Electrically conductive composites prepared from 3-methyl thiophene by the FeCl₃ oxidation method

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Abstract−Surface conductive polyurethane films from poly(propylene glycol), toluene 2,4-diisocyanate, 3-methyl thiophene and butyltin dilaurate can be successfully prepared by the diffusion-oxidative polymerization method. Various effects of the doping conditions, such as the reaction time, the FeCl₃ concentration, the weight ratio of the 3-methyl thiophene to PU and the temperature on the electrical conductivity and thickness of the conductive layer of the 3-methyl thiophene/PU composite were investigated. Decomposition temperature rises gradually from pure undoped PU to doped composite that indicates blending took place in FeCl₃/ethyl acetate solution. As oxidative reaction time increases, the electrical conductivity of the 3-methyl thiophene doped PU film increases together with the thickness of the coating layer. With increasing FeCl₃ concentration and weight ratio of the 3-methyl thiophene to PU, the thickness of the coating layer decreases, while the electrical conductivity increases. The increase of the thickness of the PU film leads to the rise of the electrical conductivity. The thickness of the coating layer decreases, while the electrical conductivity of the 3-MT doped PU film increases with increasing reaction temperature. As the reaction time and temperature increase, the polar components of the PU film increase resulting into the increase of moisture regain value.

Key words: Polymer Composite, Organic Solution, Diffusion-oxidative Reaction, Electrical Conductivity

INTRODUCTION

The saturated polymeric materials studied by Staudinger, Flory, Ziegler and Natta are insulators, and they were viewed as uninteresting from the point of view of electronic materials [Allen, 1994; Roselena et al., 1999; Meixiang et al., 1995; Omoda et al., 2006; de Barros et al., 2005]. However, the conjugated polymers with π-bonding, in which the carbon orbitals are in the sp²p_z configuration and in which the orbitals of successive carbon atoms along the backbone overlap, reveal electron delocalization along the backbone of the polymer. This electronic delocalization provides a "highway" for charge mobility structure along the backbone of the polymer chain [Yigit et al., 2003; Wiriya et al., 2002; Lee et al., 2004].

Compared with conventional polymeric materials, however, organic conductive polymers with π-conjugated system, which have delocalized electrons, making movement of electrons in molecules easier, do not have relatively wide applications due to the poor processing properties, flexibility and solubility, even if the use of bulky protonic acids, such as p-toluene sulfonic acid, makes polyaniline soluble in organic solvents in the doped state [Flandin et al., 2001].

The chemical polymerization method can overcome these disadvantages. Several procedures to obtain conductive composite films have been developed. PPY-poly(vinyl alcohol) (PVA) films were prepared by exposing PVA that contained ferric chloride to pyrrole and water vapors [Takeaki and Seizo, 1986].

PPY-poly(ethylene terephthalate) (PPY-PET) was prepared by immersing the pyrrole-swollen PET polymer into an aqueous solution of ferric chloride [Changjinag and Zhigang, 1991]. PPY-poly(methyl methacrlyate) (PMMA) films were obtained by spreading a water-insoluble solvent solution of pyrrole and PMMA over the surface of an aqueous solution of ammonium persulfate [Mitsuyuki et al., 1988]. Composite films containing PPY were also prepared by introducing polymer films at the interface between an aqueous solution of ferric chloride and a toluene solution of pyrrole [Bocchi et al., 1987]. Insulating plastics and fibers can be coated with thin films of conductive polymers by polymerizing monomers directly onto the substrates. The synthesis, structure and the modification of the properties for specific applications of polythiophenes are attracting immense interest by researchers. Poly(3-alkyl thiophenes) are both soluble and melt processible. They have good chemical and environmental stability with excellent electronic and optical properties suitable for various device applications. Polythiophenes can be prepared both by electrochemical polymerization and chemical oxidative polymerization technique. However, the polymers prepared by electrochemical method are not processible. Chemical oxidative polymerization of 3-methyl thiophene with ferric(III) chloride (FeCl₃) produces polymers in high yield [Kim et al., 2003, 2004; Singh et al., 2003].

In this study, a simple method for preparing PMT-coated PU films via condensation polymerization at room temperature is proposed. The effects of the preparation conditions, such as the reaction time, the reaction temperature, the concentration of FeCl₃, and the weight ratio of 3-methyl thiophene to PU on the electrical conductivity and thickness of the conductive layer of the 3-MT/PU composite were carefully studied. In order to investigate the relation between the electrical conductivity and surface free energy, contact angle measurement was done and scanning electron microscopy was used to study morphological features dependent on doping conditions.

EXPERIMENTAL

1. Chemical Materials and Preparation

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3-Methyl thiophene (Aldrich, 99+%) as an inherent conducting material, ferric(III) chloride (Aldrich, 97%), PPG 2000 (poly(pro-pylene glycol), Aldrich, mol. wt. 2000), toluene 2,4-diisocyanate (Aldrich, 80%), and dibutyltin dilaurate (Aldrich, 95%) as a cata-lyst were used without further purification. Anhydrous ethyl acetate (Aldrich, 99+%) and methyl alcohol (Aldrich, 98%) were used as a solvent for FeCl$_3$ solution (used an oxidizing agent) and distilled and deionized water was employed. PPG, toluene 2,4-diisocyanate, 3-methyl thiophene and butyltin dilaurate were mixed in a flask equip-ped with vacuum system for premixing. Then, the liquid mixture was poured on a horizontal plate with a good peeling ability with an area of about 40 cm^2, which was subsequently covered with a box, whose four open edges were sealed to the surface of a desk, to avoid vaporization in free air. After the condensation polymer-ization was allowed to proceed for 24 hours, the obtained PU film containing 3-methyl thiophene was peeled away from the plate. To dope the 3-methyl thiophene impregnated PU films, the film was immersed in a FeCl$_3$/ethyl acetate solution, at different temperatures with different reaction time. On doping, the surface of the film turned dark brown rapidly. The coated film was washed in methyl alcohol and water and finally dried in vacuum.

