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Characterization of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) thin film deposited through electrohydrodynamic atomization technique

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ABSTRACT

This article presents an attractive printing technique for thin film deposition of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) on flexible substrates known as electrohydrodynamic atomization (EHDA). Optimum flow rate and applied potential for stable cone jet mode has been confirmed through identification of process operating envelop. The uniformity and film thickness has been investigated by a field emission scanning electron microscope. The thin film shows nearly 75–82% transmittance in visible region. The electrical study shows good ohmic behavior of PEDOT:PSS thin film with the resistivity of approximately 49.6 mΩ cm.

1. Introduction

A π-conjugated conducting polymer of PEDOT (poly(3,4-ethylenedioxythiophene)) carries very much interest in organic optoelectronics because of its good optical transparency, high electrical conductivity and excellent stability [1]. PEDOT has many applications in solar cells, light emitting diodes, sensors and thin film transistors [1-4]. Usually the pure form of PEDOT is insoluble in most of the solvents. This problem is overcome by introducing water soluble polymeric material of poly(styrenesulfonate) (PSS). The PSS polymer has the ability to attain equilibrium with cationic charge of PEDOT under polymerization process to generate PEDOT:PSS complex with homogeneous dispersion of PEDOT in water [5].

Conventionally, the fabrication of thin film are achieved through dip and spin coating, chemical vapor deposition, physical vapor deposition and atomic layer deposition etc. [6,7]. These techniques produce good quality film but are expensive and have certain intricacies involved with them [8,9]. Therefore the development of new techniques such as electrohydrodynamic atomization (EHDA) becomes more relevant for thin film deposition [10] as it offers simple process, low cost and enables large area printing under ambient conditions. The working mechanism of EHDA is discussed in detail by Hayati et al. in [11].

In this paper, commercially available PEDOT:PSS is modified by adding isopropanol to make it suitable for electrospray deposition on polyethylene terephthalate (PET) as a substrate. A field emission scanning electron microscopy is used to determine the surface morphology and film thickness. Transparency and electrical properties of deposited film have been characterized through UV–vis spectrum and current–voltage (*I*–*V*) measurements.

2. Materials and Methods

2.1. Materials

PEDOT:PSS (Orgacon) was purchased from Agfa Materials Japan Ltd, Japan. Isopropanol ($(CH_3)_2CHOH$) was obtained from Sigma-Aldrich, South Korea. Silver nanoparticle ink was received from NPK Ink Ltd, South Korea.

2.2. PEDOT:PSS ink preparation

In EHDA technique, the stable cone-jet is achieved when the electric stress overcomes the surface tension of the liquid meniscus at the end of the capillary [12]. Liquids with high surface tension (e.g. H_2O) are very difficult to electrospray [13]. Water based inks are usually modified by adding suitable alcoholic co-solvents to reduce the surface tension of the inks [14]. Based upon this phenomena PEDOT:PSS was modified by using isopropanol as a co-solvent to achieve low surface tension (Fig. 1(a)).

PEDOT:PSS ink was prepared by diluting (2.3 wt%) PEDOT:PSS with 5 ml of isopropanol (2:1w/w) and stirring for 20 minutes at 1500 rpm. Then 2 ml of deionized-water was added drop by drop and stirring was continued for 2 hours under ambient conditions. The obtained solution was filtered through the polymeric filter (PTFE – 0.45 μm) to achieve homogeneous dispersion of modified

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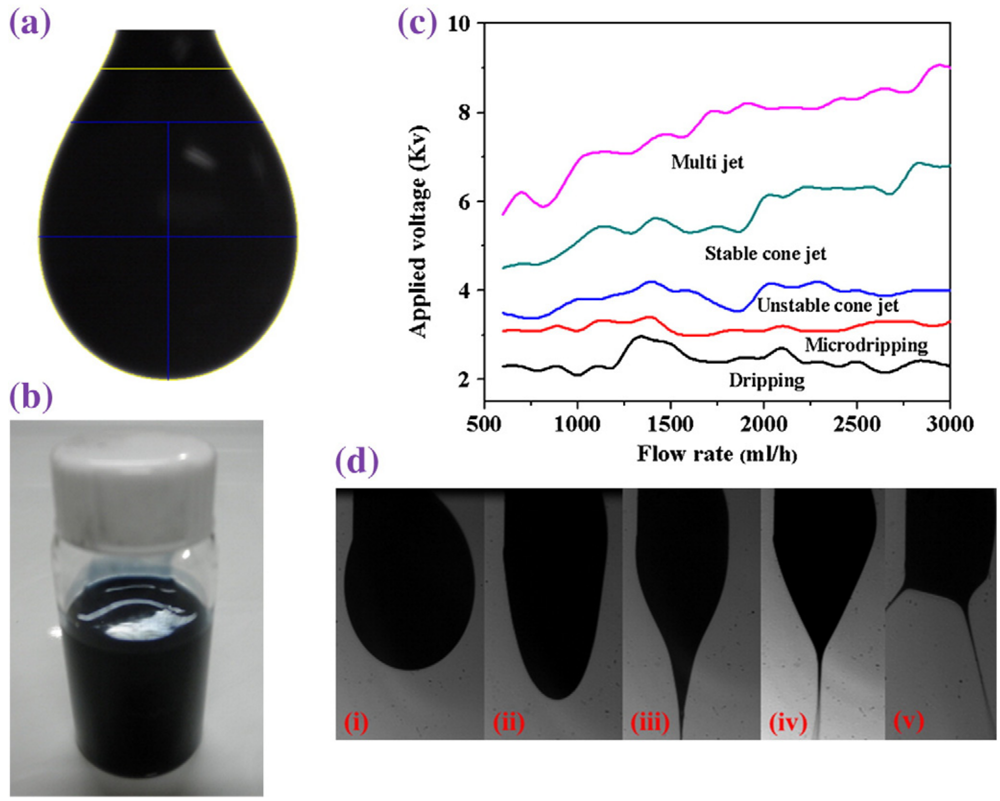

