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The processing and mechanical properties of polypyrrole/polyurethane alloy films

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Polymeric composites of polypyrrole/polyurethane (PPy/PU) were prepared by electrochemical polymerization. The resulting films had conductivities ranging from 10^{-4} to $1\,\mathrm{S\,cm^{-1}}$, and showed significant improvement in their mechanical properties. By varying the conditions of polymerization, a range of mechanical, as well as electrical, properties could be obtained.

1. Introduction

A variety of aromatic polymers can be prepared through electrochemical oxidation. Basically, the polymerization involves the substitution of hydrogen atoms in the monomer to form a fully conjugated aromatic polymer [1]. Doping by electrolytic anions occurs simultaneously during the reaction, thus resulting in highly conductive polymers. Among these polymers, PPy has very impressive characteristics. Under properly selected polymerizing conditions, its conductivity may exceed $500\,\mathrm{S\,cm^{-1}}$ [2]. It also has good stability in air [3, 4]. PPy can be made in the form of free-standing film. However, it is brittle ($\sigma = 46.3\,\mathrm{MPa}$, $\varepsilon = 2\% \sim 3\%$, $E = 862\,\mathrm{MPa}$) [5, 6] and it takes a considerably longer polymerization time to attain a practical thickness. These shortcomings limit its applicability. As a result, PPy films must be modified in order to improve their applicability.

There are various means of modification. Among these, polymerization with other polymers is the most widely used. Polymers such as PVC [7, 8], PVA [9, 10], P(VDF–TrFE) [11], Br-PVK [12], NBR [13], P(EVA–VC) [14] and polyether/polyester [15] or PU [16] were used as the host polymer matrix, which was spread on the anode, and then the electrochemical polymerizing reaction was performed in a solution of the pyrrole monomer with an appropriate electrolyte. With a proper electrolyte solution, pyrrole monomer and dopant anions can diffuse in this host polymer matrix and yield a conductive alloy film. The resulting polymer composite has stronger mechanical properties due to the polymer matrix, but has lost some of the conductivity of PPy. In this work, such a conductive composite was prepared by the electrochemical polymerization of PPy with PU as the host polymer matrix.

The objective of this research was to investigate the relationship between the mechanical properties of PPy/PU composite films and the polymerization conditions: polymerization time, monomer concentration, electrolyte concentration, solvent concentration, and current density.

2. Experimental details

The details of the electrochemical polymerization used were as follows: Pt-plated titanium meshes were used as a counter electrode (cathode), and PU (Lidyetex 904, Lidye Chemical Co., Ltd.) was spread by casting on an indium-tin oxide (ITO) coated glass substrate to form a film about $20\,\mu\mathrm{m}$ thick. Thus was dried in an oven for 30 min. After cooling, it was swollen by immersing for 3 min in an acetonitrile/N,N-dimethylformamide (MeCN/DMF) solution containing 03 M pyrrole and 0.023 M p-toluenesulphonic acid monohydrate (PTSA). Then a constant DC current was applied. During the polymerization, a PPy/PU alloy film formed on the ITO coated glass substrate (anode) and the colour changed from colourless to brown or dark black. After the reaction was complete, the anode was taken out and rinsed with acetonitrile and then vacuum-dried at room temperature for 3 h. Finally, the alloy film was carefully peeled off from the ITO coated glass.

The surface conductivity of the alloy film was measured using the 4-point probe method. Its mechanical properties were tested using a tensile tester (Tensilon UTM-3-500, Toyo Baldwin Co., Ltd.). The specimen was 5 mm wide and the grip to grip distance was 20 mm. The crosshead speed was $4\,\mathrm{mm\,min^{-1}}$. The thickness of the film was measured with a micrometer (SM-1201, Teclock Co.).

3. Results and discussion

The results showed that the conductivity of the polymerized PPy/PU was about 10^{-4} to $1\,\mathrm{S\,cm^{-1}}$ at room temperature. Although it was lower than that of pure PPy, such a polymer was still an ideal material for semiconductive film. The mechanical properties did show improvement. Figure 1 shows a comparison of