2. FT-IR Spectroscopy and Thermogravimetric Analysis (TGA)

The pure PU film and 3-methyl thiophene/PU composite were subjected to FT-IR spectroscopic studies by using a Bio Red IR spec-trometer (FTS 165, U.S.). Thermogravimetric analyzer (Shimadzu TA-50) with heating rate of 10 °C/min was used to measure ther-mal decomposition temperatures of the pure PU substrate and 3-methyl thiophene/PU films before and after doping.

3. Image and Scanning Electron Microscopy (SEM)

A thin slice cut vertically from the coated film was magnified with a microscope (SOMETECH) and its picture taken with a ICAM-SCOPE (Image analyzer system, Baestech). The thickness of the coating layer was calculated from its thickness in the picture, taking into account the magnification of the microscope. One of the pictures is presented in Fig. 1. Surface morphologies of 3-methyl thiophene/PU composites were studied from gold coated films with a JSM 6400 electron microscope at 20 kV following a sputter coating tech-nique.

4. Electrical Conductivity

The coated PU film was cut to rectangular shape (2.5×1.5 cm).
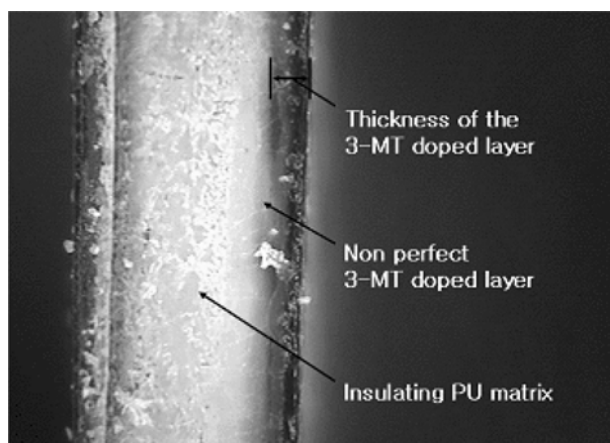

Fig. 1. Photograph of the 3-MT doped PU film.

Table 1. Surface free energy characteristics of the testing liquids

Testing liquids	γ_L^L [mJ·m^{-2}]	γ_L^{SP} [mJ·m^{-2}]	γ_L [mJ·m^{-2}]
Water	21.8	51.0	72.8
Diiodomethane	50.42	0.38	50.8

The electrical resistance was measured by the four-point probe tech-nique, where electrical contacts are four gold wires. The electrical conductivity of the coating layer was calculated from the electrical resistance and the thickness of the coating layer. The electrical con-ductivity (σ) can be defined as follows [Migahed et al., 2004]:

$$\sigma = \frac{I}{V} \times \frac{C}{b \times d}$$

where I, V, C, b and d are defined as the applied current between the inner electrodes, the output voltage between the two outer elec-trodes, the sample thickness, the distance between the two inner electrodes and the sample width, respectively.

5. Surface Energy

An SEO 300A contact angle measuring device from SEO Co. was used for measurement of the surface energy of liquid and solid phases. In this study, distilled water and diiodomethane were used as wetting liquids. Their surface free energy characteristics are shown at Table 1.

6. Moisture Regain

Moisture absorption properties of the pure PU film and doped 3-methyl thiophene/PU composite were studied by using a stan-dard technique. Weighed portions of the perfectly dried samples were exposed to a dessicator until a constant weight was reached. From the weight gain the moisture absorption (%) was calculated.

RESULTS AND DISCUSSION

1. FT-IR Spectroscopy

As the polymerization of 3-methyl thiophene at and within the surfaces of PU films proceeded, they turned rapidly dark brown. To confirm spectrally the formation of the 3-methyl thiophene in the insulating polymer matrix, IR spectra were obtained both on
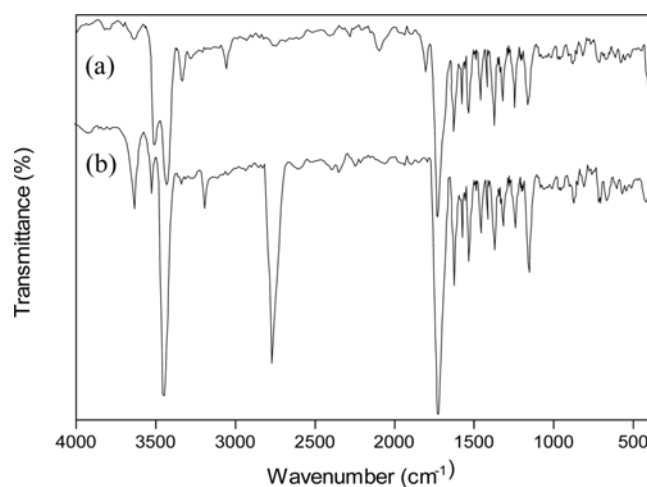

