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A 250-mm-width, flexible, and continuous roll-to-roll slot-die coated carbon nanotube/silver nanowire film fabrication and a study on the effect of anti-reflective overcoat

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ABSTRACT

Roll-to-roll (R2R) slot-die coating process for the carbon nanotube (CNT)/silver nanowire (AgNW) hybrid film and anti-reflection (AR) overcoating were performed. The R2R process was performed at an operating speed of 2 m/min at various flow rate conditions to control the wet thickness of the layer. The R2R process includes the CNT/AgNW hybrid coating, washing with a tank and spray unit, and AR coating to improve the transparency of the layer. The correlation between the washing time and the properties of the coated layer such as sheet resistance and transmittance were identified. Moreover, the changes in the sheet resistance and the transmittance performance with respect to the wet thickness of the CNT/AgNW and AR layers were studied. Finally, the relationship between the performances and the process conditions were analyzed using the developed non-dimensional numbers. A 250-mm-wide, transparent, conductive film was fabricated that has a sheet resistance of 102 Ω/□ and transmittance of 87.03%. In the case of AR coating, the sheet resistance and the transmittance were obtained as 185 Ω/□ (initial value: 139.84) and 90.65% (initial value: 87.76), respectively. It is important to understand the characteristics of the conductive layer and the AR layer that should be considered with the specifications of the final product film (device).

1. Introduction

Transparent conductive films have been used in touch screen, organic light emitting diode, liquid crystal display, and organic photovoltaic devices [1–4]. In the industry, indium tin oxide (ITO) is mainly adopted as a product based on a glass substrate [5]. The ITO has a sheet resistance of 30–80 Ω/□ and a transmittance of 90% [6], but has a restricted use in flexible substrate such as the polyethylene terephthalate (PET), polyethylene naphthalate, and polyimide (PI) films because of its brittle, unbendable structure [7,8]. To compensate the defect of the ITO film, conducting polymers such as the poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), carbon nanotube (CNT), and graphene, a conductive material based silver nanowire (AgNW), and silver or copper printed grid are used [9].

The mentioned emerging materials have an advantage that they can be deposited through a solution process, not a vacuum process. Therefore, it is possible to adopt these materials in the roll-to-roll (R2R) coating and printing process [10–13]. There are many coating and printing methods that suit the R2R system: slot-die, gravure, spray, inkjet, and rotary screen [14–19]. Among them, R2R slot-die coating process is the most suitable method for large-area film fabrication. The R2R slot-die coating process has been actively researched by Krebs research center to deposit a highly-uniform coated layer on organic photovoltaic devices [20]. Slot-die coating can coat a large area, and the thickness of the coated layer can be estimated and controlled by the pre-metered coating method [21].

The drawbacks of transparent conductive film are their mechanical (flexibility), optical (transmittance), and electrical (sheet resistance) properties. There have been many attempts at improving the performances by tuning, adding, and mixing materials including hybrid structures such as CNT/AgNW [28], AgNW/PEDOT:PSS [29], Graphene/single-walled carbon nanotube (SWCNT) [30], AgNW/graphene [31], and Ag grid/graphene [6], which are compared with the original materials as listed in Table 1 [6,22–31]. The hybrid structure could offset the impact of the disadvantages such as the high sheet resistance of the nanotube and the low transparency of the metal nanowires [9]. Moreover, a combined structure enhances the conductivity of the layer by soldering [29] and increases the flexibility of hybrid films by adding the polymer structure [28].

The conductivity of the coated layer is determined by the density of the materials such as area of a surface. A complex structure can increase the conductivity of the layer, which is called hierarchical structure [32]. However, a complex and thick structure can decrease the transmittance of the coated layer. Thus, the sheet resistance is inversely related to the transmittance value [33]. This study proposes a method to increase the

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Table 1
Performances of original and hybrid conducting materials with various fabrication methods.

Material	Method	Sheet resistance (Ω/□)	Transmittance (%)	Ref.
ITO	Evaporation	30–80	90	[6]
AgNW	Bar coating	110	87	[22]
SWCNT	Spray coating	150	90	[23]
CNT	Inkjet coating	156	81	[24]
Graphene	Vapor deposition	250	86	[25]
PEDOT:PSS	Spin coating	46	82	[26]
Ag grid	Spin coating	100	70	[27]
CNT/AgNW	Filtration	26	90	[28]
AgNW/PEDOT:PSS	Bar coating	25	90	[29]
Graphene/SWCNT	Vacuum filtration	100	80	[30]
AgNW/graphene	Vapor deposition	33	94	[31]
Ag grid/graphene	Sputtering	3	80	[6]

transparency of the layer by the overlay of anti-reflection (AR) coating. AR coating is used in the display technology to prevent the reflection of light on screens [34]. R2R AR coating was already investigated by Park et al. [35], and that can be applied to the transparent conductive film fabrication. However, it is presumed that the sheet resistance decreases when an AR layer is over coated. Therefore, it is important to deduce the optimum performance and develop a guideline by considering the R2R process condition and the target device.