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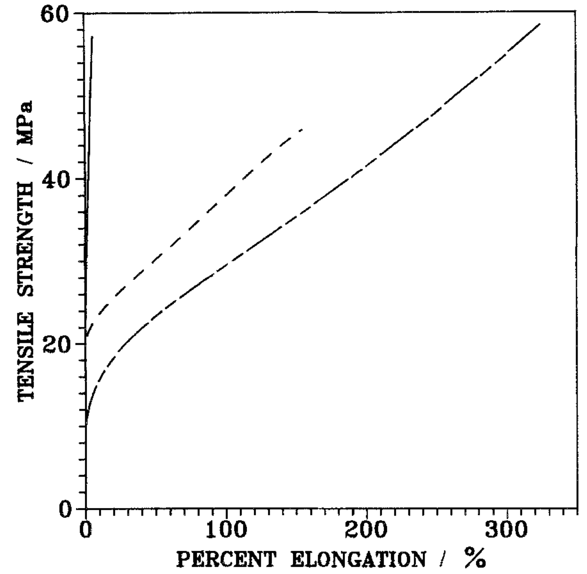

Fig. 1. Stress–strain curves for pure PPy film electro-polymerized for 48 C cm^{-2} (solid line); pure PU film (long dash); and PPy/PU alloy film electro-polymerized for 6 C cm^{-2} (short dash). (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMP/MeCN: 1/4, PU film thickness: about 20 μm.)

the stress–strain (S–S) curves of PPy/PU alloy film, pure PU and pure PPy. The calculated break strength, break elongation and modulus are listed in Table I. Pure PPy is a hard and brittle material with high modulus, low break elongation and no yield stress. On the other hand, PU is a tough material with low modulus, high break elongation and a yield stress of 18 MPa. The S–S curve of the PPy/PU alloy film was located in the region enclosed by the S–S curves of PU and PPy and it showed a yield stress of 22 MPa. Because the addition of PPy induced more microstructural defects into the PU matrix, the break strength of the alloy film was lower than that of both pure PU and PPy.

3.1. *The influence of polymerization time*

Under constant current density, the voltage declined as the time elapsed. The change of voltage was sharp at the beginning and then gradually leveled off, as shown in Fig. 2. This phenomenon was even more pronounced when the electrode had not been preimmersed for 3 min in the electrolyte solution. In other words, the PU-coated electrode without preimmersion had a higher initial voltage, and the change of voltage was sharper. This was related to the solvent-swelling of the PU matrix. At the beginning of polymerization, the rate of diffusion of pyrrole and the PTSA anions through the PU film was behind the rate of polymerization, thus the voltage was higher. As time elapsed, the swelling of the PU film by the solvent lowered the resistance to diffusion and the formation of PPy shortened the diffusion distance of pyrrole and the PTSA anions. Thus the voltage was lowered.

*Table 1. Results of the stress–strain measurements made on the conductive composites**

Material	σ_b/MPa	ε	E/MPa	$\sigma/S\,cm^{-1}$
PU	58.5	3.30	316	–
PPy	56.7	0.06	1372	10
PPy/PU	45.5	1.55	568	0.32†

* σ_b: tensile strength, ε_b: elongation at break, E: modulus at 4% ε, σ: electrical conductivity, and $\varepsilon = (L - L_0)/L_0$. The electropolymerization conditions were 20 mA cm^{-2}, DMF/MeCN = 1/4, and 6 C cm^{-2}.

† Conductive only on the side originally adjacent the ITO electrode.

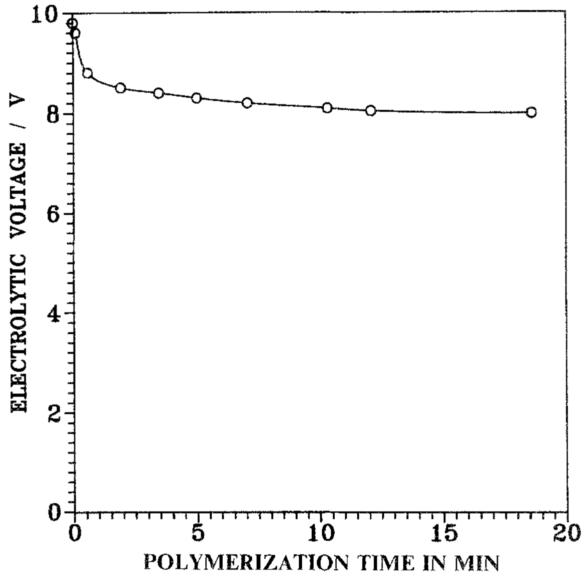

Fig. 2. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of the polymerization time. (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMP/MeCN: 1/4, PU film thickness: about 20 μm.)