Fig. 2. Infrared spectra of the pure PU substrate and 3-MT doped PU composite.

the pure films and the 3-methyl thiophene contained PU films. Fig. 2 shows the results of IR spectral studies of the pure PU substrate (a) and the 3-methyl thiophene doped PU composite (b), respectively. Compared with the IR spectrum of the pure PU, where vibration bands are observed at 3,450 cm^{-1} (N-H bending, 3,000 to 3,500 cm^{-1}), 1,730 cm^{-1} (C=O) and 1,289 cm^{-1} (N-C-O), there are regions of the composite spectra which show considerable changes [Park et al., 2000]. For example, new vibration bands are observed from 3,000 to 2,500 cm^{-1} (Fig. 3). Further, the IR spectra of the composite films showed a featureless increase in IR spectrum at 2,800 cm^{-1} which is due to the methyl group of the 3-methyl thiophene.

2. Thermogravimetric Analysis (TGA)

Fig. 3 shows the TGA curves under nitrogen atmosphere for the pure PU substrate, the undoped 3-methyl thiophene/PU blend and doped 3-methyl thiophene/PU composites, respectively. Their decomposition temperatures are 216 °C, 270 °C and 318 °C, respectively. It shows that the decomposition temperature of the blended PU substrate is higher than the pure PU substrate, while that of the
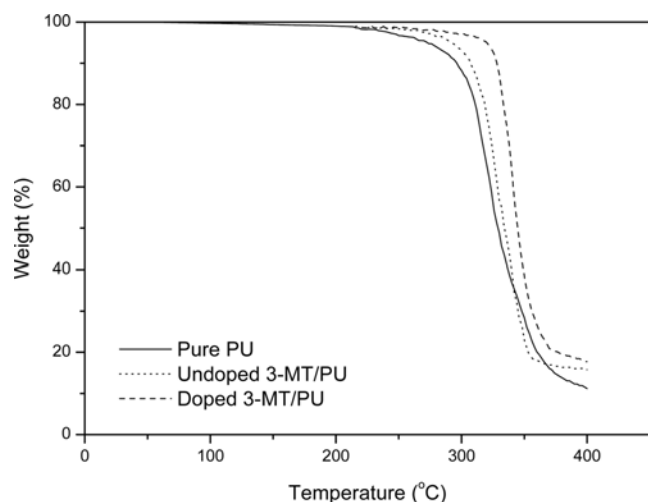

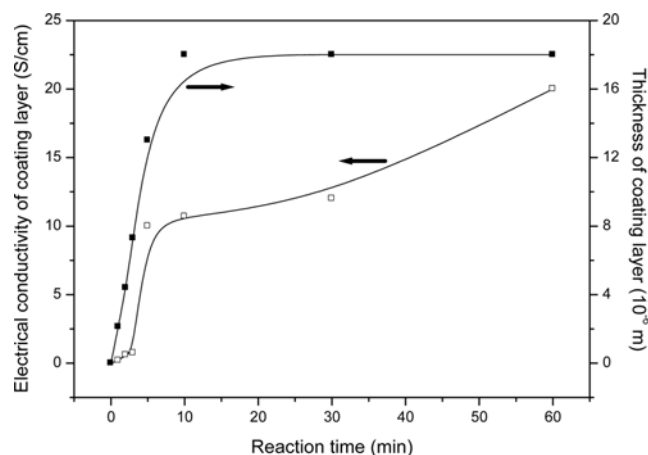**Fig. 3. TGA curves of the pure PU substrate, undoped 3-MT/PU blend and doped 3-MT doped PU composite.**

doped 3-methyl thiophene/PU composite is much higher than that of the undoped 3-MT/PU blend. From these observations, it is inferred that the blending of 3-methyl thiophene with PU matrix proceeded. Polymerization occurred when the blend was soaked in the doping FeCl$_3$ solution.

3. Electrical Conductivity

Various effects of the doping conditions were carefully investigated in this study. Fig. 4 presents the effect of oxidative reaction time on the electrical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. The weight ratio of the 3-methyl thiophene/PU film was 0.25; the molar ratio of isocyanate/hydroxyl was 1.1; the concentration of FeCl$_3$ in ethyl acetate was 0.35 g/ml; the thickness of the PU film was about 0.47 mm. The electrical conductivity was measured at room temperature. As oxidative reaction time increases, the electrical conductivity of the 3-methyl thiophene doped PU film increases together with the thickness of the coating layer. For an oxidative polymerization of about 5 min, the PU film has a coating layer with a conductivity as high as 10 S/cm. During the immersion of the 3-methyl thiophene/PU film in the FeCl$_3$/ethyl acetate solution, several processes take place: (i) the swelling of the 3-methyl thiophene/PU film by the organic solution; (ii) the diffusion of ethyl acetate into the 3-methyl thiophene/PU film and the diffusion of 3-methyl thiophene from inside towards the surface of the film; (iii) the oxidative polymerization of 3-methyl thiophene by FeCl$_3$. Generally speaking, a diffusion-oxidative polymerization process takes place. As soon as the amount of the PMT (poly(methylthiophene)) becomes large enough, a network is generated in the neighborhood of the surface of the film. The surface conductivity of the film increases from 0 to 5 min. The conducting 3-methyl thiophene network forms a shield near the PU surface which prevents the counter diffusion of 3-methyl thiophene and FeCl$_3$, and hence prevents additional oxidative polymerization. As a result, when the oxidative reaction time increases from 10 to 60 min, the thickness of the coating layer hardly changes. However, the amount of the additionally produced PMT is small and appears not to be included in the network surface layer, since the electrical resistance does not change appreciably.

