

동시 공-증발 기상중합을 이용한 PPy-PAN 전도성 복합 박막제조

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Novel Preparation Route of Conductive PPy-PAN Hybrid Thin Films Using Simultaneous Co-vaporized Vapor Phase Polymerization

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초록: 본 연구에서 서로 다른 중합 메커니즘을 가진 두 개의 단량체(즉, 산화 커플링 중합과 라디칼 중합)를 동시에 공-증발 기상 중합(SC-VPP) 수행하여 유기-유기 전도성 복합 박막을 제조하는 새로운 접근법을 보고한다. SC-VPP 공정을 통해 폴리피롤(PPy)과 폴리아크릴로니트릴(PAN)로 구성된 PPy-PAN 복합 박막을 제조하였다. 두 종류의 유기-유기 전도성 복합 박막의 제조는 FTIR 및 ¹H NMR 분석을 통해 확인되었다. PPy-PAN 박막은 입자 크기가 작고 PPy 박막보다 상대적으로 매끄러운 표면을 가졌다. PPy-PAN은 부드러운 표면 형태로 인해 PPy와 유사한 전기 전도성을 보였다. PPy-PAN의 접촉각은 30° 이하로 표면 특성을 친수성으로 조절하였다. 본 고에서 제안된 SC-VPP 기반 전도성 하이브리드 박막 소재의 개질 기술로 다양한 디바이스 계면에서의 특성을 조절가능하리라 기대한다.

Abstract: A new approach for the fabrication of organic-organic conducting composite thin films using simultaneous co-vaporization vapor phase polymerization (SC-VPP) of two monomers that have different polymerization mechanisms (i.e., oxidation-coupling polymerization and radical polymerization) has been reported for the first time. In this study, a PPy-PAN composite thin film consisting of polypyrrole (PPy) and polyacrylonitrile (PAN) were prepared by the SC-VPP process. The preparation of the two types of organic-organic conducting composite thin films was confirmed through FT-IR and ¹H NMR analysis. The PPy-PAN thin film had a smaller grain size and relatively smoother surface than the PPy thin film. PPy-PAN showed similar electrical conductivity to PPy due to its smooth surface morphology. The contact angle of PPy-PAN was below 30°, which means the surface property was changed to hydrophilic character. The proposed SC-VPP-based hybrid materials allow for control of the surface properties, such as hydrophilicity, of the resulting thin films.

Keywords: organic-organic conducting hybrid thin film, polypyrrole, polyacrylonitrile, simultaneous co-vaporized vapor phase polymerization, electrical property.

Introduction

Since the discovery of polyacetylene in 1977,¹ the class of intrinsic conducting polymers (ICPs) with conjugated double bonds has expanded to include polyaniline (PANi), polypyrrole (PPy), and poly(3,4-ethylenedioxythiophene) (PEDOT). ICPs

have been widely applied to “green electronics”,² biomedical materials,^{3,4} displays,^{5,6} and energy storage⁷⁻⁹ because of their excellent electrical conductivity and stability in their natural states. In particular, PEDOT and PPy are among the most successful ICPs with excellent electrical conductivity, stability, and flexibility.¹⁰⁻¹⁴ Vapor phase polymerization (VPP) has been applied to the production of crystalline conductive polymer thin films with high conductivity (>4000 S/cm).¹⁵ After Mohammadi *et al.* introduced the VPP technique for making PPy thin films,¹⁶ various VPP-based ICPs have led to a great

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deal of research on device application.¹⁷⁻²³ VPP is a method of forming an electroconductive polymer thin film *in situ* by coating an oxidant onto a substrate and then exposing the conductive monomer to a gas phase. The application field of the ICP can be greatly expanded because VPP can be used to form conductive films for various micro- and nanostructures (i.e. spheres,²⁴ fibers,¹⁹ nanoporous carbon,²⁵ and woven fabrics),^{26,27} as well as various flat materials such as poly(ethylene terephthalate) (PET), polyimide, glass, and silicon wafer. In addition, the VPP method can prevent environmental problems caused by the use of solvents because the conductive polymer thin film is formed directly on the solid substrate. Meanwhile, non-conductive organic polymers can also be prepared by gas phase polymerization. The VPP process is capable of polymerizing not only vinyl monomers made by radical polymerization mechanisms, but can also generate PEDOT, PPy, and PANi, which are produced by polymerization mechanisms with oxidative coupling.²⁸⁻³⁰ Tenhaeff *et al.* successfully obtained alternating PSMa thin films by evaporating styrene (St) and maleic anhydride (Ma) monomers with *tert*-butylperoxide.²⁸ Chan *et al.* reported that poly(methyl methacrylate) thin films were obtained by the simultaneous evaporation of methyl methacrylate monomer and triethylamine initiator.²⁹ Recently, it has been suggested that various non-conductive vinyl polymers and polyolefins can also be prepared by a VPP process.³⁰

