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Microstructure-mechanical properties relationship in conducting polypyrrole films

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In this paper, the microstructures of electrochemically synthesized conducting polypyrrole (PPy) films were studied by scanning electron microscopy (SEM). It was found that the polymer film growth condition has strong effects on mechanical properties of the polymer film. The relationship between mechanical properties (such as tensile strength and brittle—tough properties) and the microstructures of PPy films was described for the first time. The effect of electrochemical polymerization condition including temperature and electrolyte composition on the strength and brittle—tough properties was also studied. Films deposited both on the surface of the anode facing the counter electrode and on the back surface were characterized. In order to improve the mechanical properties of PPy films, an optimal condition of electrochemical synthesis of conducting PPy films has been recommended.

1. Introduction

It is well recognized that the novelty of the functions provided by electrochemical synthesis technologies for organic thin films is emphasized as an area in which thin film research and development have a significant impact. Remarkable advances have been made in recent years in the science and technology of thin film formation processes. Up to the present time, thin films have been extensively studied from the viewpoint of the relationship between their microstructure/nanostructures and properties.

On the other hand, the commercial use of thin films has been growing at a surprisingly rapid rate in the last two decades and in almost all the industrial fields such as optics, electronics, mechanics and even biotechnology. These films are practically formed by depositing materials onto a supporting substrate to build up thin film through a complicated thin film process rather than by thinning down bulk materials by simple methods.

Conducting thin films based on polypyrrole (PPy) have been the subject of interest in polymer materials because of their important electro-optical and chemical stability properties and potential as versatile display members and as coatings to protect against oxidation and corrosion and as chemical sensors and biosensors [1]. Among the different strategies to synthesize conducting PPy films reported in the literature, the three-electrode system is an elegant and general approach [2]. As is well known, the physical and mechanical properties of thin films are closely related to their microstructures. For example, the tensile strength of the material is strongly dependent on the microstructure. If the density of the material is high, the strength is high because there are fewer defects in the microstructure. And strictly speaking, the microstructure is related to the electrochemical synthesis of the polymer film. Recently, Wang and coworkers [3, 4] investigated experimentally the mechanical properties of conducting polythiophene films by using an electronic speckle pattern interferometry method and the SEM technique. Significant effects of thickness on the strength and Young's modulus of conducting polythiophene films were found. Similar results from the variation of microstructures including the distribution of defects and residual stress development in a bi-layer coating [5, 6] as well as structure-property relationships were reported [7–10]. Although a doped PPy film in a general synthesis shows good conductivity and stability, their brittleness and other mechanical properties directly cause problems for larger scale industrial applications [11–14]. Therefore, the mechanical properties of the new polymer films have observably affected these films in industrial applications. But there is still a lack of investigation on the relationship between the mechanical properties and microstructures of conducting PPy films.

Recently, PPy films with high conductivity and chemical stability have been synthesized by an electrochemical method [15, 16]. The mechanical properties of the PPy films were experimentally investigated in this paper by using a tensile experimental method and the SEM technique. The relationship between mechanical properties (tensile strength and brittle-tough properties) and the microstructures of PPy films was first described with SEM fracture-sections and free surface

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images. The effect of the electrochemical synthesis process, which varied with the deposited temperatures and solution composition, on the strength and brittle-tough properties was analyzed. In order to improve the mechanical properties of PPy films, this paper recommended the optimal condition of electrochemical synthesis of conducting PPy films.

2. Experimental

2.1. Conducting polypyrrole film preparation processing

The electrochemical polymerization and examinations were performed in a one-compartment cell by the use of a Model 283 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control with a three-electrode system. In preparation of PPy films platinum sheet plate (80 mm × 10 mm) was used as the working electrode which was placed 5mm apart from the counter electrode, stainless steel plate (100 mm × 20 mm). During polymerization PPy films were deposited on both sides of the anode. It is found that the properties of the film on the anode surface facing the counter electrode (film A) are quite different from those on the back surface of the anode (film B), which will be discussed later. All potentials were referred to a saturated calomel electrode (SCE).

