Abstract: Recently, active research has been conducted on the development of flexible electronic devices. Hence, the transparent conductive film (TCF), an essential component of the device, must also be flexible. However, the commonly used indium tin oxide (ITO) TCF lacks flexibility and contains rare metal, making resource depletion an issue. Therefore, we focused on poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), which has high flexibility and conductivity. Flexible TCFs have been fabricated by coating PEDOT:PSS on polyethylene naphthalate substrates using an inkjet printer. However, the current issue in such fabrication is the effect of the interface state on the transparency and conductivity of the thin film. In this study, we investigated the effect of surfactant in addition to polar solvents on the properties of thin films fabricated with PEDOT:PSS ink. Although the electrical conductivity was reduced, the transmittance remained above 90%. Thus, these results are comparable to those of ITO TCFs for practical use in terms of optical properties.

Keywords: transparent conductive film; surfactant; polar solvent; inkjet printing; transmittance; resistance; thin-film surface; optical properties

1. Introduction

Flexible devices using organic materials have recently attracted attention [1–4]. These organic electronic devices can be fabricated at a low cost through low-temperature processes, such as coating and printing [5,6]. Although vacuum evaporation and sputtering are widely used deposition methods for fabrication, the production requires vacuum equipment, leading to high initial investment and energy and raw material consumption.

TCFs are an important component in display devices, such as smartphones and solar cells. Therefore, for flexible devices, the TCF must be flexible as well. Indium tin oxide (ITO) is commonly used as a TCF. ITO with high conductivity and good transparency in the visible range (T > 90%) [7,8]. However, rapid price fluctuations and lack of flexibility are its disadvantages. Moreover, ITO TCFs contain indium, a rare metal, making resource depletion an issue [9]. Therefore, various materials, such as organic materials and carbon nanotubes, have been investigated as alternatives to ITO [10–17]. In particular, the practicality of organic materials has been recognised in organic electroluminescence devices and organic thin-film solar cells [18–21]. Hence, we focused on poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), which is an organic conductive material with high flexibility and conductivity, as an alternative to ITO. We are also working on fabricating inexpensive and flexible TCFs by coating the materials on plastic substrates using an inkjet printer.
Uniformity of the film surfaces and improvement of the thin-film properties are the key issues in fabricating organic TCFs by inkjet printing [22]. If these challenges are resolved and practical TCFs are fabricated, it will be possible to produce flexible devices, including electrodes and interconnects using only printing technology. Furthermore, we have shown that ultraviolet/ozone (UV/O₃) cleaning of the substrate, heat treatment method, and treatment with polar solvents is effective for PEDOT:PSS thin films. Moreover, the use of ethylene glycol as a polar solvent improves the properties of the films. However, the optical and electrical properties of the thin films were affected by the interfacial conditions owing to the surface roughness of each layer [23]. In this study, we investigated the addition of surfactants to polar solvents in thin films prepared with PEDOT:PSS inks to improve the properties of the films by improving their uniformity.

2. Materials and Methods
2.1. PEDOT:PSS and Additives

CLEVIOS (Clevios™ PH500), based on PEDOT:PSS, was used in the present study. It is a conductive polymer with excellent electrical conductivity and high transmittance in the visible light spectrum, which has attracted attention due to its excellent mechanical flexibility. Figure 1 and Table 1 show the molecular structure and physical properties of PEDOT:PSS, respectively.

![Figure 1. The molecular structure of the PEDOT:PSS.](image)

| Material Property | Typical Values | SI Unit |
|-------------------|----------------|---------|
| PEDOT:PSS ratio   | 1:2.5          | w/w     |
| Viscosity at 20°C | 25             | mPa     |
| pH at 20°C        | 1.5–2.5        |        |
| Density at 20°C   | 1              | g/cm³   |
| Average particle size | 30    | nm      |
| Bolling Point     | approx 100     | °C      |

Table 1. Material property of the PEDOT:PSS.

PEDOT:PSS has been reported to improve the properties of thin films with the addition of additives [24,25]. The addition of low-boiling-point solvents lowers the surface tension of the ink and improves the wettability of the substrate. Further, the addition of high-boiling-point solvents improves the conductivity due to the secondary doping effect of...
PEDOT and the bonding of conductive regions. Dimethyl sulfoxide (DMSO) is a high-boiling-point solvent with a low viscosity. Therefore, it was added to the ink to control the viscosity and prevent coagulation. It is also known that the addition of ethylene glycol, a high-boiling-point solvent, removes the insulating PSS and forms a conductive area of PEDOT [26,27].

