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Effects of various imidazole-based weak bases and surfactant on the conductivity and transparency of poly(3,4-ethylenedioxythiophene) films

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ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT)-based conductive thin films with improved transparency and surface resistance can be prepared by using adequate weak bases and non-ionic surfactants. Among the imidazole-based weak bases, 2-ethyl-4-methyl-substituted imidazole showed the best performance in terms of surface resistance and transparency. It is speculated that 2-ethyl-4-methyl-imidazole causes reduced particle size because polymerization kinetics are retarded by the electron donating effect of ethyl and/or methyl groups in the imidazole ring. Addition of Triton X-100 may stabilize nanoscopic PEDOT particles in the coating solution resulting in low surface resistance (172 Ω/□) and enhanced transparency (>90%) of the PEDOT film.

1. Introduction

Numerous studies on the use of conductive polymers to replace metallic materials have recently been reported because of the low cost, light weight, and flexibility of conductive polymers. Among conductive polymers, poly(3,4-ethylenedioxythoiphene) (PEDOT) is a π-conjugated polymer having high conductivity, transparency, and stability [1–4]. These properties make it possible to apply PEDOT in many applications including photovoltaic applications, electrochemical/electronic devices, and optical displays [5–8]. However, PEDOT has processing limitations because it is relatively insoluble in most solvents. Nevertheless, one of the most widely used systems is an aqueous dispersion of poly(3,4-ethylenedioxythoiphene)–poly(styrenesulfonate) (PEDOT–PSS), which is soluble in water. However, PEDOT–PSS exhibits a relatively low conductivity (0.1–10 S/cm) that does not meet the high conductivity requirements of many applications [9]. Therefore, several studies have been conducted to overcome the disadvantages of PEDOT–PSS. To increase the conductivity of PEDOT films, De Leeuw et al. introduced an effective method for improving conductivity up to 300 S/cm using imidazole as a weak base in the direct oxidative PEDOT polymerization [10]. Recently, Y.-H. Ha et al. investigated optimal conditions by manipulating various parameters of the intrinsic PEDOT polymerization process such as the content of imidazole (weak base) and oxidant ($Fe(OTs)_3$), types of solvent and monomer, and solution concentration [11]. They achieved fairly high transparent (~80%) and conductive (~900 S/cm) PEDOT films [11]. More recently, pyridine as a weak base has also been used to produce highly transparent and conductive PEDOT films (500–1000 S/cm) [12–14]. The role of weak base has been elucidated that reduction potential of Fe^{III}/Fe^{II} couple and thus a decrease in the PEDOT polymerization kinetics. In other words, base-inhibited PEDOT polymerization results in a decrease of the size of PEDOT particles in the solution and thus increased connectivity between PEDOT domains in the film state [11]. Highly transparent and conductive PEDOT films can therefore be achieved due using a weak base. In the case of surfactant, Y. Kudoh et al. found that a good yield of the highly conductive aqueous PEDOT solution could be obtained by emulsion polymerization with an anionic surfactant such as sodium alkylnaphthalene sulfonate [15]. However, there has not been sufficient research on the effects of substituents in the weak base and/or a combination of weak base and surfactant on the conductivity of PEDOT films.

In this study, PEDOT films were prepared by adding various imdazole derivatives and a non-ionic surfactant by a simple spin-coating method. The effects of the imidazole derivative substituent

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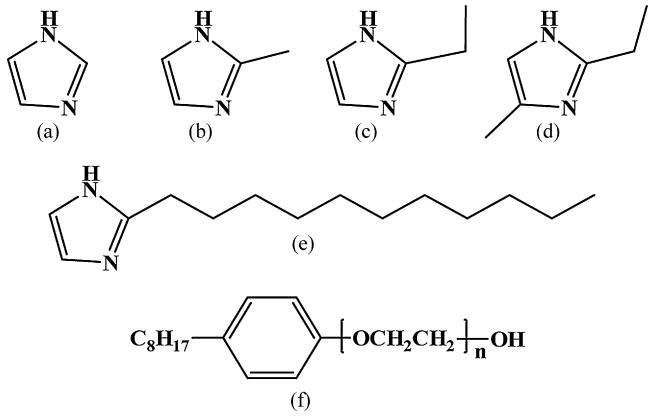