In this study, we present a CNT/AgNW hybrid film coating and an AR coating process in the R2R slot-die coating system. It demonstrates the CNT/AgNW hybrid film coating in one coating process by using the mixed material and not a filtration method [28]. Kim et al. investigated the same film with twice the coating layers by using a spray or slot-die coating method [36]. The R2R process of CNT/AgNW slot-die coating, washing, and AR coating were performed in a large-scale R2R system (films of width 250 mm and length more than 1000 m) with systemic coating guidelines such as the roll machining accuracy, eccentricity minimization, and circumferential slot. The relationship between the performance (sheet resistance and transmittance) and process conditions such as the washing time, hybrid film, and AR thickness were identified.

2. Experimental setup

The R2R system used in this experiment has tension in the range of 9.8–98 N, transfer speed in the range of 0.5–10 m/min, and drying temperature ranging from room temperature to 150 °C. Bare substrate (web) has a transmittance of 90.32% at 550-nm wavelength, a width of 300 mm, and a thickness of 187 μm. A flexible film is linked from an unwinder to a rewinder as shown in Fig. 1 [7]. The CNT/AgNW hybrid and the AR solution coating process consist of several steps (a)–(h) as depicted in Fig. 1 (photograph of a real system is shown in Fig. 2(a)). Sequentially these steps include: (a) unwinding of a flexible web; (b) infeeding with tension control by a dancer and load cell; (c) first slot-die coating process for the CNT/AgNW hybrid layers [slot-die coater can coat a layer of width 250 mm and control the gap precisely from a backup roller to a nozzle, as shown in Fig. 2(b)]; (d) hot-air drying of the coated layer; (e) washing process of the coated layer using a spray unit and a tank [photograph in Fig. 2(c)]; (d) hot-air drying of deionized water-washed web; (f) second slot-die coating process for the AR layers; (d) hot-air drying of the coated layer; (g) out-feeding with tension and lateral control by an edge position controller, a dancer and load cell; and (h) rewinding of the final product (photograph in Fig. 2(d)). In this study, all these processes were not performed continuously. The system can coat a single layer in one-step. For multi-layer coating, additional rewinding and unwinding processes were performed after the first slot-die coating.

To coat a uniform layer, there are systemic guidelines (elements) in R2R process as shown in Fig. 3.

First, a transfer web should have a constant velocity and tension. The synchronization of the velocity and tension at the coating zone, which affects the coating quality, should be confirmed [8]. For an accurate web transportation, an adjacent roll with a slot-die nozzle called a backup roll is set as a master speed drive to maintain the reference velocity (v_{ref}) using the proportional-integrator (PI) control of input u.

Second, the accuracy of the roll machining surface was considered. The surface roughness and roundness of the backup roll are affected by the change in coating gap with web transportation. The coating gap value can be derived by a roll eccentricity model [37] as shown in Eq. (1) where h_0, H, t_w, R_{mean}, θ, e, and Φ are the coating gap (slot-die to film surface), distance between the slot-die and the axis of the backup roll, thickness of the web, distance between the web and the centroid of geometric shape, distance between a and b, and angle between a and b (a: centroid of geometric shape and b: axis of rotation in Fig. 3), respectively.

$$h_0 = H - [t_w + R_{mean} + e\sin(\theta + \phi)]. \quad (1)$$

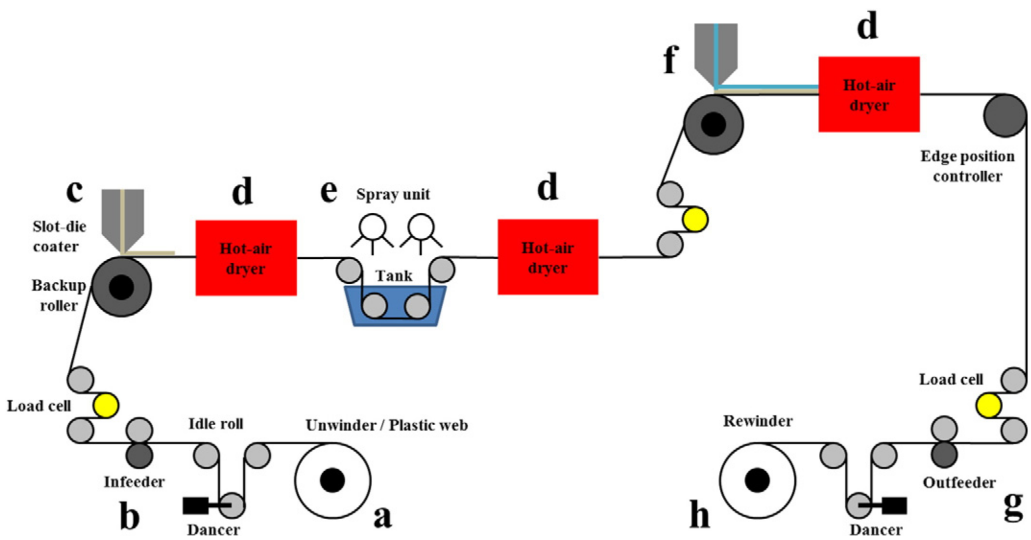

Fig. 1. Process logic of CNT/AgNW, AR coating process in R2R slot-die coating system. (a) unwinding (b) in-feeding (c) slot-die coating of CNT/AgNW layer (d) hot-air drying (e) washing of first layer (f) slot-die coating of AR layer (g) out-feeding (h) rewinding.