

## Electrical Properties and Characterization of 3-Methylthiophene Impregnated Polyurethane films

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### 3-Methylthiophene이 함유된 폴리우레탄 필름의 전기적 특성 연구

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**ABSTRACT** : The elastomeric and conductive polyurethane (PU) films were prepared by poly(propylene glycol) (PPG), toluene 2,4-diisocyanate, 3-methylthiophene (3-MT) at various preparation conditions, such as the reaction time, the FeCl<sub>3</sub> concentration, the weight ratio of the 3-MT to PU and the reaction temperature for the diffusion-oxidative reaction. The conductive poly (3-methylthiophene) (PMT) layers via the diffusion-oxidative reaction of 3-MT and ferric chloride were formed by immersing the film in organic solution of FeCl<sub>3</sub>/ethyl acetate. The preparation conditions greatly affected the electrical conductivity of the 3-MT/PU composite. The effects of the reaction time and temperature on morphology and surface free energy were investigated by scanning electron microscopy (SEM) analysis and contact angle measurement, respectively. The conductivity of the composite was as high as 42 S/cm.

요 약 : 본 연구에서는 poly(propylene glycol) (PPG), toluene 2,4-diisocyanate, 3-methylthiophene (3-MT)으로부터 반응시간, FeCl<sub>3</sub>의 농도, 3-MT와 PU의 무게비, 반응온도 등의 다양한 조건에 따라 전도성 폴리우레탄 필름을 제조하였다. FeCl<sub>3</sub>와 ethyl acetate로 구성된 유기용매에 제조한 필름을 함침 시킨 결과 3-MT와 FeCl<sub>3</sub>의 확산-산화 반응을 통해 급속한 전도성 PMT 층이 형성되었다. 전도성 복합체의 전기 전도도는 제조조건에 따라 많은 영향을 받고 SEM 분석과 접촉각 측정으로부터 반응시간과 반응온도가 모폴로지와 표면 자유에너지에 미치는 영향을 조사하였으며 제조된 복합체의 전도도는 최대 42 S/cm 인 것으로 확인되었다.

*Keywords* : conductive polyurethane, diffusion-oxidative reaction, electrical conductivity

## I. Introduction

The conjugated polymers with  $\pi$ -bonding, in which the carbon orbitals are in the  $sp^2p_z$  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 the "highway" for charge mobility structure along the backbone of the polymer chain.<sup>1,2</sup>

The conjugated polymers must possess not only charge carriers but also an orbital system in which

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the charge carriers can move. The charge carriers can be provided by partial oxidation (p-doping) of the polymer chain with appropriate electron-acceptor or by partial reduction (n-doping) with electron-donors while the conjugated structure can meet the second requirement through overlapping  $\pi$ -orbitals to provide reasonable carrier mobility along the polymer backbone. Conductivity of conjugated polymers which are in redox by n-doping or p-doping can be changed into the range of semiconductor to conductor and has been reported to have electrochromism (EC) as well as continuous electrical activation due to thermodynamic oxidation and reduction state.<sup>3,4</sup>

In the last two decades, the conductive polymers, heterocyclic conjugated polymers, such as polypyrrole (PPY), polyaniline (PANI), polythiophene (PT) and their derivatives, have received considerable attention due to their high conductivity, high thermal and chemical stability and, particularly, their potential applications in batteries, catalysts, biosensors, chemical detectors, actuators, electrochromic devices, electromagnetic shielding and antistatic coatings.<sup>5</sup> Compared with conventional polymeric materials, however, organic conductive polymers with  $\pi$ -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.<sup>6,7</sup>

The synthesis, structure and the modification of the properties for specific applications of polythiophenes are attracting immense interest of the researchers. Poly(3-alkyl thiophenes) are both soluble and melt processable. 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 processable. Chemical oxidative polymerization of 3-methyl thiophene with iron(III) chloride ( $\text{FeCl}_3$ ) produces polymers in high yield.

