Electrochemical Preparation of Electrically Conducting Polyurethane / Polyaniline Composite

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Synopsis

Composite films from polyaniline (PANi) and polyurethane (PU), with high flexibility and mechanical strength similar to pure PU and conductivity close to pure PANi, have been obtained by electropolymerizing aniline on a PU/Pt electrode in water/acetonitrile/ethylene glycol electrolyte solution. In the composite films, PANi is dispersed, in the form of particulate, inside and on the inner surface of the PU substrates. It is found that the electropolymerization reaction of aniline proceeds much faster in basic solution and composite film as prepared shows higher conductivity than that in acidic solution. PANi in PU/PANi composite film is protonic-acid-doped and is conducting even in case it is electropolymerized in a basic electrolyte solution.

INTRODUCTION

Polyaniline with high conductivity has been studied for exactly twenty years.[1-7] Currently it is arousing considerable interests as a novel conducting polymer.[2-7] Polyaniline is usually synthesized by chemical or electrochemical oxidative polymerization of aniline in aqueous acid solutions.[3-7] Chemical synthesis gives powder,[3,8] while electrochemical synthesis results in cohesive films.[1,3] Moreover, it is reported to electropolymerize aniline in basic media which produces polyaniline or oligomers of aniline.[9,10] Polyaniline promises to have interesting properties as materials for rechargeable batteries,[3,11] modified electrodes,[12,13] electrochromic display devices,[14] etc. However, no free-standing film of PANi, which is easy to handle, has been obtained up to now. Thus its practicality is greatly limited.

By electrooxidatively polymerizing aniline on a nonconducting, mechanically superior polymer film-coated electrode, composite film which contains the high conductivity and stability of PANi to ambient conditions associated with the good mechanical properties of the polymer substrate is expected to be obtained. Here we report the conducting composite films of polyaniline and polyurethane prepared with this method.

EXPERIMENTAL

A polyurethane-coated Pt electrode (PU/Pt) was prepared by depositing a 5 wt % solution of PU (polyester-based resin) in THF onto a Pt slice and allowing the solvent to evaporate. The thickness of the as-prepared PU film was ca. 10 μm if not mentioned. With a bare Pt slice as counter electrode and an aqueous saturated calomel reference electrode (SCE), constant potential of

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2.00 V was applied to a PU/Pt working electrode, which has been immersed in the electrolyte solution for 3 min. The electrochemical polymerization was conducted in a one-compartment cell containing water/acetonitrile/ethylene glycol solution (volume ratio 1 : 1 : 1) of $0.2M$ purified aniline and $0.25M$ supporting electrolyte. As aniline was being electropolymerized onto the PU/Pt electrode, the transparent PU film coated on Pt gradually darkened. Soluble brown by-product was observed around the working electrode in 2 min. The counter electrode bubbled much hydrogen. Working current rapidly decreased after polarization current pulse, and tended to be stable in a while. After 30 min of electropolymerization, the as-grown composite polyurethane/polyaniline films (PU/PANi) were easy to peel off the Pt slice with a razor and were rinsed with anhydrous acetonitrile and then dried by airing. A composite PU/PANi film is green or black. Its mechanical strength and flexibility are high and similar to those of a polyurethane/polypyrrole composite film.[15] By extracting a PU/PANi film with THF, we obtained some dark-green powder of polyaniline which was rinsed with anhydrous acetonitrile and then dried at 50°C.

The electrical conductivity was measured using the conventional four-probe method. The adsorption spectra in the visible region were taken from a KBr pellet via an Opton DMR-22 UV-visible spectrophotometer, or recorded *in situ* with a Nanometrics Nanospec/10 microspectrophotometer. To obtain the *in situ* visible spectra, the Pt slice was replaced by a conducting In_2O_3–SnO_2-coated glass (CG). It was found that the electropolymerization reactions of aniline on a CG or PU/CG electrode were identical to those on a Pt or PU/Pt electrode, respectively. Other instruments were the same as described in literature.[15]

