

The morphology and conductivity of polypyrrole/polyurethane alloy films

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Polymeric composites with conductivities ranging from 10^{-4} to 1 S cm^{-1} were prepared by electrochemically polymerizing pyrrole in a matrix of polyurethane. The polypyrrole/polyurethane alloy films obtained were characterized by element analysis, electron microscopy and electrical conductivity measurements. The morphology of the films depended on the solvent, the electrolyte and the current density. The mechanism of the electrochemical polymerization showed that PPy grew in a treelike structure, with molecular chains extending from the electrode surface into the solution. The transition temperature of the PPy/PU increased with the PPy content.

1. Introduction

Electrochemically polymerized polypyrrole (PPy) films show good electrical conductivity of about 100 S cm^{-1} [1] and are relatively stable over long periods of time under ambient conditions [2]. However, being a highly conjugated polymer, polypyrrole is difficult to fabricate into a desired shape. In addition, polypyrrole has poor mechanical properties as indicated by its low elongation at breaking point and its brittleness. These properties severely restrict its application. The mechanical properties can be enhanced by forming composite polymers through electrochemically incorporating polypyrrole into a polymeric matrix with superior mechanical properties, for example, poly(vinyl chloride) [3], poly(vinyl alcohol) [4], P(VDF-TrFE) [5], Br-PVK [6], NBR [7], P(EVA-VC) [8] and polyether/polyester [9]. Samples prepared by this method show a conductivity as high as 50 S cm^{-1} . The conductivity in the surface direction is highly non-uniform across the thickness, with the electrode side being the most conductive and the side adjacent to the solvent being the least. The non-uniformity persists even after a conductive polypyrrole layer begins to form and grow on the free surface of the film.

PPy/PU films have good electrical conductivity similar to pure PPy films and they retain the favourable mechanical properties of the host PU films. This paper describes the effect of the preparation conditions on the conductivity of polypyrrole films, as well as the electrochemical method for producing flexible, free-standing composite films from polyurethane (PU) and polypyrrole (PPy). In addition, results are presented from a study of the relation between the conductivity and the structure of PPy/PU composite film, and the conducting mechanism and the controlling factors are discussed.

2. Experimental details

It is known that polypyrrole films can be prepared by the anodic oxidation of pyrrole in a polar organic electrolytic solvent in the presence of a conducting salt. The effects of various factors in the electrochemical preparation make possible the optimization of the different growth conditions that produce the various properties of conductivity, mechanical strength, morphology and flexibility. The factors that can be controlled in the electrochemical environment are the electrode material, the solvent, the electrolyte, the water content and the current density. In this study, polypyrrole films 20 to $50 \mu\text{m}$ thick were prepared on a titanium surface ($2 \text{ cm} \times 6 \text{ cm}$) by applying a current density of 4 mA cm^{-2} for 30 min in a two-electrode cell containing 0.3 M pyrrole and 0.015 M electrolyte in a solvent, as shown in Table 1. The reaction system was held at room temperature during the preparation of the films. These films gradually adhere to the titanium surface and can be removed intact from the surface of the metal by careful peeling.

A piece of the sample, about 2-5 mg, was examined with an Elemental Analyser (CHN-O-Rapid) to find the percentage weight fractions of C, H, N, S and Cl. The composition was then calculated.

The densities of the films were measured by the flotation method in a tetrachloromethane-xylene mixture. The conductivities of the PPy films were measured by four probes according to the equation

$$\sigma = I \frac{\ln 2}{\pi dV}$$

where I is the current, V the voltage, and d the thickness.

The surface morphology was examined by means of a scanning electron microscope (SEM) (Cambridge Steroscan S4-10), operated at 20 kV.

