Preparation and Characterization of Conductive Polyurethane Films

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Abstract: In this study, conductive polyurethane (PU) films were prepared by the condensation of poly(propylene glycol) (PPG), toluene 2,4-diisocyanate, and 3-methylthiophene (3-MT) under various preparation conditions. The immersion of the film in an organic solution of ferric chloride (FeCl₃)/ethyl acetate led to the rapid formation of the conductive poly(3-methylthiophene) (PMT) layers via the diffusion-oxidative reaction of 3-MT and ferric chloride. We found that the electrical conductivity and the mechanical properties were affected significantly by the time, the FeCl₃ concentration, the weight ratio of the 3-MT to PU, and the temperature of the diffusion-oxidative reaction. The effects that the reaction time and temperature have on the morphology and surface free energy were investigated by scanning electron microscopy (SEM) analysis and contact angle measurements, respectively. The mechanical properties, such as tensile strength and elongation at break, were also studied. The conductivity of the composite was as high as 42 S/cm.

Keywords: conductive polyurethane, 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 [1-3]. However, conjugated polymers featuring π-bonding, in which the carbon orbitals are in the sp³p₂ 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 along the backbone of the polymer chain [4,5]. During the last two decades, conductive polymers and heterocyclic conjugated polymers, such as polypyrrole (PPY), polyaniline (PANI), polythiophene (PT), and their derivatives, 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 [6-8]. Compared with conventional polymeric materials, however, organic conductive polymers having π-conjugated systems, which have delocalized electrons, making movement of electrons in molecules easier, do not have relatively wide applications because of their 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 [9].

Much research has been performed to prepare composites containing a conductive polymer and an insulating, but flexible, polymer, especially in the form of films. Various anionic soluble polymers can be used as dopants in the electrochemical polymerization of pyrrole to prepare polyelectrolyte-PPY composites at the anode. Similarly, latex particles having anionic surfaces were precipitated together with electrochemically polymerized PPY on an anode to generate composite films [10]. Most conductive composite films have been prepared electrochemically by coating an anode with a polymer film and then immersing it in a solution containing an electrolyte and a monomer. The monomer, which imbibes the polymer, is polymerized electrochemically, to generate a composite film. However, the electrochemical method cannot provide large films and it is also expensive.

The chemical polymerization method can overcome
these disadvantages. Several procedures have been developed to obtain conductive composite films. PPY-poly(vinyl alcohol) (PVA) films have been prepared by exposing PVA that contained ferric chloride to pyrrole and water vapors [11]. PPY-poly(ethylene terephthalate) (PPY-PET) has been prepared by immersing the pyrrole-swollen PET polymer into an aqueous solution of ferric chloride [12]. PPY-poly(methyl methacrylate) (PMMA) films have been obtained by spreading a water-insoluble solvent solution of pyrrole and PMMA over the surface of an aqueous solution of ammonium persulfate [13]. Composite films containing PPY have also been prepared by introducing polymer films at the interface between an aqueous solution of ferric chloride and a toluene solution of pyrrole [14]. 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 ability to modify the properties toward specific applications of polythiophenes are attracting an immense amount of interest from researchers. Poly(3-alkyl thiophenes) are both soluble and melt processible. They have good chemical and environmental stability with excellent electronic and optical properties that are suitable for various device applications. Polythiophenes can be prepared both by electrochemical polymerization and chemical oxidative polymerization techniques. However, the polymers prepared by the electrochemical method are not processible. Chemical oxidative polymerization of 3-methylthiophene with ferric(III) chloride (FeCl₃) produces polymers in high yield.

In this study, a simple method for preparing PMT-coated PU films through 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-MT to PU, were carefully studied. Moreover, the surface free energy was examined. To determine the mechanical properties, the tensile strength and elongation at break were also estimated and studied. Scanning electron microscopy was used to study the morphological features and their dependence on the doping conditions.

Because the PUs have good mechanical properties, PUs having conductive surfaces could be employed in new fields, for example, as keyboards or buttons for calculators and computers. Due to the easy dissipation of electricity, the conducting surfaces have the advantage of avoiding dust deposition from air. In contrast, conductive rubber, such as carbon rubber, accumulates dust from the air because of the presence of the insulating rubber at the surface of the material. The PU coated with PMT also constitutes a good material for electromagnetic shielding.