The typical electrolytic solutions were mixtures of isopropyl alcohol (IPA), which was made by Tianjin No. 1 Chemical Regent Plant, China, boron trifluoride diethyl etherate (BFEE), (Beijing Changyang Chemical Plant, China), diethylene glycol (DEG) or poly(ethylene glycol) (PEG), (PGE, MW = 400 or 1000, Beijing Yili Fine Chemical Corporation Ltd.). All solutions were deaerated by a dry nitrogen stream for 10 minutes before the experiment and a slight nitrogen over-pressure was maintained during the experiment. The polymerization of pyrrole was performed at ice bath temperature of 0°C except when indicated otherwise.

PPy films were grown potentiostatically, and their thicknesses were determined by plastic film thickness gauge (CH-1-ST, Shanghai Liuling Instrumental Plant). After polymerization, PPy films were washed repeatedly with acetone to remove the electrolyte and monomer and then were peeled off the electrode surfaces. The density of polymer films was estimated according to the equation:

$$\rho = W/(L \times T \times d) \quad (1)$$

Where ρ, W, L and d are the density (kg/m^3), the mass (kg), length (m), thickness (m) and width (m) of the same PPy film, respectively.

2.2. Measurement of conductivity and mechanical properties of conducting PPy films

After being well washed by acetone, the polymer films were stripped from the electrodes and dried in air at ambient temperature for several days before making measurements. Electrical conductivity of PPy films was determined by using the four-probe method where copper was used as the electode and indium shot paste was used to fix the copper wire on the polymer.

The tensile strength and elongation of PPy film was determined at room temperature using AGS-10kN(G) Autograph (Shimadzu, Japan) at the stretching rate of 0.5 mm/min. The width of the sample of PPy film was 5 mm and the length of sample was about 60 mm. The sample of conducting PPy film was gripped with the flexible tensile grip in order to satisfy the effective breakage of PPy film.

The surface morphology and cross section fracture of PPy films were obtained from SEM (Superscan SS-550 Shimadzu Corporation, Japan).

The results of measured conductivity and mechanical properties of PPy films are shown in Table I. It shows that there is a relation of high conductivity in concordance with high tensile strength. The effect of PPy film thickness on the strength and conductivity of the film is also obvious because the strength of the film decreases with the film thickness increasing from 4 micrometers to 65 micrometers [4].

TABLE I Influence of PEG(DEG) Molecular weight on the properties of PPy films produced in mixed electrolytes

	Electrolyte composition and temperature							
			IPA + 5%BFEE					
	IPA + 5%BFEE		+5%DEG		+5%PEG400		+5%PEG1000	
	0°C	15°C	0°C		0°C		15°C[a]	
Thickness (μm)	46(A) 19(B)	65(A) 22(B)	37.5(A)	15(B)	42(A)	15.5(B)	68(A)	31(B)
Density (kg/m^3)	866.5(A) 1151(B)	739.7(A) 987.8(B)	1533(A)	2061(B)	1464(A)	2100(B)	1472(A)	1685(B)
Conductivity (S/cm)	14(A) 15.6(B)	10(A) 12.4(B)	41.6(A)	64.4(B)	75.4(A)	80(B)	41.2(A)	57.4(B)
Tensile strength (MPa)	11.0(A) 24.5(B)	5.5(A) 8.5(B)	60.3(A)	83.7(B)	62.6(A)	68.3(B)	36.1(A)	51.5(B)
Elongation (%)	1.15(A) 1.68(B)	0.57(A) –	6.38(A)	6.81(B)	4.72(A)	6.30(B)	4.47(A)	5.56(B)

Notes: (A) means the PPy films deposited on the anode surface facing the counter electrode (film A). (B) means deposited simultaneously on the back of the working electrode (film B).

