

VAPOR-PHASE THIN-FILM COATING OF PEDOT ON POLYMERIC SUBSTRATE FOR ELECTROLUMINESCENCE DEVICE

Truong Thuy Le, Dong-Wook Kim, Youngkwan Lee, Jae-Do Nam*

Department of Polymer Science and Engineering; Sungkyunkwan University; 300 Chunchun-dong, Jangan-gu, Suwon; Kyonggi-do, 440-746, Korea.

Phone Number: + 82-31-290-7299; Fax: +82-31-292-8790

* To whom correspondence should be addressed (email: jdnam@skku.edu)

ABSTRACT

Transparent thin coating of poly(3,4-ethylenedioxythiophene) (PEDOT) was investigated through vapor-phase deposition of 3,4-ethylenedioxythiophene (EDOT) on flexible polyethyleneterephthalate (PET) plastic substrates coated by Fe(III)-tosylate (FTS). High conductivities were obtained ($\sim 200 \text{ S.cm}^{-1}$) with moderate transmission in the UV-visible range 350–700 nm. The roughness of PEDOT film was also investigated by Atomic Force Microscopy (AFM). The method relies on the use of organic ferric sulfonates as oxidant so that these salts easily form smooth and noncrystalline films. The described technique can easily be adapted to different patterning techniques in organic electroluminescence device and others.

Keywords: Poly(3,4-ethylenedioxythiophene); vapor-phase deposition; polyethyleneterephthalate; Fe(III)-tosylate

1. INTRODUCTION

PEDOT has been extensively studied in the recent years due to its many advantageous properties such as high conductivity, transparency and stability.^[1-3] It makes PEDOT very attractive for various applications including electrochromic windows,^[4] organic electrodes for photovoltaics^[5,6] or capacitors and specifically a hole transport layer of OLED.^[7,8]

The oxidized PEDOT can be found in a variety of forms with different polymerization techniques. In order to make thin films, solution processing is most common being used in the form of spin-coating, solvent-casting, or ink-jet printing. The PEDOT system is, however, hardly dissolved in most solvents. It is often necessary to derivatize PEDOT with soluble side chains or dope the polymer with stabilizing polyelectrolytes.^[9] Most widely used is an aqueous dispersion of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)

(PEDOT-PSS), or Baytron P, proven to be a stable polymer system with ease to process with a high transparency up to 80%.^[10,11] However, the PEDOT-PSS film exhibits a relatively low electrical conductivity of approximately 10 S/cm,^[10] which does not usually meet the requirements of high conductivity in most applications.

Alternatively, PEDOT can be deposited by the in situ polymerization directly on the substrate surface. This can be achieved by electrochemical polymerization which enhances conductivity but typically results in poor transparency.^[12] In addition, the electrochemical polymerization should be carried out on conducting substrates, which consequently limits the practical use of this method.^[13] On the other hand, oxidative chemical polymerization is more versatile and less restricted by the substrate because chemical oxidation can be performed simply by coating the surface with a mixture of monomer and oxidant. Often such mixtures have a limited pot-life time, but more degree of freedom in the

design of the coating process can be achieved if the monomer and oxidant are applied separately. One way to achieve this is to apply the oxidant by solvent coating and subsequently exposing the coated surface to monomer vapor, which is often referred as vapor phase polymerization (VPP).^[14] It has been reported that the VPP gives the highest conductivity of PEDOT.^[13,15,16] We used the base-inhibited VPP method to produce PEDOT film and investigated the conductivity, transparency as well as surface topology of PEDOT-coated PET films

2. EXPERIMENTAL SECTION

2.1. Materials

Fe(III) tosylate (40% solution in n-butanol, Baytron C) as an oxidizing agent and dopant were received from Bayer AG. EDOT was obtained from Aldrich. The thickness of PET films used in this study was 100 μm . The solvents were alcohols such as ethanol, butanol, acetone and DI water.

2.2. Oxidative polymerization of EDOT with FTS by VPP

The PET was cleaned twice in acetone before using. Vapor-phase polymerization of EDOT was carried out in a simple chamber set-up as shown in Fig. 1. The chamber was flushed with nitrogen during polymerization, and heated up 50 $^{\circ}\text{C}$ in order to speed up the process. The samples to be covered with PEDOT were initially coated with the oxidant ferric tosylate. Ferric tosylate diluted in butanol has an adequate concentration for coating. After drying at 60 $^{\circ}\text{C}$ in air for 2 min, the samples were transferred to the polymerization chamber. The vapor-phase polymerization lasted for 30 min, and thereafter the samples were heated to 50-90 $^{\circ}\text{C}$ in an oven for 30 min and washed in ethanol and DI water, respectively. Finally, PEDOT film was removed residual solvents at 80 $^{\circ}\text{C}$ for 20 min.

