이미다졸과 계면활성제가 기상중합법으로 제조된 PEDOT 박막의 광-전기적 특성에 미치는 영향

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Effect of Imidazole and Surfactant on the Opto-Electrical Properties of PEDOT Thin Films *via* Vapor Phase Polymerization

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초록: 본 논문은 ferric *p*-toluenesulfonate를 산화제에 약 염기인 이미다졸과 poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) 계면활성제를 동시 첨가하여 기상중합법으로 제조된 poly(3,4-ethylenedioxythiophene) (PEDOT) 박막의 광-전기적 특성 향상에 대한 것이다. 여러 가지 조건에서 제조된 PEDOT 박막 특성과 산화제의 첨가제로 사용된 약 염기와 계면활성제의 조합 효과의 상관관계를 규명하고자 하였다. 이미다졸과 PEG-PPG-PEG로 구성된 첨가제를 사용하여 제조된 PEDOT 박막은 1300 S·cm^{-1} 이상의 전도성을 가졌다. PEG-PPG-PEG계 계면활성제의 분자량이 기상 중합을 이용한 PEDOT 박막의 특성에 미치는 영향도 조사하였다.

Abstract: This paper reports the combined effects of the triblock copolymer surfactant poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) and imidazole on the opto-electrical and mechanical properties of poly(3,4-ethylenedioxythiophene) (PEDOT)-based thin films prepared *via* vapor phase polymerization (VPP) using ferric *p*-toluenesulfonate as a catalyst. Various PEDOT-based thin films were synthesized using PEG-PPG-PEG and imidazole alone and in combination to compare and correlate their effects on film properties. The improved conductivity of the PEDOT films was higher than 1300 S·cm^{-1} when the surfactant and imidazole were used together. The PEG-PPG-PEG chain length was also varied to identify the best conditions for the VPP-based preparation of PEDOT thin films.

Keywords: PEDOT, conductivity, surfactant, imidazole, opto-electrical properties.

Introduction

The discovery of inherently conducting polymers (ICPs) by Shirakawa and co-workers[1,2] spurred the development of myriad organic/inorganic electronic materials over the past several decades.[3-5] By virtue of their potential applications in flexible electronic devices such as biosensors,[6] OLED displays,[7] electrochromic windows,[8] and photovoltaics,[9] electrically conducting polymers have recently become the objects of intensive research. Nonetheless, their high contact resistance, difficulties with organic/inorganic patterning, poor adhesion,

and several other major and minor issues are still yet to be addressed prior to their fruitful and advantageous use.[10-12]

Among the distinct ICPs used for practical applications, PEDOT is, by consensus, very attractive because of its many worthwhile properties. Its high conductivity, transparency, and stability make it the most favored conducting polymer for many realistic applications.[13] An abundance of methods have been described for the production of PEDOT-based thin films using various synthesis techniques, including electrochemical synthesis,[14] liquid-phase polymerization (LPP),[15] micellar polymerization,[16] and vapor-phase polymerization (VPP).[17-19] Recently, VPP has drawn close consideration as a means for the *in situ* synthesis of PEDOT thin films on variously shaped substrates, due to its ability to overcome issues associated with film processing/coating, performance, and pot-life. Through

VPP, a PEDOT thin film can be synthesized on any conducting or non-conducting substrate.[19-21] Various non-conductive materials such as glass and poly(ethylene terephthalate) (PET) can be used as coating substrates.[20] The typical oxidants used in the VPP of PEDOT are iron(III)-based halides[19] or salts such as ferric p-toluenesulfonate (FTS).[22-24] Contemporary research on PEDOT thin films has predominantly focused on testing various additives in the FTS solution to improve the electrical conductivity of the conductive films. Winther-Jensen and West demonstrated the use of the FTS oxidant with pyridine as a weak base inhibitor during VPP to strengthen the electrical conductivity of PEDOT films.[18,25] Further studies employing imidazole to raise the pH of the oxidant also determined that, as the base evaporates from the oxidant, a more controlled polymerization was triggered.[15,26] Meanwhile, Fabretto et al. suggested the role of water during the VPP process.[27] An appropriate amount of water is necessary for proton scavenging for efficient monomer polymerization. The presence of excess water, however, degrades the quality of the VPP-based PEDOT due to the formation of FTS crystallites.[28] Therefore, the effects of a surfactant, PEG-ran-PPG, were systematically investigated to determine an optimum loading in the FTS oxidant solution for a high quality PEDOT film (conductivity > 700 S·cm^{-1}).[29] The addition of the surfactant PEG-PPG-PEG to the FTS oxidant solution was also found to inhibit the deleterious effects of water absorption and prevent the oxidant from forming crystalline structures.[30,31]