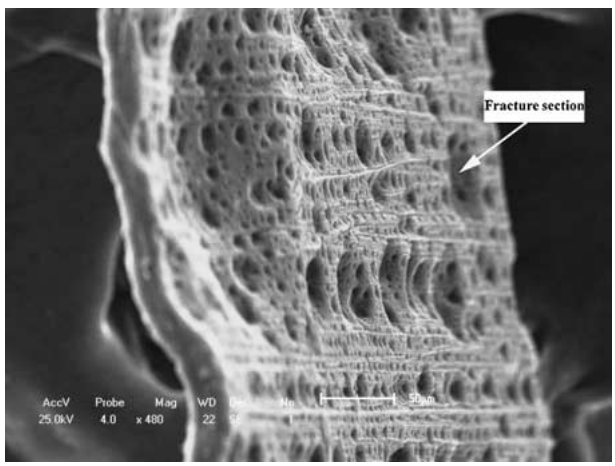
[a]The experiment was performed at 15°C because of the low solubility of PEG1000 in IPA at low temperature.

3. Results and discussion

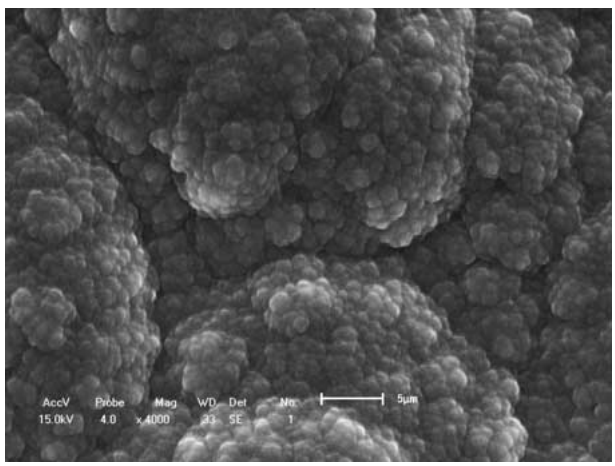
3.1. Effect of the PPy films microstructures on the mechanical properties

In order to describe the effect of the PPy films microstructures on the tensile strength and brittle-tough properties, we used one class BFEE concentration (5%, by value) to analyze the relation and the effect of different temperatures and PEG concentrations on the mechanical properties were discussed.

Fig. 1a and b show the fracture and free surface of thin film, which was prepared in mixed electrolytes of IPA + 5%BFEE in an ice bath at 0°C. When the film thickness is 19 micrometers, their mechanical properties $\sigma_b = 24.5$ MPa (the tensile strength), $\delta = 1.68\%$ (the elongation at break) are better than another in mixed electrolytes of IPA +5%BFEE as shown in Table I. It is observed that there are plentiful honeycomb pattern cavitations in the fracture section (as shown in Fig. 1a), which will lead to decrease in the binding energy and load-carrying ability. This honeycomb pattern microstructure of PPy film produces inferior strength and toughness. We see clearly that the electrochemical synthesized free surface shows a relatively greater polymer agglomeration and formed inferior interdependent adhesion, easily producing structural flaws such as voids, cracks. It is obvious that the microstructure of PPy film is not suitable as a thin film coating on the devices.

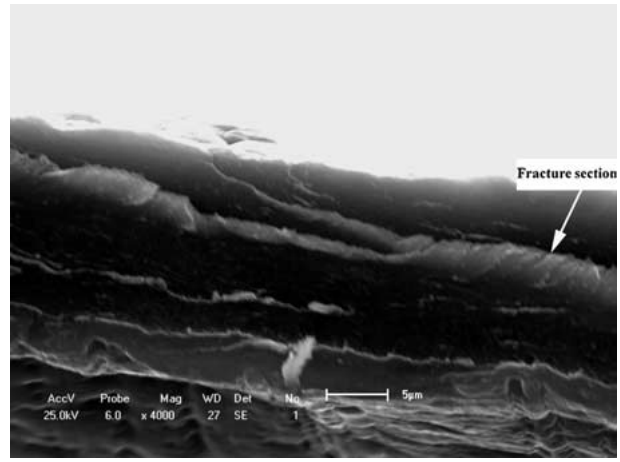


(a)