Most conductive composite films were electrochemically prepared by coating an anode with a polymer film and then immersing them in a solution containing an electrolyte and a monomer. The monomer, which imbibes the polymer, was electrochemically polymerized, thus generating a composite film. However, the electrochemical method cannot provide large films and is also expensive. The chemical polymerization method can overcome these disadvantages.

In this study, a simple method for chemically preparing PMT-doped PU films via the condensation polymerization at room temperature is proposed. The film was peeled away from the plate and immersed into a organic solution of  $\text{FeCl}_3$ . The PU film was thus coated with a conductive film containing PMT via the oxidative polymerization of 3-MT. The preparation conditions, such as the reaction time, the reaction temperature, the concentration of  $\text{FeCl}_3$ , and the weight ratio of 3-MT to PU were carefully studied. Moreover, surface free energy was examined by contact angle measurement. Scanning electron microscopy was used to study morphological features dependent on doping conditions.

Since the PUs have good mechanical properties, the PU with conductive surfaces could be employed in new fields, for example, as keyboards or buttons for calculators and computers. The PU coated with PMT also constitutes a good material for electromagnetic shielding. The preparation procedure is not complicate and the amount of 3-MT required is small.

## II. Experimental

### 1. Chemicals

3-MT (Aldrich, 99+%) as an inherent conducting

material, ferric(III) chloride (Aldrich, 97%), PPG 2000 (poly(propylene glycol), Aldrich,  $M_n = 2000$ ), toluene 2,4-diisocyanate (Aldrich, 80%), and dibutyltin dilaurate (Aldrich, 95%) as a catalyst 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 as an oxidizing agent) and distilled and deionized water was employed.

## 2. Preparation

In a typical experiment, PPG, toluene 2,4-diisocyanate, 3-MT and butyltin dilaurate were mixed in a flask equipped 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  $40\text{ cm}^2$ , which was subsequently covered with a box, whose four open edges were sealed to the surface of a desk, to avoid the vaporization in free air. After the condensation polymerization was allowed to proceed for 24 hrs, the obtained PU film containing 3-MT was peeled away from the plate. To dope the 3-MT impregnated PU films, the film was immersed in a  $FeCl_3$  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.

## 3. Characterizations

Thermogravimetric analyser (Shimadzu TA-50) with heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  was used to measure thermal decomposition temperatures of the pure PU substrate and 3-MT/PU films before and after doping.

A thin slice cut vertically from the coated film was magnified with a microscope (SOMETECH) and its picture taken with a ICAMSCOPE (Image analyzer system, Baestech). The thickness of the coating layer was calculated from its thickness in the picture taking into account the magnification of

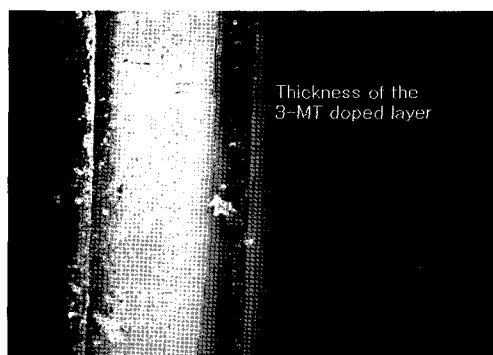


Figure 1. Photograph of the 3-MT doped PU film.

the microscope. One of the pictures is presented in Figure 1. Scanning electron microscopy (SEM, JSM 6400, Japan) was used to study the effects of the different reaction and reaction temperature on the morphologies of the 3-MT/PUs.