Our group has studied the use of organic-inorganic hybrid materials using SC-VPP.³¹⁻³⁸ The oxidizing agent used in VPP for conducting polymers is typically an iron (III)-based salt such as ferric (III) *p*-toluenesulfonate (FTS).^{18,39} The key to the production of organic-inorganic hybrid materials using SC-VPP is the two complementary roles of FTS: (i) a strong acid catalyst that catalyzes the hydrolysis/condensation of various alkoxy silane precursors; and (ii) an oxidant catalyst for polymerizing conductive monomers such as 3,4-ethylenedioxythiophene (EDOT), which polymerizes via an oxidation-coupling route. Thus, the fabrication of an organic-inorganic hybrid conductive thin film on an oxidizer-coated substrate can be simply implemented in a VPP reactor with co-evaporation of EDOT and alkoxy silane precursors. SC-VPP can homogeneously produce multifunctional organic-inorganic composites at the molecular level that cannot be achieved by simple solution-solution or solid-solution mixing. That is, the mixing of various species in the gas phase can effectively overcome the solubility limit in the liquid/solid mixture. In addition, the SC-VPP process facilitates the incorporation of organic-inorganic

hybrid conductive coatings with excellent mechanical properties to a variety of substances having complicated shapes, since gaseous monomers can easily approach solid interfaces and form a uniform polymer layer.^{35,36,38}

In this study, we report, for the first time, an effective approach for the preparation of conductive organic-organic hybrid composites using SC-VPP, which simultaneously evaporates two monomers that are polymerized by different polymerization mechanisms (i.e. oxidation-coupling polymerization and radical polymerization) in order to control characteristics of composite thin films. A mixed solution of FTS (oxidizing agent for oxidation-coupling polymerization) and α,α' -azobisisobutyronitrile (AIBN) (radical initiator for radical polymerization) is applied to the substrate by spin coating. Moreover, PPy-PAN hybrid thin films were prepared by the SC-VPP process using pyrrole (Py) and acrylonitrile (AN) as monomers on the substrate coated with the same hybrid catalyst as the above process (Scheme 1(a)). The chemical composition and surface morphology of the two types of organic-organic hybrid conductive thin films were analyzed by Fourier transform infrared (FTIR), ¹H nuclear magnetic resonance (NMR), and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). The optical, electrical, and surface hydrophilic properties of the composite thin films were compared and analyzed.

Experimental

Chemicals. Pyrrole (Py, Aldrich) were used without purification for the preparation of conductive hybrid thin films. Acrylonitrile (AN, Aldrich) were purified using a column packed with aluminum oxide (~50-200 μ m) to remove the polymerization inhibitor. Ferric (III) *p*-toluenesulfonate (FTS, Aldrich) was used without further purification. The radical initiator α,α' -azobisisobutyronitrile (AIBN, Samchun) was used after recrystallization. The polymerization solvent, acetone (Junsei) was used without purification. A square (5×5 cm) PET film and glass (2.5×2.5 cm) were used as substrates for the conductive hybrid thin films.

Preparation of PPy-PAN Conductive Hybrid Thin Films. PPy thin films were prepared by VPP. FTS, an oxidizing agent for oxidative-coupling polymerization, was dissolved in acetone at 15 wt% for about 10 min with stirring. It was then dissolved in acetone with stirring for about 10 min, fixing the solid contents at 15 wt%. The mixed oxidant solution was spin-coated on the PET film at 300 rpm for 20 s. After spin-coating, it was transferred directly into the VPP reactor without

Table 1. Monomer Composition of SC-VPP for PPy-PAN Conductive Hybrid Films

Sample name	PPy-based hybrid	
	Monomer composition	Initiator composition
	Py : An (molar fraction)	FTS : AIBN (molar fraction)
PPy	1.0 : 0.0	1.0 : 0.0
PPy-PAN1	1.0 : 1.0	1.0 : 0.5
PPy-PAN2	1.0 : 1.0	1.0 : 1.0

drying. The VPP reactor was then filled with nitrogen at a flow rate of 500 mL/min, and the internal temperature was set to a constant (60–65 °C). The Py was placed at the bottom of the reactor and exposed to the gas phase in the FTS-coated PET film. The VPP process was carried out at atmospheric pressure for 30 min. After polymerization, the unreacted oxidant and monomers were washed away with distilled water. After washing, the film was dried at room temperature.