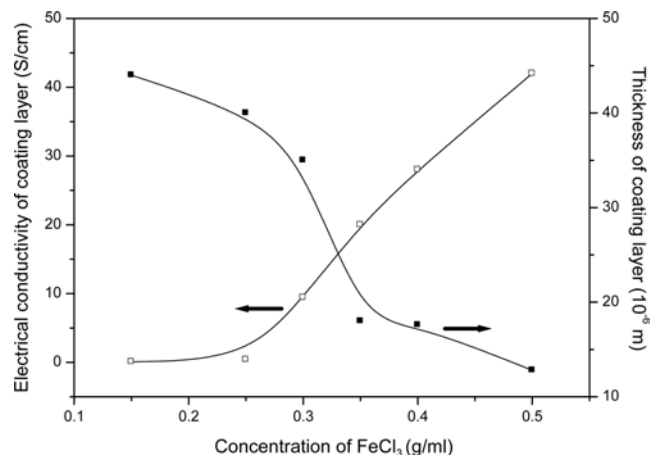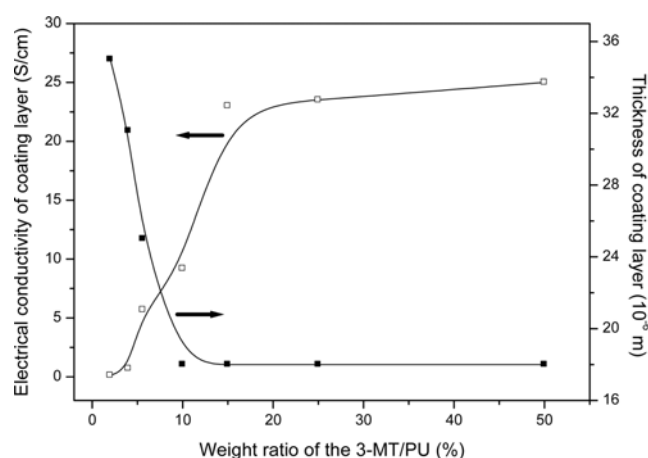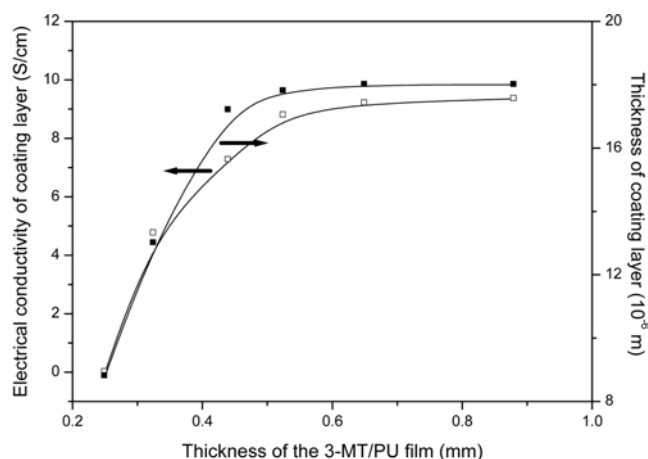Fig. 5 shows the effect of the concentration of FeCl$_3$ on the elec-

Fig. 4. The effects of the reaction time on the electrical conductivity and the thickness of the coating layer of the 3-MT doped PU film.

Fig. 5. The effect of the concentration of FeCl$_3$ on the electrical conductivity and the thickness of the coating layer of the 3-MT doped PU film.

trical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. The reaction time was 1 h. Other preparation conditions were as in Fig. 5. With increasing concentration, the thickness of the coating layer decreases, while the electrical conductivity increases. The electrical conductivity becomes large at a critical concentration between 0.30 and 0.35 g/ml. These observations can be explained as follows: first, the oxidation potential increases with increasing $FeCl_3$ concentration and only at a suitable oxidation potential can 3-methyl thiophene be oxidized to PMT. Second, at higher concentrations, more $FeCl_3$ diffuses in the PU film in a short time and the PMT layer, which retards the further reaction, is formed more rapidly. As a result, the electrical conductivity is high (42 S/cm) and the coating layer is thin (13 μm). For low $FeCl_3$ concentrations, the diffusion into the PU film is slower. It takes therefore a longer time for a PMT network to be formed and $FeCl_3$ can penetrate deeper into the film. This leads to both thicker coating layer and lower conductivities. It is known that oxidation reaction of a conducting material with a doping agent is closely related to the formation of appropriate thickness of conducting layer and conductivity. Therefore, maximum electrical conductivity can be obtained by adjusting the concentration of doping solution.

