1 mm, respectively. The slot die used for this experiment is shown in figure 2. It has a die that allows printing of patterns 3 mm wide and 2 mm apart. This die enables us to make 16 such parallel patterns as shown in Fig. 3. The ink from a positive displacement pump is pumped at a constant rate into the slot die setup. Slot die is a precisely machined ink dispensing unit that issues ink onto the web moving underneath it. It is widely preferred because of the simplicity of the whole process and because it is a non-contact process.

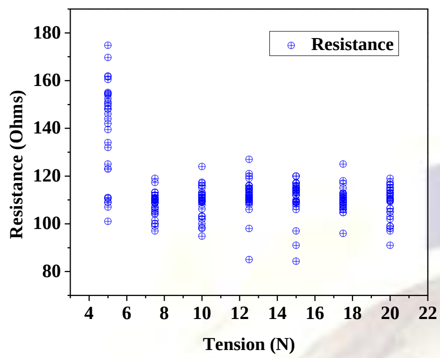

Figure 4 Resistance vs. tension plot.

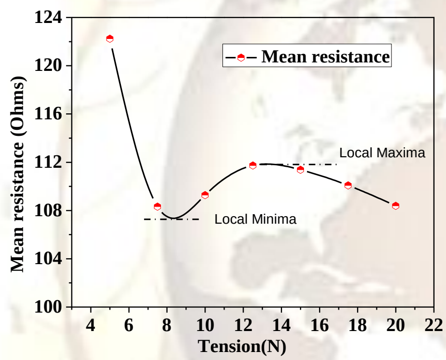

Figure 5(a) Mean resistance vs. tension.

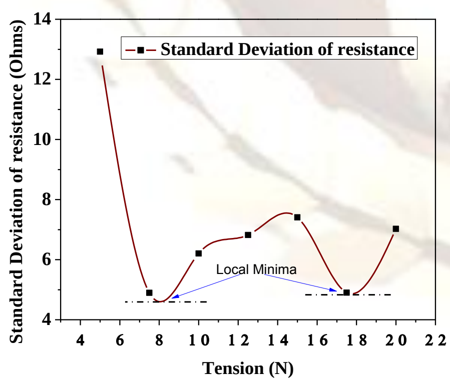

Figure 5(b) Standard deviation of resistance vs. tension.

3. EXPERIMENT DESIGN

The objective of the experiment is to understand the relation between the web tension and the resistance of PEDOT: PSS ink coated on PET substrate for a constant flow rate of ink flowing into the slot die. For this purpose the flow rate of positive displacement pump is kept constant at 13.3 ml/min. Typically there is a lower limit below which the coating is non-uniform, the set flow rate was just above this value and was arrived at by iteratively raising the flow rate from zero. The velocity of the web was maintained at 0.012 m/s. During the initial adjustments to achieve a uniform coating the web tension was set at 5 N. This value is the minimum stable tension capability of the R2R system. Also it is important to maintain the minimum possible tension during the processing stage as subsequent removal of tension is bound to cause contraction of the web. Once steady state coating is achieved the web tension is incremented in steps of 2.5 N up to a maximum of 20 N. The amplitude of noise in the tension is less than of 0.5 N. This noise value tends to be a constant for all set tensions. Soon after the slot die coating, the web enters IR curing unit maintained at 120 °C.

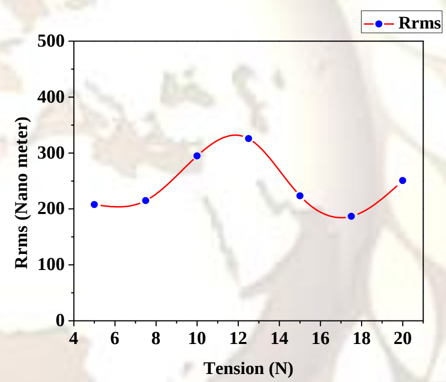

Figure 6 Surface roughness vs. tension

4. Results and discussion

4.1. Resistance

The results from the experiments were analyzed with respect to the resistance of the coating. The sheet resistance was measured for each of the samples that were obtained by operating the R2R system at the 7 different tensions. Resistance was measured using the four point probe at different locations on the surface of the pattern and the plotted as shown in fig. 4 and it revealed significant changes with respect to tension. To interpret this data, statistical techniques were used and the mean (μ) and standard deviation (σ) of resistance corresponding to each tension is found and plotted in Fig.5 (a) and (b) respectively. Statistically σ is a measure of the variation about the mean. The resistance range $\mu \pm 3\sigma$ will account for 99.7% of the sampled population. Therefore it can be a useful tool