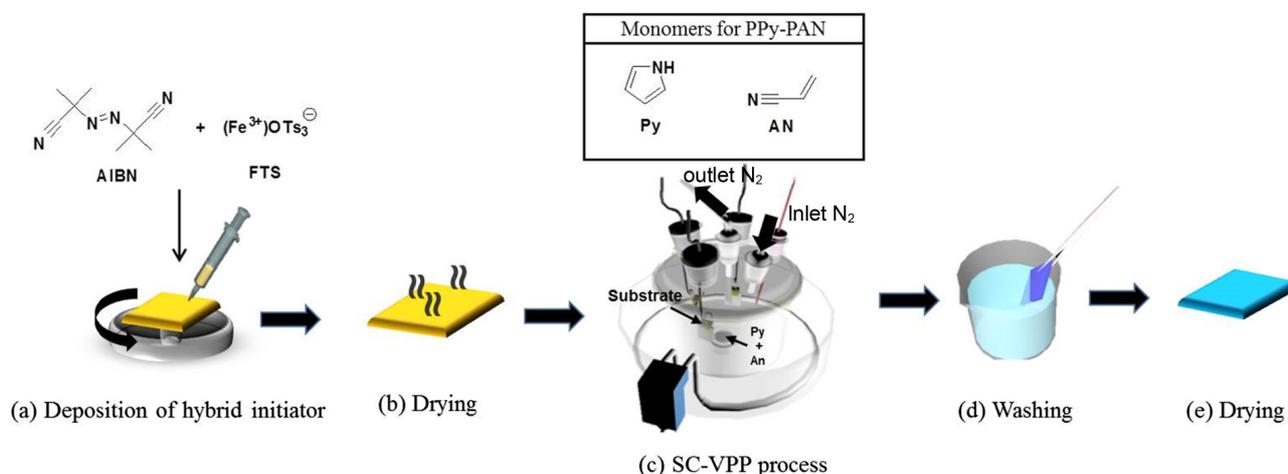
PPy-PAN conductive hybrid films were prepared by the almost same procedure as described above. FTS/AIBN (1:1 and 1:0.5 molar ratios) as a catalyst and Py/AN monomers (1:1 molar ratio) were used for making PPy-PAN hybrid film. Table 1 summarizes the composition of SC-VPP mixed catalysts and monomers in the conductive thin films prepared in this study.

Characterization. The surface resistances of the various prepared PPy-PAN films were measured using a 4-probe point conductivity meter (AiT) with a 100 g load and a radius of 100 μm . The transmittance and absorbance of the films were measured in the range of 400–800 nm using UV-Vis spectroscopy (Optizen 2120 UV plus, Mecasys). The SEO CTA

400 was used to measure the contact angle of the film surface. The morphology, thickness, and elements of the hybrid films were analyzed using field emission scanning electron microscopy (FE-SEM, MIRA LMH, TESCAN, voltage of 50 kV) and energy-dispersive spectroscopy (EDS). The molecular structure of the prepared films was analyzed using ATR-FTIR (Perkin Elmer Spectrum 100) and ^1H NMR spectroscopy (Bruker, 400 MHz, in CDCl_3). ATR-FTIR spectra were measured using potassium bromide (KBr) thin plates.

Results and Discussion

Characterizations of Physico-chemical Structure of Organic-organic Hybrid Thin Films. Organic-organic hybrid composites using SC-VPP have been known to combine two kinds of conductive polymers with oxidation-coupling mechanisms.^{40,41} A PPy/PEDOT blend made by the SC-VPP process of PEDOT-PPy (58 S/cm) was prepared and reported to have an electrical conductivity higher than PPy (4 S/cm).⁴⁰ In addition, PEDOT/P3HT composite thin films, which control bandgap, electrical conductivity, and surface hydrophilicity, were reported by SC-VPP using EDOT and 3-hexylthiophene.⁴¹ In this study, we investigated the possibility of organic-organic conductive hybridization, which would facilitate control of the hydrophilicity of the surface of the hybrid thin film prepared with conductive monomers such as Py, and vinyl-based monomers such as An, using SC-VPP. The process for preparing the PPy-PAN hybrid conductive thin films is shown in Scheme 1. A substrate coated with a mixed catalyst (a radical initiator and an oxidizer) was placed in a VPP reactor, and an SC-VPP process was performed using a conductive monomer (Py) and a