The coated PU film was cut to rectangular shape ( $2.5 \times 1.5\text{ cm}$ ). The electrical resistance was measured by the four-point probe technique, where electrical contacts are four gold wires. The conductivity of the coating layer was calculated from the electrical resistance and the thickness of the coating layer. The electrical conductivity ( $\sigma$ ) can be defined as follows:<sup>8</sup>

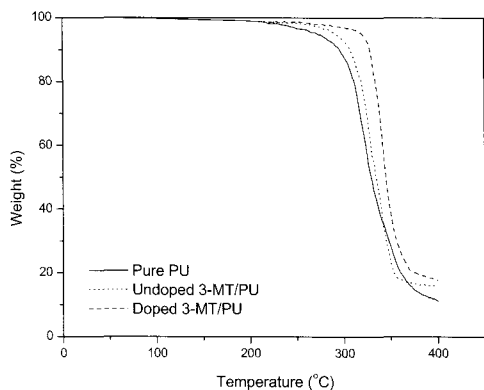
$$\sigma = \frac{I}{V} \times \frac{C}{b \times d}$$

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

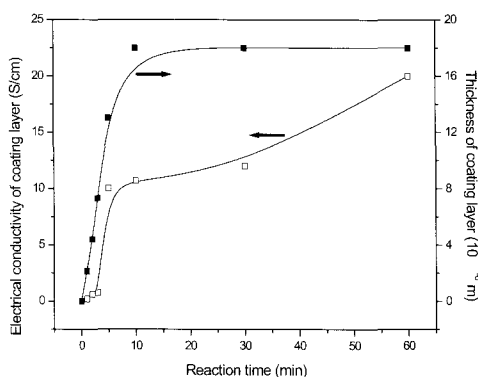
SEO 300A contact angle measuring device from SEO Co. was used for measurement of the surface energy of liquid and solid phases. In this study, distilled water and diiodomethane were used as wetting liquids.

## III. Results and Discussion

Figure 2 shows the TGA curves under nitrogen



**Figure 2.** Infrared spectra of the pure PU substrate.



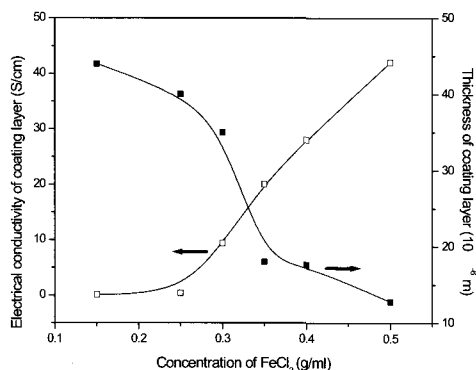
**Figure 3.** Infrared spectra of the 3-MT doped PU composite.

atmosphere for the pure PU substrate, the undoped 3-MT/PU blend and doped 3-MT/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 that of the pure PU substrate, while that of the doped 3-MT/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-MT with PU matrix proceeded. Polymerization occurred when the blend was soaking in the doping  $\text{FeCl}_3$  solution.

Various effects of the doping conditions were carefully investigated in this study. Figure 3 presents the effects of the oxidative reaction time on the

conductivity and the thickness of the coating layer of the 3-MT doped PU film. The weight ratio of the 3-MT/PU film was 0.25; the molar ratio of isocyanate/hydroxyl was 1.1; the concentration of  $\text{FeCl}_3$  in ethyl acetate was 0.35 g/ml; the thickness of the PU film was about 0.47 mm. The conductivity was measured at room temperature. As reaction time increases, the electrical conductivity of the 3-MT 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-MT/PU film in the  $\text{FeCl}_3$ /ethyl acetate solution, several processes take place: (i) the swelling of the 3-MT/PU film by the organic solution; (ii) the diffusion of ethyl acetate into the 3-MT/PU film and the diffusion of 3-MT from inside towards the surface of the film; (iii) the oxidative polymerization of 3-MT by  $\text{FeCl}_3$ . Generally speaking, a diffusion-oxidative polymerization process takes place. As soon as the amount of the PMT (poly(methylthiophene)) becomes larger 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-MT network forms a shield near the PU surface which prevents the counter diffusion of 3-MT and  $\text{FeCl}_3$ , and hence prevents additional oxidative polymerization. As a result, when the reaction time increases from 10 to 60 min, the thickness of the coating layer hardly changes.