Fig. 1. Chemical structures of various imidazole derivatives and the non-ionic surfactant (Triton X-100) used in this study: (a) Im, (b) 2-Me-Im, (c) 2-Et-Im, (d) 2-Et-4-Me-Im, (e) 2-undecyl-Im, and (f) Triton X-100 ($n \sim 10$).

were investigated to enhance the performance of the transparent conductive films. To improve the performance of the transparent conductive PEDOT films, Triton X-100, a non-ionic surfactant, was added to improve the transparency of the PEDOT-based conductive films. The PEDOT-based conductive films were characterized using Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and X-ray Photoelectron Spectroscopy (XPS) to elucidate the effect of a substituent in the imidazole derivative and the effect of the combination of a weak base and surfactant.

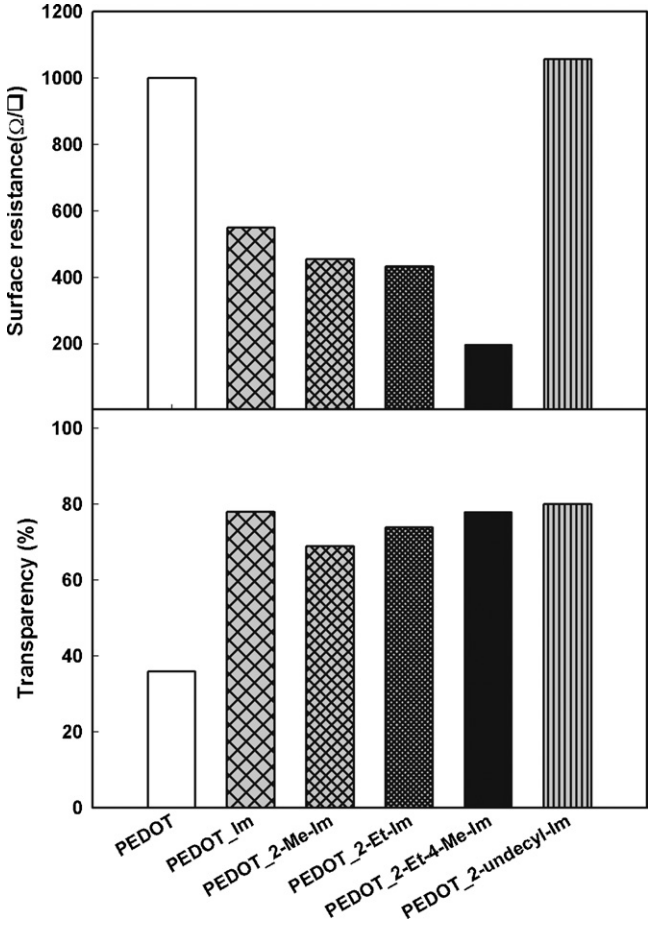

Fig. 2. Surface resistance and transparency of PEDOT-based films prepared with various weak bases.