RESULTS AND DISCUSSION

Conductivity of PU/PANi Composite Films

With the electrolyte solution having different supporting electrolytes, PU/PANi composite films as prepared show different conductivities (Table I). The pH value of the solution also exerts a great influence on conductivity. A composite film prepared in a basic solution shows much higher conductivity than that in an acidic solution with the expectation in a TsONa electrolyte solution. The results from a neutral medium are close to those from a basic medium. The basicity of electrolyte solutions is adjusted by adding NaOH, but if in an NaOH solution which does not contain any other supporting electrolyte, aniline does not electropolymerize on a PU/Pt electrode. Composite films prepared from $NaClO_4$ electrolyte solution, symbolized as PU/PANi–ClO_4^-, or PU/PANi for abbreviation, bears the highest conductivity. The following discussion is aimed at these composite films.

With $NaClO_4$ as supporting electrolyte, the electrooxidative polymerization of aniline on a PU/Pt electrode gets faster and faster and conductivity of composite PU/PANi–ClO_4^- films as grown gets higher and higher if we steadily increase the pH value of the electrolyte solution (Fig. 1). In a solution of pH 13, a PU/PANi–ClO_4^- film is obtained whose conductivity is as high as 3 S/cm, which is on the same level as pure PANi. This film is flexible and

TABLE I
Effects of Supporting Electrolytes on Electropolymerization Current and Conductivity (Performed in Solution Containing 0.2*M* Aniline and 0.25*M* Supporting Electrolyte at a Constant Potential of 2.00 V vs. SCE for 30 min)

	pH value of electrolyte solution					
	pH 12		pH 7		pH 4	
Supporting electrolyte	Average current density (mA/cm^2)	Conductivity (S cm^{-1})	Average current density (mA/cm^2)	Conductivity (S cm^{-1})	Average current density (mA/cm^2)	Conductivity (S cm^{-1})
$NaClO_4$	3	1	2.5	0.5	0.5	3×10^{-3}
Bu_4NBF_4	5	0.3	5	0.01		
KCl	1.5	0.01	2	0.01	0.5	6×10^{-3}
TsONa	1.8	3×10^{-3}	1.5	3×10^{-3}	0.6	0.01
$NaNO_3$	0.9	1×10^{-6}	0.9	1×10^{-6}	0.2	1×10^{-7}
KPF_6	1.6	2×10^{-7}	1.4	2×10^{-7}	0.2	6×10^{-8}
$\frac{1}{2}Li_2SO_4$	0.1	Nonconducting	0.1	Nonconducting	0.2	Nonconducting
NaOH	Very little	Nonconducting				

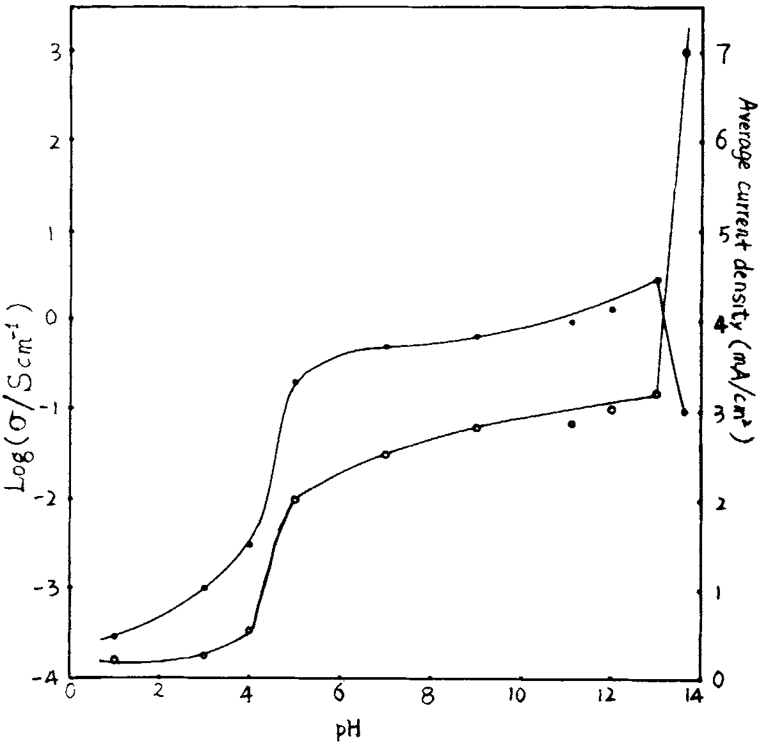


Fig. 1. Effects of pH value on (○) average electropolymerization current and (●) conductivity (performed by the means used in Table I with $NaClO_4$ as supporting electrolyte).