Figure 4 shows the effects of the concentration of  $\text{FeCl}_3$  on the conductivity and the thickness of the coating layer of the 3-MT doped PU film. The reaction time was 1 h. Other preparation conditions were as in Figure 3. The conductivity was measured at room temperature. With increasing concentration, the thickness of the coating layer decreases, while the conductivity increases. The conductivity becomes large at a critical concentration between 0.30 and 0.35 g/ml. These observations can be explained as follows: firstly, the oxidation potential increases with increasing  $\text{FeCl}_3$  concentration and only at a

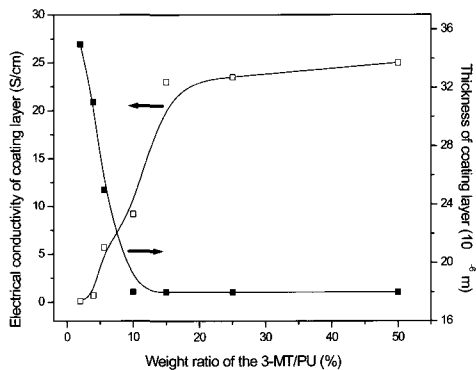


**Figure 4.** TGA curves of the pure PU substrate, undoped 3-MT/PU blend and doped 3-MT doped PU composite.

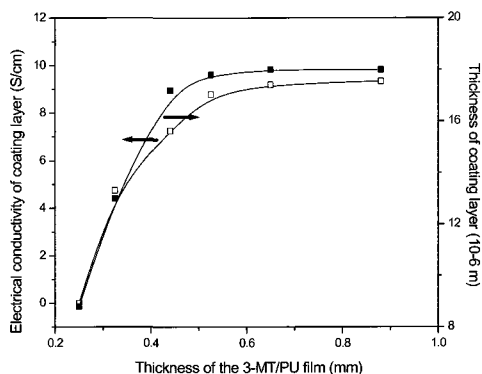
suitable oxidation potential can 3-MT be oxidized to PMT. Secondly, at higher concentrations, more  $\text{FeCl}_3$  diffuses in the PU film in a short time and the PMT layer, which retards the further reaction, is formed more rapidly. As a result, the conductivity is high (42 S/cm) and the coating layer is thin (13  $\mu\text{m}$ ). For low  $\text{FeCl}_3$  concentrations, the diffusion into the PU film is slower. It takes therefore a longer time for a PMT network to be formed and  $\text{FeCl}_3$  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 conductivity can be obtained by adjusting the concentration of doping solution.

Figure 5 shows the effects of the weight ratio of the 3-MT/PU on the conductivity and the thickness of the coating layer of the 3-MT doped PU film. The reaction time was 1 hr. Other preparation conditions were as in Figure 3. The conductivity was measured at room temperature. With increasing weight ratio, the thickness of the coating layer decreases, while the conductivity increases. This is as expected since, for higher weight ratio, the content of 3-MT near the surfaces of the film is higher. Therefore, in a short time, more 3-MT participates in the reaction with  $\text{FeCl}_3$  and forms a



**Figure 5.** The effects of the reaction time on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.



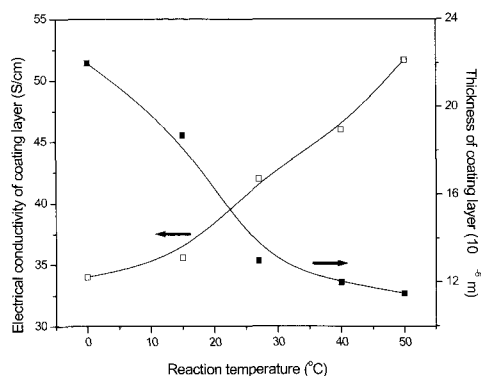
**Figure 6.** The effect of the concentration of  $\text{FeCl}_3$  on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

conductive network and also a reaction-preventing shield. When the content of 3-MT is low, the slow diffusion of 3-MT plays an important role in its reaction with  $\text{FeCl}_3$ . In the latter case,  $\text{FeCl}_3$  penetrates deeply into the film. As a result, the coating layer is thick, but its conductivity is low because of the loose network of PMT generated from the smaller amount of 3-MT. Figure 5 shows that for a relatively low weight ratio of 3-MT/PU, namely, 0.50, the conductivity of the coating layer is already 5.7 S/cm.