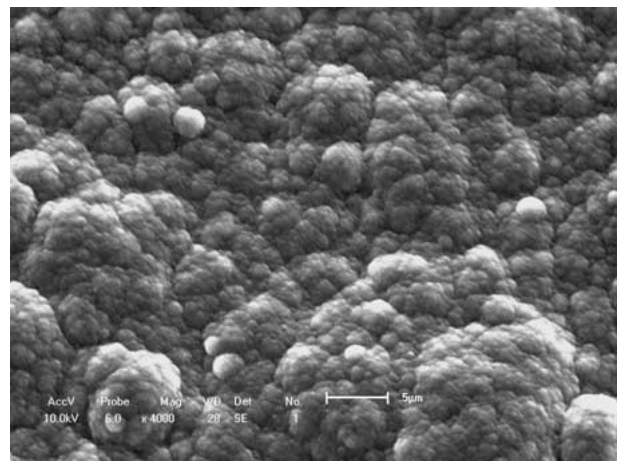


(b)

Figure 1 SEM images of the conducting PPy film grown in IPA + 5%BFEE at 0°C. (a) SEM image of the fracture section, (scale bar-20 μm ?) or 50 μm? (b) SEM image of the free surface.



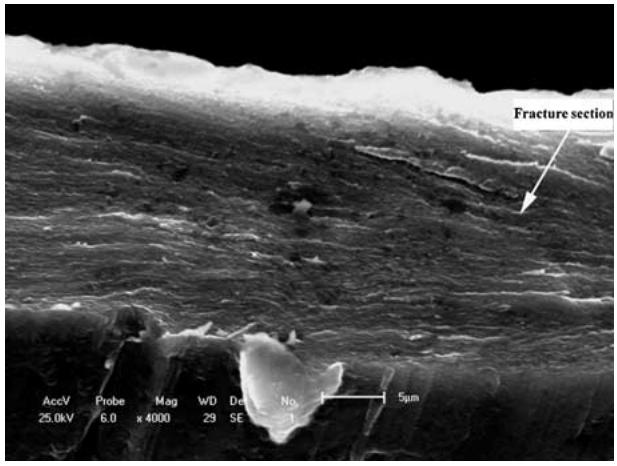
(a)



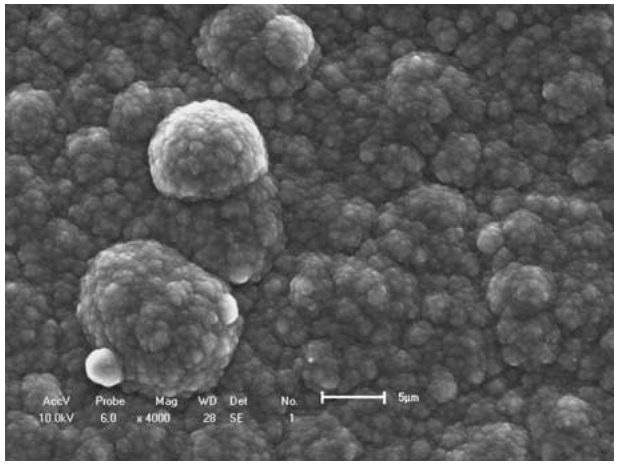
(b)

Figure 2 SEM images of the conducting PPy film B grown in IPA + 5%BFEE + 5%DEG at 0°C. (a) SEM image of the fracture section, (b) SEM image of the free surface.