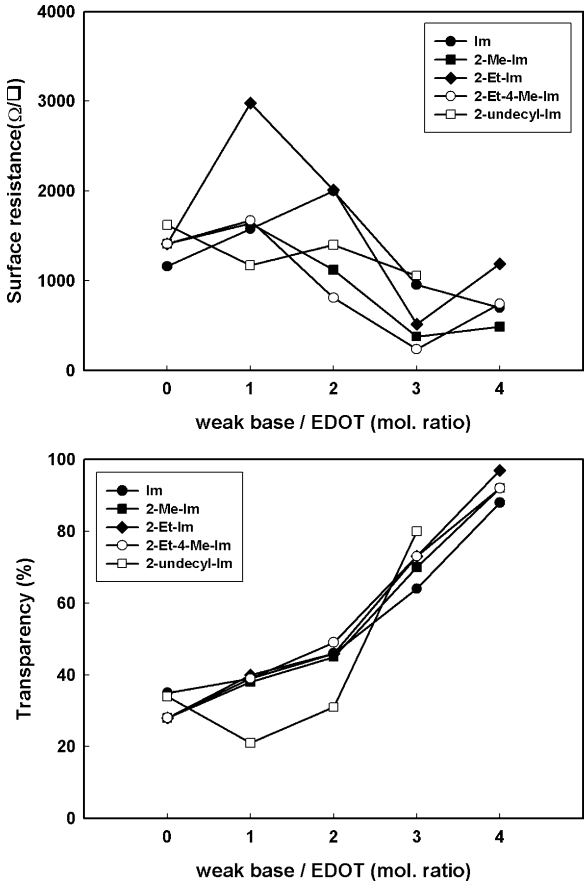

Fig. 3. Surface resistance and transparency of PEDOT-based films as a function of the molar ratio of weak base/EDOT.

2. Experimental

2.1. Reagents and materials

3,4-Ethylenedioxythiophene (EDOT, ALDRICH) as a synthesis monomer of PEDOT, iron(III) *p*-toluene sulfonate (FTS, ALDRICH) as a oxidizing agent/dopant, and 1-butanol (JUNSEI) were used as received. Imidazole (Im, SAMCHUN), 2-methylimidazole (2-Me-Im, ALDRICH), 2-ethylimidazole (2-Et-Im, ALDRICH), 2-ethyl-4-methyl-imidazole (2-Et-4-Mt-Im, ALDRICH), 2-undecyl-imidazole (2-undecyl-Im, KASEI) as a weak base, and Triton X-100 (ALDRICH, Mw: ~647) as a non-ionic surfactant were also used as received. The chemical structures of the various Im derivatives and non-ionic surfactants are shown in Fig. 1.

2.2. Preparations of PEDOT film

PEDOT was synthesized by using the chemical oxidative polymerization method. The molar ratio of FTS/EDOT was 3 and the solid content was fixed at 40 wt%. The content of the various Im derivatives was varied by adjusting the molar ratio of Im/EDOT in the range of 0–4. The effect of surfactant was also studied by varying the weight ratio of surfactant/EDOT over the range of 0–2.5. After FTS and weak base were dissolved in 1-butanol, EDOT and Triton X-100 were added. The mixed solutions were stirred for 10 s and then filtered by using a Teflon syringe filter (0.2 μm). The filtered solutions were continuously spin-coated at 300 rpm for 10 s and at 500 rpm for 30 s on the poly(ethyleneterephthalate) (PET, 3 M) film and p-type Si wafer (Wafer Works Corp./Helitek Company Ltd.), respectively. The films were then polymerized in an oven for 2 min