Ethylene glycol is also a highly polar solvent. It has been reported that high polarity solvents control the molecular structure and orientation of PEDOT in PEDOT:PSS and improve its conductivity. Hence, ethylene glycol was used as the polar solvent to improve the conductivity of the films [28].

Fluorosurfactants can lower the surface tension of a solvent when added in small concentrations. In addition, it has been reported that surfactants can improve the wettability of PEDOT:PSS [29]. There are two types of surfactants: ionic and non-ionic. Ionic surfactants are further classified as amphoteric, anionic, or cationic. We used an ionic amphoteric fluorosurfactant (Surflon S-231, AGC Seimi Chemical Co., Ltd., Chigasaki, Japan), which also reduced the viscosity and surface tension of ethylene glycol.

2.2. Preparation and Evaluation of PEDOT:PSS Thin Films

A piezoelectric pigment inkjet printer (PX-105; Seiko Epson Co., Suwa, Japan) was used to produce the PEDOT:PSS thin film, with the printing pattern set to 40 mm (Length) × 15 mm (Width). A heat-resistant transparent film (Teonex Q65FA; DuPont Teijin Films, Tokyo, Japan) was selected as the substrate. Q65FA is a polyethylene naphthalate film with excellent thermal stability, chemical resistance, and high transparency. A UV/O₃ cleaning system (ASM401N; Asumi Giken, Ltd., Tokyo, Japan) was used to clean the substrate before the deposition to reduce organic contaminants and improve hydrophilicity. The UV/O₃ cleaning conditions were a UV irradiation distance, low-pressure mercury lamp output, and cleaning time of 30 mm, 40 W, and 20 min, respectively. The composition of the ink was PEDOT:PSS:DMSO:ethylene glycol = 70:20:10 wt%, which exhibited the best properties to date [30]. Similar to a previous study, PEDOT:PSS thin films were formed in two to four printing cycles [23]. Polar solvents were applied by inkjet printer for each PEDOT:PSS layer printed. The thin film was annealed at 90 °C for 60 min using a constant-temperature drying oven (EOP-300B; As One Co., Ltd., Osaka, Japan) after the entire printing process was completed.

We evaluated the resistance, transmittance, and surface observation results of the PEDOT:PSS thin films. The resistance of the PEDOT:PSS thin film was determined by measuring the vertical ends of the printed pattern using a digital multimeter (VOAC7521H; Iwatsu Electric Co., Ltd., Tokyo, Japan). The film thickness was measured with a variable-angle spectroscopic ellipsometer (M-2000V-Te; J. A. Woollam Co., Ltd., Lincoln, NE, USA) at multiple angles of incidence, and the resistivity was calculated using the average of the resistance values. The transmittance was measured at a wavelength of 550 nm using a spectrophotometer (U-3900; Hitachi High-Technologies Co., Tokyo, Japan). The wavelength of about 550 nm has the highest spectral luminous efficiency, corresponding to the sensitivity of the human eye, and is therefore the wavelength most often used in papers. The surface of the thin film was observed under a microscope (VHX-1000; Keyence Co., Ltd., Osaka, Japan), while the surface roughness was measured using an atomic force microscope (AFM) (SPM-9700; Shimadzu Co., Kyoto, Japan).

3. Results and Discussion

The surfactant was added to ethylene glycol at concentrations ranging from 0 to 2.0 wt%, as it was difficult to achieve a stable coating when the concentration was more than 2.0 wt%.

Figure 2 shows the change in resistance and transmittance with the printing cycles when Surflon S-231 is added. Two printing cycles have higher transmittance than three printing cycles, and particularly a significant increase in resistance. Therefore, three printing cycles are suitable for Surflon S-231-doped thin films.
Figure 2. Resistance value and transmittance as a function of the printing cycles. The surfactant (Surflon S-231) was added at a concentration of 2.0 wt% in a polar solvent (ethylene glycol). Figure 3 shows the resistance of the film when Surflon S-231 is added to the polar solvent. The resistance increased with the increasing surfactant concentration. This was due to the electronegative fluorine atoms present in Surflon S-231. Electronegativity is a measure of the attraction of electrons by the nucleus of an atom, and fluorine has the strongest electronegativity among all the atoms. Therefore, it attracts electrons in the PEDOT:PSS thin film, which prevents the transfer of electrons and increases the resistance.