pliable, similar to pure PU film. However, in an electrolyte solution with even higher pH value, e.g., pH 13.6, dozens of minutes of immersion in the solution will cause the PU layer coated on Pt slice to crumble and, to some extent, to lose adhesion to the Pt slice. In a solution of pH $\leq$ 4, the electropolymerization of aniline on PU/Pt electrode is very slow, and composite films as prepared show much lower conductivity. In contrast, on a bare Pt working electrode, aniline must be electropolymerized in a strong protonic acidic solution in order to prepare conducting PANi. Moreover, the mechanism of conduction in PANi is based upon protonic acid doping, and if conducting PANi is washed with an aqueous solution of pH > 4, it undergoes a metal–insulator transition resulting from deprotonation.

It is supposed that after the PU coating of a PU/Pt electrode is sufficiently swollen by an electrolyte solution, aniline and supporting electrolyte penetrate through the PU layer onto the Pt surface. As a result, aniline is electrooxidatively polymerized on the Pt surface and a large number of protons are released during the reaction. Since the PU layer exerts a strong limitation on the diffusion rate of ions through it, the protons released cannot rapidly diffuse from the interface of Pt and PU (PU–Pt) into the bulk electrolyte solution. Hydroxide ions from the bulk solution cannot rapidly diffuse into the PU–Pt interface either to completely neutralize the remaining H^+ at the same time. Accumulation of H^+ makes the PU–Pt interface strong acidic.

Therefore, in an electrolyte solution with any pH value, electropolymerization of aniline is actually conducted in strong acidic circumstances, and conducting PANi is thus produced. In an acidic electrolyte solution, low concentration differences of H and OH between PU–Pt interface and bulk solution results in a much slower diffusion rate of H^+ and OH^- through the PU layer. Consequently, the acidicity of the PU–Pt interface is so strong that the electropolymerization rate of aniline is limited to a larger extent instead, which will be further investigated in another paper. After PU/PANi-ClO_4^- composite film is peeled off prepared from an electrolyte solution with pH 3–13, the Pt slice is immersed into 10 mL of neutral water. The small amount of liquid and a very thin layer of PANi remaining on the Pt slice make the pH value of water decrease from 7 to 2.7–3.0. This fact confirms that, even in basic solution, the PU–Pt interface is strong acidic after electropolymerization reaction of aniline has started.

Mechanical Properties of PU/PANi Composite Film

Figure 2 shows the results of a stress–strain mechanical test of PU/PANi composite film in comparison with pure PU film. A pure PU film is flexible and strong with high tensile strength at break (68 N/mm^2), large elongation at break (840%) and low Young's modulus [Fig. 2(b)] typical for rubbers. On the contrary, pure PANi is usually prepared as powders. Although free-standing films of PANi have been obtained by McDiarmid et al.,[3,7] these films are too fragile to handle. Thus it is impossible to get any data for their mechanical properties. The composite film of PANi and PU remains the high flexibility and strength of PU substrate. Its stress–strain curve [Fig. 2(a)] is very similar to that for pure PU film, with tensile strength and elongation at break being 40 N/mm^2 and 570%, respectively. Moreover, Young's modulus of the composite film is identical to that of pure PU, which implies that, in the composite film, PANi is dispersed in PU matrix in the form of particulate.