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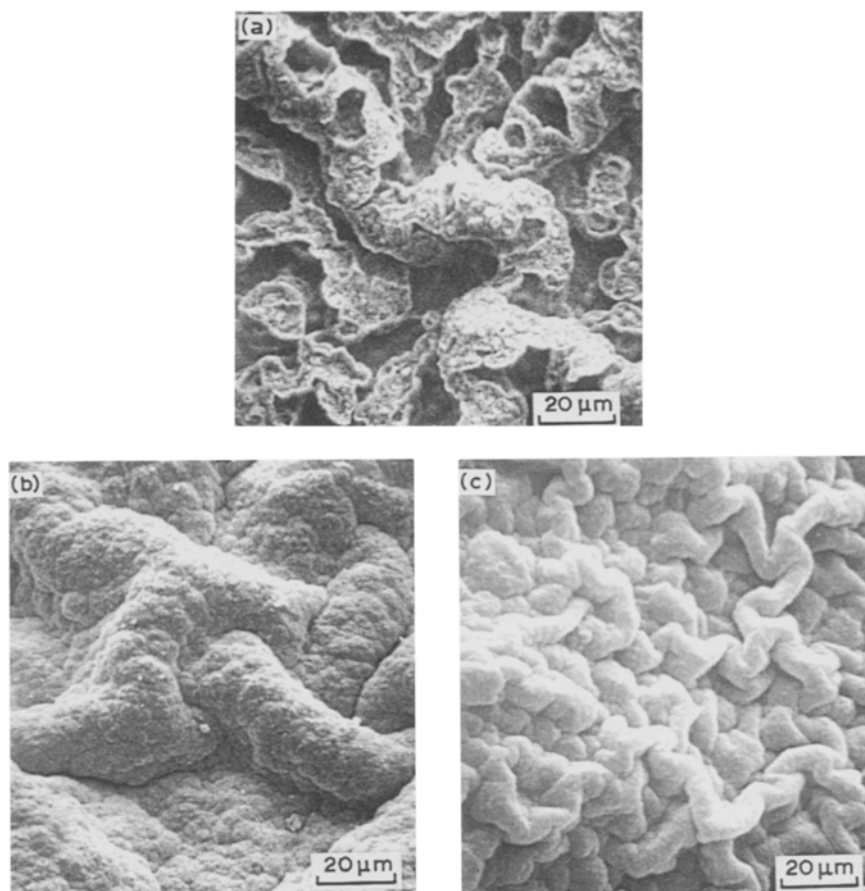


Fig. 1. Scanning electron micrographs of polypyrrole perchlorate films prepared from various solvents: (a) CH_2Cl_2 , (b) CH_3CN , (c) $\text{C}_6\text{H}_5\text{NO}_2$.

3. Results and discussion

3.1. Morphology of PPy films

The growth rate of the film was found to be proportional to the current density and was linearly dependent on time. When the current density was increased, the PPy film became brittle and its surface became rough. The densities of the films as determined by the flotation method in a tetrachloromethanexylene mixture, ranged from 1.33 to 1.48 g cm^{-3} (Table 2). The film density was greater when using tetraethyl ammonium perchlorate as the electrolyte.

The morphology of the film depended on the solvent, the electrolyte, the current density and other factors. For instance, the films containing ClO_4^- prepared in acetonitrile and dichloromethane were

bulky and brittle, whereas the films prepared in nitrobenzene were dense and tough (Fig. 1). Thus the role of the solvent in the electropolymerization process is important. There appears to be some form of specific solvation which stabilizes the α -segments of intermediate length along the PPy chain.

The chemical composition of the films depended on the preparation conditions. The results of the elemental analysis of the films are shown in Table 3. The

Table 2. The effect of electrolyte on polypyrrole densities

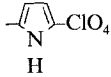
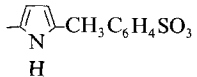
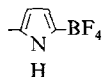
| Electrolyte | Polymer | Polymer density/ g cm^{-3} |
|---|---|-------------------------------------|
| $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ |  | 1.48 |
| $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ |  | 1.37 |
| $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ |  | 1.33 |

Table 1. Composition of the reaction system

| Supporting electrolyte | Solvent |
|---|-----------------------------------|
| $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ | CH_3CN |
| $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ | $\text{C}_6\text{H}_5\text{NO}_2$ |
| $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ | CH_2Cl_2 |