Experimental

Chemicals

3-MT (Aldrich, 99+% as an inherent conducting material, ferric(III) chloride (Aldrich, 97%), PPG 2000 [poly(propylene glycol), Aldrich, mol. wt. 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 solvents for the FeCl₃ solution (used as an oxidizing agent), and distilled and deionized water was also employed.

Preparation and Characterizations

In a typical experiment, PPG, toluene 2,4-diisocyanate, 3-MT and butyltin dilaurate were mixed in a flask equipped with a vacuum system for premixing. The liquid mixture was then poured on a horizontal plate having a good peeling ability over an area of ca. 40 cm², 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 polymerization had proceeded for 24 h, 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 FeCl₃ solution at different temperatures and for different reaction times. On doping, the surface of the film turned dark-brown rapidly. The coated film was washed in methyl alcohol and water and finally dried under vacuum.

IR spectra, recorded from 4000 to 400 cm⁻¹, of the pure PU film and 3-MT/PU composite were obtained on a Bio Red FT/IR (FTS 165, U.S.). A thermogravimetric analyzer (Shimadzu TA-50), operating at a heating rate of 10°C/min, was used to measure the 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 image recorded with an ICAMSCOPE (Image analyzer system, Baestech). The thickness of the coating layer was calculated from its thickness in the image and taking into account the magnification of the microscope. One of these images is presented in Figure 1. Scanning electron microscopy (SEM, JSM 6400, Japan) was used to study the effects of the different reaction conditions on the morphologies of the 3-MT/PU.

The coated PU film was cut into a rectangular shape (2.5 × 1.5 cm). The electrical resistance was measured using the four-point probe technique, where the electrical contacts were 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 (σ) can be defined as follows [15]:
\[ \sigma = \frac{I}{V} \times \frac{C}{b \times d} \]

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.

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

The sample sheet was cut to the size required by the ASTM D412. The mechanical properties, such as tensile strength and elongation at break, were performed using a universal testing machine (UTM, Lloyd) at room temperature and at a cross-head speed of 20 mm/min.

**Results and Discussion**

As the polymerization of 3-MT on and within the surface of the PU film proceeds, the rapidly sample turned dark-brown. To confirm spectrally the formation of the 3-MT in the insulating polymer matrix, IR spectra were obtained both on the pure films and the 3-MT-containing PU films. Figures 2 and 3 show the results of IR spectral studies of the pure PU substrate and the 3-MT-doped PU composite, respectively. Compared with the IR spectrum of the pure PU, where vibration bands are observed at 3450 cm\(^{-1}\) (N-H bending, 3000 to 3500 cm\(^{-1}\)), 1730 cm\(^{-1}\) (C=O), and 1289 cm\(^{-1}\) (N-C-O), there are regions of the composite’s spectrum that show considerable changes [16]. For example, new vibration bands are observed from 3000 to 2500 cm\(^{-1}\) (Figure 3). Furthermore, the IR spectrum of the composite film shows a featureless increase at 2800 cm\(^{-1}\) that is due to the methyl group of 3-MT.

Figure 4 shows the TGA curves recorded under a nitrogen atmosphere for the pure PU substrate, the undoped 3-MT/PU blend, and doped 3-MT/PU composites, respectively. Their decompositions occur at 216, 270, and 318°C, respectively. These findings show that the decomposition temperature of the blended PU substrate is higher than 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, we infer that blending of 3-MT with the PU matrix proceeded. Polymerization occurred when the blend was soaked in the doping FeCl\(_3\) solution.

Various effects of the doping conditions were carefully investigated in this study. Figure 5 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 FeCl\(_3\) in ethyl acetate was 0.35 g/mL; the thickness of the PU film was ca. 0.47 mm. The con-
conductivity was measured at room temperature. As the 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 FeCl₃/ethyl acetate solution, several processes take place: (i) swelling of the 3-MT/PU film by the organic solution; (ii) diffusion of ethyl acetate into the 3-MT/PU film and diffusion of 3-MT from inside toward the surface of the film; and (iii) oxidative polymerization of 3-MT by FeCl₃. 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-MT network forms a shield near the PU surface that prevents the counter-diffusion of 3-MT and FeCl₃, and, hence, prevents additional oxidative polymerization. As a result, when the reaction time increased from 10 to 60 min, the thickness of the coating layer hardly changed.