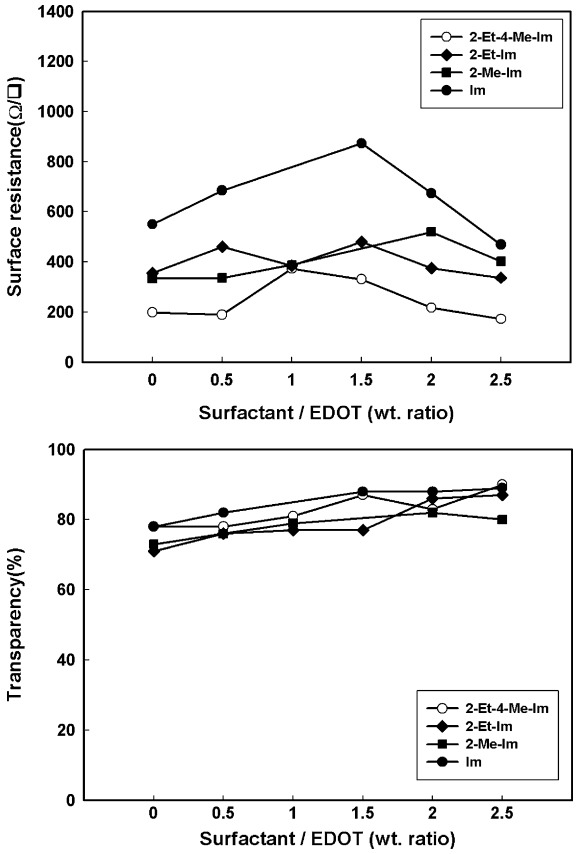

Fig. 4. Surface resistance and transparency of PEDOT-based films as a function of the amount of Triton X-100.

at 80 °C, washed 3 times with distilled water, and dried at room temperature.

2.3. Characterization of prepared PEDOT films

The surface resistance of the samples was measured by the 4-probe point (CHANGMIN) method. The thickness of the PEDOT film was measured using a JSM-6335F scanning electron microscope (JEOL). The conductivity was calculated from the surface resistance and thickness of the PEDOT films by using the following Eq. (1).

$$\sigma = \frac{1}{SRt} \tag{1}$$

In Eq. (1), *SR* is the surface resistance (Ω/□) and *t* is the thickness of the film (cm). The transparency measurement was carried out by means of UV–vis/8453 (Hewlett Packard) from 380 to 780 nm in the visible light region. Atomic Force Microscopy (SPA-400, SEIKO) was carried out in the tapping mode with a silicon tip to analyze the surface morphology. The surface roughness value used in this study was the root-mean-square roughness. An X-ray photo-