Table 3. Elemental analysis of polypyrrole films prepared by using different electrolytes

| Electrolyte | C/% | H/% | N/% | Cl/% | S/% | Structure |
|--|-------|------|-------|-------|------|---|
| (C ₂ H ₅) ₄ NBF ₄ | 46.32 | 3.67 | 13.39 | | | (C ₄ H ₄ N)X |
| (C ₄ H ₉) ₄ NClO ₄ | 43.32 | 3.36 | 12.71 | 10.40 | | C ₄ H _{3.69} N(ClO ₄) _{0.31} |
| CH ₃ C ₆ H ₄ SO ₃ H · H ₂ O | 58.93 | 4.58 | 10.68 | | 8.24 | C ₄ H ₃ N(CH ₃ C ₆ H ₄ SO ₃) _{0.34} |

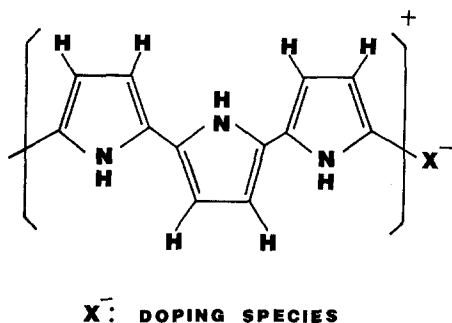


Fig. 2. A possible structure of polypyrrole.

existence of ClO₄⁻ anions suggests that the pyrrole units carry a partial positive charge, with the ratio of anion to pyrrole unit about 1:3. The film is believed to be a polymer of pyrrole formed by linkages occurring at the α -carbon [10], the possible structure being illustrated in Fig. 2.

3.2. Effect of the electrolytic solution on conductivity

The electrical conductivity of the thick films (20 to 50 μ m) removed from the electrode were measured by the four-probe method. The conductivities at room temperature ranged from 10 to 200 S cm⁻¹. The conductivity of the PPy film depended on the nature of the electrolyte and the quantity of the doping of the counter-ion. For example, the PPy film obtained with (C₄H₉)₄NClO₄ had better conductivity than that obtained with (C₂H₅)₄NBF₄. In addition, when the quantity of the doping in the PPy films increased, the conductivity became higher.

The conductivity also varied with the nature of the solvent. For example, the conductivity was higher when using the solvent CH₃CN than when using CH₂Cl₂. The reason is that the surface is full of irregular holes (Fig. 1). The conductivity of the films varied with the water content of the electrolyte solution. The more water in the solution, the lower the conductivity of the film. This is due to the disruption of the extended π structure in the PPy chain. With toluenesulfonate as the counter-ion, the conductivity of the polypyrrole may be reduced by exposing it to a NaOH solution. The decrease in the conductivity is

related to the elimination of the toluenesulfonate counter-ions (Table 4). The UV-visible spectra of the polypyrrole toluenesulfonate films are shown in Fig. 3. The absorption band that appears above 750 nm suggests the formation of free carriers, and the absorption band around 500 nm is due to π - π^* transition [11, 12]. The conductivity decreases when the absorption band of the u.v.-visible spectrum moves toward shorter wavelengths.

3.3. Relationship of conductivity and structure

As the polymerization charge density increased, the conductivity of the alloy film also increased. At the beginning, the change of the conductivity was sharp, but then it gradually levelled off (Fig. 4). With a polymerization current density of 20 mA cm⁻², if the polymerization charge density dropped to less than 24 C cm⁻², the solvent side of the alloy film ceased to be conductive (or, exceeded the measurable range of our equipment); when the charge density was higher than 24 C cm⁻², both the solvent side and the electrode side of the alloy film had about the same conductivity. With a current density of 5 mA cm⁻², if the polymerization charge density was less than 54 C cm⁻², the solvent side of the alloy film ceased to be conductive. With a charge density of 54 C cm⁻², the solvent side had only partial conductivity, in other words on the surface of the solvent side, only the region with PPy molecules was conductive and had conductivity equal to that of the electrode side.