In this paper, we report our investigations concerning the co-addition of a base inhibitor and a surfactant to the oxidant solution, and attempt to reveal their combined effects on the physicochemical and opto-electrical properties of PEDOT thin films. Imidazole[15,26] as base inhibitor was used to increase the pH of the oxidant solution and initiate a more controlled polymerization, and PEG-PPG-PEG triblock copolymer[30,31] was used as the surfactant to moderate the polymerization rate while preventing problems associated with water absorption and the formation of crystallites. In addition, two PEG-PPG-PEG surfactants having different molecular weights were investigated with imidazole and the oxidant solution to identify the most favorable combination for the preparation of VPP-based PEDOT thin films.

Experimental

Materials & Reagents. In this study, 3,4-ethylenedioxythiophene (EDOT) as monomer, pyridine as base inhibitor,

FTS as oxidant, and two poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) (PEG-PPG-PEG) triblock copolymers as surfactants (number average molecular weight (M_n) = 5800 and 14600) were purchased from Aldrich and used as received. The base inhibitor, imidazole (Samchun Chemicals), and 1-butanol (Junsei) were purchased and used without further purification. Poly(ethylene terephthalate) (PET) films were purchased from Dongseo and used as the substrates for PEDOT coating.

Vapor Phase Polymerization and Analysis. A constant flow of N_2 gas at 7.5 mL s^{-1} was circulated through the VPP chamber before and during the polymerization reaction. The vessel was heated to 80 °C and the EDOT monomer was placed in a Petri dish at the bottom of the polymerization chamber. To prepare the substrate, a solution of FTS, surfactant, and base inhibitor was prepared in 1-butanol by stirring for ~20 min. The prepared solution was spin-coated on a PET substrate at 300 rpm for 10 s and 500 rpm for 30 s sequentially. The spin-coated PET samples were immediately dried in an oven at 60 °C for ~15 min. After drying, the samples were inserted into the VPP chamber and exposed to the EDOT vapor, allowing the controlled polymerization of EDOT to PEDOT on the PET films. Soon after polymerization, the PEDOT-coated PET samples were washed in distilled water to remove unreacted and excess reagents, and then dried at room temperature.

The transparency of the PEDOT films was measured using an Optizen 2120UV Plus UV/Vis spectrophotometer (MECA-SYS). The transmittance at 550 nm, the average wavelength of light in the visible region, was recorded. Surface resistance (Ω·sq[-1]) was calculated by averaging 10 resistances values obtained using a 4-point probe conductivity meter (AiT Co., Ltd.) with a 100 nm tip radius and a 100 g load. The thickness and surface morphology of the PEDOT films were characterized using a TESCAN MIRA II LMH field-emission scanning electron microscope (SEM), and a Bruker Quantax system was used for energy dispersive spectroscopy (EDS). The average thickness (nm) value of different positions was taken for a precise thickness measurement. In addition, a Dektak 150 Veeco instrument was used for α-step measurements in the analysis of the thickness and roughness of the PEDOT films. The thickness data from the SEM and α-step measurements were compared and averaged to determine the accurate thickness of the film. The samples for SEM were mounted on aluminum studs using adhesive tape and sputter-coated with platinum studs before analysis. The pencil hardness was deter-

mined using a pencil hardness tester conforming to ASTM D3363 and applied force for scratch was measured by scratching the films at various forces (N) with a 3090 sclerometer hardness tester (Elcometer®).

Results and Discussion

Many papers have reported the use of a base inhibitor such as pyridine[18] or imidazole[15,26] with an oxidant solution to achieve greater control during PEDOT synthesis *via* LPP or VPP. Similarly, several experiments have employed PEG-*ran*-PPG or PEG-PPG-PEG surfactants to improve the conductivity of PEDOT films prepared *via* atmospheric or vacuum VPP.[29-31] To our knowledge, a systematic study of additive combinations consisting of a base inhibitor and a surfactant has not been reported for the VPP-based preparation of highly conductive thin films (>1000 S·cm^{-1}). Therefore, we studied the combined effects of a surfactant and base inhibitor with a view to producing homogenously coated uniform PEDOT thin films with enhanced opto-electrical properties.