**Scheme 1.** Preparation of PPy-PAN hybrid conductive films by SC-VPP.

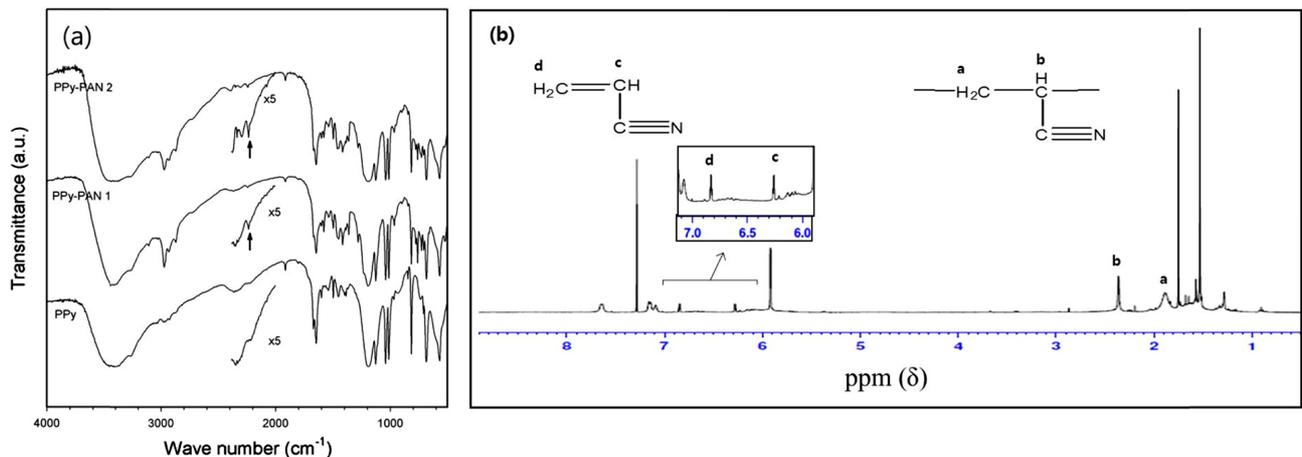


Figure 1. FTIR and ^1H NMR spectra for PPy-based films (a) FTIR; (b) ^1H NMR spectrum in CDCl_3 .

vinyl monomer (AN), resulting in the hybrid conductive thin film. A PPy polymerized by oxidation-coupling and a PAN produced by radical polymerization were simultaneously polymerized *in situ* on a substrate coated with a mixed catalyst, resulting in an organic-organic polymer blend thin film exhibiting conductivity.

Figure 1(a) shows the FTIR spectra of the PPy-PAN composite films prepared under various conditions. The peaks near 1540 and 1452 cm^{-1} are due to the vibrations of a typical PPy ring; the peaks near 1352 and 1045 cm^{-1} correspond to the in-plane stretching vibrations of $=\text{CH}$; and the peak near 1197 cm^{-1} is the stretching vibration of $\text{C}-\text{N}$.^{42,43} Moreover, the peak at 1654 cm^{-1} is characteristic of the $\text{C}=\text{N}$ stretching vibration of PPy. On the other hand, intrinsic characteristic peaks of PAN are observed at 2237 cm^{-1} due to $\text{C}\equiv\text{N}$ group vibrations.⁴³ In the samples of PPy-PAN 1 and PPy-PAN 2, the $\text{C}\equiv\text{N}$ peak at 2237 cm^{-1} is indicative of PPy-PAN composite thin films. In particular, as the content of AIBN coated on the substrate increased, the $\text{C}\equiv\text{N}$ peak gradually intensified, indicating that PAN was further formed in the composite thin film (Figure 1 (a)).

^1H NMR analysis was performed to confirm the fabrication of PPy-PAN composite thin films (Figure 1(b)). Most ICPs, such as PEDOT and PPy, are insoluble in common organic solvents. Therefore, the composite thin films were dissolved in CDCl_3 , and the undissolved solids were removed by a $0.2\text{ }\mu\text{m}$ syringe filter prior to NMR analysis. The methylene and methine peaks of PAN were observed at 1.89 and 2.36 ppm , respectively, confirming the formation of the PPy-PAN composite thin film.⁴⁴ Two peaks were observed at 6.28 and 6.84 ppm , which are not attributed to the PAN polymer, but to