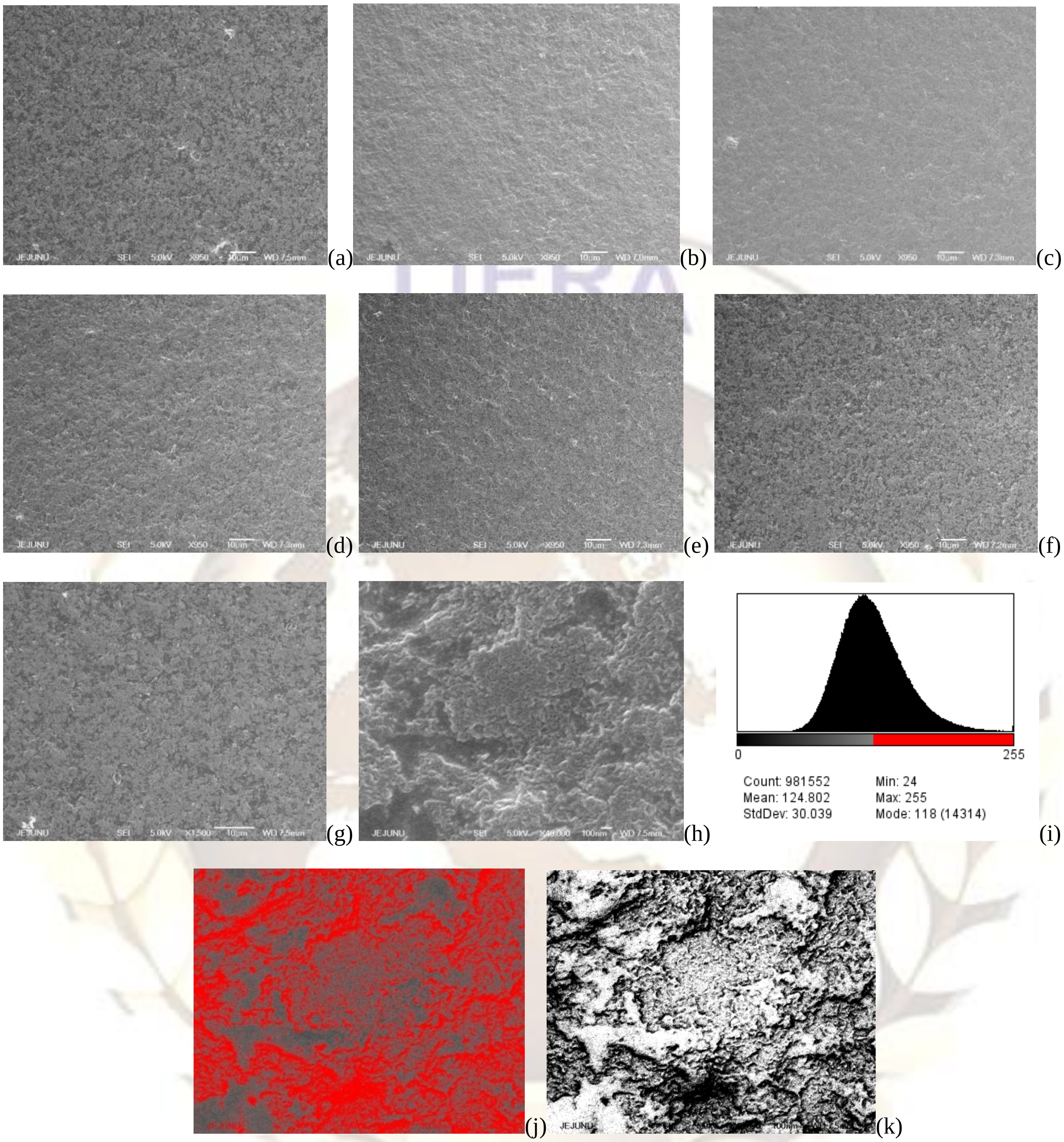

Figure 7 SEM images of coatings made at different tensions: (a)Tension=5N; (b)Tension=7.5N; (c)Tension=10N; (d)Tension=12.5N;(e)Tension=15N;(f)Tension=17.5N; (g)Tension=20N; Image processing:(h) SEM image of a sample at 40000x magnification;(i) Frequency histogram of the image(j) Thresholding process, red pixels indicate peak, while black pixels indicate valley;(k) Black and white image after thresholding.

to optimize the tension to achieve desired pattern resistance.