Figure 3 shows that during polymerization, as the charge density or the concentration of PPy increased, the modulus of the alloy film increased, while its break strength and the break elongation decreased. In other words, it approached the characteristics of pure PPy. In contrast, as the charge density decreased, the

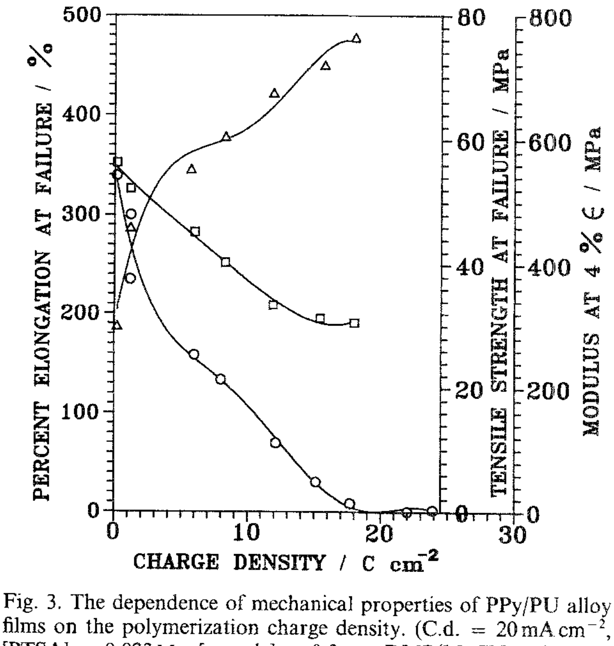

Fig. 3. The dependence of mechanical properties of PPy/PU alloy films on the polymerization charge density. (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMP/MeCN: 1/4, PU film thickness: about 20 μm.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

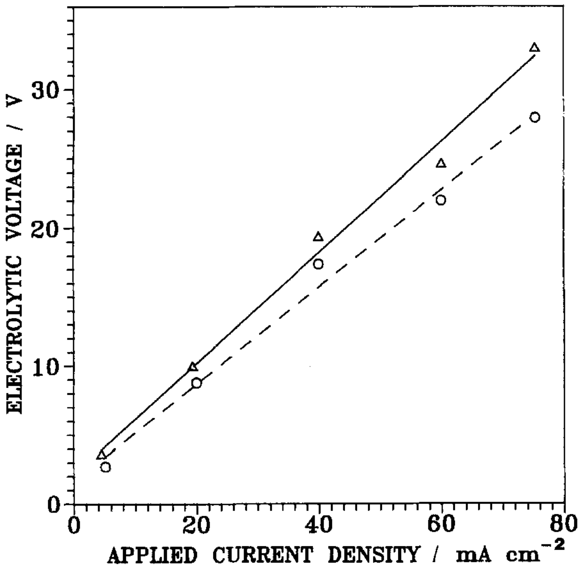

Fig. 4. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of applied current density. ([PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMF/MeCN: 1/4, PU film thickness: about 20 μm.) (○) At the beginning of the polymerization, and (△) at 6 C cm^{-2}.

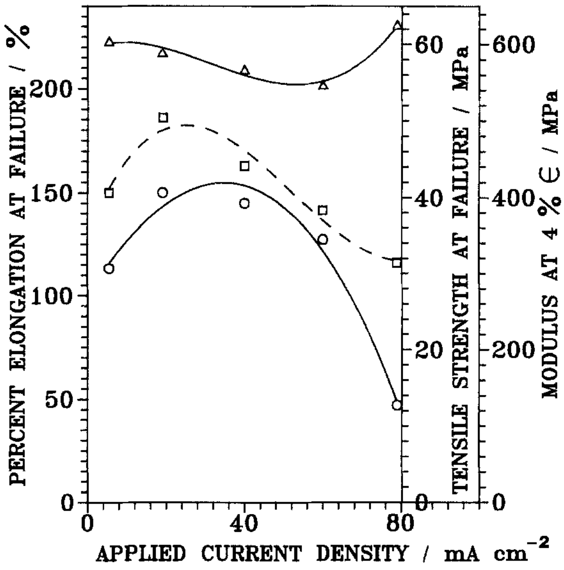

Fig. 5. The dependent of the mechanical properties of PPy/PU alloy films on the polymerization current density. (Charge density: 6 C cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMF/MeCN: 1/4, PU film thickness: about 20 μm.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

modulus decreased while the break strength and the break elongation increased: it became more like pure PU. Again, the break strength and the break elongation of the alloy film were lower than those of pure PU or PPy. This was probably because more defects were induced in the alloy film by the electrochemical-polymerization which introduced PPy to the PU film.