Figure 6 presents the effects of the thickness of the PU film on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

The reaction time was 0.5 h and the weight ratio of the 3-MT/PU was 0.5. Other preparation conditions were as in Figure 3. The conductivity was measured at room temperature. As the thickness of the PU film increases, the conductivity increases. For a thickness of 0.25 mm, the coated film is an insulator; when it increases to 0.32 mm, the 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-MT 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-MT in the film decreases so much that a conductive network can no longer be generated; hence, the conductivity is zero. When the film becomes thicker, for example, 0.32 mm, even though the content of 3-MT on the surface of the film is low, it is still possible for a conductive network to be generated because the 3-MT present inside can diffuse to the surface and react. After the formation of the coating layer, the surplus of 3-MT 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 paper, only PU films thicker than 0.32 mm can be well coated with a conductive layer. Decreasing the volume of the box and introducing a small container containing 3-MT in the box to supply 3-MT vapor may prevent the diffusion of the 3-MT from the PU in the atmosphere and, thus, allow the decrease of the minimum thickness of the PU film needed to obtain surface conductive PU films.

Figure 7 shows the effects of the reaction temperature on the conductivity and the thickness of the coating layer of the 3-MT doped PU film. Preparation conditions are same as in Figure 3. Only the reaction temperature is different; 0°C, 15°C, 27°C, 40°C, and 50°C. With increasing reaction tem-



**Figure 7.** The effects of the weight ratio of the 3-MT to PU on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

perature, the thickness of the coating layer decreases, while the conductivity of the 3-MT doped PU film increases. This results are almost same as in the concentration effect of FeCl<sub>3</sub> on the conductivity and the thickness of the coating layer of the 3-MT doped PU film. The increase of the reaction temperature in the limited dimension of the container for doping brings higher concentration of FeCl<sub>3</sub>, which results into the more diffusion of FeCl<sub>3</sub> in the PU film in a short time and the sudden formation of the PMT layer which retards the further reaction.

According to Fowkes,<sup>9</sup> the surface free energy is expressed by the sum two components: a dispersive component,  $\gamma_S^L$ , attributable to London attraction, and a specific (or polar) component,  $\gamma_S^{SP}$ , 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 and Kaoble developed the Fowkes' concept using contact angle from two liquids with great different features on solid surface.<sup>10</sup>

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

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

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

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

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

To get 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,  $\gamma_S^L$ , and specific (or polar) components,  $\gamma_S^{SP}$ , 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.

Figures 8 and 9 present the effect 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 components of the PU film increase.

These specific component increase of the surface free energy can be explained by the oxidative polymerization of the 3-MT by FeCl<sub>3</sub> at surface of

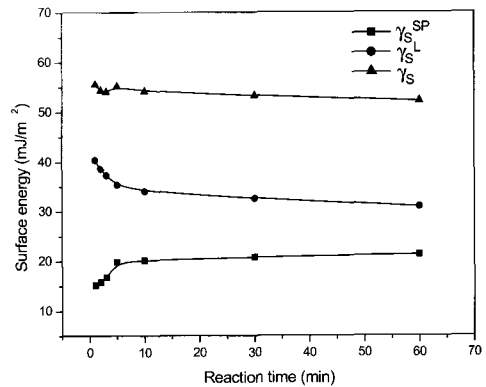


Figure 8. The effects of the thickness of the PU film on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