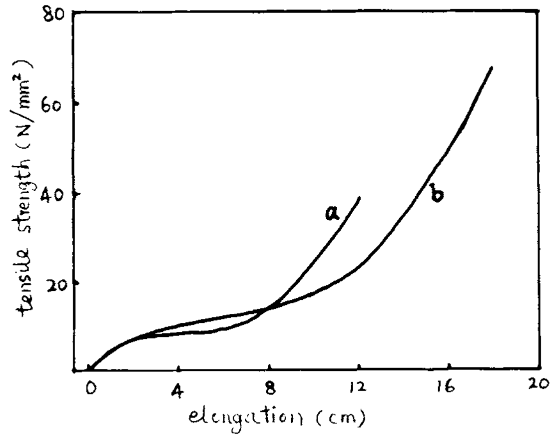
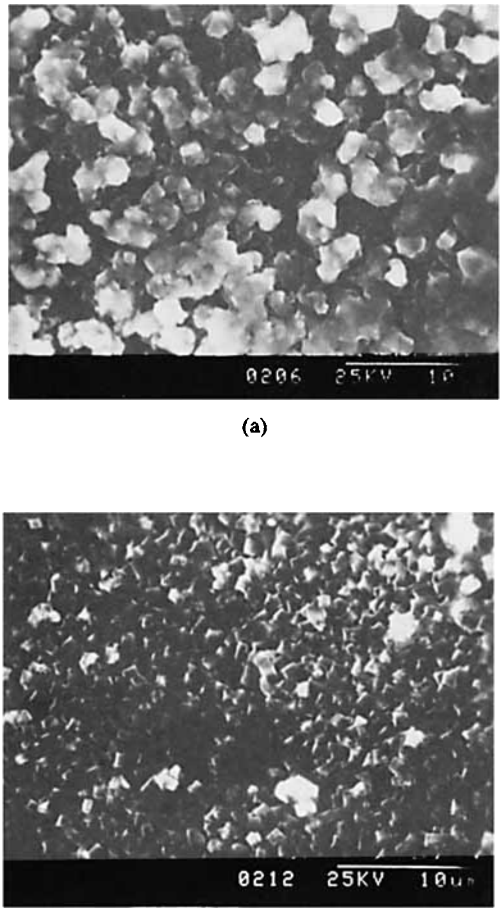


Fig. 2. Stress–strain curves (strain rate 50 mm/min) for: (a) composite PU/PANi-ClO_4^- film prepared in pH 12.7 electrolyte solution thicknesses of the original PU film and the composite film are ca. 15 and 20 μm, respectively; (b) pure PU film of 20 μm in thickness.

The particulates are separated and do not form the PANi network as in case of PU/PPy composite films.[15]

Morphology of PU/PANi Composite Films

Aniline is electropolymerized onto PU/Pt electrode in electrolyte solution with pH ranging from 3 to 13. The inner surface (the surface close to the Pt electrode) of the composite PU/PANi films as prepared is conducting, while its outer surface (close to solution) is non- or very little conducting in a wide range of reaction time. Morphologies of the inner and outer surfaces of PU/PANi composite film, prepared from a basic solution (pH 12.7), are both different from those of a pure PU film. It is observed that both surfaces of the



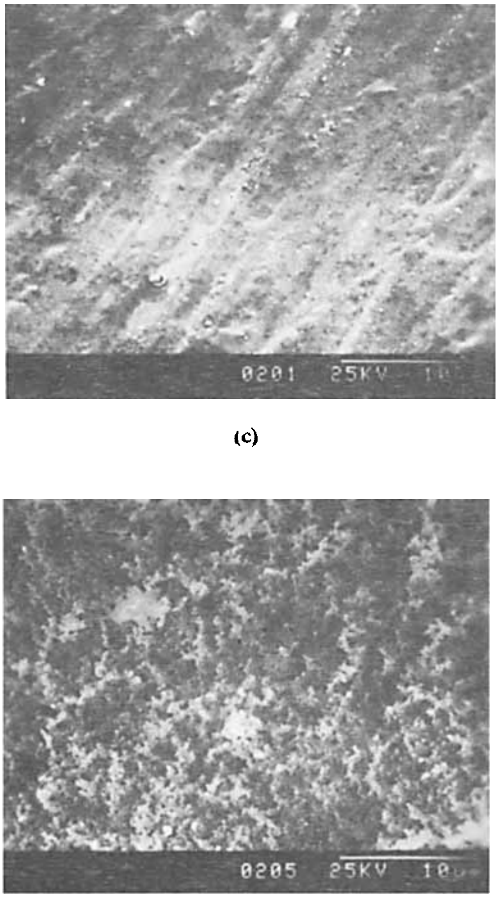
(a)