Base inhibitors, imidazole and pyridine were both tried to synthesize PEDOT thin films and the opto-electrical properties like surface resistance and transmittance were analyzed. Under same reaction conditions (FTS 30 wt%, 1:1 mole ratio of FTS:base inhibitor), the analysis showed better opto-electrical performance by imidazole (surface resistance ~0.153 KΩ·sq^{-1}, transmittance~65%) rather than pyridine (surface resistance ~0.162 KΩ·sq^{-1}, transmittance ~55%), so we selected imidazole as an appropriate base inhibitor to be used for further experiments. The reason behind this may be the more basic nature of imidazole (pk$_a$=6.9) than pyridine (pk$_a$=5.2) which led to precise and controlled polymerization process resulting

in better opto-electrical features.[26] Similarly, triblock copolymer PEG-PPG-PEG surfactant having lower and higher molecular weight (5800 and 14600) were used to know the effect of molecular length on the various properties of PEDOT thin films. Rather than PEG-*ran*-PPG, we choose PEG-PPG-PEG due to its easy availability and purchasabilty as well.

Vapor phase polymerization (VPP) is well categorized into two methods, atmospheric and vacuum-based VPP process. Vacuum VPP is known to be the standard method of PEDOT preparation in terms of high conductivities due to the vacuum based polymer growth conditions but the robustness of the films is deteriorated. In case of atmospheric VPP, the polymer thin films are grown on ambient pressure-based conditions therefore the conductivity obtained from this process cannot meet to that obtained from vacuum VPP.[32] Although most of the research these days is entirely based on vacuum-based VPP but due to the simplicity and cost effectiveness, we followed atmospheric VPP to synthesize PEDOT thin films in order to determine the combined effect of surfactant and imidazole on the PEDOT thin films. So, the results presented in this study should be viewed in this context.

Initially, PET substrates were spin-coated with 30 wt% FTS solutions containing 0 to 20 wt% PEG-PPG-PEG triblock copolymer (M_n=5800) and placed into the VPP chamber to investigate optimum surfactant loading. Table 1 describes the various electrical and physicochemical properties of the PEDOT films prepared in this manner. The sheet resistance tended to decrease with the addition of surfactant up to 5 wt%, and then increased with additional surfactant. The surfactant-containing films were thinner than the pristine sample, and their thickness decreased up to 5 wt% due to the dilution effect.[29] Then, the film thickness slowly increased to 734.5 nm

Table 1. Effect of Surfactant Loading in the FTS Solution on the Various Properties of PEDOT Films[a]

Surfactant (wt%)	Surface resistance (KΩ/sq)	Transparency (%)	Pencil hardness (H)	Applied force for scratch (N)	Thickness (nm)	Conductivity[b] (S·cm^{-1})
0	0.380	7.30	1	0.1	536.4	49.1
2	0.175	13.51	4	0.3	443.8	128.7
3	0.125	17.32	4	0.3	435.2	183.7
4	0.114	18.28	3	0.4	421.9	207.8
5	0.103	21.23	3	0.3	396.6	244.8
10	0.158	22.65	1	0.2	506.3	125.0
15	1.056	28.52	1	0.2	684.0	13.8
20	2.459	21.46	1	0.1	734.5	5.5

[a]FTS concentration=30 wt% in 1-butanol; number average molecular weight (M_n) of PEG-PPG-PEG is 5800. [b]Conductivity was calculated using the equation $\sigma=1/(SR*t)$, SR is the surface resistance and t is the film thickness.