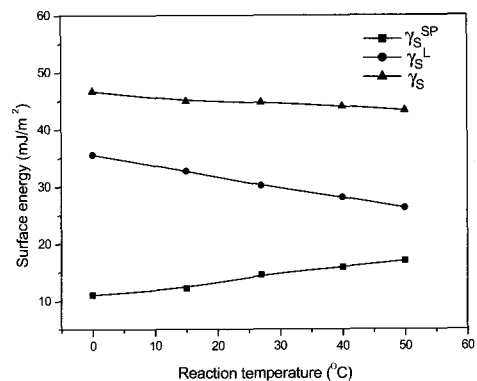


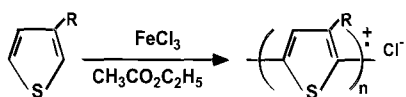
Figure 9. The effects of the reaction temperature on the conductivity and the thickness of the coating layer of the 3-MT doped PU film.

the PU film. It is well known that the specific components of the surface energy is always related to surface functional group, hydrogen bonding, coulomb and dipole-dipole interaction.

FeCl<sub>3</sub> with high electronegativity polarizes the interatomic bonds. Therefore, higher degree of functionalization at surface can influence the magnitude of polar share. In addition, as reaction temperature

increases, diffusion rate of  $\text{FeCl}_3$  into the 3-MT is activated, leading to the improvement of functionalization.

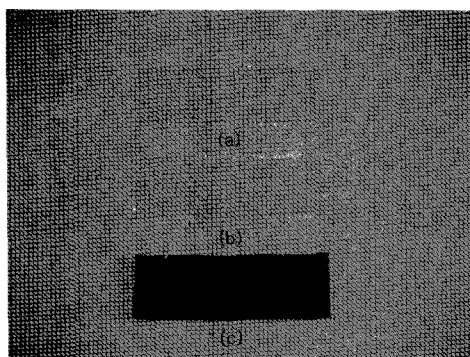
As presented in the conductivity results, conductivity with reaction time and reaction temperature increases. Hence, it is informable to relate conductivity with surface free energy. As shown in picture,  $\text{FeCl}_3$  is diffused to the surface of the 3-MT, and  $\text{S}^+$  and  $\text{Cl}^-$  groups are formed by the electronegativity difference.



With increasing reaction time, more charge separation on the surface occurs and charge mobility is faster, resulting into the enhancement of conductivity and specific component. This is obvious factor to understand how specific component of surface free energy affects the conductivity.

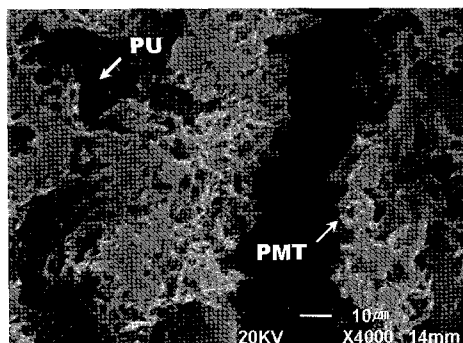
Figure 10 shows the photographs of the specimens of the pure PU film and 3-MT contained PU films before and after doping. Both the pure PU substrate (a) and 3-MT contained PU film (b) were transparent and there was no difference in sight. But the 3-MT doped PU film (c) was dark brown.

Figure 11 shows the SEM photographs of the surfaces for the composites film with different

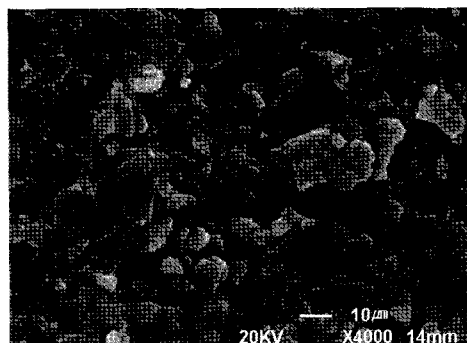


**Figure 10.** The effect of the reaction time on the surface free energy of the 3-MT doped PU film.

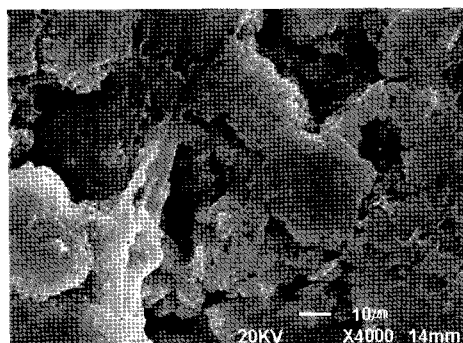
reaction time. It was reported that the rate of polymerization was comparatively lower when chloride was used as a doping anion. A lower rate of polymerization brings a higher bulk density and less porous morphology, which results in a higher