The morphology of the alloy film surface on the electrode side is generally smooth, as shown in Fig. 5a. The surface morphology of the film is related to the surface morphology of the ITO coated glass. On the other hand, as indicated in Fig. 5b, c, and d, when the polymerization charge density increased, the surface morphology of the solvent side changed from that of a smooth surface to that of a surface with loose small particles, and then to that of a surface with dense large particles. The solution side can be really conductive only when these particles are closely stacked to form a continuous conducting surface. However, because the solution side does not usually have a continuous

Table 4. Element analysis of polypyrrole toluene sulphonate films modified by treating with NaOH

| Polypyrrole toluene sulphonate | C/% | H/% | N/% | S/% | Structure | /S cm ⁻¹ |
|--------------------------------|-------|------|-------|------|---|---------------------|
| A | 58.93 | 4.58 | 10.68 | 8.24 | C ₄ H ₃ N(CH ₃ C ₆ H ₄ SO ₃) _{0.34} | 13.5 |
| B | 60.38 | 4.33 | 14.24 | 3.34 | C ₄ H ₃ N(CH ₃ C ₆ H ₄ SO ₃) _{0.10} | 0.18 |

Note: (A) original film; (B) film after the treatment with 2N NaOH for 2 min.

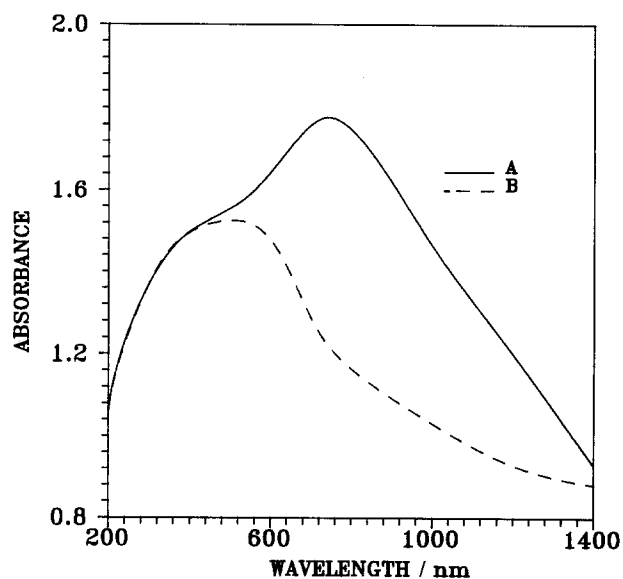


Fig. 3. UV-visible spectra of polypyrrole toluenesulphonate films. (—) Original film, ($\sigma = 0.18 \text{ S cm}^{-1}$), and (---) after treatment with 2N NaOH ($\sigma = 13.5 \text{ S cm}^{-1}$).

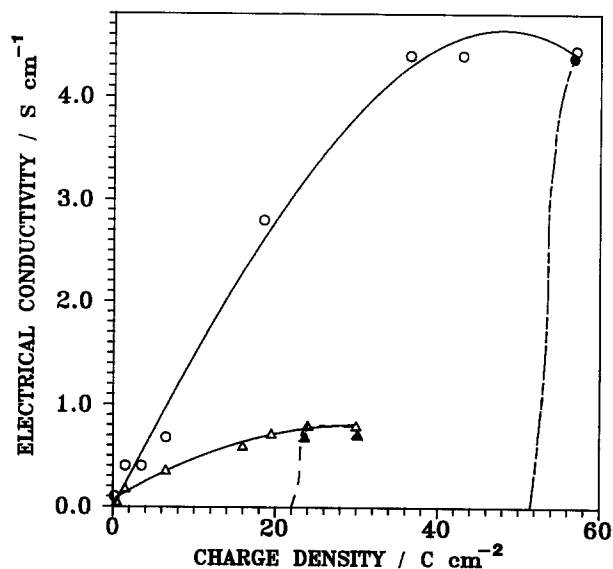


Fig. 4. Conductivity of PPy/PU alloy films prepared at 20 or 5 mA cm^{-1} with various charge densities. ([PTSA] = 0.023 M , [pyrrole] = 0.3 M , DMF/MeCN: 1/4, PU film thickness: about $20 \mu\text{m}$). (O) Electrode side: 5 mA cm^{-2} ; (●) surface side: 5 mA cm^{-2} ; (Δ) electrode side: 20 mA cm^{-2} ; (\blacktriangle) surface side: 20 mA cm^{-2} .