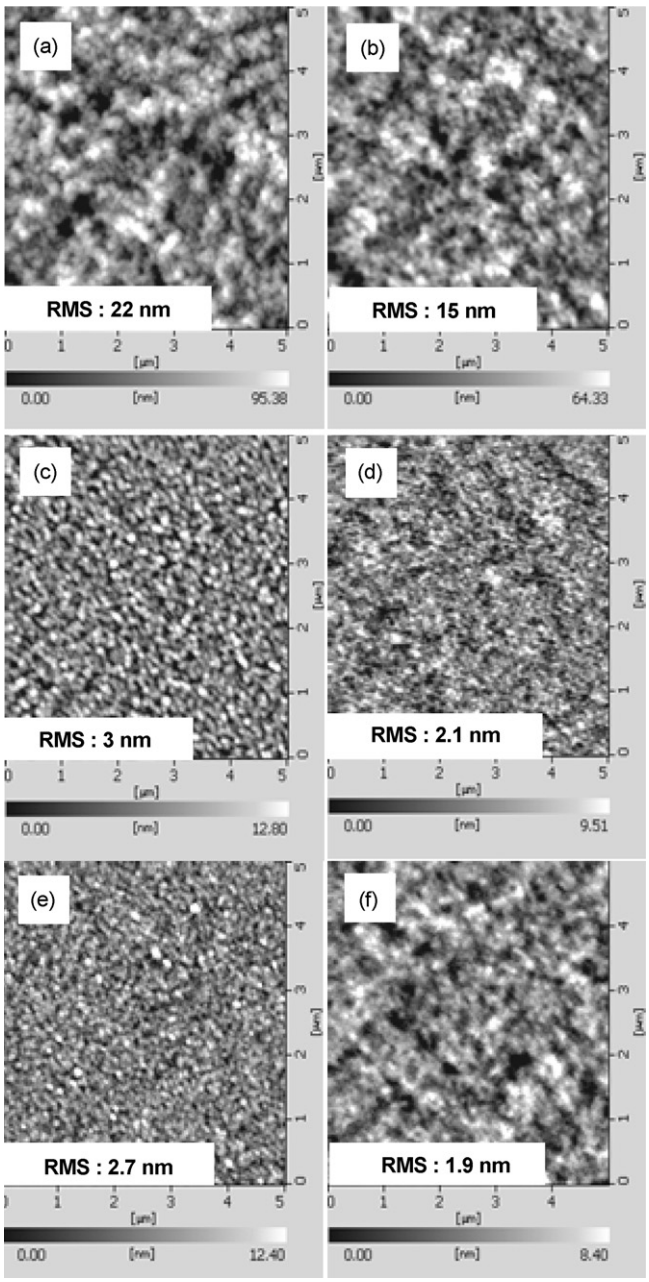

Fig. 5. AFM images of various PEDOT-based films: (a) PEDOT, (b) PEDOT_Triton X-100, (c) PEDOT_Im, (d) PEDOT_Im_Triton X-100, (e) PEDOT_2-Et-4-Me-Im, and (f) PEDOT_2-Et-4-Me-Im_Triton X-100.

Table 1
Summary of various properties of PEDOT-based films prepared with weak base and Triton X-100.

	Thickness (nm)[2]	Surface resistance (Ω/□)	Transparency (%)[3]	Conductivity (S/cm)[3]
PEDOT[1]	290	1000	36	34
PEDOT_Triton X-100[1]	569	376	51	44
PEDOT_Im	118	550	78	154
PEDOT_Im_Triton X-100	140	469	89	152
PEDOT_2-Et-4-Me-Im	120	198	78	420
PEDOT_2-Et-4-Me-Im_Triton X-100	159	172	90	365

EDOT:FTS:weak base = 1:3:3 (mole ratio) except[1], EDOT/FTS = 1:3 (mole ratio), Triton X-100/EDOT = 2.5 (wt. ratio), solid contents: 40 wt% in n-butanol, [2]Thickness was obtained by SEM, [3]Surface resistance and transparency were measured on PET film.

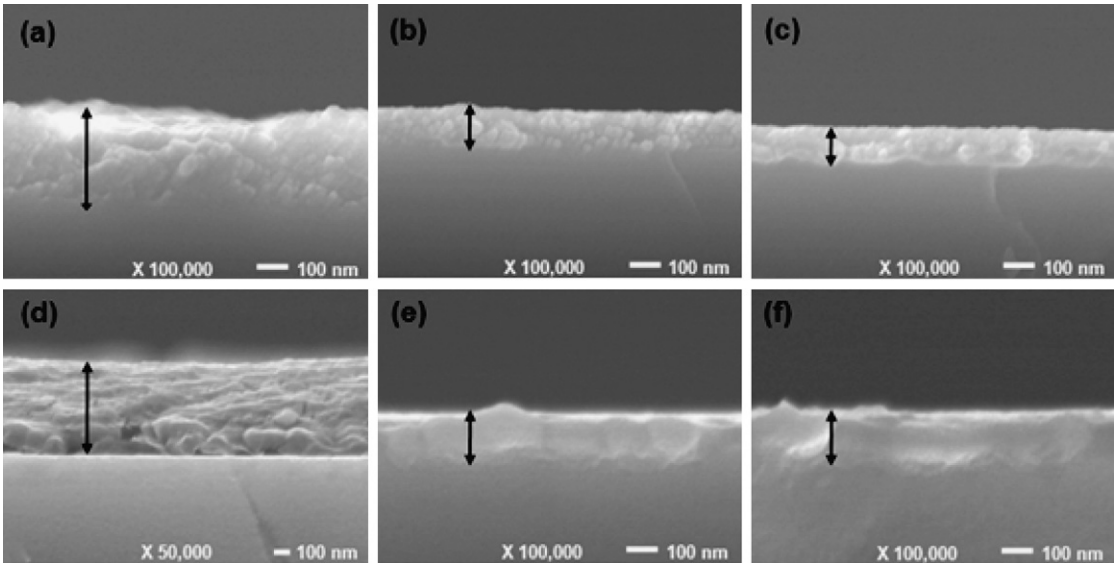

Fig. 6. Cross-sectional SEM images of PEDOT-based films prepared with weak base and Triton X-100: (a) PEDOT, (b) PEDOT_Im, (c) PEDOT_2-Et-4-Me-Im, (d) PEDOT_Triton X-100, (e) PEDOT_Im_Triton X-100, and (f) PEDOT_2-Et-4-Me-Im_Triton X-100.