3.2. *The influence of current density*

As shown in Fig. 4, curve A and curve B represent the relationship between the current density and voltage at the beginning of polymerization and at 6 C cm^{-2}, respectively. Both followed a linear ohmic relationship. At a lower current density, the difference between initial voltage and voltage at 6 C cm^{-2} was less than that at a higher current density. This was related to the ratio of the diffusion rate to the polymerization rate, written as R. During polymerization under constant current density, when the current density was low (R was large), the change in the voltage was small; while when the current density was high (R was small), the change in the voltage was much more drastic.

The stacking pattern of PPy in the PU film was also affected by the current density. As shown in Fig. 5, when the current density was increased, the break strength and the break elongation of the alloy film first increased and then decreased, while the modulus decreased and then increased. This was probably due to the current efficiency and the ratio R in the electrochemical polymerization. At a lower current density, the current efficiency of polymerization was higher and more PPy was produced, thus resulting in a higher modulus and lower break strength and break elongation. At a higher current density, R was smaller and the stacking pattern of PPy had higher modulus, but more defects were induced by the uneven stacking, hence lowering the break strength and the break elongation. In the intermediate range of current density there was a minimum for the modulus and a maximum for both the break strength and the break elongation.

3.3. *The effect of electrolyte concentration*

In Fig. 6, curve A and curve B show the relationship between the polymerization voltage and the electrolyte concentration at the beginning of polymerization and at a constant current density of 6 C cm^{-2}, respectively. At higher electrolyte concentration, the polymerization voltage was lowered by the increase in

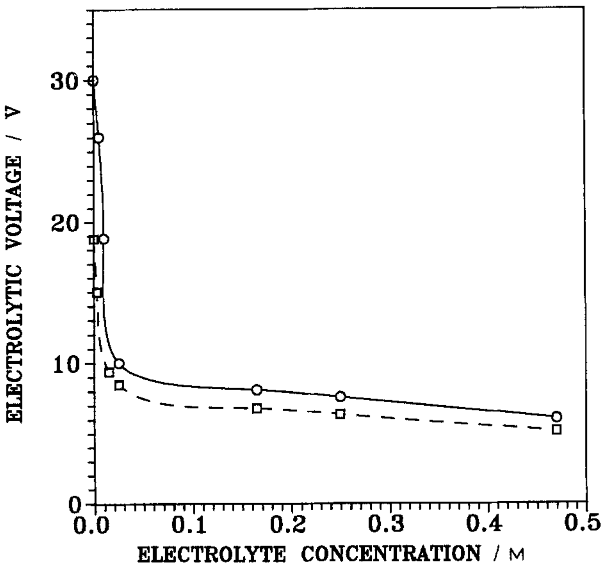

Fig. 6. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of the electrolyte concentration. (C.d. = 20 mA cm^{-2}, [pyrrole] = 0.3 M, DMP/MeCN: 1/4, PU film thickness: about 20 μm.) (○) At the beginning of the polymerization, and (□) at 6 C cm^{-2}.

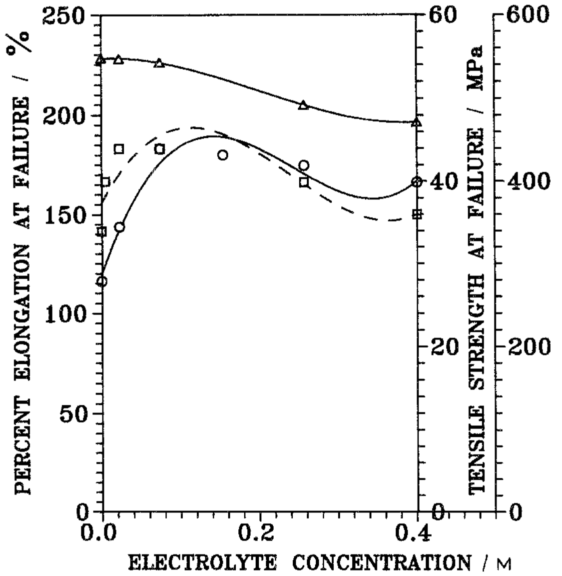

Fig. 7. Mechanical properties of PPy/PU alloy films as a function of the electrolyte concentration. (Charge density: 6 C cm^{-2}, C.d. = 20 mA cm^{-2}, [pyrrole] = 0.3 M, DMF/MeCN: 1/4, PU film thickness: about 20 μm.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