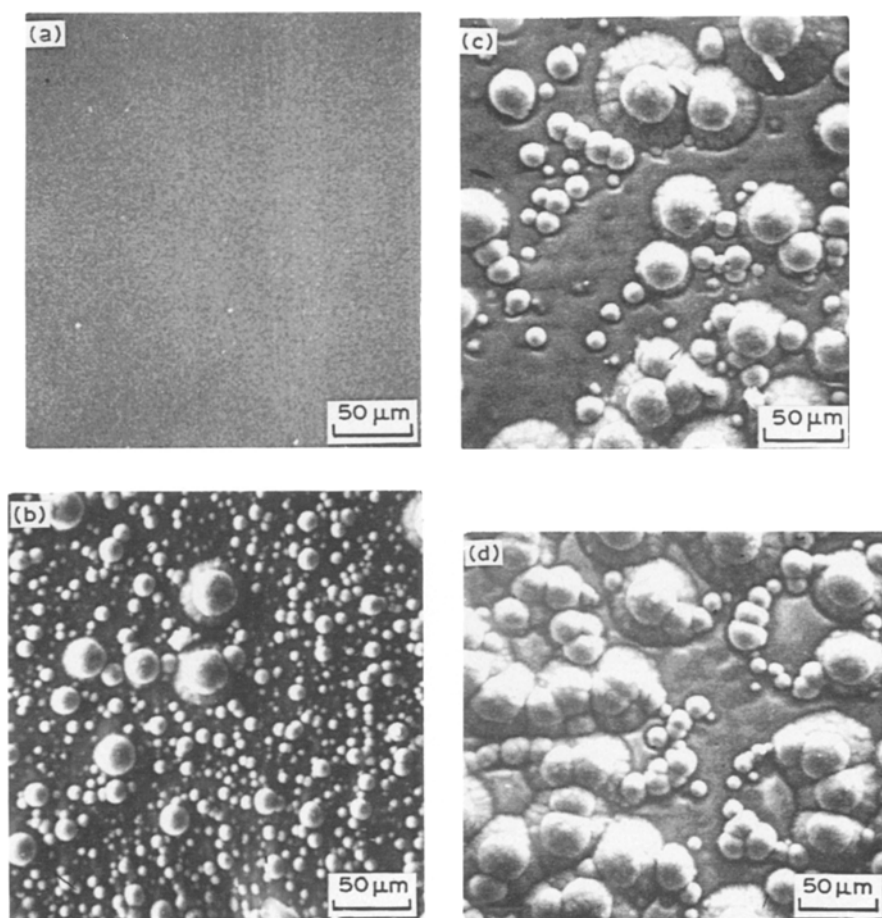


Fig. 5. SEM pictures of PPy/PU alloy films prepared at various charge densities: (a) electrode side: 0.2 C cm^{-2} ; (b) surface side: 12 C cm^{-2} ; (c) surface side, 24 C cm^{-2} ; and (d) surface side, 30 C cm^{-2} . (C.d.: 20 mA cm^{-2} , [PTSA] = 0.023 M , [pyrrole] = 0.3 M , DMF/MeCN: 1/4, PU film thickness: about $20 \mu\text{m}$).

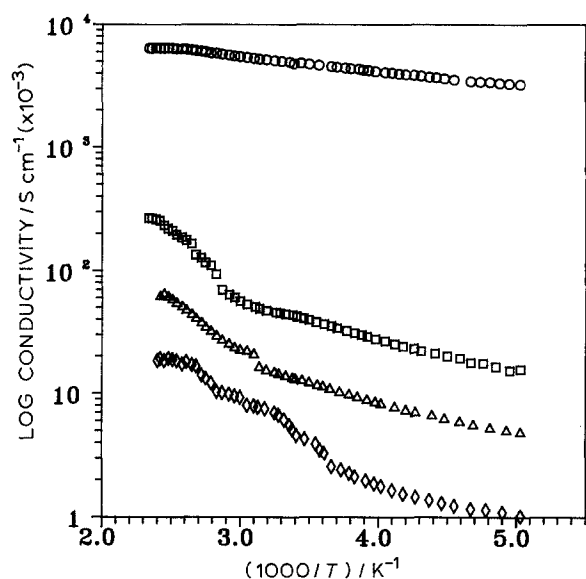


Fig. 6. Log conductivity of electrode side against $1/T$ for pure PPy film and PPy/PU alloy films electro-polymerized with various charge density. (C.d.: 20 mA cm^{-2} , [PTSA] = 0.023 M , [pyrrole] = 0.3 M , DMF/MeCN: $1/4$, PU film thickness: about $20 \mu\text{m}$). (O) Pure PPy, (□) 12 C cm^{-2} , (△) 4.8 C cm^{-2} and (◇) 1.2 C cm^{-2} .