Fig. 2a and b show the fracture surface and free surface of PPy film (B), which was mixed electrolytes of IPA + 5%BFEE + 5%DEG in an ice bath at 0°C. The thickness of sample (film B) is 15 micrometers. And the good mechanical properties are $\sigma_b = 83.7$ MPa (the tensile strength), $\delta = 6.81\%$ (the elongation) in the film (B), respectively. It is obvious the mechanical properties (tensile strength and toughness) are greatly improved as shown in Fig. 2a. The river like pattern on the PPy film reflects the fact that this microstructure film can be subjected a certain amount of elastic-plastic deformation so that it can withstand the shear stress and this can meet the requirement of the coating film applied in the practical device. And the main mechanical properties (strength and toughness) of this microstructure conducting polymer film nearly reaches that of the same thickness thin aluminum plate. At the same time, the tensile experimental results demonstrated that the addition of the 5%DEG in the mixed electrolytes composition of IPA + 5%BFEE improves the mechanical properties of the PPy film. In addition, the uniformity of material domain on the free surface is better than that shown in Fig. 1b because there are more smaller and uniform grains of microstructure. Accompanying with

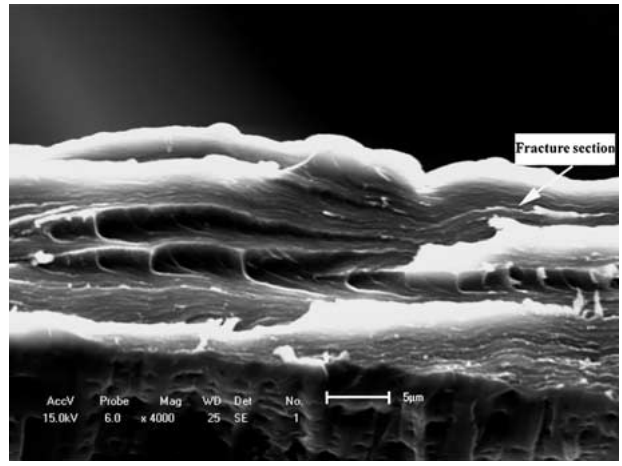


(a)

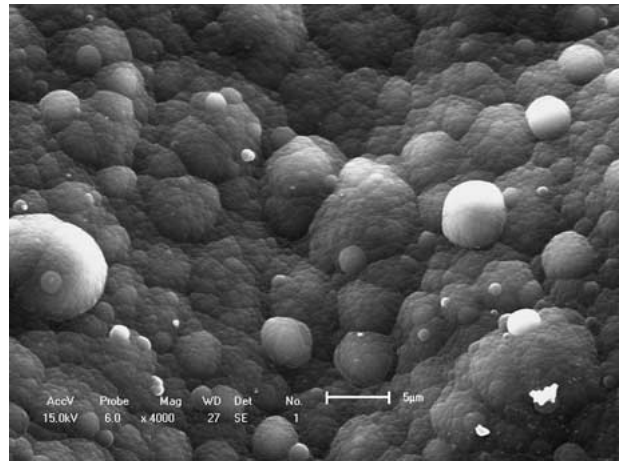


(b)

Figure 3 SEM images of the conducting PPy film A grown in IPA + 5%BFEE + 5%DEG at 0°C. (a) SEM image of the fracture section, (b) SEM image of the free surface.



(a)



(b)

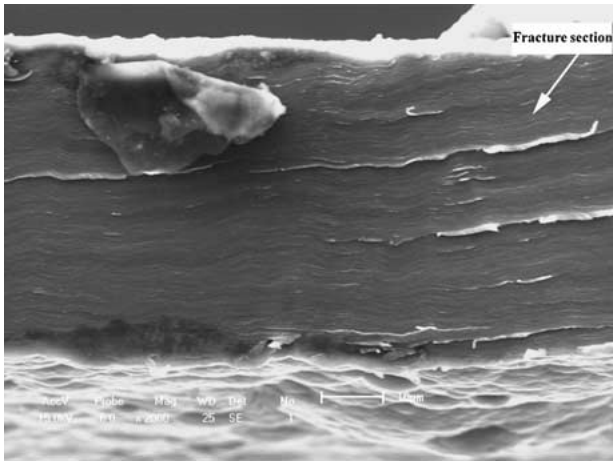
Figure 4 SEM images of the conducting PPy film B grown in IPA + 5%BFEE + 5%PEG1000 at 0°C. (a) SEM image of the fracture section, (b) SEM image of the free surface.

the improvement of the film uniformity, the mechanical properties and conductivity of the film can be greatly improved as shown in Table I.