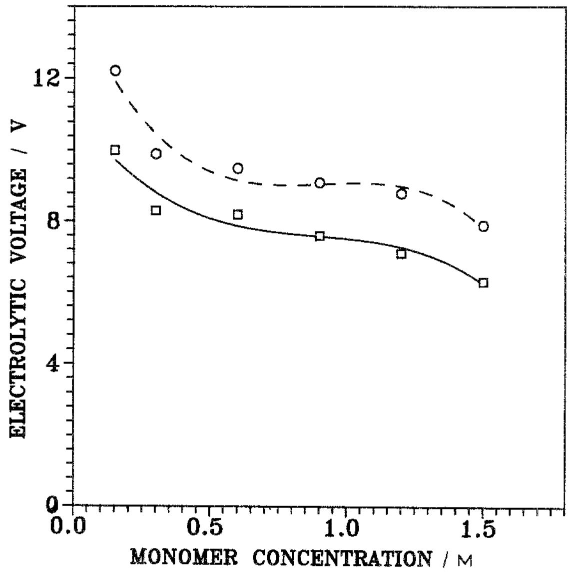

Fig. 9. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of the monomer concentration. (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, DMF/MeCN: 1/4, PU film thickness: about 20 μm.) (○) At the beginning of the polymerization, and (□) at 6 C cm^{-2}.

the conductivity of the solution. The voltage difference between curve A and curve B diminished as the electrolyte concentration increased. This was related to the ratio *R*. When *R* was large (higher electrolyte concentration), the voltage and the voltage variation were small; while when *R* was small (lower electrolyte concentration), the voltage and the voltage variation were much more significant.

The dopant content in the PPy stacking also increased with the electrolyte concentration in the solution. The dopant content affected the microstructure of the alloy film and hence the mechanical properties of the film. As shown in Fig. 7, the modulus of the alloy film decreased as the electrolyte concentration increased. This was also related to *R*. When *R* was larger, the modulus of the alloy film was smaller; when *R* was smaller, the modulus was larger. In addition, with the increase of the electrolyte concentration, the break strength and the break elongation first increased and then decreased slightly. At lower electrolyte concentration, smaller *R* created more defects in the alloy film, so the break strength and the break elongation were weaker. At higher electrolyte concentration, the increase of dopant in the alloy film also created more defects in the alloy film, so the break strength and the break elongation decreased. Consequently, there was a maximum for both the break strength and the break elongation.

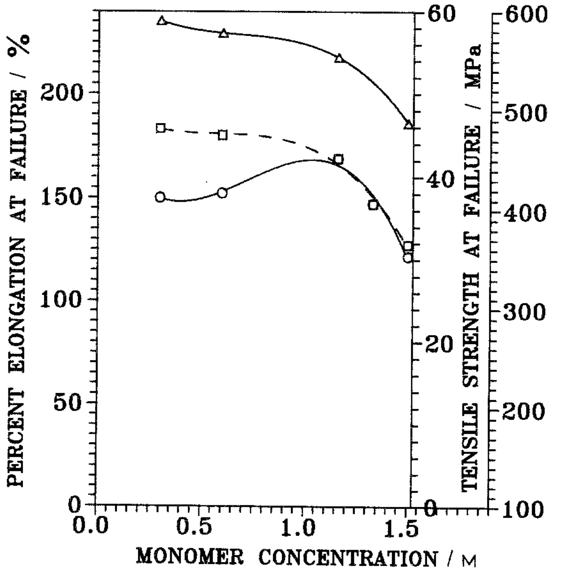

Fig. 8. Mechanical properties of PPy/PUP alloy films as a function of the monomer concentration. (Charge density = 6 C cm^{-2}, c.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, DMF/MeCN: 1/4, PU film thickness: about 20 μm.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

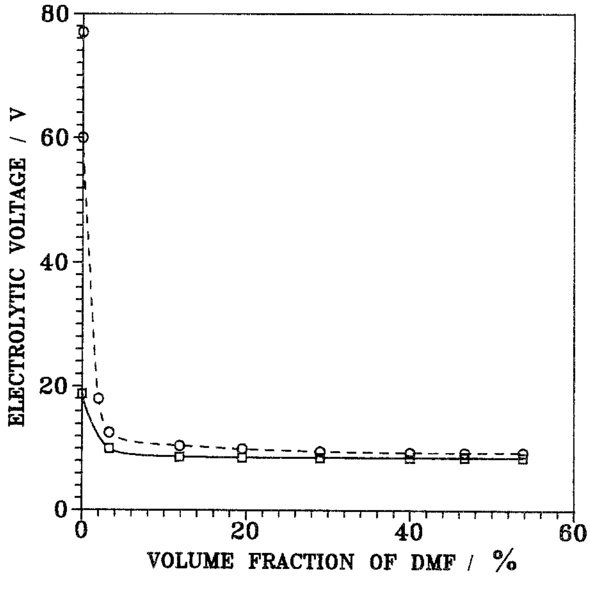

Fig. 10. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of the percent volume fraction of DMF. (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, PU film thickness: about 20 μm.) (○) At the beginning of the polymerization, and (□) at 6 C cm^{-2}.