Table 2. Effect of Surfactant and Imidazole on the Various Properties of PEDOT Thin Films[a]

Surfactant amount (wt%)	F:I (mole ratio)	Surface resistance (KΩ/sq)	Pencil hardness (H)	Applied force for scratch (N)	Thickness (nm)	Conductivity[b] (S·cm^{-1})
0	0	0.380	1	0.1	536.4	49.1
5 ($M_n \sim 5800$)	0	0.103	1	0.1	396.6	244.8
0	1:1	0.153	2	0.2	166.7	392.0
5 ($M_n \sim 5800$)	1:1	0.138	2	0.3	52.8	1372.4
5 ($M_n \sim 14600$)	1:1	0.129	2	0.3	135.9	570.4

[a]FTS concentration=30 wt% in 1-butanol. [b]Conductivity was calculated by the equation $\sigma = 1/(SR*t)$, SR is the surface resistance and t is the film thickness.
F:I=FTS:Imidazole.

at 20 wt% surfactant content. The controlled amount of surfactant was beneficial in preventing the crystallization of the FTS oxidant[29] and providing the necessary amount of water to act as a proton scavenger[31] in order to obtain efficient EDOT polymerization. When excess surfactant is used in the VPP process, a significant amount remains in the PEDOT film as an insulator.[29] This decreases the conductivity of PEDOT films prepared with high surfactant loading (>10 wt%). Thus, the conductivity calculated using the equation stated in the footnote of Table 1 reached a maximum at 5 wt% (244.8 S·cm^{-1}), and then tended to decrease up to 20 wt%. These results are consistent with the work of Fabretto et al.[29] At low concentrations of surfactant (2-5 wt%), the pencil hardness and anti-scratching properties of the film were higher than those of PEDOT prepared without surfactant. At high concentration of surfactant (>10 wt%), however, the mechanical rigidity of the films such as pencil hardness and anti-scratching properties was lost because of the considerable amount of surfactant contained in the PEDOT film. The optimum surfactant loading in the FTS oxidant solution for the preparation of PEDOT films by the VPP process was 5 wt%, in terms of the resultant electrical conductivity and mechanical properties.

Table 2 compares the effects of imidazole and surfactant alone or in combination. The pristine PEDOT film exhibits high surface resistance, considerably less transparency, mechanical weakness, and a conductivity of 49.1 S·cm^{-1}. With the addition of 5 wt% PEG-PPG-PEG ($M_n \approx 5800$), the surface resistance was significantly reduced, improving the conductivity to 244.8 S·cm^{-1}. The optimum amount of surfactant allows the amount of water necessary to commence the controlled polymerization of EDOT while inhibiting the formation of crystallite structures. For the sample produced using a 1:1 mole ratio of oxidant to imidazole, the conductivity was further improved to 392.0 S·cm^{-1} and the film thickness was reduced.

In this case, imidazole increased the pH of the oxidant solution and aided the process of controlled polymerization.[15] The most favorable results were obtained for the sample synthesized using the combination of 5 wt% surfactant ($M_n \approx 5800$) and a 1:1 mole ratio of FTS to imidazole in the oxidant solution. The surface resistance of this sample was recorded as 138 Ω·sq^{-1}, and the thickness was very low at 52.8 nm. This sample showed high transparency as well as very high conductivity (1372.4 S·cm^{-1}), and exhibited sound mechanical properties. From the mechanical analysis, properties such as pencil hardness and applied force for scratch were clearly commendable in the PEDOT films synthesized in the presence of both this surfactant and imidazole.

The effect of different PEG-PPG-PEG chain lengths ($M_n \approx 5800$ and 14600) in combination with imidazole was also inspected at the optimum concentration (5 wt%) to better confirm the results. In both cases, 5 wt% surfactant and 1:1 FTS:imidazole were employed to determine which surfactant best enhanced the PEDOT thin film properties. The results confirmed the higher conductivity in the case of the lower molecular weight PEG-PPG-PEG surfactant ($M_n \approx 5800$). As the molecular weight of the surfactant increased, surfactant incompatibility with imidazole/FTS solution mixture that resulted in slightly turbid films became apparent, which is the reason behind the decrease in conductivity. The transparency of the film was also reduced as the molecular weight of the surfactant increased. However, mechanical properties such as pencil hardness and applied force for scratch were maintained.