However, the amount of PMT additionally produced is small and appears not to be included in the network surface layer, because the electrical resistance does not change appreciably.

Figure 6 shows the effect of the concentration of FeCl₃ on the conductivity and thickness of the coating layer of the 3-MT-doped PU film. The reaction time was 1 h. Other preparation conditions were the same as those in Figure 5. The conductivity was measured at room temperature. Upon increasing the concentration, the thickness of the coating layer decreased, while the conductivity increased. The conductivity became 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 upon increasing the FeCl₃ concentration and only at a suitable oxidation potential can 3-MT be oxidized to PMT. Secondly, at higher concentrations, more FeCl₃ diffuses in the PU film within 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 μm). For low FeCl₃ concentrations, diffusion into the PU film is slower. It takes, therefore, a longer time for a PMT network to be formed and FeCl₃ can penetrate deeper into the film. This situation leads to both a thicker coating layer and lower conductivities.

It is known that oxidation of a conducting material with a doping agent is closely related to the formation of an
appropriate thickness of conducting layer and the conductivity. Therefore, maximum conductivity can be obtained by adjusting the concentration of the doping solution.

Figure 7 shows the effect of the weight ratio of the 3-MT/PU on the conductivity and thickness of the coating layer of the 3-MT-doped PU film. The reaction time was 1 h. Other preparation conditions were the same as those in Figure 5. The conductivity was measured at room temperature. Upon increasing the weight ratio, the thickness of the coating layer decreased, while the conductivity increased. This result was expected because, for a higher weight ratio, the content of 3-MT near the surface of the film is higher. Therefore, in a short time, more 3-MT participates in the reaction with FeCl₃ and forms a 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 FeCl₃. In the latter case, FeCl₃ 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 7 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 8 presents the effect of the thickness of the PU film on the conductivity and 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 the same as those in Figure 5. The conductivity was measured at room temperature. As the thickness of the PU film increased, the conductivity increased. For a thickness of 0.25 mm, the coated film was an insulator; when it increased to 0.32 mm, the conductivity became 4.8 S/cm; when it increased further, from 0.43 to 0.88 mm, the conductivity moderately increased. 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 diffused into the air of the box and, therefore, its actual concentration in the film was much lower. As a result, when a PU film is too thin, e.g., 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, e.g., 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 3-MT seldom takes part in the reaction. This theory explains why the thickness of the coating layer increased very little when the thickness of the PU film increased 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 coated well 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 diffusion of 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 9 shows the effect of the reaction temperature on the conductivity and thickness of the coating layer of the 3-MT-doped PU film. The preparation conditions were the same as those in Figure 5. Only the reaction temperature was changed: 0, 15, 27, 40, and 50°C. With increasing reaction temperature, the thickness of the coating layer decreased, while the conductivity of the 3-MT-doped PU film increased. This result is almost
same as that observed for the effect of the concentration of FeCl₃ on the conductivity and thickness of the coating layer of the 3-MT-doped PU film. The increase in the reaction temperature in the limited dimensions of the container for doping provides a higher concentration of FeCl₃, which results in more diffusion of FeCl₃ in the PU film within a short time and the sudden formation of a PMT layer that retards further reaction.

According to Fowkes [17], the surface free energy is expressed by the sum of two components: a dispersive component, $\gamma_S^{LP}$, 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)

$$\gamma_S = \gamma_L^{LP} + \gamma_L^{SP}$$

Similarly, for the liquid,

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

where the superscripts $L$ and $SP$ refer to the London dispersive and specific components, respectively, and the subscripts $S$ and $L$ represent solid and liquid phases, respectively. Owens and Wendt [19] developed Fowkes’ concept using the contact angle from two liquids with significantly different features on a solid surface.