(a)



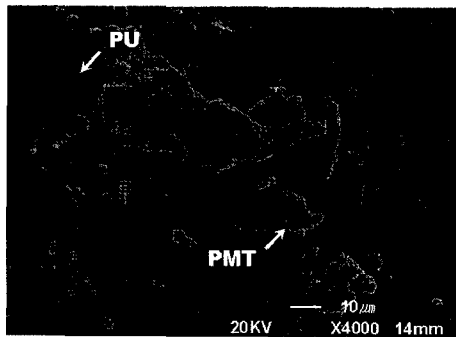
(b)



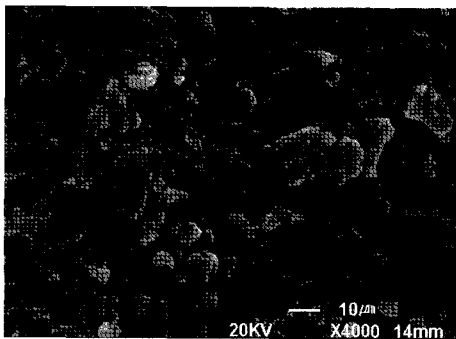
(c)

**Figure 11.** The effect of the reaction temperature on the surface free energy of the 3-MT doped PU film.

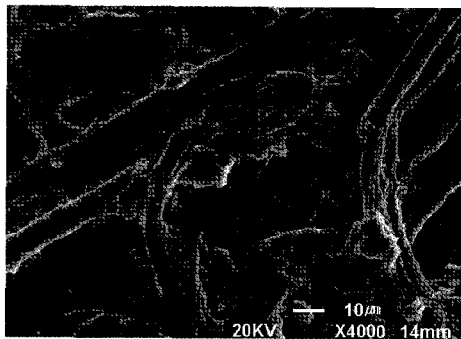




(a)



(b)



(c)

**Figure 12.** The photographs of the specimens of (a) the pure PU film and 3-MT contained PU films before (b) and after (c) doping.

conductivity. In contrary, a lower bulk density and more porous morphology will result in lower 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 the more

3-MT, resulting in the formation of the more 3-MT aggregates on the PU surface. The dark region of the SEM photograph displays the 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-MT content affects the morphology of the composite films, and hence, the surface morphology must greatly affect the conductivity.

Figure 12 represents the influence of the reaction temperature on the changes of the morphologies of the 3-MT doped PU films. Reaction temperature was varied at three regions; (a) 0°C, (b) 27°C, and (c) 50°C. But reaction time was 30 min and not changed. With increasing reaction temperature, effect of the increased concentration of  $\text{FeCl}_3$  reveals the more PMT aggregates on the surface of the PU film by the more diffusion-oxidative polymerization, which more conducting network is generated in the neighborhood of the surface of the film.

As the 3-MT/PU film was immersed into the  $\text{FeCl}_3$  solution, 3-MT was diffusion-oxidative polymerized to PMT. 3-MT 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.

#### IV. Conclusion

Surface conductive polyurethane films can be successfully prepared from poly(propylene glycol), toluene 2,4-diisocyanate, 3-MT and butyltin dilaurate by the diffusion-oxidative polymerization method proposed in this paper. A mixture of the precursors of PU containing 3-MT was cast and transformed into a film by condensation polymerization followed by immersion of the film containing 3-MT into a ferric chloride solution. As a result, in a short time, the PU film was coated with a conductive layer near its surface. Preparation conditions, such as the reaction time, the  $\text{FeCl}_3$

concentration, the weight ratio of the 3-MT to PU and the temperature for the diffusion-oxidative reaction are factors that affect the electrical conductivity.

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