Fig. 6 shows the effect of the weight ratio of the 3-methyl thiophene /PU on the electrical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. The reaction time was 1 h. Other preparation conditions were as in Fig. 5. With increasing weight ratio, the thickness of the coating layer decreases, while the electrical conductivity increases. This is as expected since, for higher weight ratio, the content of 3-methyl thiophene near the surfaces of the film is higher. Therefore, in a short time, more 3-methyl thiophene participates in the reaction with $FeCl_3$ and forms a conductive network and also a reaction-preventing shield. When the content of 3-methyl thiophene is low, the slow diffusion of 3-methyl thiophene plays an important role in its reaction with $FeCl_3$. In the latter case, $FeCl_3$ penetrates deeply into the film. As a result, the coating layer is thick, but its electrical conductivity is low because of the loose network of PMT generated from the smaller amount of 3-methyl thiophene. Fig. 6 shows that for a relatively low weight ratio of 3-methyl thiophene /PU, namely, 0.50, the electrical con-

Fig. 7. The effects of the thickness of the PU film on the electrical conductivity and the thickness of the coating layer of the 3-MT doped PU film.

ductivity of the coating layer is already 5.7 S/cm.

Fig. 7 presents the effect of the thickness of the PU film on the electrical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. The reaction time was 0.5 h and the weight ratio of the 3-methyl thiophene/PU was 0.5. Other preparation conditions were as in Fig. 4. As the thickness of the PU film increases, the electrical conductivity increases. For a thickness of 0.25 mm, the coated film is an insulator; when it increases to 0.32 mm, the electrical conductivity becomes 4.8 S/cm; when it increases further from 0.43 to 0.88 mm, the conductivity moderately increases. An explanation is as follows: In the 24 h process of condensation polymerization of PPG 2000 to form the PU film, the 3-methyl thiophene from the film diffuses into the air of the box and therefore its actual concentration in the film is much lower. As a result, when the PU film is too thin, for example, 0.25 mm, the content of 3-methyl thiophene in the film decreases so much that a conductive network can no longer be generated; hence, the electrical conductivity is zero. When the film becomes thicker, for example, 0.32 mm, even though the content of 3-methyl thiophene on the surface of the film is low, it is still possible for an electrical conductive network to be generated because the 3-methyl thiophene present inside can diffuse to the surface and react. After the formation of the coating layer, the surplus of 3-methyl thiophene seldom takes part in the reaction. This is why the thickness of the coating layer increases very little when the thickness of the PU film increases from 0.32 to 0.88 mm. Under the preparation conditions used in this study, only PU films thicker than 0.32 mm can be well coated with an electrical conductive layer. Decreasing the volume of the box and introducing a small container containing 3-methyl thiophene in the box to supply 3-methyl thiophene vapor may prevent the diffusion of the 3-methyl thiophene from the PU in the atmosphere and, thus, allow the decrease of the minimum thickness of the PU film needed to obtain a surface conductive PU films.

Fig. 8 shows the effects of the reaction temperature on the electrical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. Preparation conditions are the same as in Fig. 4. Only the reaction temperature is different: 0 °C, 15 °C, 27 °C, 40 °C, and 50 °C. With increasing reaction tempera-

Fig. 6. The effects of the weight ratio of the 3-MT to PU on the electrical conductivity and the thickness of the coating layer of the 3-MT doped PU film.
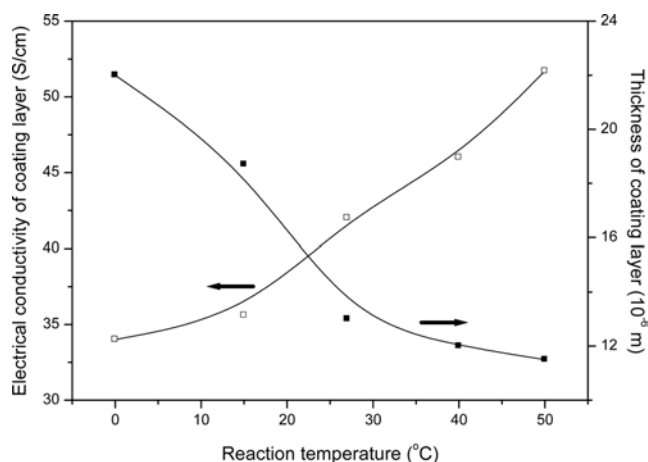
Fig. 8. The effects of the reaction temperature on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

ture, the thickness of the coating layer decreases, while the conductivity of the 3-methyl thiophene doped PU film increases. These results are almost the same as in the concentration effect of FeCl₃ on the electrical conductivity and the thickness of the coating layer of the 3-methyl thiophene doped PU film. The increase of the reaction temperature in the limited dimension of the container for doping brings higher concentration of FeCl₃, which results in more diffusion of FeCl₃ in the PU film in a short time and the sudden formation of the PMT layer which retards the further reaction.