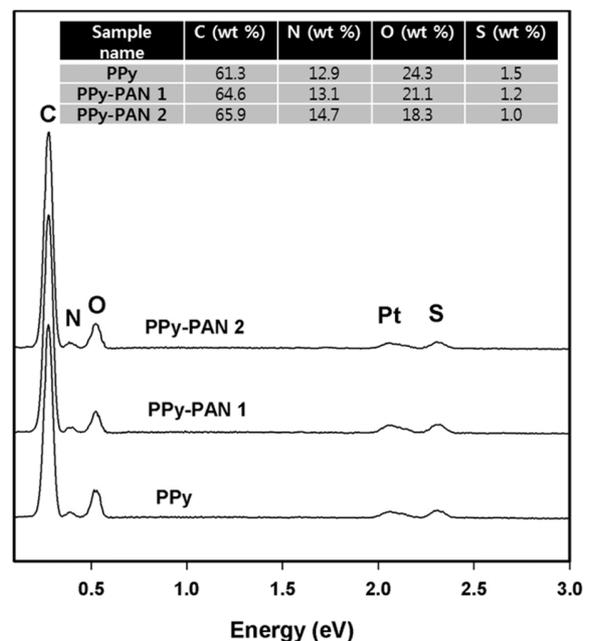


Figure 2. EDS spectra for PPy-based films.

the proton of the AN monomer hydrogen bonded between the $\text{C}\equiv\text{N}$ group of some AN monomers and the $\text{N}-\text{H}$ bond of PPy.

The chemical composition of PPy-PAN composite thin films were also investigated by EDS analysis (Figure 2). The PPy thin film and the PPy-PAN conductive hybrid thin film exhibited peaks for C, N, O, Pt, and S at 0.27 , 0.39 , 0.52 , 2.00 , and 2.30 keV , respectively. Sulfur and oxygen detected in the PPy thin film and the PPy-PAN conductive hybrid thin film were attributed to FTS because *p*-toluenesulfonate derived from FTS is *p*-doped into the main chain of PPy as shown in Figure 3(a). The composition of the hybrid catalysts during the prepa-

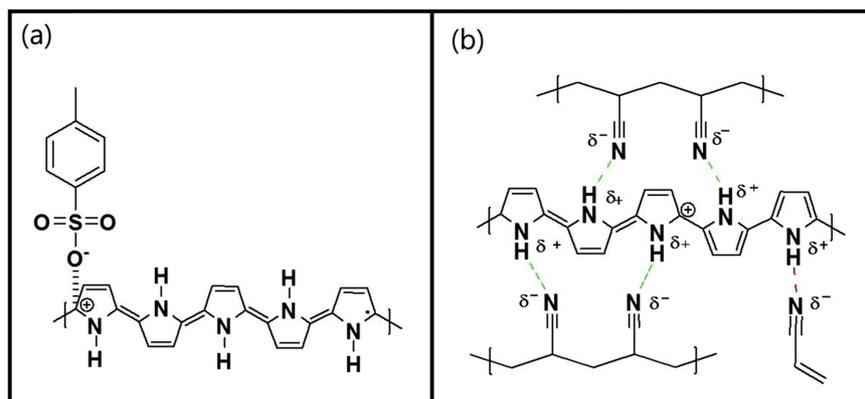


Figure 3. Plausible chemical structures of (a) *p*-doped PPy by *p*-toluene sulfonic acid; (b) hydrogen bonding between PPy and PAN/AN monomer.