electron spectroscope (VG scientific MultiLab. ESCA 2000, Thermo Electron Corporation) equipped with a Mg Kα radiation source (1253.6 eV) was used to obtain the $R_{S/T}$ value. The base pressure used was 1×10^{-8}–10^{-9} Torr.

3. Results and discussion

3.1. Effect of a substituent in the Im derivatives

Several Im derivatives having one or two alkyl substituents at the 2 and/or 2, 4 positions in the Im ring structure were used, as shown in Fig. 1. Comparisons considering the effects of the number of alkyl groups and the length of hydrocarbon chains in the Im ring structure were made.

Fig. 2 shows the surface resistance and transparency values of the conductive polymer films made from various Im-based weak bases. The addition of weak bases significantly reduced the surface resistance and increased the transparency as compared with pristine PEDOT, except in the case of 2-undecyl-Im. These results are consistent with previous studies which considered the improvement of PEDOT's properties due to adding weak base [10–14]. Y.-H. Ha et al. explained the roles of the weak base as follows [11]. First, Im retards the polymerization rate by reducing the reactivity of FTS by coordination and/or lowering of the pH of the polymerization medium. Secondly, Im promotes higher molecular weights of the PEDOT chains. Finally, Im prevents overdoping of the PEDOT chains. Hence, it is obvious that weak bases not only reduce surface resistance but also increase the transparency of films. Imidazole derivatives with short chain substituents (2-Me-Im, 2-Et-Im, and 2-Et-4-Mt-Im) in particular show superior performance compared to Im. This result can be explained by the electron donating effect of ethyl and/or methyl groups. In general, an alkyl group is an electron donating group as compared to hydrogen. Therefore, nitrogen atoms in the Im ring containing an alkyl group may have a more basic character. In fact, 2-Et-4-Me-Im which has two alkyl groups showed the lowest surface resistance among the imidazole derivatives, while 2-undecyl-Im showed the highest surface resistance among the weak bases. In the case of 2-undecyl-Im, the alkyl chain of the imidazole ring is much longer than the other derivatives. Hence, the undecyl chain in the 2-undecyl-Im should act as a steric hindrance in the interaction with FTS in the PEDOT polymerization. On the whole, the use of short chain-substituted Im decreases surface resistance and increases the transparency of PEDOT films compared to pristine Im.

3.2. Effect of amounts of Im derivatives

The molar ratio of Im derivatives/EDOT was varied in the range of 0–4 to optimize the amount of Im-based weak bases. Fig. 3 shows the surface resistance and transparency of the PEDOT films as a function of the amount of weak base. Short alkyl chain-substituted Im exhibited the lowest surface resistance at a weak base/EDOT molar ratio of 3. These results closely agree with a previous report of Y.-H. Ha et al. [11]; these authors found the highest conductivity and lowest surface resistance when the molar ratio of weak base/oxidant was nearly the same. The weak base may coordinate oxidant equivalently in accordance with the previously reported PEDOT polymerization scheme [11] thereby reducing the oxidant potential. Also, transparency tends to increase consistently with increasing amounts of weak base. This may be due to the significant reduction of the thickness of the PEDOT layer with increasing weak base amount as reported previously [11]. The tendency for transparency to increase was largely similar regardless of substituent type.