conducting surface during polymerization, the formation of PPy molecules on the solution side emerges in the form of particles; in other words PPy molecules can only attach to the conductive region. From this electrochemical polymerizing mechanism, we conclude that PPy grows in a tree-like structure extending from the electrode side to the solution side and the density of the stack decreases from the electrode side towards the solution side. This phenomenon is consistent with the observed electrical properties. The solvent sides of the samples in this research do not have real conductivities since the stacks of PPy particles are not dense enough. As for the samples prepared at 24 C cm^{-2} and 54 C cm^{-2} , the reason for the solution-side conductivity is that, in the 4-probe method, the measuring current formed a loop to the electrode side in the direction of the film thickness.

3.4. Relationship between conductivity and temperature

The temperature dependence of the conductivity of the polymers is shown in Fig. 6. The conductivity of the pure PPy and PPy/PU films increased with temperature. The temperature dependence of the pure PPy film can be described by the relationship $\sigma \propto e^{-E/T}$, and the PPy/PU film shows a transition between 267 and 330 K. Through thermal analysis it is known that PPy in a PPy/PU film has no transition within this temperature range, so this transition must be attributed to the PU. As Fig. 7 shows, this transition temperature moved upward as the charge density (or the PPy content) increased. This phenomenon can be explained by the molecular motion of the PU matrix. The motion of the PU molecule chain was blocked due to the formation of the PPy particles, thus raising the transition temperature. In addition, from the acti-

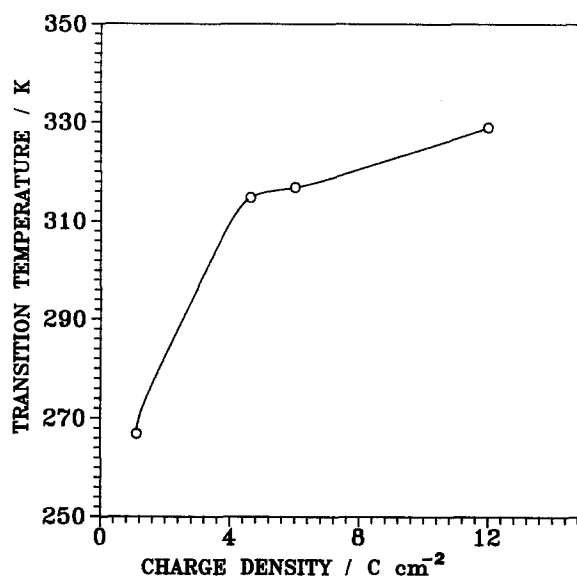


Fig. 7. Transition temperature of PPy/PU alloy films as a function of charge density. (C.d.: 20 mA cm^{-2} , [PTSA] = 0.023 M , [pyrrole] = 0.3 M , DMF/MeCN: $1/4$, PU film thickness: about $20 \mu\text{m}$). (O) T_g .

vation energies calculated from the slopes of the curves in Fig. 8, pure PPy had the lowest activation energy (53.6 meV). For PPy/PU films, as the PPy content increased, the temperature sensitivity of the conductivity decreased. Above the transition temperature, the activation energy tended to first increase and then to decrease as the charge density increased. On the other hand, when the temperature was below the transition point, the activation energy was lower than it was above the transition point.

There are two conducting mechanisms in the PPy/PU composite: hole conduction of PPy and ionic conduction of PU. The ionic conductivity of PU is much lower compared with that of PPy, thus the total conductivity is dominated by the hole conduction. In