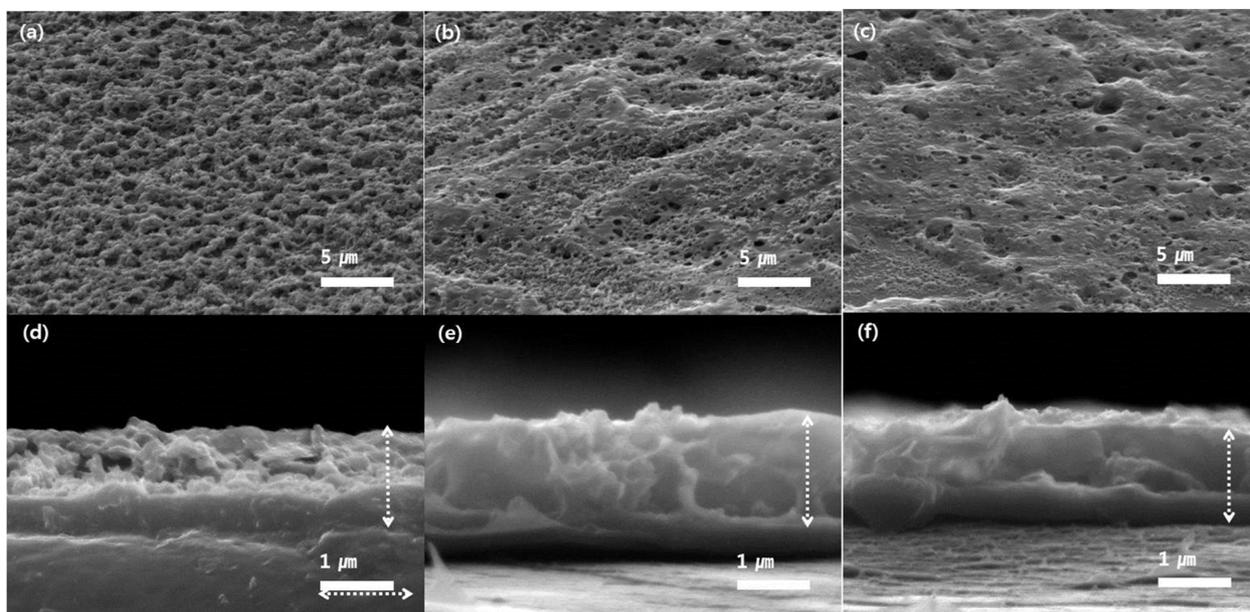


Figure 4. SEM images of the surface of (a) PPy film; (b) PPy-PAN 1 film; (c) PPy-PAN 2 film ($\times 1,000$); a cross-section of (d) PPy film; (e) PPy-PAN 1 film; (f) PPy-PAN 2 film ($\times 50,000$).

ration of the PPy-PAN conductive hybrid thin film increases with the amount of AIBN resulting in the increased formation of PAN in the composite thin film.

In Figure 4, SEM analysis of PPy and PPy-PAN composite thin films was performed to compare their surface morphology. The PPy-PAN thin film had a smaller grain size and a relatively smoother surface compared to that of the PPy thin film. These effects are due to the compatibility of hydrophilic PPy and the PAN. In addition, PPy, PAN, N-H groups capable of hydrogen bonding, and C \equiv N groups are considered to be uniformly hybridized to form a uniform thin film (Figure 3(b)). Also, the AN monomer is considered to be coordinated to FTS at the time of SC-VPP to prevent the rapid oxidation-coupling

reaction of the PPy polymerization from producing a composite particle with a small grain. In other words, it is presumed that Im is a weak base in PEDOT polymerization and that the AN monomer plays a similar role in PPy polymerization.^{45,46}

Table 2. Opto-electrical Properties of PPy and PPy-PAN Films

Sample name	Surface resistance ($k\Omega \cdot sq^{-1}$)	Thickness (nm)	Conductivity (S/cm)	Transparency (%)
PPy	2.17×10^2	1278	3.61×10^{-2}	23
PPy-PAN 1	2.51×10^2	1512	2.64×10^{-2}	34
PPy-PAN 2	2.11×10^2	1601	2.96×10^{-2}	37

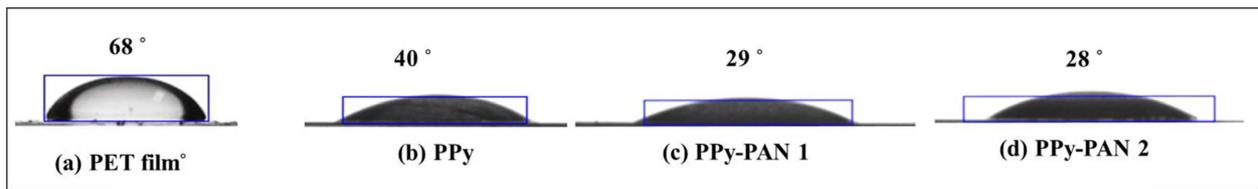


Figure 5. Contact angles of (a) PET film; (b) PPy; (c) PPy-PAN 1; (d) PPy-PAN 2 by DI-water.

Characterizations of Opto-electric and Hydrophilic Properties for PPy-PAN Hybrid Conductive Thin Films. Table 2 summarizes the opto-electric properties of PPy and PPy-PAN conductive hybrid thin films. The surface resistance, thickness, conductivity, and transparency of PPy and PPy-PAN conductive hybrid thin films were measured and are shown in Table 2. PPy exhibited a conductivity of 0.0361 S/cm, and PPy-PAN 1 composite exhibited 0.0264 S/cm. The electrical conductivity of PPy-PAN hybrid film was comparable to PPy alone. This phenomenon can be explained in two ways. The first factor is that the two components in the PPy-PAN blend combination can interact more with each other by hydrogen bonding (see Figure 3(b)), thus providing excellent compatibility to facilitate uniform hybridization. The second reason is that the AN can be coordinated to the oxidizing agent and can act as a polymerization rate-controlling agent for the oxidation-reduction reaction. This is due to the fact that the PEDOT thin film has high conductivity and transparency because of the lower rate of oxidation-reduction polymerization accomplished by the addition of the weak base as a reaction inhibitor during the VPP of PEDOT.^{45,46} The transmittance was slightly increased as the content of PAN increased.