(b)

Fig. 3. Scanning electron micrographs of (a) the inner surface (the surface close to the Pt electrode) of a composite PU/PANi film prepared in an electrolyte solution with pH 12.7; (b) the outer surface (the surface close to the solution) of the composite film; (c) the inner surface of a pure PU film which was immersed in the electrolyte solution for 30 min; (d) the outer surface of the pure PU film.

composite film are PANi particulates, and the particulate diameter on the inner surface is about twice as large as that on the outer surface [Figs. 3(a),(b)]. The inner surface of a pure PU film is compact and takes the shape of the Pt electrode surface [Fig. 3(c)]; yet its outer surface is porous [Fig. 3(d)]. As to composite film prepared from an acidic electrolyte solution (pH 4), its inner surface is similar to composite film prepared from basic solution, whereas its outer surface is similar to that of a pure PU film.

As has been reported, aniline and supporting electrolyte penetrate through the PU layer of a PU/Pt electrode and are electropolymerized on the Pt electrode surface. The large amount of protons released during the reaction make PANi as polymerized conducting. PANi continuously grows and piles up in the PU substrate. Having grown throughout the inside of the PU substrate, PANi grows out of the outer surface of PU. In the pH 12.7 basic electrolyte solution, PANi grown out of the PU substrate is exposed to the bulk solution and becomes nonconducting. In the pH 4 acidic solution, the electropolymer-



(c)

(d)

Fig. 3. (*Continued from the previous page.*)

ization of aniline is very slow and PANi does not grow throughout inside PU substrate for the same reaction time as in the basic solution. Thus the outer surface of the composite film as obtained is still composed of pure PU and is nonconducting.

Construction of PU/PANi Composite Film

Soaking and swelling in a water/acetonitrile/ethylene glycol electrolyte solution containing 0.25*M* $NaClO_4$ with various pH values do not change the FTIR spectrum of a pure PU film. During the electropolymerization process of aniline on a PU/Pt electrode, the FTIR spectrum of the PU coating does not change either. So it can be concluded that polyurethane resin used is electrochemically stable and cannot be electrooxidized during electropolymerization of aniline.

FTIR spectrum is shown in Figure 4 of PANi particulates obtained from PU/PANi-ClO_4^- composite by extracting with THF. It is similar to IR spectra of pure PANi prepared on bare Pt electrode in aqueous acidic electrolyte solution[16] except for the adsorption peak at 1683 cm^{-1} in the former case. The FTIR spectrum changes little when pH value of the electrolyte solution varies between 3 and 13. The PANi particulates from composite films prepared in pH 4-13 electrolyte solutions are all dark green and conducting and transit to dark blue, nonconducting ones by washing with water or aqueous base solution, which indicates that the PANi also bears a protonic acid doping conduction mechanism like pure PANi in the literature.[3-5] Adsorption spectra in visible region of the PANi particulates taken from a KBr pellet and of PU/PANi composite film *in situ* are typical for conducting PANi (an adsorption peak near 420 nm and strong adsorption from 600 nm upwards as shown in Fig. 5).

If we assume tentatively that all of the oxygen is in the form of H_2O, then elemental composition of the PANi particulates from the composite films prepared in pH 12 electrolyte solutions in the form of atomic ratio with

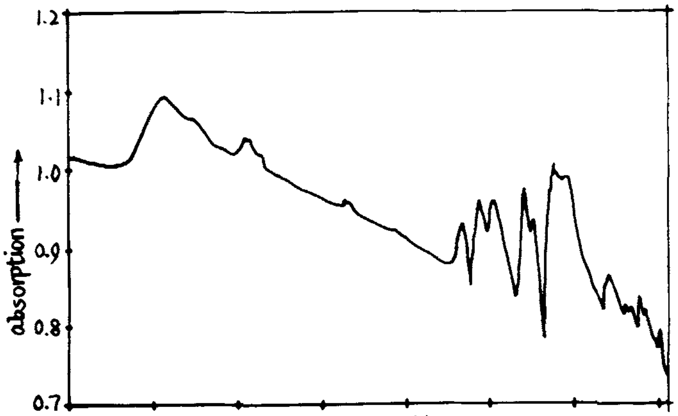


Fig. 4. FTIR spectrum for the PANi component in PU/PANi-ClO_4^- composite film prepared in an electrolyte solution with pH 12.7.

