

High-Strength Metallic Plastic Sheet Prepared by Electrochemical Polymerization of Thiophene on Stainless Steel

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ABSTRACT: Conducting polythiophene films hundreds of micrometers thick was first obtained by electrochemical polymerization of thiophene in freshly distilled BF_3 -diethyl ether solution at stainless steel electrode. The tensile strengths of these films were much higher than those of some widely used engineering plastics such as polypropylene and poly(vinyl acetate). These films can be easily cut by conventional mechanical methods into a variety of structures like a metallic sheet. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1027–1029, 1998

Key words: metallic plastic sheet; electrosynthesis; thiophene; stainless steel

INTRODUCTION

Much work has already been devoted to the synthesis of conducting polymers, such as polythiophene (Pth), polypyrrole, and polyaniline.^{1–3} The high electrical conductivity of these materials provides potential applications in fabricating many kinds of microelectrical devices.^{4–7} Usually, thin films of the conducting polymer are obtained by electrochemical synthesis,⁸ and powders are obtained by chemical oxidative polymerization.⁹ However, as we know, the conducting polymer film with a thickness of hundreds of micrometers has never been obtained.

Recently, we synthesized a thin Pth film with great strength by electrochemical polymerization of thiophene in freshly distilled BF_3 -diethyl ether (BFEE) solution at 1.3 V versus Ag/AgCl with a stainless steel working electrode.¹⁰ This led us to try and study the possibility of preparing thick

conducting film like a metallic sheet from the same system. This article reports experimental results.

EXPERIMENTAL

Materials

BFEE solution (Huangyan Chemical Plant, Shanghai, China) was purified by distillation. Analytical grade thiophene (Tianjing Xiqing Kelong Chemical Plant, China) was distilled twice before use.

Pth Film Preparation

Electrochemical syntheses were performed in a one-compartment cell with the use of an EG&G potentiostat model 273 under computer control. The working and counter electrodes were AISI 304 stainless steel sheets (3 cm × 4 cm) placed 0.5 cm apart. The anodic potentials of 1.4 V were measured versus a Ag/AgCl electrode (AgCl coated on Ag directly in the solution). To provide a more

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Table I Conductivities, Tensile Strengths, and Thicknesses of the Pth Films Obtained by Direct Oxidation of Thiophene at 1.4 V and 25°C in BFEE Solution with Various Monomer Concentrations

No.	Monomer Concentration (M)	Film Thickness (μm)	Tensile Strength (kg cm^{-2})	Conductivity (s cm^{-1})
1	0.03	11	1000	0.26
2	0.03	35	924	0.26
3	0.03	50	542	0.10
4	0.10	50	527	0.50
5	0.10	470	447	

general reference, we examined a ferrocene–ferrocenium redox couple in freshly distilled BFEE, and its half-wave potential [$\frac{1}{2}(E_{p,a} + E_{p,c})$, where a is anodic and c is cathodic] was found at 0.331 V (versus Ag/AgCl). Thus, a correction of 0.069 V ($-0.331 + 0.400$ V) was needed to bring the measured potentials in BFEE originally versus Ag/AgCl to potentials versus the standard hydrogen electrode.¹¹ The electrodes were carefully polished with Al_2O_3 (Presi, 1 μm) before each synthesis. The electrolyte was freshly distilled BFEE solution (no other solvent added) containing 0.03 and 0.1M thiophene, respectively. BFEE may exist in diethyl ether as a polar molecule,¹² $(\text{C}_2\text{H}_5)_3\text{O}^+$, BF_4^- , which furnishes the conducting medium. All solutions were deaerated by bubbling a dry nitrogen stream for 10 min and then maintained at a light overpressure during the experiments. The integrated charge passed during film growth was used to control the thickness of deposited films. Electrochemical syntheses of thick films were performed by an alternate immersion of the electrodes in a new electrolyte solution containing the monomer every 3 h. Pth films were peeled off the electrode surface and washed repeatedly with distilled ethyl ether, and then dried for 24 h at 50°C under vacuum before our characterizations.

Film Property Tests

Film thicknesses were determined with a “Heiderrham” thickness monitor. Tensile strength of the films was carried out by using a electronic drawing machine (WD-1, Changchun) at a stretching rate of 0.5 cm s^{-1} . Scanning electron microscopy pictures were taken out by using an X-560 electron micrographer.

RESULTS AND DISCUSSION

Table I lists a series of experimental condition parameters, conductivities, tensile strengths, and

thicknesses of the Pth films obtained at 1.4 V. According to this table, the Pth films with different thicknesses obtained at various monomer concentrations were semiconductors, and their conductivities were in the order of $10^{-1} \text{ s cm}^{-1}$.

Films described previously were very shiny and metallic. Figure 1 shows the scanning electron micrographs of the thickest Pth film prepared by electrolysis of BFEE solution containing 0.1M thiophene for 30 h. The cross-sectional view (Fig. 1C) of the film revealed that the film has a thickness of $\sim 470 \mu\text{m}$. It is clear that the morphologies of the two sides of the film are different. The side in contact with the electrode (Fig. 1A) was very smooth and compact, and that in contact with the solution (Fig. 1B) of the film was rough and irregular. A thin film prepared in the same medium was smooth and compact in both sides.¹⁰ It should be noted herein that a thick film is also obtainable from the BFEE solution with lower monomer concentration, but it will take a longer time because of the low polymerization rate.