The wettability of the thin coating is very important in the fabrication of many bio-medical, optoelectronic, energy devices, where multilayers should be consisted of many heterogeneous layers. Regarding device reliability, hydrophilicity control would be crucial matter to design interface between multilayers. The contact angle of water was measured to confirm that hydrophilicity was imparted to the surface by PAN hybridization of the PPy-PAN conductive hybrid thin film (Figure 5). The contact angle of the PET film is 68°. PPy-PAN conductive hybrid thin films exhibited a change in hydrophilicity as PAN was hybridized. The contact angles of PPy-PAN 1 and 2, in which PAN was hybridized with PPy, were 29° and 28°, which were 11–12° lower than those of PPy. The hydrophilic properties are thought to increase because the dipole is charged according to the difference in electronegativity of the carbon and nitrogen atoms in the cyano group

(C≡N) of PAN. The SC-VPP-based PPy-PAN hybrid thin films proposed in this study were able to effectively improve the hydrophilic properties of the thin films while minimizing the degradation of the original electrical conductivity of PPy.

Conclusions

PPy-PAN hybrid of conductive thin films were successfully prepared by co-evaporation of each monomer using vapor phase polymerization at atmospheric pressure. PPy-PAN thin film had a smaller grain size and relatively smoother surface than the PPy thin film. PPy-PAN showed similar electrical conductivity to PPy due to its smooth surface morphology. The contact angle of PPy-PAN was below 30°, as compared to 40° for PPy. The proposed SC-VPP-based organic-organic hybrid conductive materials allow for control of the surface properties, such as hydrophilicity, of the resulting thin films. The demonstrated methodology for preparing an organic-organic conductive hybrid thin film is also expected to be useful for adjusting the ICP's surface property such as mechanical, optical, roughness properties.

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References

1. C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, and A. G. MacDiarmid, *Phys. Rev. Lett.*, **39**, 1098 (1977).
2. M. Irimia-Vladu, *Chem. Soc. Rev.*, **43**, 588 (2014).
3. M. Gerard, A. Chaubey, and B. D. Malhotra, *Biosens. Bioelectron.*, **17**, 345 (2002).
4. N. K. Guimard, N. Gomez, and C. E. Schmidt, *Prog. Polym. Sci.*, **32**, 876 (2007).
5. P. A. Levermore, L. Chen, X. Wang, R. Das, and D. D. C. Bradley, *Adv. Mater.*, **19**, 2385 (2007).