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

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

$$\gamma_S^{LP} = \frac{1}{4} \left\{ \frac{(1 + \cos\theta_L) \gamma_L \cdot (\gamma_L^{LP})^{1/2} + (1 + \cos\theta_S) \gamma_S \cdot (\gamma_S^{LP})^{1/2}}{(\gamma_L^{LP} \cdot \gamma_L^{LP})^{1/2} + (\gamma_S^{LP} \cdot \gamma_S^{LP})^{1/2}} \right\}$$

$$\gamma_S^{SP} = \frac{1}{4} \left\{ \frac{(1 + \cos\theta_L) \gamma_L \cdot (\gamma_L^{SP})^{1/2} + (1 + \cos\theta_S) \gamma_S \cdot (\gamma_S^{SP})^{1/2}}{(\gamma_L^{LP} \cdot \gamma_L^{LP})^{1/2} + (\gamma_S^{LP} \cdot \gamma_S^{LP})^{1/2}} \right\}$$

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

To obtain the properties of the diffusion-oxidative surface characteristics of the PU film, analysis of the surface free energy is evaluated through physical studies divided into two components. The London dispersive, $\gamma_L^{SP}$, and specific (or polar) components, $\gamma_L^{SP}$, of the surface free energy of the PU film were determined by measuring the contact angle of a variety of testing liquids that have known values for their London dispersive and specific components of surface free energy.

Figures 10 and 11 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 components of the PU film increased.

These specific component decreases of the surface free energy can be explained by the oxidative polymerization of 3-MT by FeCl₃ 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 interactions.

FeCl₃, with its high electronegativity, polarizes the interatomic bonds. Therefore, a higher degree of functionalization at the surface can influence the magnitude of the polar share. In addition, as the reaction temperature increases, the diffusion rate of FeCl₃ into 3-MT is
activated, leading to the improvement of functionalization.

As presented earlier, the conductivity increased upon increasing the reaction time and reaction. Hence, it is informative to relate conductivity to the surface free energy. As shown in the picture, FeCl₃ to the diffused to the surface of the 3-MT, and Cl⁻ and Cl⁻ groups are formed by the electronegativity difference.

With increasing reaction time, more charge separation occurs on the surface and charge mobility becomes faster, resulting in enhanced conductivity and the specific component [20]. These factors obviously must be studied to understand how the specific component of surface free energy affects the conductivity.

Figure 12 shows photographic images of the specimens of the pure PU film and the 3-MT-containing PU films before and after doping. Both the pure PU substrate (a) and 3-MT-containing PU film (b) were transparent and there was no difference to the naked eye, but the 3-MT-doped PU film (c) was dark brown.

Figure 13 shows SEM images of the surfaces of the composite films with respect to the reaction time. It was reported that the rate of polymerization was comparatively lower when chloride was used as the doping anion. A lower rate of polymerization provides a higher bulk density and a less-porous morphology, which results in a higher conductivity. In contrast, a lower bulk density and more-porous morphology will result in lower conductivity. As the reaction time increases, a higher bulk density occurs on the surface of the insulating PU matrix. This situation is due to oxidation of more 3-MT, resulting in the formation of more 3-MT aggregates on the PU surface. The dark region of the SEM image displays the continuous PU matrix. On the other hand, the white regions reveal the formation of more PMT aggregates on the PU surface. Therefore, it is obvious that the reaction time, as well as 3-MT content, affects the morphology of the composite films, and, hence, the surface morphology must affect the conductivity significantly.

Figure 14 represents the influence of the reaction temperature on the changes of the morphologies of the 3-MT-doped PU films. The reaction temperature was varied at five regions: (a) 0°C, (b) 27°C, and (c) 50°C. The reaction time was kept constant at 30 min. With increasing reaction temperature, the effect of the increased concentration of FeCl₃ reveals the more PMT aggregates appeared on the surface of the PU film by the more diffusion-oxidative polymerization, which resulted in more conducting network being generated in the neighborhood of the surface of the film.

As the 3-MT/PU film was immersed into the FeCl₃ solution, 3-MT was diffusion-oxidative polymerized to PMT. 3-MT particles tend to form aggregates on and inside the PU matrix and the sizes of these aggregates depend upon the reaction time and temperature.