Fig. 1. (a) Surface tension analysis of PEDOT:PSS ink, (b) photographic image of modified PEDOT:PSS ink, (c) operating envelop of PEDOT:PSS ink by using EHDA, (d) modes of atomization: (i) dripping, (ii) micro dripping, (iii) unstable cone jet, (iv) stable cone jet, (v) multi-jet mode.

PEDOT:PSS ink as shown in Fig. 1(b). The physical properties of modified PEDOT:PSS ink were given in Table 1.

2.3. EHDA system

The EHDA setup consisted of a metallic nozzle with internal diameter of 410 μm and external diameter of 680 μm fixed at the bottom of nozzle holder. It was directly connected to a high voltage DC power supply (NanoNC, 30 kV). The top of the nozzle holder was connected to syringe pump (Harvard Apparatus, PHD 2000 Infusion) through teflon tube for ink supply. The whole experiment was observed by using a high speed CCD camera (MotionPro X) (Supplementary Fig. 1).

2.4. Fabrication of PEDOT:PSS thin film

Before the deposition, the substrates were plasma treated in order to confirm the possibility of improving the adherence of PEDOT:PSS with the substrate. As expected, the oxygen plasma treated substrates showed less contact angles (47°) than untreated (72°), which gave us an indication for the possibility of improved thin film deposition (Supplementary Fig. 2). Thin film deposition of PEDOT:PSS was carried out on PET substrates through EHDA technique at ambient conditions. During EHDA process, the stand-off distance between metallic nozzle and the substrate (PET) was maintained at 15 mm with the substrate velocity of 8 mm/sec to achieve uniform deposition and the film were sintered at 110 °C for 10 minutes after deposition.

Table 1
Properties of modified PEDOT:PSS ink for EHDA technique.

Physical property	Values
Viscosity	114 mPa s
Surface tension	14 mN m^{-1}
Electrical conductivity	7.2 μS cm^{-1}

2.5. Characterization techniques

The electrical conductivity of the PEDOT:PSS ink was measured by a conductivity meter (EUTECH Instruments, ECOSCAN CON 6). The surface tension of the ink was measured by a surface tension meter (SEO-Phoenix). The viscosity of the ink was measured through a viscometer (ARES, TA Instruments, USA). The transparency of the film was recorded by a UV–vis spectrometer (Shimadzu UV-3150) with a range of 200–800 nm. The surface morphology and cross-section of the deposited thin film were analyzed by field emission scanning electron microscope (FESEM JEOL. Ltd., JEM 1200EX II). The *I–V* characteristics of the thin film were measured by a semiconductor device (B1500A, Agilent, USA) parameter analyzer.

3. Results and discussion

Before the actual deposition process, working operating envelope [12] was identified as shown in Fig. 1(c). At different flow rate and applied voltages, different spray modes such as dripping, micro-dripping, unstable cone jet, stable cone jet and multi jet were obtained. Fig. 1(d) illustrates the different atomization modes which exist at constant flow rate of 1200 μl/h at varying voltages. Until 3.3 kV, only natural dripping appeared. Above 3.3 kV micro-dripping occurred until 3.9 kV. Further increase in voltage resulted in the ejection of unstable cone when the stable cone jet appeared at 5.4 kV which was maintained until 7.1 kV. Increasing the voltage beyond 7.1 kV resulted in multi jet mode. The thickness of the as-deposited thin films can be controlled by different parameters such as concentration of ink, flow rate, standoff distance, substrate velocity and spray time [15].