3.3. Effect of addition of non-ionic surfactant and Im derivatives

To determine the effect of a non-ionic surfactant, Triton X-100, on the transparency and conductivity of PEDOT films, the amount of Triton X-100 was varied by adjusting the surfactant/EDOT weight ratio over the range of 0–2.5 while fixing the molar ratio of EDOT:FTS:weak base at 1:3:3. Fig. 4 shows the surface resistance and transparency values of the PEDOT films as a function of the amount of Triton X-100. The transparency of PEDOT-based films increased slightly with increasing amounts of Triton X-100 which indicates that Triton X-100 as a surfactant can effectively disperse PEDOT particles in the solvent. In other words, the PEDOT particle size decreased as the amount of Triton X-100 increased. By the way, surface resistance of the films was nearly sustained with addition of Triton X-100. To quantitatively determine PEDOT particle size, the surface morphology of the PEDOT-based films produced using

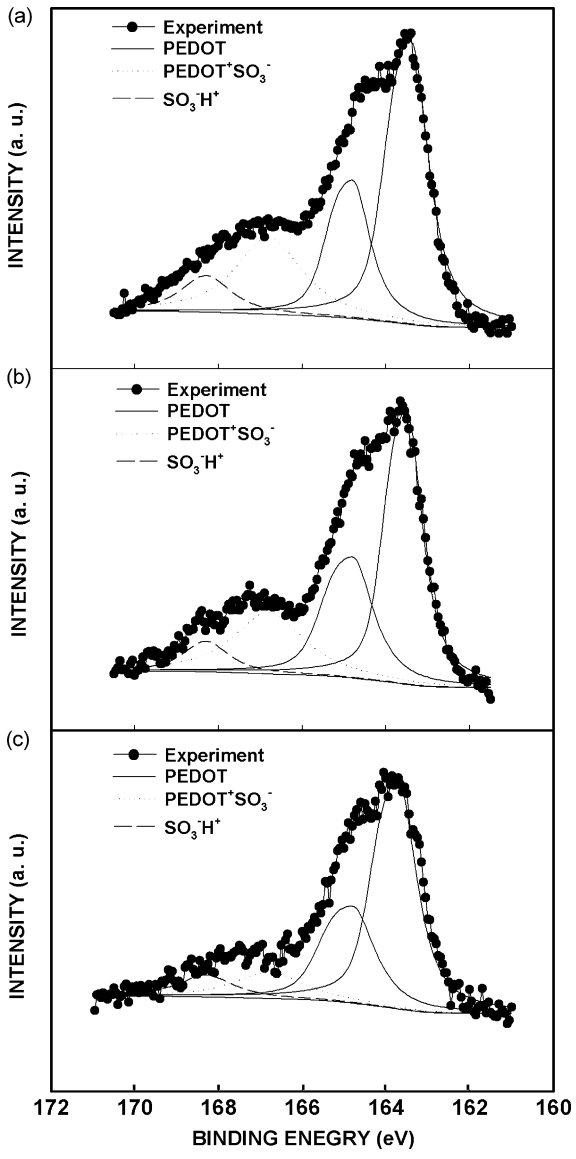

Fig. 7. XPS curves of PEDOT-based films prepared with weak base and Triton X-100: (a) PEDOT ($R_{S/T}$ = 0.31, conductivity = 34 S/cm), (b) PEDOT_Triton X-100 ($R_{S/T}$ = 0.23, conductivity = 44 S/cm), and (c) PEODT_2-Et-4-Me-Im_Triton X-100 ($R_{S/T}$ = 0.19, conductivity = 365 S/cm). The XPS sample was prepared as a type of film on PET. $R_{S/T}$ was calculated using a previously reported method [16,17].

weak base and Triton X-100 was investigated by means of AFM. The AFM images of various PEDOT-based films are given in Fig. 5. The surface roughness of PEDOT films made using Triton X-100 was slightly decreased (15 nm) as compared with pristine PEDOT (22 nm). Meanwhile, the surface roughness of the PEDOT film using Im derivatives and/or Im derivatives and Triton X-100 decreased significantly from 22 nm to below 3 nm. The surface roughness is related to the PEDOT particle size in solution – the lower the roughness, of the smaller the PEDOT particles in solution. The reduction of PEDOT particle size using Triton X-100 was minor compared to the reduction in particle size achieved using a combination of weak base and Triton X-100.