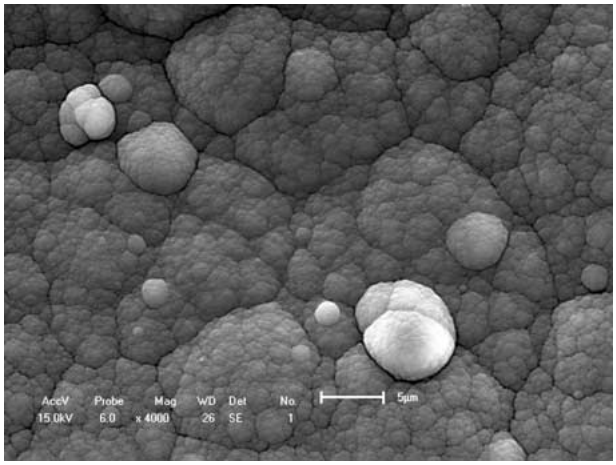
Fig. 3a and b show the free surface and fracture surface of PPy film (A), in the mixed electrolytes of IPA + 5%BFEE + 5%DEG at 0°C; the synthesis method is the same as that of PPy film (B) in Fig. 2. The differences between the film (A) and film (B) are the different separations from the counter electrode and the difference of positive (face) and negative (back) surface of the anode. The thickness of sample is 37.5 micrometers (film A) and 15 micrometers (film B), respectively. And the mechanical properties are $\sigma_b = 60.3$ MPa (the tensile strength), $\delta = 6.38\%$ (the elongation) in the film (A), respectively. The main reason may be related to the difference of film growth rate. Owing to the difference of film growth rate, the mechanical properties are somewhat affected. Especially, the toughness and brittle properties vary with the change of the film growth rate. This is obvious compared with the Figs 2a and 3a. There is almost no difference between the free surfaces of the film (B) and film (A) as shown in Figs 2b and 3b. The final free surface microstructure is not affected for the above mentioned reason.

In order to obtain the excellent mechanical properties, we changed the PEG molar mass and temperature parameters to obtain the new PPy films, for which the fracture and free surface SEM images are shown in Figs 4 and 5.

Fig. 4a and b show the free surface and fracture surface of PPy film (B) in the mixed electrolytes of IPA + 5%BFEE + 5%PEG1000 at 15°C. The experiment was performed at 15°C because of the low solubility of PEG1000 in IPA at low temperature. The thickness of the sample is 31 micrometers (film B), which is less than that of film (A). And the mechanical properties are $\sigma_b = 51.5$ MPa (the tensile strength), $\delta = 5.56\%$ (the elongation) in the film (B), respectively, which is better than that in film (A). There is an apparent change of mechanical properties of PPy film, which is analogous to that of the conducting film prepared from the electrolyte with a mixed electrolyte composition of IPA + 5%BFEE + 5%DEG at 0°C. The mechanical properties of the film synthesized in the medium of IPA + 5%BFEE + 5%PEG1000 at 15°C are observed to be the inferior to those obtained from mixed electrolytes of IPA + 5%BFEE + 5%DEG at 0°C. The fracture surfaces show that the efficient area withstood the shear stress despite having the river patterns similar to the result in Fig. 2a. The mechanical properties of PPy film depend strongly on the PEG molar mass, and the tensile strength and toughness of the PPy film decreases



(a)



(b)

Figure 5 SEM images of the conducting PPy film A grown in IPA + 5%BFEE + 5%PEG1000 at 0°C. (a) SEM image of the fracture section (scale bar - ? μm), (b) SEM image of the free surface.

with increasing the PEG molar mass and temperature. The mechanical properties of the PPy film also depend on the film growth rate, the tensile strength and toughness of PPy film increase when the film grows slowly.