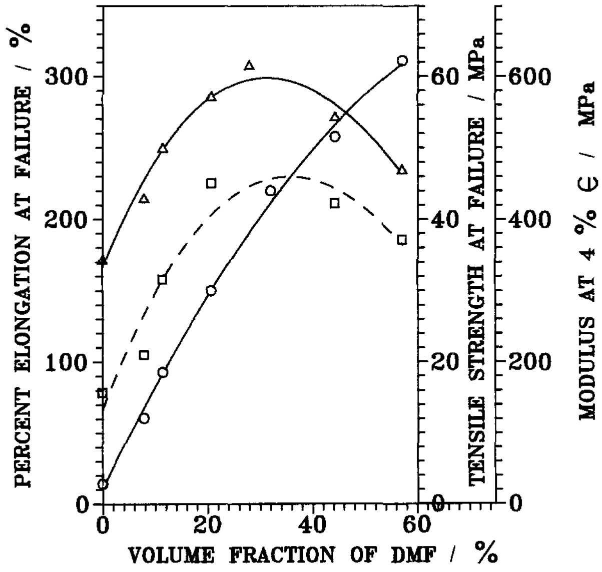

Fig. 11. Mechanical properties of PPy/PU alloy films as a function of the percent volume fraction of DMF. (Charge density = 6 C cm^{-2}, c.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, PU film thickness: about 20 μm.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

3.4. *The effect of monomer concentration*

In Fig. 8, curve A and curve B illustrate the relationship between the polymerization voltage and the concentration of pyrrole at the beginning of polymerization and at 6 C cm^{-2}, respectively. As the monomer concentration increased, the increase in the diffusion rate of the monomer lowered the polymerization voltage. This was also related to *R*. When *R* was larger (higher monomer concentration), the polymerization voltage was lower; when *R* was smaller (lower monomer concentration), the polymerization voltage was higher.

The increase of the monomer concentration slightly accelerated the production rate of PPy in the alloy film. Therefore the change in the monomer concentration could influence the mechanical properties of the film. Figure 9 shows that the modulus of the alloy film decreased as the concentration of monomer (pyrrole) increased. Once again, this is related to *R*. When *R* was larger (higher monomer concentration), the alloy film had a lower modulus; when *R* was smaller, the modulus was larger. In addition, as the monomer concentration increased, the break elongation first increased and then decreased. At lower monomer concentration, smaller *R* created more defects in the alloy film and thus yielded a lower elongation. At higher monomer concentration, the efficiency of the electrochemical polymerization was

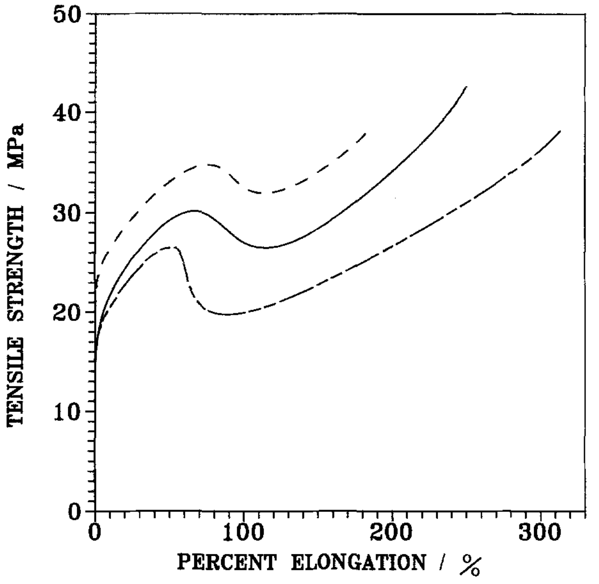

Fig. 13. Stress–strain curves for PPy/PU alloy films prepared at various solvent compositions: the percent volume fraction of DMF was (----) 28, (——) 44, (- - -) 56. (Charge density = 6 C cm^{-2}, c.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, PU film thickness: about 20 μm.)