4. Surface Energy

According to Fowkes [1962], the surface free energy is expressed by the sum of two components: a dispersive component, γ_S^L, attributable to London attraction, and a specific (or polar) component, γ_S^{SP}, owing to all other types of interactions (Debye, Keesom, hydrogen bonding, and other polar effects):

$$\gamma_S = \gamma_S^L + \gamma_S^{SP}$$

Similarly, for the liquid,

$$\gamma_L = \gamma_L^L + \gamma_L^{SP}$$

where the superscripts L and SP refer to the London dispersive and specific components, respectively, and subscripts S and L represent solid and liquid phases, respectively. Owens, Wendt [Park et al., 1999] and Kaeble [Owens and Wendt, 1969] developed the Fowkes concept using a contact angle from two liquids with greatly different features on the solid surface.

$$\gamma_L(1+\cos\theta) = 2(\gamma_L^L \times \gamma_S^L)^{1/2} + 2(\gamma_L^{SP} \times \gamma_L^{SP})^{1/2}$$

Assuming the above equation to hold for a two-liquid system, it is then possible to describe the surface free energy components, γ_S^L and γ_S^{SP} of the 3-MT/PU composite as

$$\gamma_S^L = \frac{1}{4}\left\{\frac{(1+\cos\theta_1)\gamma_{L1}\cdot(\gamma_{L2}^{SP})^{1/2} - (1+\cos\theta_2)\gamma_{L2}\cdot(\gamma_{L1}^{SP})^{1/2}}{(\gamma_{L1}^L\cdot\gamma_{L2}^{SP})^{1/2} - (\gamma_{L2}^L\cdot\gamma_{L1}^{SP})^{1/2}}\right\}^2$$

$$\gamma_S^{SP} = \frac{1}{4}\left\{\frac{(1+\cos\theta_2)\gamma_{L2}\cdot(\gamma_{L1}^{SP})^{1/2} - (1+\cos\theta_1)\gamma_{L1}\cdot(\gamma_{L2}^{SP})^{1/2}}{(\gamma_{L1}^L\cdot\gamma_{L2}^{SP})^{1/2} - (\gamma_{L2}^L\cdot\gamma_{L1}^{SP})^{1/2}}\right\}^2 .$$

The determination of the surface characteristics of a solid can be performed by measuring the surface energy of use of the contact angle method.

To get the properties of the diffusion-oxidative surface characteristics of the PU film, analysis of the surface free energy is evaluated in the physical energetic studies divided by two components. The London dispersive, γ_S^L, and specific (or polar) components, γ_S^{SP}, of surface free energy of PU film studied are determined by measuring the contact angle of a variety of testing liquids, having known their London dispersive and specific components of surface free energy.

Figs. 9 and 10 present the effects of the oxidation reaction time and temperature on the surface free energies and their London dispersive and specific components of the coated PU film, respectively. With increasing reaction time and temperature, the specific com-
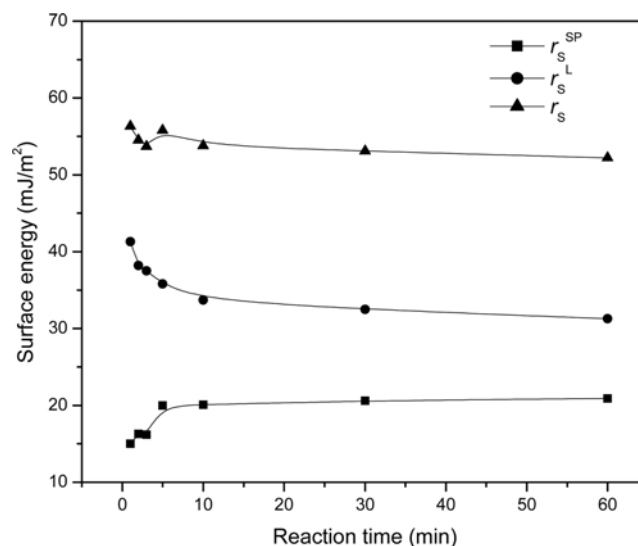

Fig. 9. The effect of the reaction time on the surface free energy of the 3-MT doped PU film.
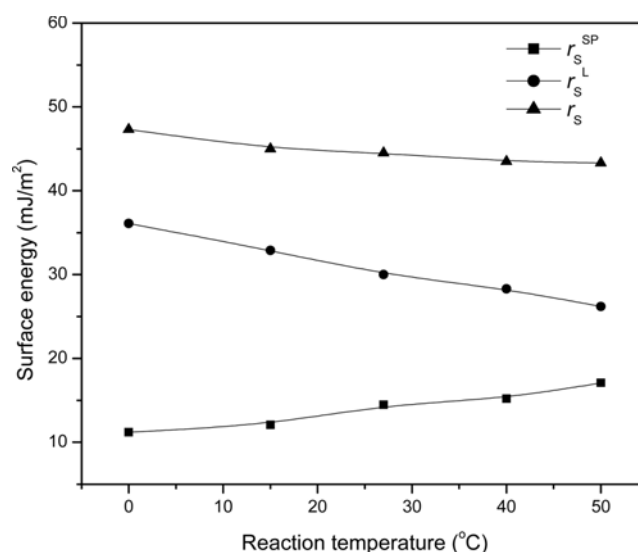

Fig. 10. The effect of the reaction temperature on the surface free energy of the 3-MT doped PU film.

ponents of the PU film increase. Specific component increase of the surface free energy can be explained by the oxidative polymerization of the 3-methyl thiophene by $FeCl_3$ at the surface of the PU film. It is well known that the specific components of the surface energy are always related to surface functional group, hydrogen bonding, coulomb and dipole-dipole interaction. $FeCl_3$ with high electronegativity polarizes the interatomic bonds. Therefore, higher degree of functionalization at the surface can influence the magnitude of the polar share. In addition, as reaction temperature increases, diffusion rate of $FeCl_3$ into the 3-methyl thiophene is activated, leading to the improvement of functionalization. As presented in the conductivity results, conductivity with reaction time and reaction temperature increases. Hence, it is informative to relate conductivity with surface free energy. As shown in the picture, $FeCl_3$ is diffused to the surface of the 3-methyl thiophene, and ⬡ and Cl^- groups are formed by the electronegativity difference.
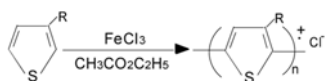
With increasing reaction time, more charge separation on the surface occurs and charge mobility is faster, resulting in the enhancement of conductivity and specific component. This is an obvious factor to understand how a specific component of the surface free energy affects the conductivity.