The Pth film with a thickness of 11 μm showed a great tensile strength of $1000 \pm 50 \text{ kg cm}^{-2}$, and it mechanically behaved like aluminum foil. The tensile strength of the films decreased with the increasing of film thickness (as shown in Table I). It is also clear from this table that the mechanical property of Pth film became worse when higher monomer concentration was used for electrolysis. The deposition rate of Pth film on the electrode increased with the increasing of the monomer concentration, which resulted in the formation of loosely accumulated films (as shown in Fig. 1). But, it should be pointed out that even the film with a thickness of $\sim 470 \mu\text{m}$ has a tensile strength as high as $447 \pm 50 \text{ kg cm}^{-2}$. This value was much higher than those of some generally used important engineering plastics, such as poly(vinyl acetate) ($\sim 260 \text{ kg cm}^{-2}$) and polypropylene ($\sim 300 \text{ kg cm}^{-2}$).¹³ Therefore, the thick Pth films can be called “metallic plastic sheet.”

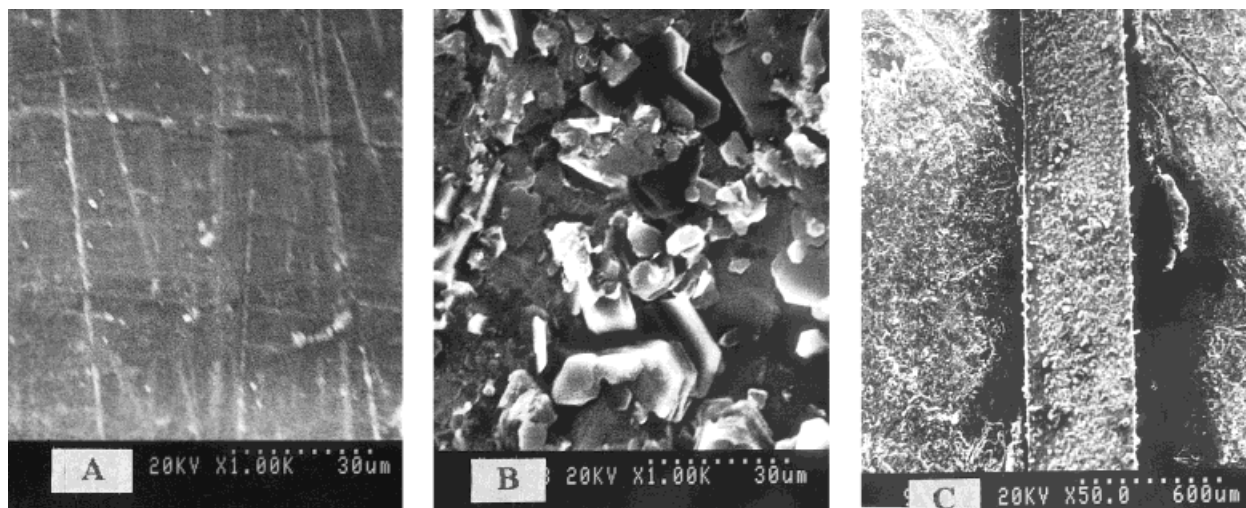


Figure 1 Scanning electron micrographic images of Pth film prepared by electrolysis of BFEE solution containing 0.1M thiophene for 30 h. (A) Side contacted to the electrode. (B) Side exposed to the solution. (C) Cross-sectional view.

CONCLUSIONS

Conducting polymer films hundreds of micrometers thick was first obtained by electrochemical polymerization of thiophene in BFEE solution at stainless steel. It showed high tensile strength and flexibility, and can be easily cut by conventional mechanical methods into a variety of structures like a metallic sheet.

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REFERENCES

1. J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
2. N. Toshima and S. Hara, *Progr. Polym. Sci.*, **20**, 155 (1995).
3. W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal, and E. W. Meijer, *Polymer*, **37**, 5017 (1996).
4. H. Yoneyama, H. Wakomoto, and H. Tamura, *J. Electrochem. Soc.*, **132**, 2414 (1985).
5. E. W. Panl, A. J. Ricco, and M. S. Wrighton, *J. Phys. Chem.*, **89**, 1441 (1985).
6. A. Tsumura, H. Koezuka, S. Tsunoda, and T. Ando, *Chem. Lett.*, 683 (1986).
7. M. Aizawa, T. Yamada, H. Shinohara, K. Akagi, and H. Shirakawa, *J. Chem. Soc., Chem. Commun.*, 1315 (1986).
8. K. Kaneto, Y. Kohno, K. Yoshino, and Y. Inuishi, *J. Chem. Soc., Chem. Commun.*, 382 (1983).
9. T. Yamamoto, K. Sanechika, and A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 9 (1980).
10. G. Shi, S. Jin, G. Xue, and C. Li, *Science*, **267**, 994 (1995).
11. R. R. Gagne, J. L. Allison, R. S. Call, and C. A. Coval, *J. Am. Chem. Soc.*, **99**, 7170 (1977).
12. D. D. Eley, in *Chemistry Cationic Polymerization*, P. H. Plesch, Ed., Macmillan, New York, 1963, p. 393.
13. J. Brandup and E. H. Immergut, Eds., *Polymer Handbook*, John Wiley & Sons, Inc., New York, 1975, pp. V-23, V-51.