The transparency graph in Figure 1 shows results for the highly transparent PEDOT films prepared by various combinations of reactants. The PEDOT films synthesized using only FTS and FTS/surfactant exhibit very low transparency (Figure 1(a)). On the other hand, the transparency dramatically increases in the presence of the weak base. The role of imi-
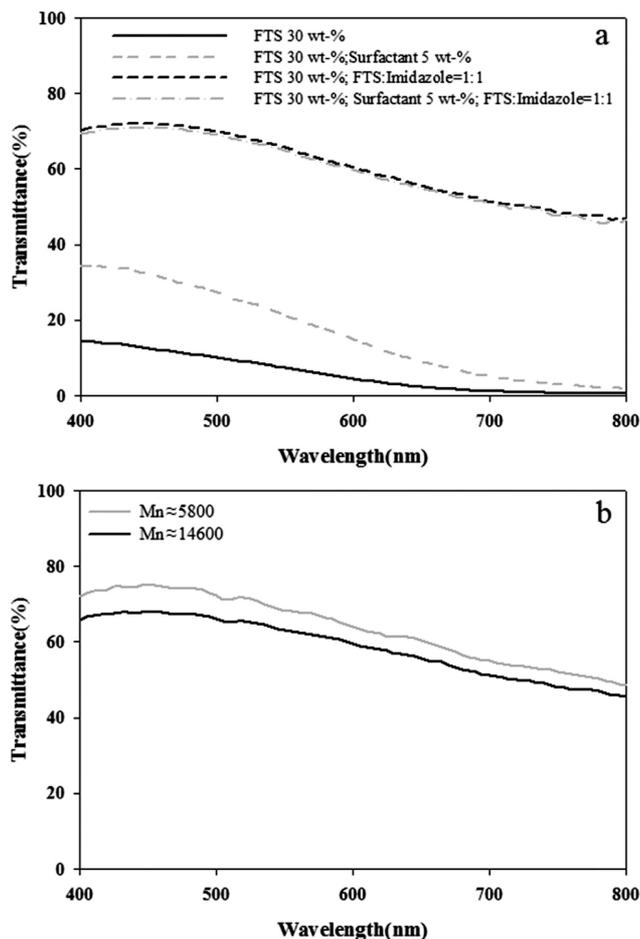
Figure 1. UV-Vis spectra of PEDOT films prepared by VPP with (a) 30 wt% FTS; FTS/PEG-PPG-PEG ($M_n \approx 5800$); FTS/imidazole; and FTS/surfactant/imidazole; (b) 30 wt% FTS, imidazole (1:1) and 5 wt% surfactants ($M_n \approx 5800$ or 14600).

dazole is well known: it retards the polymerization rate by reducing the reactivity of FTS by coordination and/or increasing the pH of the polymerization medium.[15] Eventually, a thinner film with higher transparency is formed when imidazole is used as an additive. Similarly, in Figure 1(b), it is clear that the low molecular weight surfactant with imidazole yields a high transparency, exceeding 65%. We can confirm that PEDOT films with high transparency can be obtained when using both the low molecular weight surfactant and imidazole. Slightly lower transparency was observed for the higher molecular weight surfactant with imidazole.

In the EDS spectra, C, N, O, Fe, Si, Pt, and S peaks are assigned at 0.27, 0.40, 0.52, 0.71, 1.60, 2.00, and 2.30 keV, respectively. The Pt detected in the EDS spectra originates from the sample preparation steps for the SEM-EDS measurements. Figure 2 reveals the presence of the basic elements
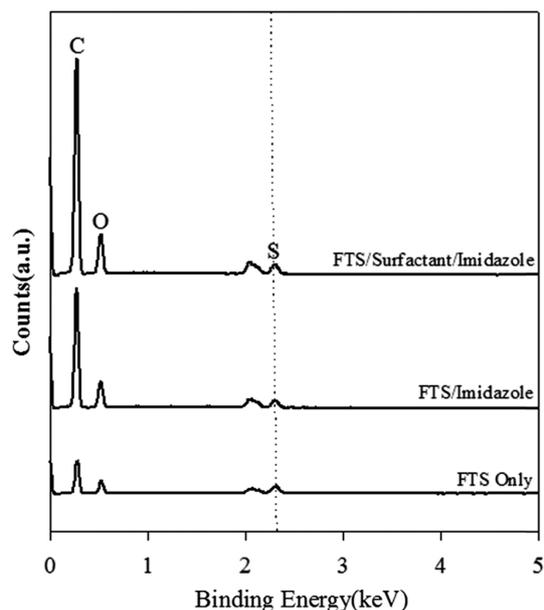

Figure 2. EDS spectra of PEDOT thin films prepared using various additives in FTS oxidant solution.