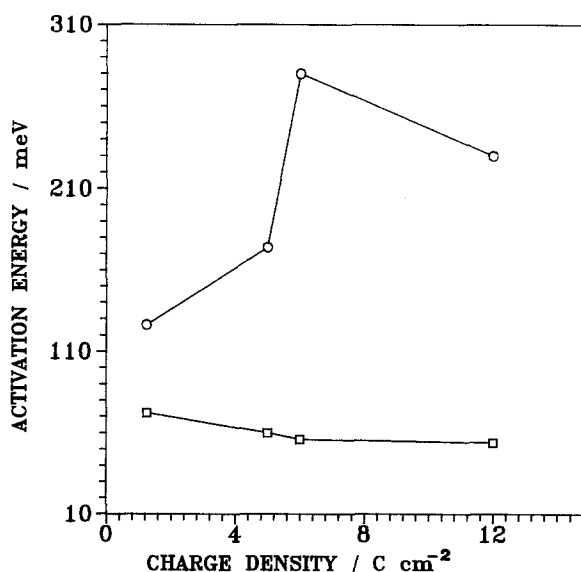


Fig. 8. Activation energy of conductivity of PPy/PU alloy films as a function of charge density. (C.d.: 20 mA cm^{-2} , [PTSA] = 0.023 M , [pyrrole] = 0.3 M , DMF/MeCN: $1/4$, PU film thickness: about $20 \mu\text{m}$). (O) $T > T_g$ and (□) $T < T_g$.

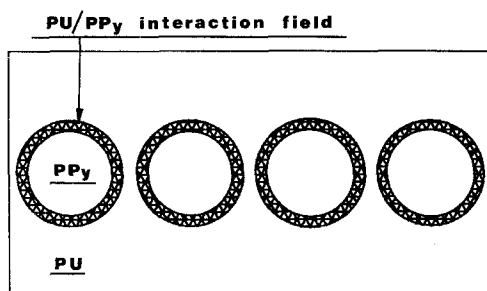


Fig. 9. Schematic illustration of the interaction between the PU and PPy in the PPY/PU alloy film.

general, the conductivity, σ , of a polymer is controlled by two factors: the carrier concentration per volume, n , and the carrier drift mobility, μ . The carrier concentration is determined by the applied external energy and the characteristics of the carrier. For the same material, n is constant. When the temperature goes up, n tends to increase, thus increasing σ . In addition, at higher temperatures μ is larger, making σ larger. In addition, the activation energy on the lower temperature side is less than that on the higher temperature side. This phenomenon can be explained by the relationship between the molecular movement and μ . The molecules of the PU matrix at lower temperatures are immobile, thus facilitating the transportation between holes. At higher temperatures, the increasing mobility of the PU matrix blocks the transportation between holes, thus increasing the activation energy of the system.

Figure 7 shows that the transition temperature goes up as the charge density increases. This is because the introduction of PPy molecules in the PU matrix restricts the intermolecular interaction between the PU molecule chains.

The activation energy of the conductivity of PPY/PU increases as the polymerization charge density increases (i.e. the content of PPy increases) and then decreases. This can be explained by the interaction mode of the material, as illustrated in Fig. 9. When the content of PPy on the surface of PPY/PU is small, PPy molecules exist within the PU matrix in a dispersed mode and the interaction force between the molecules of PPy and PU is small. As the content of PPy increases, the interaction field between PU and PPy also increases. This interaction field affects the motion of the conductive carrier and causes an increase in the activation energy. When a continuous conductive path is formed by PPy molecules, the activation energy again decreases.

4. Conclusion

From the above analysis, it may be concluded that the

properties of polypyrrole films depend on the solvent, the electrolyte, the anode electrode and the current density. The film with ClO_4^- prepared in acetonitrile is bulky and brittle, while the film prepared in nitrobenzene is dense and tough. In addition, this work has demonstrated that polypyrrole films are influenced by the counter anion. The observations are summarized as follows:

1. Based on the measurements of conductivity and SEM, it is deduced that PPy grows in a tree-like form from the electrode side of the PU matrix towards the solution side. The closer to the electrode, the higher the density of PPy stacked in the PU. The reason why the solution side of the alloy film has conductivity is that the measuring current forms a loop to the electrode side in the direction of the film thickness.
2. Because the rigid PPy chain blocks the molecular motion of the PU molecule chain, the transition temperature goes up as the PPy content increases.
3. The conducting mechanism is dominated by the transportation between holes. The transportation at lower temperatures is restricted by the motion of the PU molecules, while the transportation at higher temperatures is related to the interaction between the molecules of PU and PPy.

Acknowledgement

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