Fig. 5a and b show the fracture and free surface of PPy film (A) synthesized in the electrolyte of IPA + 5%BFEE + 5%PEG1000 at 15°C. The results shown in Figs 4 and 5 are similar to those in of Figs 2 and 3. But there are differences of the microstructure on the free surface under the two electrochemical synthesis processes. When the PEG weight in the mixed electrolyte and temperature increase, the agglomerating microstructure on surface of PPy film seems more pellets because of the homogeneous nucleation. The surface cohesive force of this microstructure may be weaker than that of cap-shaped aggregates formed by capillarity or island microstructure formed by three-dimensional nucleation.

Fig. 6 shows the SEM images of PPy film in contact with the substrate surface. The striations on the film surface reflect the metallic substrate machining patterns. This microstructure has no effect on the mechanical properties of the conducting polymer film. Therefore, this result means the electrochemical synthesized deposition mechanism of the conducting polymer film may be the same in the initial stages. The deposition mechanism mainly depends on the substrate material and the three-electrode system such as a voltage parameter, etc. It shows that the above mentioned mechanical properties varied with the electrochemical synthesis procedure, as indicated in Table I.

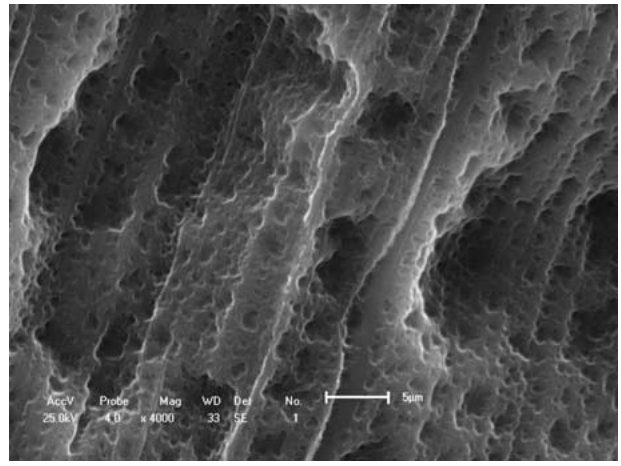


Figure 6 SEM image of the conducting PPy film surface in contacted with the substrate.

4. Conclusions

In this study, various attempts have been made to elaborate conducting PPy film electrochemical synthesis to provide good conductivity and mechanical properties. Our work focused on the analysis of the relationship between the microstructure of conducting PPy film and mechanical properties (tensile strength and toughness parameters) using the SEM fracture and free surfaces images. The effects of the mixed electrolytes of IPA + 5%BFEE + 5%PEG (DEG) on the mechanical properties were discussed with the experimental technology. Through these analyses and discussions, the conclusions are as follows:

(1) Compared with the mixed electrolyte composition of IPA + 5%BFEE + 5%PEG (DEG), the better mechanical properties of conducting PPy films were given by the mixed electrolyte composition of IPA + 5%BFEE + 5%DEG.

(2) The mechanical properties of the conducting PPy films on the anode front and back surfaces (film A and film B) (front-facing the counter electrode) have significant differences. The mechanical properties and conductivity of film (B) is better than that of film (A) because the growth rate in film (A) is faster than that in film (B).

(3) The conducting films on the anode front and back surface mainly lead to the fracture differences in the brittleness-toughness.

(4) The fracture analyses of the conducting PPy film with SEM shows the relationship between the microstructure of PPy film and their mechanical properties. The river patterns and cap-shaped aggregation structure formed by capillarity or island microstructure formed by three-dimensional nucleation mean excellent mechanical properties (tensile strength and toughness) are obtained.

We are currently investigating in more detail the effect of the electrochemical synthesis process on the mechanical properties/behavior. These results will be reported later.

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