6. D. M. Welsh, A. Kumar, E. W. Meijer, and J. R. Reynolds, *Adv. Mater.*, **16**, 1379 (1999).
7. K. S. Lee, J. H. Yun, Y.-H. Han, J.-H. Yim, N.-G. Park, K. Y. Cho, and J. H. Park, *J. Mater. Chem.*, **21**, 15193 (2011).
8. J. M. D'Arcy, M. F. El-Kady, P. P. Khine, L. Zhang, S. H. Lee, N. R. Davis, D. S. Liu, M. T. Yeung, S. Y. Kim, C. L. Turner, A. T. Lech, P. T. Hammond, and R. B. Kaner, *ACS NANO*, **8**, 1500 (2014).
9. J. Ahn, J. S. Yoon, S. G. Jung, J.-H. Yim, and K. Y. Cho, *J. Mater. Chem. A*, **5**, 21214 (2017).
10. A. M. Nardes, M. Kemerink, M. M. D. Kok, E. Vinken, K. Maturova, and R. A. J. Janssen, *Org. Electron.*, **9**, 727 (2008).
11. B. Somboonsub, M. A. Invernale, S. Thongyai, P. Praserttham, D. A. Scola, and G. A. Sotzing, *Polymer*, **51**, 1231 (2010).
12. Y. Wei, J.-M. Yeh, D. Jin, X. Jia, J. Wang, G.-W. Jang, C. Chen, and R. W. Gumbs, *Chem. Mater.*, **7**, 969 (1995).
13. X. Zeng, T. Zhou, C. Leng, Z. Zang, M. Wang, W. Hu, X. Tang, S. Lu, L. Fang, and M. Zhou, *J. Mater. Chem. A*, **5**, 1749 (2017).
14. Y. S. Ko and J.-H. Yim, *Polymer*, **93**, 167 (2016).
15. J.-Y. Kim, M.-H. Kwon, Y.-K. Min, S. Kwon, and D.-W. Ihm, *Adv. Mater.*, **19**, 3501 (2007).
16. A. Mohammadi, M. Hasan, B. Liedberg, I. Lundstrom, and W. Salaneck, *Syn. Met.*, **14**, 189 (1986).
17. J. Kim, E. Kim, Y. Won, H. Lee, and K. Suh, *Syn. Met.*, **139**, 485 (2003).
18. B. Winther-Jensen, D. W. Breiby, and K. West, *Syn. Met.*, **152**, 1 (2005).
19. J. P. Lock, S. G. Im, and K. K. Gleason, *Macromolecules*, **39**, 5326 (2006).
20. M. Fabretto, M. Muller, C. Hall, P. Murphy, R. D. Short, and H. J. Griesser, *Polymer*, **51**, 1737 (2010).
21. F. D. M. Fernandez, Y. S. Ko, and J.-H. Yim, *Polym. Korea*, **42**, 513 (2018).
22. J. S. Choi, K. Y. Cho, and J.-H. Yim, *Eur. Polym. J.*, **46**, 389 (2010).
23. Y.-H. Han and J.-H. Yim, *Polym. Korea*, **34**, 450 (2010).
24. J. Jang and B. Lim, *Angew. Chem.*, **115**, 5758 (2003).
25. M. Choi, B. Lim, and J. Jang, *Macromol. Res.*, **16**, 200 (2008).
26. W. E. Tenhaeff and K. K. Gleason, *Adv. Funct. Mater.*, **18**, 979 (2008).
27. A. Asatekin, M. C. Barr, S. H. Baxamura, K. K. S. Lau, W. Tenhaeff, J. Xu, and K. K. Gleason, *Materials Today*, **13**, 26 (2010).
28. W. E. Tenhaeff and K. K. Gleason, *Sur. Coat. Tech.*, **201**, 9417 (2007).
29. K. Chan and K.K. Gleason, *Chem. Vap. Dep.*, **11**, 437 (2005).
30. A. T. Lawal and G. G. Wallace, *Talanta*, **119**, 133 (2014).
31. Y.-H. Han, J. T-Sejdic, B. Wright, and J.-H. Yim, *Macromol. Chem. Phys.*, **212**, 521 (2011).
32. J.-H. Yim, *Compos. Sci. Tech.*, **86**, 45 (2013).
33. R. Khadka and J.-H. Yim, *Macromol. Res.*, **23**, 559 (2015).
34. Y. S. Ko and J.-H. Yim, *Polymer*, **93**, 167 (2016).
35. S. W. Kim, S. W. Lee, J. Kim, J.-H. Yim, and K. Y. Cho, *Polymer*, **102**, 127 (2016).
36. J. S. Choi, J. S. Park, B. Kim, B.-T. Lee, and J.-H. Yim, *Polymer*, **120**, 95 (2017).
37. J. Ahn, S. Yoon, S. G. Jung, J.-H. Yim, and K. Y. Cho, *J. Mater. Chem. A*, **5**, 21214 (2017).
38. S. K. Jung, K. Y. Cho, and J.-H. Yim, *J. Ind. Eng. Chem.*, **63**, 95 (2018).
39. B. Winther-Jensen and K. West, *Macromolecules*, **37**, 4538 (2004).
40. D. O. Kim, P.-C. Lee, S.-J. Kang, K. Jang, J.-H. Lee, M. H. Cho, and J.-D. Nam, *Thin Solid Films*, **517**, 4156 (2009).
41. K.-S. Jang, D. O. Kim, J.-H. Lee, S.-C. Hong, T.-W. Lee, Y. Lee, and J.-D. Nam, *Org. Electron.*, **11**, 1668 (2010).
42. T. K. Vishnuvardgan, V. R. Kulkarni, C. Basavaraja, and S. C. Raghavendra, *Bull. Mater. Sci.*, **29**, 77 (2006).
43. X. Li, X. Hao, H. Yu, and H. Na, *Mater. Lett.*, **62**, 1155 (2008).
44. P. Enzel and T. Bein, *Chem. Mater.*, **4**, 819 (1992).
45. Y. H. Ha, N. Nikolov, S. K. Pollack, J. Masstrangelo, and B. D. Martin, *Adv. Funct. Mater.*, **14**, 615 (2004).
46. D. M. de Leeuw, P. A. Kraakman, P. F. G. Bongaerts, C. M. J. Mutsaers, and D. B. M. Klaassen, *Syn. Met.*, **66**, 263 (1994).