Figure 15 shows the effect of the reaction time on the tensile strength and elongation at break of the 3-MT/PU film. With increasing reaction time, both the tensile strength and the elongation at break decreased. The explanation of these results is as follows: At a short reaction time, such as 1, 2, or 3 min, the PMT aggregates are dispersed randomly and are small. The amorphous PU matrix is relatively large. On the other hand, at a long reaction time, the formation of extended PMT ag-
Figure 13. SEM images of the surfaces of the composite films as a function of reaction time: (a) 3 min, (b) 10 min, and (c) 30 min.

Figure 14. The influence of the reaction temperature on the morphologies of the 3-MT-doped PU films: (a) 0°C, (b) 27°C, and (c) 50°C.
gregates occurred. Moreover, the separation distance between these aggregates is small. In other words, phase separation between the PMT and PU matrix takes place. These results cause a decrease in the tensile strength and an elongation at break.

Figure 16 presents the effect of the FeCl$_3$ concentration on the tensile strength and elongation at break of the 3-MT/PU film. As the concentration of FeCl$_3$ increased, there was a significant increase in the tensile strength and elongation at break in two regions of the FeCl$_3$ concentration (0.15 and 0.5 g/mL). It is important to study the change of the thickness of the FeCl$_3$ coating layer with respect to concentration. With increasing FeCl$_3$ concentration, the thickness gradually decreased. Regarding the sensitivity to the thickness, the mechanical properties, such as the tensile strength and elongation at break, can be explained as follows: The formation of the conductive layer by the diffusion-oxidative polymerization is not made perfectly at an FeCl$_3$ concentration of 0.15 g/mL, even if the thickness of the coating layer is the highest. This situation leads to only a small variation of the pristine mechanical properties of the PU matrix, which causes the low electrical conductivity. Meanwhile, at an FeCl$_3$ concentration of 0.5 g/mL, an almost perfect conductive network having a thin layer is formed, resulting in an increase in the mechanical properties as well as the electrical conductivity.

Figure 17 shows the effects of the weight ratio of 3-MT/PU on the tensile strength and elongation at break of the 3-MT/PU composite. With increasing the weight ratio of the 3-MT/PU, the amount of 3-MT that changes into PMT by diffusion-oxidative polymerization increases. Consequently, this situation leads to the same result as that for the effect of the concentration of FeCl$_3$. 

Figure 18. The effect of the thickness of the 3-MT/PU film on the tensile strength and elongation at break of the 3-MT-doped PU film.
Figure 19. The effect of the reaction temperature on the tensile strength and elongation at break of the 3-MT-doped PU film.

Figure 18 presents the effects of the thickness of the 3-MT/PU film on the tensile strength and elongation at break of the 3-MT-doped PU film. As the thickness of the film increases, two different regions are seen: (a) 0.25 to 0.43 mm than (b) 0.52 to 0.88 mm. In region (a), the thickness of the coating layer increased faster than the thickness of the film, resulting in the decrease of the mechanical properties. On the other hand, in region (b), there is little change in the thickness of the coating layer, leading to the increase of the mechanical properties upon increasing the thickness of the film.

Figure 19 shows the effect of the reaction temperature on the tensile strength and elongation at break of the 3-MT-doped PU film. With increasing reaction temperature, the tensile strength decreases, as does the elongation at break. This result is due to the increased phase separation between the PU matrix and the PMT, as we observed for the reaction time effect, although the thickness of the coating layer decreased upon increasing oxidation temperature.

**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. First, a mixture of the precursors of PU containing 3-MT was cast and transformed into a film by condensation polymerization. Secondly, the film containing 3-MT was immersed into a ferric chloride solution. As a result, within a short time, the PU film was coated with a conductive layer near its surface. The preparation conditions, such as the reaction time, the FeCl₃ concentration, the weight ratio of 3-MT to PU, and the temperature for the diffusion-oxidative reaction, are all factors that affect the electrical conductivity and the mechanical properties. The conductivity of the composite was as high as 42 S/cm and the amount of FeCl₃ required was small.

**References**