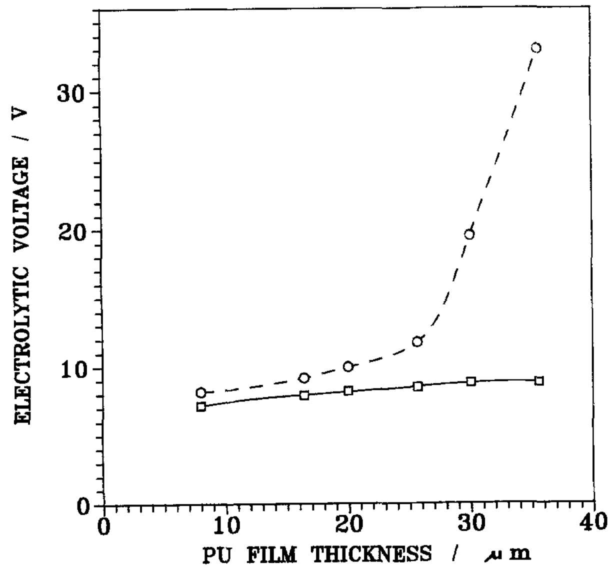

Fig. 12. Electric voltage in the polymerization of pyrrole on a PU-coated electrode as a function of the PU film thickness. (C.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMF/MeCN: 1/4.) (○) At the beginning of the polymerization, and (□) at 6 C cm^{-2}.

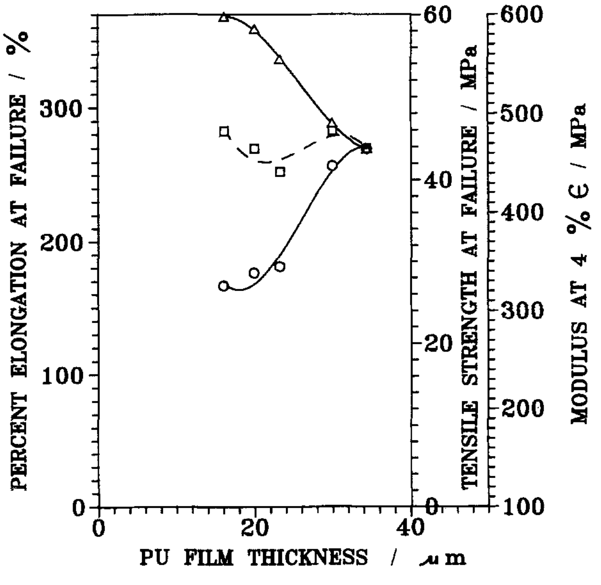

Fig. 14. Mechanical properties of PPy/PU alloy films as a function of the PU film thickness. (Charge density = 6 C cm^{-2}, c.d. = 20 mA cm^{-2}, [PTSA] = 0.023 M, [pyrrole] = 0.3 M, DMF/MeCN: 1/4.) (○) Percent elongation at failure, (□) tensile strength at failure, and (△) modulus at 4% ε.

Table 2. Relationship between the polymerization conditions and the mechanical properties of the PPy/PU alloy films obtained.*

Polymerization condition	*Increasing or decreasing*	*Electrolytic voltage*	*R*	*E*	ε_b	σ_b
Current density	⇑	⇑	⇓	⇑	⇓	⇓
	⇓	⇓	⇑	⇑	⇓	⇓
Pyrrole concentration	⇑	⇓	⇑	⇓	⇓	⇓
	⇓	⇑	⇓	⇑	⇓	↑[†]
PTSA concentration	⇑	⇓	⇑	⇓	↓	↓
	⇓	⇑	⇓	⇑	⇓	⇓
DMF concentration	⇑	⇓	⇑	⇓	⇑	↓
	⇓	⇑	⇓	⇓	⇓	⇓
PU thickness	⇑	⇑	⇓	⇓	⇑	↓
	⇓	⇓	⇑	⇑	⇓	↑

* σ_b: tensile strength, ε_b: elongation at break, *E*: modulus at 4% ε, *R*: the ratio of the diffusion rates of pyrrole and the PTSA anion to the polymerization rate.

[†] Symbols ⇑, ↑, ⇓, and ↓ represent increasing, slightly increasing, decreasing, slightly decreasing, respectively.

higher, and thus the content of PPy in the alloy film was increased. This induced more defects in the alloy film, hence the break elongation was decreased. Consequently, there was a maximum. Furthermore, the break strength decreased with increase in the monomer concentration. In summary, the increase of *R* reinforced the break strength, but the increase of the pyrrole concentration increased the content of PPy in the alloy film and thus reduced the break strength.

3.5. *The effect of solvent concentration*

In Fig. 10, curve A and curve B depict the relationship between the polymerization voltage and the composition of DMF/MeCN (the solvent) at the beginning of polymerization and at $6\,\mathrm{C\,cm^{-2}}$, respectively. At higher DMF concentration, the PU matrix swelled more quickly. A PU matrix with a higher degree of swelling may facilitate the diffusion of monomer and electrolyte, thus the polymerization voltage may be lowered. Furthermore, the voltage difference between curve A and curve B narrowed with increase of DMF concentration. This again was related to *R*. When *R* was larger (higher DMF concentration), the voltage and the change in voltage were small. When *R* was smaller (lower DMF concentration), the voltage was higher and the change in voltage was more significant.