C, O, and S in all the synthesized thin films, which indicates the successful coating of the PEDOT films on the substrates. Fe and N atoms are not detected in any of the prepared samples, reflecting the complete elimination of FTS and imidazole after the films are washed. The carbon content of the PEDOT films produced with the additive combination is much higher than that produced with FTS only. The C/S atomic ratios of PEDOT layers produced with FTS, imidazole, and surfactant *versus* FTS only are 65.1 and 16.5, respectively. The reason behind this is the presence of the hydrocarbon-based polymeric surfactant in the PEDOT film produced with FTS, imidazole, and surfactant. Fabretto *et al*. reported the influence of the surfactant PEG-*ran*-PPG on VPP-based PEDOT films.[27] Similarly to our results, they confirmed the presence of residual copolymer within the PEDOT film after washing by means of an X-ray photoelectron spectroscopy study.

The SEM images in Figure 3 clearly show the surfaces and cross-sections of the various PEDOT thin films synthesized using FTS, FTS/surfactant, FTS/imidazole, and FTS/surfactant/imidazole. The differences in the surface morphologies of the prepared films are apparent. Large blisters are evident in the PEDOT film prepared with FTS only (Figure 3(a)), whereas the blister sizes are reduced for the PEDOT film produced using FTS/surfactant ($M_n \approx 5800$) (Figure 3(b)). In Figure 3(c), blisters are absent but the surface is not perfectly homogenous and smooth. However, the films shown in Figure 3(d)
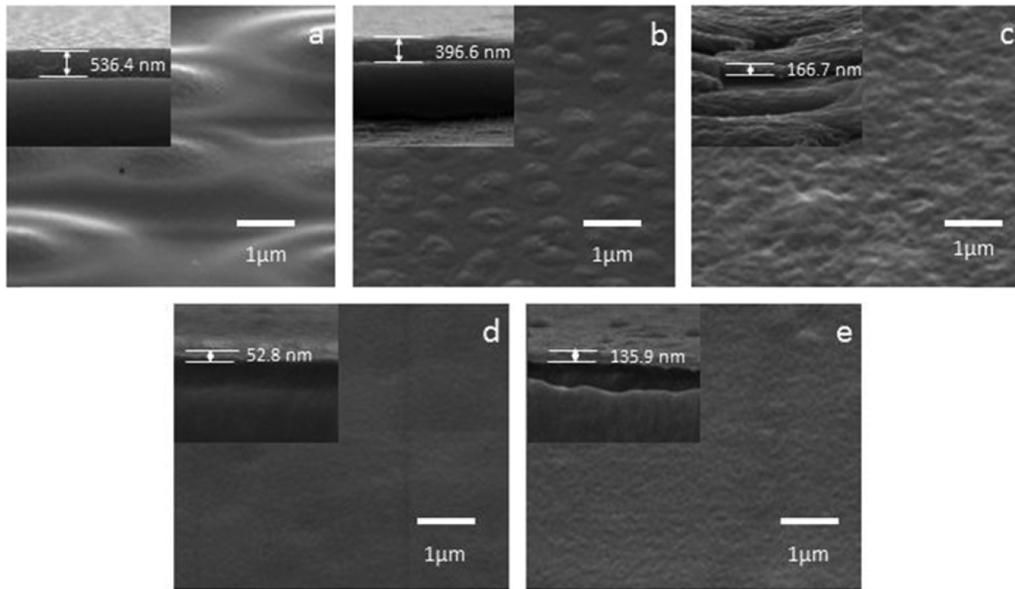
Figure 3. Surface and cross-sectional SEM images (scale: 1 μm; 50000x magnification) of various PEDOT-based films prepared using 30 wt% FTS in 1-butanol: (a) FTS only; (b) FTS/surfactant ($M_n \approx 5800$); (c) FTS/imidazole; (d) FTS/surfactant ($M_n \approx 5800$)/imidazole; (e) FTS/surfactant ($M_n \approx 14600$)/imidazole.

and (e), produced using both surfactant and imidazole, appear very smooth and homogeneous. Among these images, Figure 3(d) shows the most uniform and homogeneous morphology, which indicates that the $M_n \approx 5800$ surfactant is the most appropriate for the synthesis of satisfactory PEDOT-based thin films. This is because of the controlled polymerization as well as inhibition of crystal formation induced by the combined effects of the base inhibitor and surfactant.