5. Image and Scanning Electron Microscopy

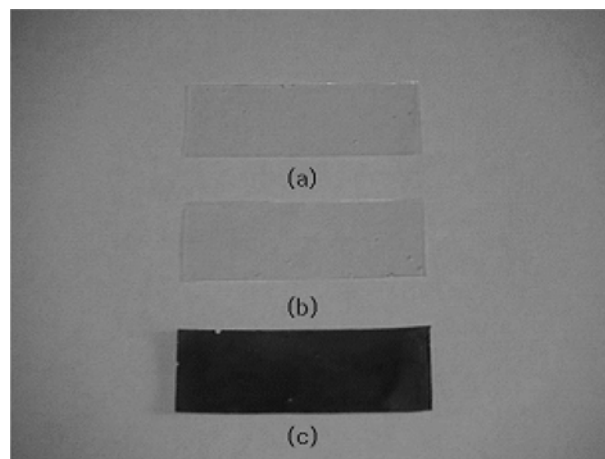Fig. 11 shows photographs of the specimens of the pure PU film

Fig. 11. The photographs of the specimens of (a) the pure PU film and 3-MT contained PU films before (b) and after (c) doping.

and 3-methyl thiophene containing PU films before and after doping. Both the pure PU substrate (a) and 3-methyl thiophene containing PU film (b) were transparent and there was no visual difference. But the 3-methyl thiophene doped PU film (c) was dark brown.
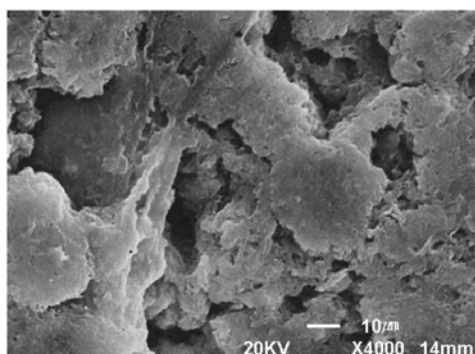
Fig. 12 shows the SEM photographs of the surfaces for the composites film with different reaction time. It was reported that the rate of polymerization was comparatively lower when chloride was used as doping anion. A lower rate of polymerization brings a higher
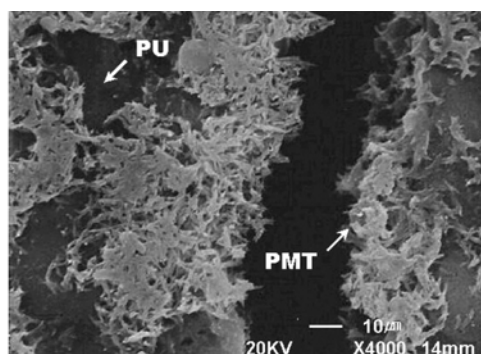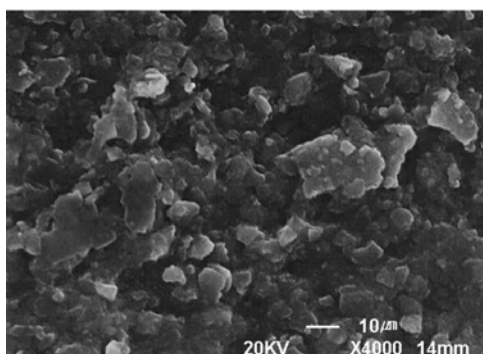
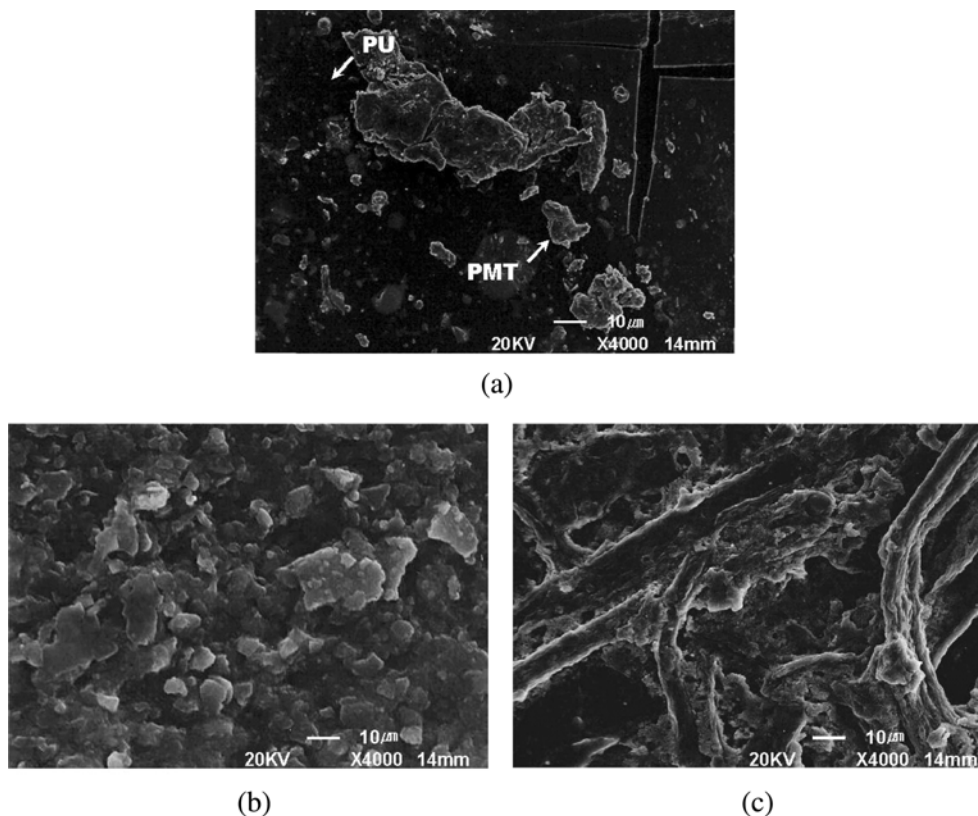**Fig. 12. The SEM photographs of the surfaces for the composites film with reaction time; (a) 3 min, (b) 10 min and (c) 30 min.**