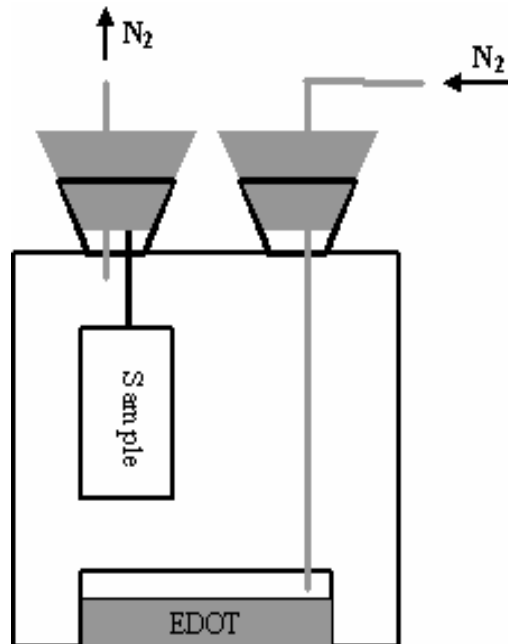


Fig. 1. Vapor-phase polymerization chamber

The conductivity of the samples was measured using a four-point probe from Jandel Engineering Ltd. Connected to a Keithly 2400 source meter. The probe is equipped with four spring-loaded tungsten carbide needles spaced 1 mm apart. The bulk resistivity of the films was calculated from the surface resistivity using the film thickness

3. RESULTS AND DISCUSSION

The oxidative polymerization of EDOT into a polymer is depicted in Fig 2. The FTS used as a stoichiometric oxidant oxidizes the EDOT, transforms it into a cation radical that dimerizes and is rapidly stabilized by base-assisted removal of two protons whereas the Fe^{III} is reduced to the Fe^{II} . Additional FTS oxidizes the dimers, and chain growth proceeds as a classical step-polymerization. It also oxidizes the growing chains, leaving the PEDOT in its dope (conducting) state.

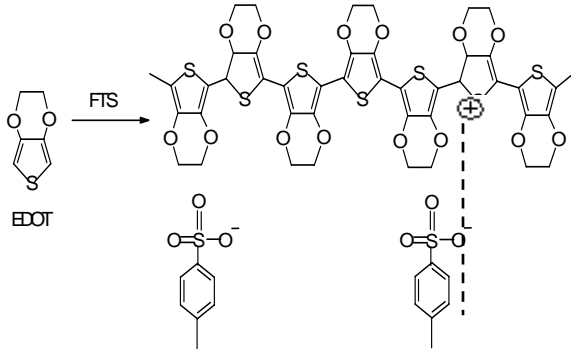


Fig. 2. Schematic description of the oxidative chemical polymerization of EDOT into PEDOT.

3.1. CONDUCTIVITY

The conductivities of PEDOT at different FTS concentrations are summarized in table 1. This implies that they vary according to FTS concentration and layer number. In detail, this property of single layer is higher than that of double layer at the same FTS concentration.

Table 1. Summary of the conductivities of PEDOT

Sample	Layer number	Thickness (Å)	Surface Resistivity (ρ_s) Ω/cm^2	Resistivity (ρ) $\Omega \cdot \text{cm}$	Conductivity (σ) (S/cm)
PET/FTS 12wt% in BuOH	2	4000	150	6×10^{-3}	160
PET/FTS 12wt% in BuOH	1	3000	140	4.2×10^{-3}	238
PET/FTS 10wt% in BuOH	2	4000	130	5.2×10^{-3}	192
PET/FTS 20wt% in BuOH	2	7200	80	5.76×10^{-3}	174

3.2. Transparency

Fig. 3 shows UV-Vis Spectra of PEDOT-coated PET films comparing the number of layer. As it can be seen, the resulting conducting polymer film is over 50% for single layer transparent in the wavelength ranging from 350 nm to 700 nm and the transmittance depends on the thickness of PEDOT.

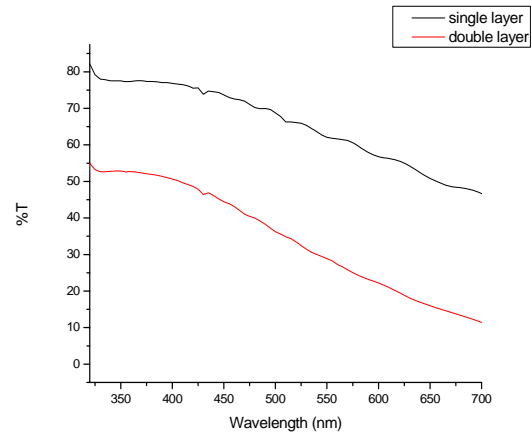


Fig. 3. UV-Vis Spectra of PEDOT film

3.3. Morphology

Fig. 4 shows the topographic image of a PEDOT surface on PET substrate examined by AFM. The thin film has a roughness of ~ 17 nm in the $5 \times 5 \mu\text{m}^2$ scan area. The morphological smoothness reveals that physical defects like holes are not noticeable in this study.