The RMS roughness values for the different PEDOT thin films are illustrated in Figure 4(a), and the divergence in RMS values using the different chain length PEG-PPG-PEG surfactants in combination with imidazole are shown in Figure 4(b). Figure 4(a) clearly shows that the RMS value for the PEDOT film synthesized using surfactant and imidazole together is very low. The numerical roughness values are 15.9, 12.1, 6.7, and 2.3 for the samples produced using only FTS, FTS/surfactant, FTS/imidazole, and FTS/imidazole/surfactant, respectively.

Similarly, in Figure 4(b), the RMS values of the films produced using the different molecular weight surfactants with imidazole are illustrated. The roughness increases with the increase in the chain length of the PEG-PPG-PEG surfactant. Figure 4(b) also supports the result that films with low roughness values can be produced using surfactant and imidazole together in the oxidant solution. Thus, PEDOT thin films with smooth and homogeneous morphologies can be obtained by
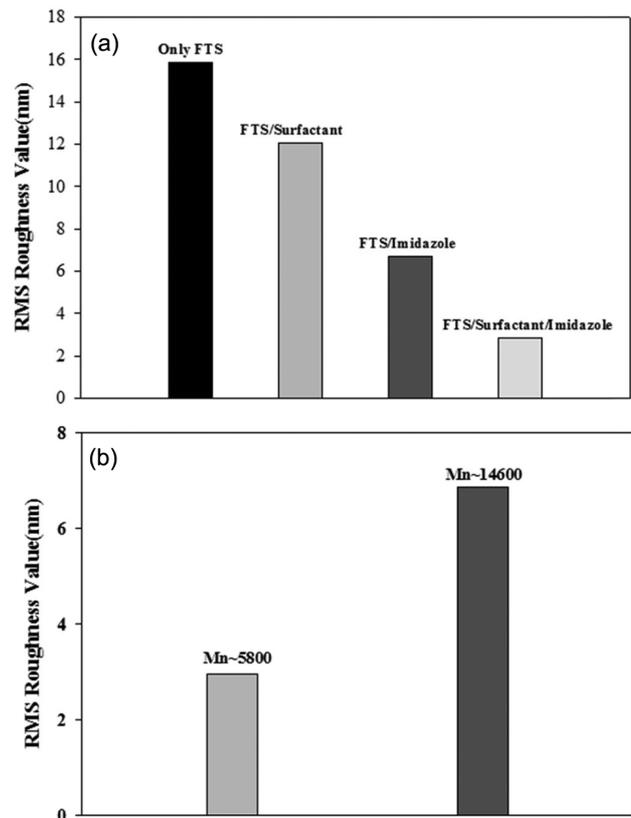

Figure 4. Graphs showing the RMS roughness values for PEDOT films prepared using (a) FTS; FTS/surfactant ($M_n \approx 5800$); FTS/imidazole; and FTS/surfactant ($M_n \approx 5800$)/imidazole; (b) FTS with imidazole and surfactants ($M_n \approx 5800$ or 14600).

the combined effects of a base inhibitor and a surfactant added to the oxidant solution.

Conclusions

PEDOT thin films with highly improved opto-electrical and mechanical properties were successfully prepared when both a surfactant and a base inhibitor were added to the oxidant solution. The two additives may work synergistically: the imidazole as base inhibitor increases the pH of the oxidant which initiates a more controlled polymerization, and the PEG-PPG-PEG triblock copolymer moderates the polymerization rate and prevents the problems of water absorption and crystallite formation. The VPP-based PEDOT film prepared on the PET substrate coated with the imidazole, PEG-PPG-PEG surfactant, and the FTS mixture showed the highest conductivity ($>$1300 S·cm^{-1}), transparency ($>$ 65%), pencil hardness (~2 H), and scratch resistance (~0.3 N). The homogeneous surface morphology of the prepared PEDOT, which was confirmed by SEM and α-step measurements, results in a high quality PEDOT film. In future studies, this method may be efficaciously applied in the preparation of other conductive polymers.

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