However, when the concentration of surfactant reached 2.0 wt%, the resistance decreased. It has been reported that the resistivity decreases with the even distribution of PEDOT:PSS [31,32]. It is hypothesised that the addition of surfactant improved the wettability of PEDOT:PSS thin film and promoted the uniformity of the thin film, thereby resulting in a decrease in resistance.

Figure 4 shows the transmittance when Surflon S-231 is added to the polar solvent. The transmittance increased with the increasing surfactant concentration. When 2.0 wt% of
Surflon S-231 was added, the transmittance was 94.6% after three printing cycles, which was 10% more than the previous thin films.

![Figure 4](image-url) Transmittance as a concentration of Surflon S-231. All transmittances are for thin films with three printing cycles.

Table 2 shows the variation in the electrical and optical properties and thickness of the films with and without Surflon S-231. The transmittance and resistivity increased with the addition of Surflon S-231. When Surflon S-231 was added (2.0 wt%), the thickness of the PEDOT:PSS film was approximately 40 nm, layered per print. Conversely, in the absence of Surflon S-231, the thickness was found to be approximately 70 nm per print. It can be inferred that the addition of the surfactant improved the wettability of the PEDOT:PSS thin film, making it easier to spread and form a uniform film, thus reducing the film thickness.

Figure 5 shows the variation in transmittance with the number of printing cycles for the films with and without Surflon S-231. Here, we compare printing twice without Surflon S-231 and printing thrice with Surflon S-231, which are relatively closer in thickness. The transmittance increased by 6.5% (from 88.1% to 94.6%) when the thickness of the film decreased by 13 nm (from 140 to 127 nm).

Table 2. The electrical and optical properties and thickness of the films with and without Surflon S-231. All values are for thin films three printing cycles.

| Surflon S-231 (wt%) | Resistivity ($\times 10^{-3} \ \Omega \cdot \text{cm}$) | Transmittance (%) | Film Thickness (nm) |
|---------------------|---------------------------------|------------------|--------------------|
| 0                   | 1.98                            | 83.4             | 213                |
| 2.0                 | 3.44                            | 94.6             | 127                |

In the absence of Surflon S-231, the transmittance is reduced by approximately 5.0% per print (film thickness ~70 nm). This behavior is not consistent with the 13 nm decrease in film thickness and 6.5% increase in transmittance. These results suggest that factors other than film thickness play a significant role in the increase in transmittance.

Figure 6 shows the images of PEDOT:PSS thin-film surfaces observed using a microscope. The addition of Surflon S-231 improved the overall transparency of the films. The micrographs show that the addition of Surflon S-231 to polar solvents results in a uniform thin film with little difference between light and dark regions. Moreover, the addition of a surfactant improved the wettability of the PEDOT:PSS thin film and made it more uniform.
It is inferred that the addition of surfactant suppresses the scattering of light and increases the transmittance.

![Graph](image)

**Figure 5.** The variation in transmittance with the printing cycles for the films with and without Surflon S-231.

![Microscope images](image)

**Figure 6.** Microscope image of the surface of a thin film. The surface of a PEDOT:PSS at 300× magnification. (a) Only ethylene glycol as polar solvent. (b) Surflon S-231 added to polar solvent at a concentration of 2 wt%.

Figure 7 shows the surface roughness of the film measured using an AFM. A significant reduction in surface roughness was observed when Surflon S-231 was added at 2.0 wt%. Furthermore, it was observed that the polar solvent containing the surfactant smoothened the surface of the thin film. Therefore, the smoothness of the thin-film surface may also be a factor for the increase in transmittance.
Figure 6. Microscope image of the surface of a thin film. (a) Only ethylene glycol as polar solvent. (b) Surflon S-231 added to polar solvent at a concentration of 2 wt%.

Figure 7. AFM image of the surface of a thin film. (a) Only ethylene glycol as polar solvent. (b) Surflon S-231 added to polar solvent at a concentration of 2 wt%.

4. Conclusions

The addition of a fluorosurfactant to a polar solvent reduced the conductivity. This may be due to the electronegative fluorine atoms in the surfactant, which prevents the transfer of electrons in the film. Further, the transmittance significantly increased because the improved wettability of the PEDOT:PSS film resulted in a uniform film and decreased surface roughness, thereby decreasing the scattering of light. When 2.0 wt% Surflon S-231 was added, the transmittance was 94.6% after three printing cycles. Thus, the values obtained in this study are comparable to those of ITO films for practical use in terms of optical properties.

In the future, the addition of silver nanowires will be investigated to improve the conductivity of thin films.

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