From Fig.5 (a) and (b) the relation between tension and resistance and standard deviation of resistance were found to be highly nonlinear. As seen in Fig. 5(a) the resistance first decreased as tension was increased from 5 N and reached local minima at around 8 N. From 8 N onwards the resistance increased and reached local maxima at around 12 N and decreases till 20 N. When examining the standard deviation of resistance in Fig. 5(b), it can be seen that there are two local minima; one at 8 N and the other at 17.5N. The quality of a conductive coating can be determined using two criteria. First, conductive electrodes should have the least possible resistance. Second, the resistance should be as consistent as possible. Standard deviation is a good measure of consistency. The lesser the standard deviation lesser is its variation about the mean resistance. There are two local minima points in the standard deviation plot and 8 N is the optimum tension for the process, because it coincides with the minima of the web resistance. There may be other optima if tests were done at higher tensions as is evident from the highly non-linear relation of resistance and the standard deviation of resistance with the web tension. But it is always advisable to apply the least possible tension while printing on a flexible substrate as the internal stresses is also bound to increase with tension. Following the above optimum tension it should be possible to make coatings with a resistance of 107 ± 13.5 Ω.

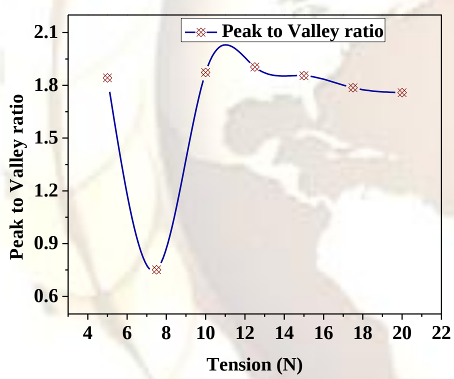

Figure 8 Peak to valley ratio vs. web tension

4.2. Surface characterization

In view of the considerable variation observed in resistance it is worthwhile to study the surface and microstructure of the coating. It has been reported that surface forces between the web and ink are affected by tension [5]. These should inevitably have an effect on the surface roughness as shown in Fig. 6.

Image processing techniques can be used to find quantitative measure of features that are recognizable on an image by human eyes. Fig. 7(a)-(g) show the scanning electron microscope (SEM) image of the coating made under different tension. Fig. 7(h) is one of those images examined closely. The histogram of the image can be seen in Fig. 7(i). It can be distinctly seen that there are smooth valleys in darker shade and peaks that have a mesa like structure which are somewhat rough and brighter. For convenience we shall refer to these formations as valleys and peaks respectively. In this paper image processing techniques will be used to quantitatively measure the influence of peak like features that are seen on the surface of the PEDOT:PSS coating. The SEM images were gray scale images. This means that the image was made up of pixel units that represent brightness of a point on a scale of 0-255. Thresholding is a process whereby the gray scale image can be converted into a black and white image by setting a threshold value such that all the pixels within this threshold were converted to a brightness of 0, and the remaining were converted to a brightness of 255. As seen in Fig. 7(j), the threshold of the image in Fig. 7(h) was adjusted such that all the peaks and valleys were separated. The peaks can be seen in red color while valleys are black in color. After the thresholding process the final black and white image looks as can be seen in Fig. 7(k). Now the pixels corresponding to the peaks and valleys can be easily counted. Each pixel contributes to the area of the image, thus the number of pixels in a feature was directly proportional to the area of that feature. Here a new term is defined, called the peak to valley ratio given as follows:

η= Number of pixels corresponding to peak / Number of pixels corresponding to valley ………..(1)

The same process was repeated for all the images in Fig. 7(a)-(g) and their η values were calculated. The plot between the peak to valley ratio and web tension was as shown in Fig. 8.

Comparison of the plot of peak to valley ratio (η) and resistance against tension suggests a strong relation between the two as they show similar trends. Comparing Fig. 5(a) and 8, it can be said that the as tension is increased from 5 N to 7.5 N, both η and the resistance values decreased followed by a rise. Also in the range 12 N to 22 N both values fall steadily. Thus it can be said that η is a function of tension. And η has a strong contribution to the resistance. Heuristically it can be stated that as peak features increase the resistance also increases and that peaks probably don't or contribute to a lesser extent to the conduction of electrons compared to the valleys.

5. CONCLUSIONS

In this paper PEDOT:PSS is coated on PET substrate using slot die coating. During the coating process the flow rate of ink and web velocity were kept constant and the web tension alone was varied from 5N to 20 N in steps of 2.5 N. The resistance of the resulting coatings made at different tensions was measured and analyzed. The result indicated that the relation between resistance and tension was highly non-linear. Further the measured resistance varied about a mean for a given tension. This variation was studied by plotting the standard deviation of the resistance against the tension. Based on the resistance and standard deviation of resistance, the optimum tension was found to be 8 N. Examination of SEM images revealed that the surface of coating had clearly distinguishable peak and valley like features. Further the SEM images were analyzed using image processing techniques and it was established that peak like features played a significant role in the resistance of coating. It can be stated that tension change had altered the surface texture which in turn affected the resistance. Future work in this field will be directed at finding the cause of the effect that tension has on the surface of coating.

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