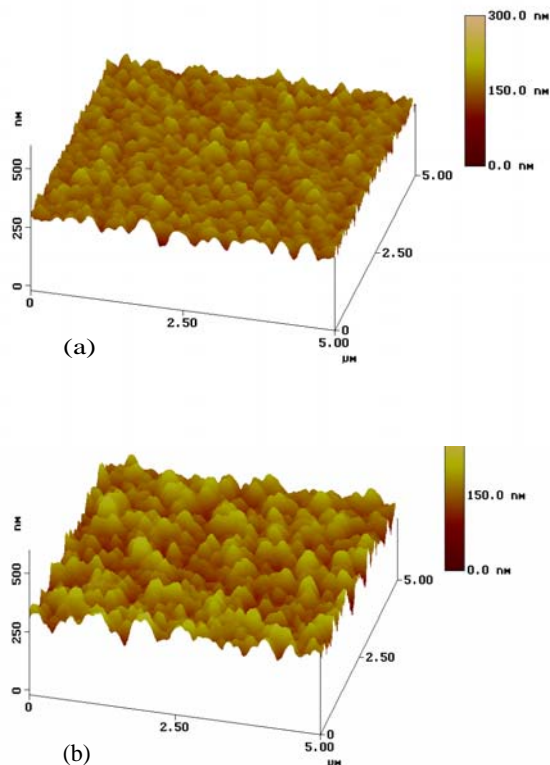


Fig. 4. AFM images of the PEDOT surface on PET substrate: (a) single layer and (b) double layer

4. CONCLUSION

Vapor-phase polymerization of PEDOT was successfully performed on PET. It has been shown here that a transparent PEDOT film with high conductivity has been prepared using EDOT vapor as a precursor. We have also demonstrated that the use of Fe (III) tosylate as a

good oxidant and dopant can form the smooth and coherent surface of PEDOT.

REFERENCE

1. F. Jonas, L. Schrader, *Synth. Met.*, **1991**, 41, 831.
2. M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electroanal. Chem.*, **1994**, 369, 87.
3. Winter, C. Reece, J. Hormes, G. Heywang, F. Jonas, *Chem. Phys.*, **1995**, 194, 207.
4. D. M. Welsh, A. Kumar, E. W. Meijer, J. R. Reynolds, *Adv. Mater.*, **1999**, 11, 1379.
5. J. Gao, G. Yu, A. J. Heeger, *Adv. Mater.*, **1998**, 10, 692.
7. D.M. de Leeuw, P.A. Kraakman, P.F.G. Bongaerts, C.M.J. Mutsaers, D.B.M. Klaassen, *Synth. Met.*, **1994**, 66, 263.
8. M. Granstrom, K. Petrisch, A. C. Arias, A. Lux, M. R. Andersson, R. H. Friend, *Nature* **1998**, 395, 257
9. M. D. McGehee, A. J. Heeger, *Adv. Mater.*, **2000**, 12, 1655.
10. W. H. Kim, A. J. Mäkinen, N. Nikolov, R. Shashidhar, H. Kim, Z. H. Kafafi, *Appl. Phys. Lett.*, **2002**, 80, 3844.
11. J R. Menon, C. O. Yoon, D. Moses, A. J. Heeger, In *Handbook of Conducting Polymer*, Marcel Dekker, New York, Second Edition, p. 27.
12. B. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, 12, 481
13. F. Jonas, G. Heywang, *Electrochim. Acta*, **1994**, 39, 1345
14. L. Groenendaal, G. Zotti, F. Jonas, *Synth. Met.*, **2001**, 118, 105.
15. B. Winther-Jensen, K. West, *Macromolecules*, **2004**, 37, 4538.
16. Bjorn Winther-Jensen, Jun Chen, Keld West, and Gordon Wallace; *Macromolecules*, **2004**, 37, 5930-5935
17. Jinyeol Kima, Eungryul Kima, Youngsoon Won, Haeseong Lee, Kwangsuck Suhc, *Synthetic Metals*, **2003**, 139, 485-489
18. Shimelis Admassiea, Fengling Zhanga, A.G. Manoja, Mattias Svenssonc, Mats R. Anderssonc, *Solar Energy Materials & Solar Cells* (In press), **2005**