Because PU has different degrees of swelling in different solvents, a change in the composition of the solvent used in the electrochemical polymerization affects the microstructure of the alloy film and so the mechanical properties. As shown in Fig. 11, with increase in the concentration of DMF, the modulus of the alloy film first increased and then decreased. This was probably also related to *R*. A smaller *R* (lower concentration of DMF) augmented the modulus, but if *R* was too small, the degree of swelling of the matrix was too low, so the diffusion of monomer and electrolyte was hindered. As a result, the alloy film had a lower modulus. In contrast, when *R* was larger, the diffusion was easy, thus making the modulus lower. Therefore, a larger *R* reduced the modulus, a smaller *R* augmented the modulus, and an extremely small *R* reduced the modulus again.

In addition, the break elongation increased with the concentration of DMF. At lower DMF concentration, the diffusion was difficult, which induced more defects in the alloy film and hence reduced the break elongation. On the other hand, at higher DMF concentration, the PU matrix swelled quickly, which made the diffusion of pyrrole and electrolyte easier. Hence, the alloy film had fewer defects, making the break elongation higher. Furthermore, the break strength also was related to the degree of swelling of the PU matrix. When the concentration of DMF increased, the break strength first increased and then decreased slightly. But at high DMF concentration, the S–S curve of the alloy film had a yield stress as well as a yield point (as shown in Fig. 12). As the concentration of DMF increased, the yield point moved towards lower elongation. This suggested that as the concentration of DMF increased, the molecular chains of PPy in the alloy film might break more simultaneously and have a lower elongation. If the PU matrix had a higher degree of swelling, the mechanical performance of the alloy film would be closer to that of pure PPy.

3.6. *The influence of the thickness of the PU matrix*

As shown in Fig. 13, curve A and curve B represent the relationship between the polymerization voltage and the thickness of the PU matrix at the beginning of polymerization and at $6\,\mathrm{C\,cm^{-2}}$, respectively. As the thickness increased, the diffusion rates of the monomer and the electrolyte decreased; thus the polymerization voltage increased. The voltage difference between curve A and curve B also increased with the thickness. This can be related to *R*. When *R* was larger (thinner PU matrix), the voltage and the change in voltage were smaller. In addition, the change in curve A was more noticeable, while curve B changed little and remained almost a horizontal line. It seemed that the 3 min pre-immersion before the electrochemical polymerization in this research was not enough to form a stable polymerization voltage. Therefore the pre-immersion time must be extended so as to produce a PU matrix fully swollen with solvent, thus resulting in an even alloy film and a stable voltage.

The thickness of the PU matrix influences the diffusion rate of the monomer and PTSA electrolyte through the matrix. Alloy films with different microstructures and mechanical properties can be obtained by changing the thickness of the matrix. As shown in Fig. 14, when the thickness increased, the modulus decreased and the elongation increased. For larger *R*, the fewer defects in the alloy film might yield a higher elongation and a smaller modulus, yet this factor was outweighed by the increase of the content of PPy in the alloy film, resulting in a lower elongation and a larger modulus. In contrast, a smaller *R* might lead to a lower elongation and a larger modulus, yet it was outweighed by the thicker PU matrix and lower concentration of PPy, thus the elongation increased and the modulus decreased. Therefore, the thickness of the PU matrix was the dominating factor. In addition, the break strength changed little withn this range. This probably was also related to *R*. For small *R*, the larger number of defects decreased the break strength; for large *R*, the fewer defects increased the break strength.

4. Conclusion

The conclusions are as follows:

1. The polymerization conditions and the thickness of the PU matrix can affect both the rate of polymerization and the balance between the polymerization rate and the diffusion rates of pyrrole and the PTSA anions through the matrix. All these factors influence the microstructure and the mechanical properties of the PPy/PU alloy film.
2. When the ratio *R* was increased by the polymerization conditions, the polymerization voltage was decreased, the polymerization efficiency was increased, and the content of both PPy and PTSA in the alloy film was increased.
3. As summarized in Table 2, by increasing the concentrations of the monomer, PTSA and DMF or decreasing the current density and the thickness of the PU matrix, the polymerization voltage could be decreased, *R* could be increased, and hence the mechanical properties of PPy/PU could be affected.

Acknowledgement

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