respect to six carbon atoms is:

$$C_6H_{4.38}N_{0.98}(H_2O)_{0.69}(HClO_4)_{0.45}$$

close to conducting PANi prepared on a bare Pt electrode in acidic solution.[17]

From the above results it is considered that PANi and PU in a PU/PANi composite are simply mechanically composited with no chemical bonding between the two components. PANi is dispersed, in the form of particulate, inside and on the inner surface of the PU substrate. There is no or little PANi on the outer surface of PU. The PANi component is conducting and is protonic acid-doped. Its structure and electrical properties have nothing to do with the pH value of electrolyte solution in which it is electropolymerized.

Preliminary study on the cyclic voltammetry (CV) of PU/PANi composite films shows that the composite films can be reduced and reoxidized nearly

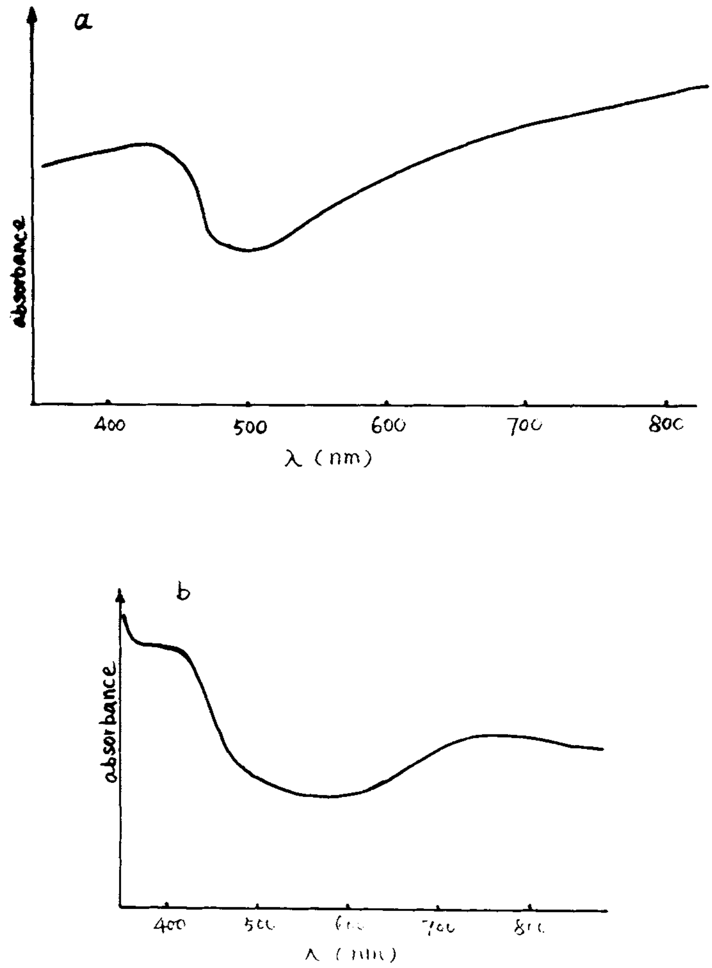


Fig. 5. Optical absorption of (a) the PANi component from KBr pellet in a PU/PANi composite film prepared in an electrolyte solution with pH 12.7; (b) the PU/PANi composite film *in situ* electropolymerized in pH 12 electrolyte solution at 2.00 V for 0.5 min.

reversibly in 0.25M $NaClO_4$ water/acetonitrile/glycol electrolyte solution of pH 1.0. The CV curves for the composite films prepared in pH 4, 7, or 12.7 electrolyte solutions are alike in shape except that the redox current is stronger if the composite film is prepared in electrolyte solution with higher pH value.

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