(a)

(b)

(c)

Fig. 13. The influence of the reaction temperature on the changes of the morphologies of the 3-MT doped PU films; (a) 0 ℃, (b) 27 ℃ and (c) 50 ℃.

bulk density and less porous morphology, which results in a higher electrical conductivity. On the contrary, a lower bulk density and more porous morphology will result in lower electrical conductivity. As reaction time increases, higher bulk density is made on the surface of the insulating PU matrix. This is due to the oxidation of more 3-methyl thiophene, resulting in the formation of more 3-methyl thiophene aggregates on the PU surface. The dark region of the SEM photograph displays a continuous PU matrix. On the other hand, the white region of the photograph reveals the formation of more PMT aggregates on the PU surface. Therefore, it is obvious that reaction time as well as 3-methyl thiophene content affects the morphology of the composite films, and hence, the surface morphology must greatly affect the electrical conductivity.

Fig. 13 represents the influence of the reaction temperature on the changes of the morphologies of the 3-methyl thiophene doped PU films. Reaction temperature was varied at three regions: 0 ℃ (a), 27 ℃ (b), and 50 ℃ (c). But reaction time was 30 min and not changed. With increasing reaction temperature, the effect of the increased concentration of FeCl₃ reveals more PMT aggregates on the surface of the PU film by more diffusion-oxidative polymerization, for which more conducting network is generated in the neighborhood of the surface of the film. As the 3-methyl thiophene/PU film was immersed into the FeCl₃ solution, 3-methyl thiophene was diffusion-oxidative polymerized to PMT. 3-methyl thiophene particles tend to form aggregates on and inside the PU matrix and the size of their aggregates depends upon the reaction time and reaction temperature.

6. Moisture Regain
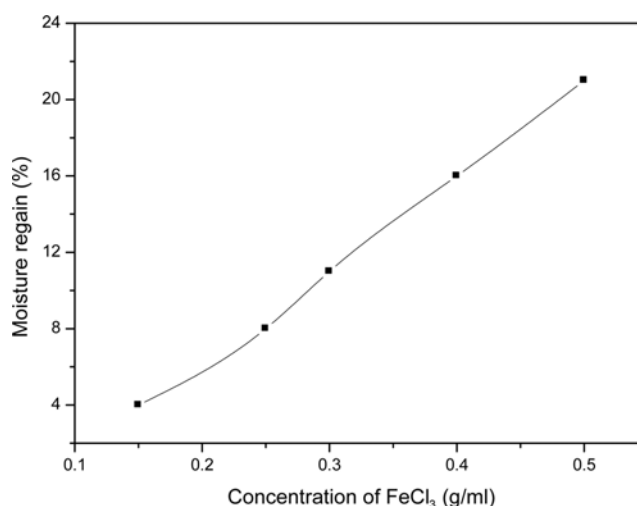
Fig. 14. Dependence of moisture regain capacity of the 3-MT doped PU composite on the concentration of FeCl₃.

Moisture regain capacity of a 3-methyl thiophene/PU composite with concentration of FeCl₃ is presented in Fig. 14. As Polar component, χ_S^{SP}, expressed as one of the surface properties increases with increasing reaction time in Fig. 10, the moisture regain value is significantly increased. This trend can be explained by the oxidative polymerization of the 3-methyl thiophene-impregnated PU film. As explained earlier, a higher degree of functionalization at the surface of the PU composite can influence the magnitude of the polar

share, resulting in an increase of the specific component.

CONCLUSION

Preparation conditions, such as the reaction time, the $FeCl_3$ concentration, the weight ratio of the 3-methyl thiophene to PU and the temperature, are factors that affect the electrical conductivity and the mechanical properties. The electrical conductivity of the composite was as high as 42 S/cm and the amount of $FeCl_3$ required was small. The electrical conductivity of the 3-methyl thiophene doped PU film can be improved by an oxidizing agent, oxidative reaction time and temperature. It is shown that there is a close relationship between the surface free energy and electrical conductivity of the conductive polymer composite.

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