Table 1 shows the thickness, surface resistance, transparency, and conductivity of typical PEDOT films produced in this study. The conductivity was calculated using Eq. (1) described in Section 2. As stated previously, the conductivity of the films increases as the thickness decreases. The thickness of the films increased when adding Triton X-100, as shown in Table 1. The conductivity increased slightly when adding Triton X-100 due to a decrease of surface resistance, although the PEDOT films made using Triton X-100 were thicker than the pristine PEDOT films (see Table 1). In contrast, the surface resistance and thickness of the films decreased when weak base was added, resulting in increased conductivity. Moreover, the transparency of the films improved when a combination of Triton X-100 and a weak base was applied. Among the combinations of Triton X-100 and weak base, films made using Triton X-100/2-Et-4-Me-Im were excellent in terms of conductivity and transparency. Small PEDOT particles increase connectivity between the PEDOT grains in the film and lead to smoother surface morphology, resulting in the observed increase in conductivity and transparency. Addition of Triton X-100 caused increased transparency due to smaller particle sizes, but the conductivity was not increased. The cross-sectional images of the PEDOT films obtained by SEM were compared (see Fig. 6). As discussed in Table 1, an increase of the thickness of the PEDOT-based film was observed by adding Triton X-100. Triton X-100, which is a high molecular weight non-ionic surfactant, may have increased the viscosity of the PEDOT solution. Interestingly, the morphology of the cross-section of the films changed from a granular type surface to a smooth surface after Triton X-100 was added. This result seems to be related to the size of the PEDOT particles, as discussed in the AFM results.

3.4. XPS study

Fig. 7 shows S(2p) XPS spectra of various PEDOT films. The $R_{S/T}$ values of the various films, calculated by the intensity ratio between the signal from tosylate (around 169.9.0 eV) and PEDOT (163.4 eV), as reported in previous studies [16,17], are somewhat different although the shape of the S(2p) XPS spectra of the various PEDOT films are similar. The value of $R_{S/T}$ of pristine PEDOT is 0.31 while the value of $R_{S/T}$ of PEDOT with Triton X-100 added was reduced from 0.31 to 0.23. Additionally, the value of $R_{S/T}$ was further reduced from 0.23 to 0.19 by adding 2-Et-4-Me-Im. This is in agreement with previous studies [16,17] which reported that an increase of conductivity is related to the $R_{S/T}$ values.

Nitrogen atoms cannot be detected around 398 eV, as seen in the N(1s) bonding in the XPS spectrum of PEDOT using 2-Et-4-Me-Im and Triton X-100 (data not shown). This suggests that the Im-based weak base does not remain in the PEDOT polymer chains after polymerization because it is thoroughly removed with iron salts during the washing of the film. This implies that the Im-based weak base only contributes to reducing the initial polymerization kinetics as a coordinated oxidation agent and assists coupling of cation radicals by the removal of two protons, as described in a previous report [11].

4. Conclusions

In this study, the effects of Im derivatives and Triton X-100 were investigated by measuring the conductivity, transparency, cross-sectional morphology, and surface roughness properties of various PEDOT films. 2-Et-4-Me-Im which has two alkyl groups exhibited excellent properties compared with other weak bases. It may effectively reduce the nanoscopic PEDOT particle size because polymerization kinetics are retarded by the electron donating effect of ethyl and/or methyl groups in the Im ring. Moreover, addition of weak base and Triton X-100 resulted in a reduction of the surface resistance (172 Ω/□) and a significant increase in the transparency (90%) of PEDOT films due to a smoother surface morphology with increased connectivity between the grains of PEDOT particles. The use of an Im-based weak base and non-ionic surfactant seems to be an effective combination for the preparation of high performance transparent conductive PEDOT films.

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